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Synthesis, Optical Properties and Photovoltaic Application of the SnS Quasi-one-dimensional Nanostructures

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Abstract: Low-toxicity single crystal SnS nanowires had been successfully synthesized by the catalyst-assistant chemical vapor deposition. Au nanoparticles were applied on the ITO surface as the catalysis, using SnS powder and S powder as forerunners. The structure, morphology and optical properties of the prepared SnS nanowires were characterized. The experimental results show the as-synthesized nanowires are single crystalline with a preferential orientation. The synthesized SnS nanowires show strong absorption in the visible and near-infrared spectral region, and the direct energy band gap of SnS nanowires is 1.46 eV.

Keywords: Nanostructure; Chemical vapor deposition; Crystal growth; Optical property

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Introduction

In the last several years, as one of the most important candidate materials for the solar cell, SnS has attracted much attention and recognition [1-8]. Firstly, SnS is an environment-friendly material without toxic. Secondly, the electrical conductivity of the SnS can be easily controlled by doping with others. Thirdly, the photoelectric conversion efficiency of the SnS material is very high than others, and the optical energy band gap of the SnS is suitable for the solar cell. Fourthly, the optical absorption coefficient of SnS is very large. For all of these reasons, SnS is one of the most important candidate materials for the solar cell. And yet, the solar cell’s efficiency has to be increased and the costs have to be reduced simultaneously. Nanowire is a promising material system to realize this. Due to the small size of nanowires, different materials can be more easily combined compared with bulk systems, and more sophisticated tandem cells could be fabricated. Secondly, the nanowires with long absorption path lengths maintain short distances for carrier collection/transportation. Thirdly, strong light trapping occured in high-density nanowire arrays. At last, the cost of nanowire solar cells may be reduced by using cheaper fabrication methods by the fact that less of the rare metals are being used in these nanostructured.

Crystalline tin sulfides have been prepared by various methods and most of the properties had been studied [9-12]. To our knowledge, most of them are thin films or nanoparticles, only a little report about preparing novel quasi-one-dimensional wire-like SnS nanostructures. Single crystalline SnS nanowires were synthesized using solution methods [13]. Nanorods and nanosheets of SnS were synthesized by a novel thioglycolic acid assisted hydrothermal process [14]. SnS
nanowires grown on tin foils were synthesized using surfactant-assisted process and the growth mechanism had been discussed also by S. K. Panda [15]. Superior rate capabilities of SnS nanosheet electrodes for Li ion batteries had been reported in 2010 [16]. Using the template-assisted pulsed electrochemical deposition, our group had successfully synthesized the SnS nanowire arrays, and the optical properties of the synthesized SnS nanowires had also been discussed [17].

In this paper, we present a simple method of producing single crystal SnS nanowires by a simple chemical vapor deposition method. Nanostructure and optical properties of the as-synthesized SnS nanomaterials have been studied. And with this method, the alligned SnS nanowire arrays can be synthesized easily with short reaction time or lower reaction rate.

Experimental

A conventional horizontal tube furnace was used for the synthesis. A quartz tube with an inner diameter of 30 mm, and length of 900 mm was installed in the furnace. Another alumina tube with an inner diameter of 20 mm, and length of 600 mm was inserted into the quartz tube. Sulfur (2 g), SnS (2 g) and the substrate were loaded in the alumina tube in turn, where the distance between the SnS powder and substrate was about 10 cm, and the distance between the sulfur powder and SnS powder was about 5 cm. The indium tin oxide (ITO) glass substrates were cleaned in diluted HF solution for 30 s then rinsed with deionized water. Several drops of water-dispersed colloidal Au nanoparticles with a nominal diameter of 10 nm were applied to the ITO surface with a similar amount of dilute HF solution, and left dormant for 30 s. After being rinsed with deionized water, the substrates were dried by a nitrogen gun and placed onto the CVD system.

After the quartz tube was evacuated by a vacuum system to about $10^{-3}$ Pa, the tube was backfilled with a high-purity carrier gas of Ar, and then the temperature of the furnace central region was increased with a rate of 50°C/min. The temperature of the central region of the furnace was kept for 30 min. At the same time a small hydrogen flow rate of 10 sccm (standard-state cubic centimeter per minute) was introduced into the system. And the temperature of the sulfur region was about 150°C. Afterwards, the furnace was left to naturally cooling down to room temperature. After deposition, the substrate was covered with black product. These products were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HRTEM). Energy dispersive X-ray spectroscopy (EDS) attaching to FE-SEM was used to analyze the elemental composition of the samples. In order to get the optical characterization of all deposited films, transmission and reflectance spectra measurements at room temperature were measured with a Shimadzu model 3101PC double-beam spectrophotometer. The absorption coefficient ($\alpha$) was calculated from $T(\lambda)$ and $R(\lambda)$ measurements, as well, its dependence on the photon energy ($h\nu$) and the optical band gap ($E_g$) was obtained. Photovoltaic measurements were recorded by a Keithley 2400 digital source meter. Solar cell performance was measured by utilizing an Air Mass 1.5 G (AM1.5 G) solar simulator with an irradiation intensity of 100 mW/cm² under ambient conditions.

Results and Discussion

Figure 1 shows a series of SEM and TEM images of as-grown quasi-one-dimensional SnS nanostructures. Figure 1(a-d) is the SEM images of SnS nanostructures deposited on gold particles-filled ITO substrate. The sample in Fig. 1(a) grew at 790°C for 30 min with the Ar and H₂ flow rates of 200 sccm and 10 sccm, respectively. SEM observation reveals that this sample consists of large amount of curly and uniform SnS nanowires. Figure 1(b) was the high magnification image of the Fig. 1(a), it can be found that the nanowires are uniformly with a diameter of 50 nm and length of several micrometers. The sample in Fig. 1(c) grew at 750°C for 30 min with 200 sccm Ar and 10 sccm H₂, and Fig. 1(d) was the high magnification image of the Fig. 1(c). From the Fig. 1(c) and Fig. 1(d), it can be found that the nanowires are messily piled up and the diameter of the nanowires changed from 10 nm to 100 nm, as the reaction temperature was 750°C. When the reaction temperature changes to 700°C, there appears the nanobelts and the comb-like nanostructure. This kind of phenomenon has appeared in our work with the ZnO nanostructure [18]. The nanostructures of the sample which grew at 790°C for 30 min with the Ar and H₂ flow rates of 200 sccm and 10 sccm were further studied by TEM and found to be nanowires. As shown in Fig. 1(e), the inset is the selected area electron diffraction (SAED) pattern of the nanowires, which indicates the nanowire is single crystalline orthorhombic SnS in structure. HRTEM was used for further insight into the structure of the nanowires. Figure 1(f) is obtained from HRTEM recorded on an individual nanowire and which is acquired by enlargement of a selected area of a single nanowire from the Fig. 1(e). It is indicated that the SnS nanowire sample exhibits good crystalline and continuous lattice fringes over a larger area. This image clearly reveals that the as-synthesized nanowire has no obvious defect of dislocation. The interplanar spacing for the orthorhombic structure, confirming the
crystalline nature of the produced SnS nanowires [16]. EDS attached to SEM was used to investigate the chemical composition of the products. The molar ratio of Sn and S in the sample is 48.15 and 51.85, respectively. Therefore, the tin atom quantity is insufficient in the as-synthesized SnS nanowires.

XRD analysis shows that all the samples are orthorhombic SnS with lattice parameters of $a = 4.36$ Å, $b = 11.09$ Å and $c = 3.98$ Å. Figure 2 shows the presentative XRD patterns of the as-prepared samples grown at 790°C for 30 min with the Ar and H$_2$ flow rates of 200 sccm and 10 sccm, in which all the peaks are indexed to orthorhombic SnS. From Fig. 2, it can be seen that the major peak (101) is strongly dominating other peaks indicating the preferred orientation. No impurities such as SnO$_2$ and SnS$_2$ can be detected from the XRD analysis. The sharp and narrow (101) peaks indicate that the nanowires are highly crystalline and consist of only a single compositional phase, and this is corresponding to the HRTEM and SAED results. And the growth mechanism (VLS) had been discussed in our earlier work. [19]

In order to determine optic properties of the as-prepared SnS nanowires, the optic transmission ($T$) spectrum measurements at room temperature were taken in the wavelength range of 350–1100 nm. The optic transmission spectra of the samples growing at 790°C for 30 min with the Ar and H$_2$ flow rates of 200 sccm and 10 sccm are shown in Fig. 3. It is seen from the Fig. 3 (see the dotted lines) that the transmission of the samples is very low when the wavelength is in the range of 350-550 nm, and then the $T(\%)$ increases with the wavelength increasing. The variation of reflection ($R$) spectra of the same samples as a function of wavelengths are shown in Fig. 3 as well (see the solid line). It is considered that the $R(\%)$ is about 35% when the wavelength is no more than 500 nm and it also decreased rapidly first and then slowly when the wavelength is more than 1000 nm. It was well known that the transmission $T$ through an absorbing slab is related to its reflectivity $R$, thickness $d$, and absorption $\alpha$ by [17, 20]

$$T = (1 - R) \cdot e^{-\alpha d} \quad (1)$$

Or

$$\alpha = \frac{1}{d} \ln \left[ \frac{(1 - R)^2 + \sqrt{(1 - R)^4 + (2RT)^2}}{2T} \right] \quad (2)$$

Herein the thickness $d$ of the nanowires films is about 10 µm for the SnS nanowires films. Therefore, the absorption coefficient $\alpha$ can be calculated from the data of $T(\lambda)$ and $R(\lambda)$. It was found that the optic absorption coefficient calculated for SnS nanowires was higher...
than $10^5$ cm$^{-1}$ in the wavelength range from 400 nm to 800 nm (See Fig. 4(a)).

To determine the energy band gap, $E_g$, and the type of optical transition responsible for this intense optical absorption, the absorption spectrum was analyzed using the equation for the near-edge absorption \[ (\alpha h\nu)^n = A(h\nu - E_g) \] (3)

Where $A$ is a constant and $n$ characterizes the transition process. We can see $n=2$ and $2/3$ for direct allowed and forbidden transitions, respectively, and $n=1/2$ and $1/3$ for indirect allowed and forbidden transitions, respectively.

Figure 4(b) shows curves of $(\alpha h\nu)^2$ versus $h\nu$ of the SnS nanowires. The straight line had been made a good fit with the curve in the higher energy range above the absorption edge, which indicates a direct optical transition near the absorption edge. From Fig. 4, the direct energy gap $E_g$ of the sample has been calculated as 1.46 eV, which is higher than the value of SnS bulk or film. The nanowires' diameter 50 nm is far greater than the Bohr radius, therefore, and it can be suggested the increased band gap values do not exhibit quantum size effects [17,21,22]. The energy band gap at 1.46 eV detected in our study may be attributed to the surface effect of the carriers in the semiconductor nanowires. The lattice distortion inducing a smaller lattice constant or surface lattice defects will lead to a size dependent enlargement of the band gap, which results in a blue shift for the absorbance onset, as observed in this work.

In order to study the photovoltaic behavior, a grating Al electrode about 200 nm was evaporated on the SnS nanowires film. The current-voltage ($I-V$) characteristics of the SnS nanowires sandwiched between ITO and Al contacts, in the dark and under 100 mW/cm$^2$ AM1.5 solar illuminations are shown in Fig. 5. These measurements show that the SnS nanowires act as photoconductors. There is negligible photovoltaic behavior,
indicating the absence of any significant Schottky barrier formed at the nanowires/electrode interface. This result indicated that the rectifying behavior was not coming from the interface contacts, or the rectifying behavior between the nanowires/electrode interfaces is very weak and can be ignored. So, the p-n junction photovoltaic cells with homojunction or heterojunction are ongoing.

**Conclusion**

The low-toxicity SnS nanowire arrays have been successfully synthesized using the catalyst-assistant chemical vapor deposition methods. SEM and FE-SEM results indicated the diameter and morphology changed with the preparation conditions. And the best conditions indicated the diameter and morphology changed by the preparation temperatures. And the best conditions indicated the diameter and morphology changed with the preparation conditions. The as-prepared SnS nanowires have a diameter of about 50 nm and length up to several micrometer or longer. The XRD pattern indicates the nanowires are composed of SnS phase and have a highly preferential (101) orientation. According to the transmission spectra and the reflection spectra, we can calculate the properties of synthesized SnS nanowires which exhibit strong absorption in the visible and near-infrared spectral region. The direct energy gap $E_g$ of the SnS nanowires has been calculated as 1.46 eV, and the experimental optical band gap value is the evidence for the lattice distortion of the SnS nanowires. Other properties of the SnS nanowires will be coming up and the SnS combined nanodevice will be studied rapidly. The current–voltage ($I-V$) characteristics of the SnS nanowires sandwiched between ITO and Al contacts have also been studied.

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**References**

[1] N. K. Reddy, Y. B. Hahn, M. Devika, H. R. Sumana and K. R. Gunasekhar, “Temperature-dependent structural and optical properties of SnS films”, J. Appl. Phys. 101, 093522-093528 (2007).
[2] G. H. Yue, D. L. Peng and P. X. Yan, “Structure and optical properties of SnS thin film prepared by pulse electrodeposition”, J. Alloys Compd. 468(1-2), 254-257 (2009).
[3] C. W. Wolfe, “Physical Properties of Semiconductors”, Prentice-Hall, Englewood Cliffs, NJ (1989).
[4] M. Devika, N. K. Reddy and K. Ramesh, “Low Resistive Micrometer-Thick SnS:Ag Films for Optoelectronic Applications”, J. Electrochem. Soc. 153(8), G727-G733 (2006).
[5] A. Ghazali, Z. Zainal, M. Z. Hussein and A. Kassim, “Cathodic electrodeposition of SnS in the presence of EDTA in aqueous media”, Sol. Energ. Mat. Sol. C. 55(3), 237-249 (1998).
[6] G. H. Yue and W. Wang, “The effect of anneal temperature on physical properties of SnS films”, J. Alloy. Compd. 474(1-2), 445-449 (2009).
[7] M. Parenteau and C. Carlone, “Influence of temperature and pressure on the electronic transitions in SnS and SnSe semiconductors”, Phys. Rev. B 41(8), 5227-5234 (1990).
[8] B. Subramanian, C. Sanjeeviraj and M. Jayachandran, Photoelectrochemical characteristics of brush plated tin sulfide thin films”, Sol. Energ. Mat. Sol. C. 79(1), 57-65 (2003).
[9] B. Thangaraju and P. Kaliannan, “Spray pyrolytic deposition and characterization of SnS and SnS2 thin films”, J. Phys. D: Appl. Phys. 33, 1054-1059 (2000).
[10] L. S. Price, I. P. Parkin and M. N. Field, “Atmospheric pressure chemical vapour deposition of tin(II) sulfide films on glass substrates from Bun3SnO2CCF3 with hydrogen sulfide”, J. Mater. Chem. 10(2), 527-530 (2000).
[11] A. Tanusevski, “Optical and photoelectric properties of SnS thin films prepared by chemical bath deposition”, Semicond. Sci. Technol. 18, 501-505 (2003).
[12] D. S. Koktyshev, J. R. McBride and S. J. Rosenthal, “Synthesis of SnS nanocrystals by the solvothermal decomposition of a single source precursor”, Nanoscale Res. Lett. 2, 144-148 (2007).
[13] Y. K. Liu, D. D. Hou and G. H. Wang, “Synthesis and characterization of SnS nanowires in cetyltrimethylammoniumbromide (CTAB) aqueous solution”, Chem. Phys. Lett. 379(1-2), 67-73 (2003).
253(23), 9259-9266 (2007). http://dx.doi.org/10.1016/j.apsusc.2007.05.053

[15] S. K. Panda, A. Datta, A. Dev, S. Gorai and S. Chaudhuri, “Surfactant-Assisted Synthesis of SnS Nanowires Grown on Tin Foils”, Cryst. Growth Des. 6(9), 2177-2181 (2006). http://dx.doi.org/10.1021/cg0602156

[16] J. Kang, J. Park and D. Kim, “Superior rate capabilities of SnS nanosheet electrodes for Li ion batteries”, Electrochem. Commun. 12(2), 307-310 (2010). http://dx.doi.org/10.1016/j.elecom.2009.12.025

[17] G. H. Yue, L. S. Wang, X. Wang, Y. Z. Chen and D. L. Peng, “Characterization and Optical Properties of the Single Crystalline SnS Nanowire Arrays”, Nanoscale Res. Lett. 4, 359-363 (2009). http://dx.doi.org/10.1007/s11671-009-9253-6

[18] J. Z. Liu, P. X. Yan, G. H. Yue, J. B. Chang, R. F. Zhuo and D. M. Qu, “Controllable synthesis of undoped/Cd-doped ZnO nanostructures”, Mater. Lett. 60(25-26), 3122-3125 (2006). http://dx.doi.org/10.1016/j.matlet.2006.02.056

[19] G. H. Yue, Y. D. Lin and X. Wen, “Synthesis and characterization of the SnS nanowires via chemical vapor deposition”, Adv. Mater. 17(1), 87-91 (2005). http://dx.doi.org/10.1007/a00339-011-6560-4

[20] D. Avellaneda, G. Delgado, M. T. S. Nair and P. K. Nair, “Structural and chemical transformations in SnS thin films used in chemically deposited photovoltaic cells”, Thin Solid Films 515(15), 5771-5776 (2007). http://dx.doi.org/10.1016/j.tsf.2006.12.078

[21] H. Tung, G. Y. Xu, L. Q. Weng, L. J. Pan and L. Wang, “Luminescence and photophysical properties of colloidal ZnS nanoparticles”, Acta Mater. 52(6), 1489-1494 (2004). http://dx.doi.org/10.1016/j.actamat.2003.11.030

[22] T. Takagahara, “Effects of dielectric confinement and electron-hole exchange interaction on excitonic states in semiconductor quantum dots”, Phys. Rev. B 47(8), 4569-4584 (1993). http://dx.doi.org/10.1103/PhysRevB.47.4569
Large-scale Patterning of Hydrophobic Silicon Nanostructure Arrays Fabricated by Dual Lithography and Deep Reactive Ion Etching

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Abstract: We describe a simple but efficient technique to fabricate large-scale arrays of highly ordered silicon nanostructures. By coupling dual lithography using light of 351.1 nm wavelength with deep reactive ion etching (DRIE), silicon nanostructures of excellent regularity and uniform coverage were achieved. The proposed nanofabrication method not only simplified the nanofabrication process but also produced high-aspect-ratio (higher than 15) nanostructures. The scalloping problem was also controlled by regulating DRIE parameters. The process is rapid, cheap, examined to optimize the fabrication process, and has the potential to be scaled up to large areas. The contact angle of a water droplet atop the surface is larger than 150°. Moreover, by coupling black silicon process with DRIE-based microfabrication, three-dimensional nano/nano dual-scale structures which show robust and stable hydrophobicity have been achieved. This process opens new application possibilities in optical, photoelectric, microelectronic, catalytic and biomedical applications.

Keywords: Hydrophobic; Nanostructure arrays; DRIE; High-aspect-ratio

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Introduction

Fabrication of high density array of high-aspect-ratio nanostructures, especially fabrication of nanopillars, has attracted considerable attention as of late. Nanopillars have already been utilized in wide range of applications such as atom diffraction [1], surface plasmon sensor arrays [2], separation of DNA molecules [3], and nanoimprint lithography fabrication.

Usually, nanoscale patterning techniques are involved in the fabrication of nanostructures. Although the standard and conventional electron beam (e-beam) lithography and focused ion beam (FIB) lithography [4] have high resolution and can produce nanoscale structures, both technologies have the disadvantages of low throughput and being expensive. Nanoimprint lithography (NIL) [5] replicates patterns in a parallel fashion, and have the advantages of high speed, low cost, large pattern area, and high pattern density, but it still needs a master mold manufactured by means of e-beam or x-ray lithography [6]. Interference lithography is an attractive method for fabricating nanostructures, as it offers several advantages including a large exposure area and high spatial-phase coherence. However, the spatial resolution is limited by the light source. Shorter wavelength lasers and immersion techniques have been used to fabricate nanostructures [7, 8], but these two methods require complex sources and have limited exposure area.

Because of the drawbacks of aforementioned techniques, a great deal of efforts has been made to develop commercially viable technologies for nanoscale lithog-
raphy. The most commonly used is nanosphere lithography (NSL) [9-13], which has been demonstrated as an efficient way to produce nanoscale patterns over a large area with high throughput and low cost. Nanospheres can be introduced onto substrates by spin-coating [14] or created during annealing a thin metallic (Au) layer [15], or linked on wafers using self-assembling [16]. However, the shapes and the sizes of the nanoparticles created by these techniques are not as well defined as the features created by using traditional lithography, and the placing of the nanoparticles is also inexact. At the same time, the self-assembly can be very time consuming [17] and long-ranged order is still not achieved [18].

In order to overcome the drawbacks of above techniques, we present a low-cost approach to fabricate high-aspect-ratio silicon nanostructures by dual lithography and high density plasma reactive ion etching (DRIE), achieving high density uniform coverage of nanostructures over entire 4 inch wafers. The size and space between nanopillars were controlled using dual lithography. This method is fast and cheap, and could be combined with microstructures. Most importantly, it has potential to be scaled up for large areas. Eventually, nano/nano dual-scal hierarchical structures was fabricated by coupling black silicon process with DRIE-based microfabrication, and contact angle measurement and tilting test results show that the fabricated silicon surfaces were superhydrophobic, and the contact angles are all larger than 150°.

**Nanostructures patterned by dual lithography**

The pattern size of nanopillars and nanotrenches in a photomask was designed as 1 µm×1 µm and 1 µm×1 mm, which was the minimum size required for successful patternization using photoresist and a contact aligner (MA6/BA6, Karl SUSS company Ltd., Germany).

Figure 1 shows the overall fabrication process of making silicon nanostructures by dual lithography. The fabrication process started with a 4 inch polished silicon wafer which had been cleaned with a Piranha solution (H₂SO₄:H₂O₂, 4:1 by volume) and dehydrated for 10 min at 150°C. Cr (150 nm) was deposited on the silicon surface by a sputtering system. AZ5214E photoresist was then spin-coated at 3000 rpm for 1 min, which resulted in about 800 nm film thickness. After the spin-coating, a soft-bake was done at 110°C for 1 min on a hot plate (Fig. 1(a)).

The substrate was then exposed using microlithography and examined for the estimated time necessary to obtain the appropriate exposure dose, and developed by MF700 developer for 24 s. After the development, the substrate was rinsed with deionized water and blown dry with N₂ gas followed by a 1 min hard-bake at 120°C on a hot plate. The patterned photoresist was scanned by microscope to assess successful development. Finally, the Cr was etched using wet etchant and the first photoresist served as the etching mask, as shown in Fig. 1(b). These nanostructures with linewidth 1 µm also served as a fiducial pattern for subsequent lithography steps.

The first photoresist was then removed with oxygen plasma ashing, followed by the second photoresist spin-coated with the same parameters (Fig. 1(c)). Then with the same photomask, the sample was aligned and exposed at a relative offset to the fiducial pattern. The offset may be several hundred nanometers, bigger than 351.1 nm which is the wavelength of UV light, so the width of unprotected by photoresist is less than 649 nm, as shown in Fig. 1(d).

After the second photoresist developed and a hard-bake on a hot plate, the unprotected Cr was etched using the second photoresist as the etching mask. The photoresist was removed with oxygen plasma ashing, as shown in Fig. 1(e) and Fig. 1(f). Finally, the silicon substrate was then etched by DRIE using the patterned Cr as an etch mask. After the DRIE, the remaining Cr was removed and the sample was cleaned with the Piranha solution.

![Fig. 1](image-url)  
**Fig. 1** Dual lithography process of nanostructures patterned. (a) Sputter 150 nm Cr and photoresist coating. (b) First lithography and Cr etching. (c) Second photoresist coating. (d) Second lithography. (e) Cr etching. (f) Photoresist removal and DRIE.
Results and discussion

Figure 2 shows SEM images of the fabricated nanopillar or nanotrench arrays of varying heights. The fabricated nanopillars are measured to be about 0.67 µm and 0.4 µm in width, and 1.96 µm and 4.7 µm in height, respectively. The aspect ratio of the nanopillars is more than 3 and 11, as shown in Fig. 2(a) and (b). Figure 2(c) and (d) show the fabricated nanotrenches, the width are about 0.38 µm and 0.66 µm, their height are about 19.6 µm and 4.3 µm, respectively. The aspect ratio for the nanotrenches is 50 and 6. However, nanometre scale scallops were formed on the sidewalls of the nanostructures due to the etching and passivation alternating in the DRIE process, as shown in Fig. 2(b) and (d), the peak-to-valley height of scallop is over 87 nm. Although the nanostructures had been achieved by the initially chosen process condition, many studies have shown that the profile affects the scattering loss in optical devices, the electrical performances and flow resistance in fluidic devices [19-22], it is undesirable in some typical applications.

Control of profile roughness

Although nanostructures had been achieved using an inductively coupled plasma (ICP) etcher with SF$_6$+O$_2$ etch chemistry and C$_4$F$_8$ passivation, the scallops affect the performance of nanostructures, as mentioned before. Table 1 shows the parameters of normal DRIE process which had been used to fabricate nanostructures in Fig. 2.

| Etch                  | Passivate               |
|-----------------------|-------------------------|
| SF$_6$ flow rate (sccm)| C$_4$F$_8$ flow rate (sccm) |
| 130                   | 85                      |
| O$_2$ flow rate (sccm) | 13                      |
| 13                    | Cycle time (s)          |
| 600                   | 11                      |
| Platen power (w)      | Pressure (mTorr)        |
| 12                    | 22                      |
| 12                    |                         |
| 11                    |                         |

Table 1 Study of the DRIE process parameters for nanostructures.

It has been proven that several parameters, such as RF power, pressure, and gas mixture, influence the sidewall profile of nanostructures. In order to control the nanoscalloping effect, several parameters had been modified based on plenty of experiments. The etching time was decreased from 11 s to 8 s, but the passivation time was increased from 7 s to 10 s, while the other parameters are fixed. Although the etching rate became much slower than before, the roughness of sidewall profiles was improved pronouncedly, as shown in Fig. 3, decreased from tens of nanometers to several nanometers. The result shows that the roughness of sidewall can be diminished by regulating the relative duration of etch time against deposition. Maybe the total number of etch cycles is responsible for the sidewall profile control, as described in reference [23].
Nano/nano dual-scale hierarchical structures fabrication

Superhydrophobic surface has attracted a considerable amount of attention in recent years. It is suggested that dual-scale roughness patterns at different length is the key factor leading to dramatic superhydrophobicity [24-27]. Highly dense arrays of nanostructures have been successful fabricated by DRIE black silicon [28,29]. However, the uniformity and reproducibility are often more important in some applications. By coupling the dual lithography, DRIE and black silicon, we have developed an effective fabrication process for nano/nano dual-scale hierarchical structures.

Normal DRIE or black silicon is not efficient enough to fabricate dual-scale nanostructures, such as nano/nano dual-scal hierarchical structures. A hybrid etching process between the normal DRIE and black silicon format is required. After the silicon sample was patterned using the aforementioned multilevel lithography, parameters of DRIE including gas flows, coil power, platen power and total etching cycles were adjusted, as listed in Table 2. The perfect hybrid etching regime can be achieved by regulating the gas flow of SF$_6$ and C$_4$F$_8$, while keeping other parameters fixed. Figure 4 shows the SEM images of nano/nano dual-scale hierarchical structures fabricated by the hybrid etching process.

Table 2 Study of the DRIE process parameters for nano/nano dual-scal hierarchical structures.

| Etch                  | Passivate           |
|-----------------------|---------------------|
| SF$_6$ flow rate (sccm)| 35 C$_4$F$_8$ flow rate (sccm) | 50 |
| Coil power (w)        | 800                | 800 |
| Platen power (w)      | 8                  | 8   |
| Cycle time (s)        | 4                  | 5   |
| Pressure (mTorr)      | 22                 |     |
| Total cycles          | 60 (9 min)         |     |

Surface characterization results

Contact angle (CA) and contact angle hysteresis (CAH) of the fabricated nano structure arrays with various geometric parameters were measured, and the results are listed in Table 3. It is clearly seen that all the contact angles are larger than 150° and quite consistent, and CAH of them are basically less than 4°. Figure 5 shows CA measurements of the nano structure arrays and nano/nano dual-scal hierarchical structures. It is obvious that the as-prepared silicon surfaces demonstrate high contact angles and low contact angle hysteresis.

Table 3 Contact angle and contact angle hysteresis measurement results

| sample                              | CA (°) | CAH (°) |
|-------------------------------------|--------|---------|
| Nanotrench arrays                   | 149.7  | 3.6     |
| Nanopillar arrays                   | 151.4  | 3.2     |
| Nano/nano dual-scal hierarchical arrays | 154.1  | 2.8     |

To further investigate the hydrophobicity of the fabricated surface, tilting test was implemented and recorded by optical contact angle measurement device. Figure 6 shows two snapped picture of tilting test. It
Conclusions

Highly dense arrays of high-aspect-ratio silicon nanopillars have been fabricated using the dual lithography and DRIE. It has also been demonstrated that DRIE together with dual lithography simplifies the fabrication process, and makes it possible to control the size of nanostructures. The DRIE process parameters had also been adjusted to control the roughness of the sidewall profiles of nanostructure. The subsequent simple method of nano/nano dual-scale hierarchical structures’ fabrication was also introduced. Contact angle measurement and tilting test results show that the fabricated silicon surfaces were superhydrophobic, and the contact angles are all larger than 150°. This process can also be used to fabricate more complex periodic nanostructures with smooth sidewalls over a large area, it has practical advantages and new application possibilities in optical, photoelectric, microelectronic, catalytic, and biomedical applications.

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References

[1] G. Gronniger, B. Barwick and H. Batelaana, “Electron diffraction from free-standing, metal-coated transmission gratings”, Appl. Phys. Lett. 87, 124104-124106 (2005). http://dx.doi.org/10.1063/1.2053347
[2] A. D. Ormonde, E. C. Hicks, J. Castillo and R. P. V. Duyne, “Nanosphere Lithography: Fabrication of Large-Area Ag Nanoparticle Arrays by Convective Self-Assembly and Their Characterization by Scanning UV-Visible Extinction Spectroscopy”, Langmuir 201(16), 6927-6931 (2004). http://dx.doi.org/10.1021/la0494674
[3] Y. C. Chan, Y. K. Lee and Y. Zohar, “High-throughput design and fabrication of an integrated microsystem with high aspect-ratio sub-micron pillar arrays for free-solution micro capillary electrophoresis”, J. Micromech. Microeng. 16, 699 (2006). http://dx.doi.org/10.1088/0960-1317/16/4/005
[4] J. Taniguchi, K. Koga, Y. Kogo and I. Miyamoto, “Rapid and three-dimensional nanoimprint template fabrication technology using focused ion beam lithography”, Microelectron. Eng. 83(4-9), 940-943 (2006). http://dx.doi.org/10.1016/j.mee.2006.01.101
[5] L. J. Guo, “Nanoimprint Lithography: Methods and Material Requirements”, Adv. Mater. 19(4), 495-513 (2007). http://dx.doi.org/10.1002/adma.200600882
[6] G. Sun, T. Gao, X. Zhao and H. Zhang, “Fabrication of micro/nano dual-scale structures by improved deep reactive ion etching”, J. Micromech. Microeng. 20, 075028 (2010). http://dx.doi.org/10.1088/0960-1317/20/7/075028

[7] T. M. Bloomstein, M. F. Marchant, S. Deneault, D. E. Hardy and M. Rothschild, “22-nm immersion interference lithography”, Opt. Express 14(14), 6434-6443 (2006). http://dx.doi.org/10.1364/0E.14.006434

[8] H. H. Solak, C. David, J. Gobrecht, V. Golovkina, F. Cerrina and S. O. Kim, “Sub-50 nm period patterns with EUV interference lithography” Microelectron. Eng. 67, 56-62 (2003). http://dx.doi.org/10.1016/S0167-9317(03)00059-5

[9] C. L. Haynes and R. P. Van Duyne, “Nanosphere Lithography: A Versatile Nanofabrication Tool for Studies of Size-Dependent Nanoparticle Optics”, J. Phys. Chem. B 105(24), 5599–5611 (2001).

[10] D. Csontos and H. Q. Xu, “Effects of boundary roughness on the conductance of quantum wires”, Appl. Phys. Lett. 77, 2364-2366 (2000). http://dx.doi.org/10.1063/1.1311606

[11] A. V. Whitney, B. D. Myers and R. P. Van Duyne, “Sub-100 nm Triangular Nanopores Fabricated with the Reactive Ion Etching Variant of Nanosphere Lithography and Angle-Resolved Nanosphere Lithography”, Nano Lett. 4(8), 1507-1511 (2004). http://dx.doi.org/10.1021/nl049345w

[12] N. Nagy, E. A. Pap, E. Horv’ath, J. Volk, I. B’arsony, A. De’ak and Z. H’orvolgyi, “Large area self-assembled masking for photonic applications”, Appl. Phys. Lett. 89, 063104-063106 (2006). http://dx.doi.org/10.1063/1.2335668

[13] A. Sinitskii, S. Neumeier, J. Nelles, M. Fischer and U. Simon, “Ordered arrays of silicon pillars with controlled height and aspect ratio” Nanotechnology 18, 305307 (2007). http://dx.doi.org/10.1088/0957-4484/18/30/305307

[14] C. T. Black, K. W. Guarini, K. R. Milkove, S. M. Baker, T. P. Russell and M. T. Tuominen, “Integration of self-assembled diblock copolymers for semiconductor capacitor fabrication”, Appl. Phys. Lett. 79, 409-411 (2001). http://dx.doi.org/10.1063/1.1383805

[15] B. J. Y. Tan, C. H. Sow, T. S. Koh, K. C. Chin, A. T. S. Wee and C. K. Ong, “Fabrication of Size-Tunable Gold Nanoparticles Array with Nanosphere Lithography, Reactive Ion Etching, and Thermal Annealing”, J. Phys. Chem. B 109(22), 11190-11199 (2005). http://dx.doi.org/10.1021/jp045172n

[16] S. S. Mark, M. Bergkvist, P. Bhatnagar, C. Welch, A. L. Goodyear, X. Yang, E. R. Angert and C. A. Batt, “Thin film processing using S-layer proteins: Biotemplated assembly of colloidal gold etch masks for fabrication of silicon nanopillar arrays”, Colloids Surf. B 57(2), 161-173 (2007). http://dx.doi.org/10.1016/j.colsurfb.2007.01.015

[17] V. Gowrishankar, N. Miller, M. D. McGehee, M. J. Misner, D. Y. Ryu, T. P. Russell, E. Drockenmuller and C. J. Hawker, “Fabrication of densely packed, well-ordered, high-aspect-ratio silicon nanopillars over large areas using block copolymer lithography”, Thin Solid Films 513(1-2), 289-294 (2006). http://dx.doi.org/10.1016/j.tsf.2006.01.064
Influence of an Electronic Field on the GMI Effect of Fe-based Nanocrystalline Microwire

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Abstract: In this work, a Fe-based nanocrystalline microwire of 20 mm in length and 25 µm in diameter was placed in the center of a 316 stainless steel pipe. The pipe was 500 µm in diameter and a little shorter than the microwire. A series of voltages were applied on the pipe to study the influence of the electrical field on the Giant-Magneto-Impedance (GMI) effect of the microwire. Experimental results showed that the electronic field between the wire and the pipe reduced the hysteresis of the GMI effect. The results were explained based on equivalent circuit and eddy current consumptions analysis.

Keywords: GMI; Eddy consumptions; Electronic field; Equivalent circuit

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Introduction

A giant change of alternating current (AC) impedance with respect to an external direct current (DC) magnetic field was discovered by Mohri in 1992 [1]. This phenomenon was called magneto-inductance effect at that time. Two years later, Machado found that the AC resistance of ferromagnetic material was also changed obviously with the change of the applied external field [2]. This change was called AC magneto-resistance (MR) effect. Then, Panina et al [3] thought that both the magneto-inductance effect and AC magneto-resistance effect concerned on same physical principle. This phenomenon was called Giant-Magneto-Impedance (GMI) effect. Because GMI effect (up to 500%/Oe) [4] is more sensitive than other magnetic sensors, such as tunnel magneto-resistance (<3%/Oe) [5], it has attracted much interest to develop magnetic sensors. Many effects such as suitable thermal treatments, development of new soft magnetic materials and so on, had been done to improve the sensitivity of GMI sensing element [6-9].

Previous study on GMI effect was focused on the influence of magnetic fields on the GMI ratio [10, 11]. Only few works was related to the influence of electronic field on the GMI effect. However, not only magnetic fields but also electronic fields are distributed in the practical application environments. Therefore, it is meaningful to study how the electrical fields affect the GMI effect.

In this work, we aimed at establishing a structure to study the influence of the electronic fields on the GMI effect. GMI ratio was measured with and without the applied electronic field. Through comparing the experimental results, it was found that the applied electronic fields can reduce the hysteresis of the GMI effect. The results were explained based on equivalent circuit analysis and eddy current consumptions.

Experiment Details

As shown in Fig. 1, a Fe73.5Cu11Nb3Si13.5B9 microwire of 20 mm in length and 25 µm in diameter was
placed in the center of 316 stainless steel pipe. The Fe_{73.5}Cu_{13.5}Si_{13.5}B_{9} microwire is annealed at 550°C and very fine nanocrystalline bcc-FeSi grains are homogeneously formed in the amorphous matrix [8]. The pipe was 500 µm in diameter and a little shorter than the wire. A series of voltages were applied on the metal pipe. The MI effect of the microwire was carried out using a precision impedance analyzer (HP4294 A). The root-mean-square (rms) value of the AC driving current was kept constant at 10 mA, and its frequency was varied from 40 Hz to 25 MHz. The GMI ratio profiles were defined as,

\[ \frac{\Delta Z}{Z} = \frac{Z(H_{\text{ext}}) - Z(H_{\text{max}})}{Z(H_{\text{max}})} \times 100\% \]  

(1)

where \( Z(H_{\text{max}}) \) was the impedance value measured at the maximum field of 73 Oe. The external magnetic field was provided by a pair of Helmholtz coils. The sign of increasing GMI curves (\( H_{\text{ext}} \) changed from −73 Oe to 73 Oe) were “up” and the sign of decreasing GMI curves (\( H_{\text{ext}} \) changed from 73 Oe to −73 Oe) were “down”.

Firstly, the GMI ratio of the microwire was measured without applying a voltage on the metal pipe. Then the ratio was measured with different voltages applied on the metal pipe.

![Fig. 1 The measurement system.](image)

**Results and discussion**

Figure 2(a) and (b) show the GMI profiles of the microwire tested at 21 MHz, where \( V_{nc} \) and \( V_{3V} \) mean no voltage and a voltage of 3 V was applied on the metal pipe, respectively. It can be seen from Fig. 2(a) that all of the GMI profiles showed a single peak characteristic, which means the microwire has no defined circumferential anisotropy.

In addition, it can be seen clearly that there is a hysteresis for increasing and decreasing fields in Fig. 2(b) [12, 13]. The magnitude of the GMI for an increasing field is smaller than that for a decreasing field. When there is no voltage applied on the pipe, the difference of maximum GMI ratio for increasing and decreasing fields is 40%. After a voltage was applied on the pipe, the difference of maximum GMI ratio for increasing and decreasing fields is only 30%. Hence, it can be concluded that the hysteresis of GMI profile is reduced when a voltage was applied on the metal pipe.

![Fig. 2 (a) GMI ratio variations as a function of magnetic field measured at 21 MHz with and without voltage applied the pipe. (b) The enlarging of the peak in (a).](image)

Figure 3 shows that the GMI ratio of the microwire changes as a function of external magnetic fields with different voltage applied on the pipe tested at 15 MHz. It can be seen from Fig. 3 that no much difference was found in GMI ratios with the applied voltage of 0 V, 3 V, 5 V and 10 V. The difference of maximum GMI ratio with respect to different applied voltages is very small.

![Fig. 3 GMI ratio variations as a function of magnetic field measured at 15 MHz with different voltage applied.](image)
small. The possible causes of this phenomenon will be analyzed hereinafter.

Electromagnetic interaction will affect the impedance as long as there is a ferromagnetic material around a conductor [14]. So the reduction of GMI hysteresis may be caused by the electromagnetic interaction between the microwire and the pipe. An equivalent circuit, as shown in Fig. 4, was used to analyze the experimental results. In the equivalent circuit, the microwire and the pipe were evenly divided into n sections. Here, $R_p$ and $L_p$ are the resistance and inductance of each section of the stainless steel pipe. $R$ and $L$ are the resistance and inductance of each section of the microwire. $Z_r$ and $Cap$ are the radial impedance and capacitance of each section, respectively.

When no voltage was applied on the pipe ($V_{DC}$ did not exist), the current flowed in the equivalent circuit was shown as the black thin arrows. The value of voltage drops successively on each section. Then the current $I_{section,n}$, which flowed in each section of $R_p$, $L_p$, $Z_r$ and $Cap$ was the same. Ignoring the phase difference of each $I_{section,n}$, the adjacent $I_{section,n}$ in each $Cap$ were just opposite to each other. So there was almost no current flowing through the $Cap$ and $Z_r$ from the microwire to the pipe except for the two ends of the structure. The total effect of $Cap$ was every weak in this situation.

When a voltage was applied on the pipe, the current in the equivalent circuit flowed via the red thick arrows as shown in Fig. 4. An AC current flowed through all of the $Cap$ and $Z_r$ from every section of the microwire to the pipe. Then, there is a relatively strong effect of capacitance. Since the capacitances always hinder the change of the voltage on the microwire, they would hinder the change of the impedance [15]. It can be believed that energy stored in the capacitance of $Cap$ will compensate the energy consumption in the microwire. Hence, the hysteresis of the GMI was reduced.

To study the influence of the frequency on the reduction of GMI hysteresis, the maximum GMI spectrum is shown in Fig. 5. The hysteresis of GMI profile increased with the frequency increasing. However, the hysteresis became smaller in all frequency range when a voltage was applied on the pipe. It is well known that the eddy consumption increases with the frequency. So the reduction of GMI hysteresis with the applied voltage maybe is relative to the overcoming of eddy consumption.

Figure 6 shows the cross-section of the microwire and the top view of the microwire’s surface. When an AC current, $I = I_m \sin \omega t$, flowed through the microwire, it would generate a circumferential magnetic flux density $B$. At the same time, there was a voltage decrease on the microwire from left end to right end. According to Lenz’s law, an induced electromotive force always gave rise to a current whose magnetic field $B'$ opposes the original change in magnetic flux $B$. The direction of the induced field $B'$ was circumferential, but opposite to $B$ when the amplitude of the current $I$ increased, in first ($0-\pi/2$) and third ($\pi/2-\pi$) quarter of the cycle. In contrast, the direction of the induced field $B'$ was circumferential, but parallel to $B$ when the amplitude of the current $I$ decreased, in second ($\pi/2-\pi$) and forth ($3\pi/2-2\pi$) quarter of the cycle. The eddy current consumptions were mainly relative to the $B'$.

When a voltage was applied on the metal pipe, a mutative electric field $E$ was distributed between the microwire and metal pipe. An AC radial conduction current $J_f$ will flow through the microwire to the metal pipe based on the above-mentioned equivalent circuit analysis. If we ignore the displace current, the current $J_f$ will induce a magnetic field $B''$ according to Maxwell equation (2).

$$\nabla \times \vec{H} = \vec{J}_f$$

(2)
Fig. 5 GMI spectrum of the microwire with and without voltage applied the pipe.

In first (0-\(\pi/2\)) quarter of the cycle, the direction of \(J_f\) was from the microwire to the pipe. Then the direction of \(B''\) can be confirmed by right-hand screw rule. It can be seen from Fig. 6 that the longitudinal component of \(B''\) was counteracted by its adjacent \(B''\). The circumferential component of \(B''\) has a total effect of \(B'''\). Since the amplitude of the voltage on wire decreased from left end to right end, then the circumferential component of \(B''\) at left part was larger than that at right part. Therefore, the direction of \(B'''\) was in circumferential and parallel to \(B\) in first (0-\(\pi/2\)) quarter of the cycle. Then the direction of \(B'''\) was in circumferential and opposite to \(B'\) in first (0-\(\pi/2\)) quarter of the cycle.

It is easy to analyze the whole cycle in the same way. In the whole cycle, the direction of \(B'''\) was in circumferential direction and parallel to \(B\) when the amplitude of \(I\) increased. And \(B'''\) was in circumferential direction and opposite to \(B\) when the amplitude of \(I\) decreased. So the direction of \(B'''\) was always against to that of \(B'\). Then the eddy current energy consumptions were decreased.

A conclusion can be made that the structure with an applied voltage decreased the eddy current consumptions partly. This conclusion agrees with the experimental phenomenon shown in Fig. 5. So it is reasonable to believe that the reduction of the GMI hysteresis was due to the decrease of the eddy current consumptions. Since the value of voltage applied on the pipe didn’t influence \(J_f\), the effects of different applied voltages were similar.

Conclusions

The GMI hysteresis was reduced when the microwire was placed in the center of a metal pipe on which a voltage was applied. A radial capacitance distributed between the microwire and the pipe hindered the energy change. When a DC voltage was applied on the pipe, the effect of the capacitance was strong enough to reduce the GMI hysteresis of the microwire. In detail, the corresponding magnetic flux density \(B'''\) induced by the radial mutative electric field \(E\) which gave rise to conductive current \(J_f\) fights against the \(B'\) which was just relative to the eddy current energy consumptions. So the eddy current energy consumptions were decreased. The structure is meaningful to reduce the hysteresis of the GMI sensors.

References

[1] K. Mohri, K. Kawashima, T. Kohzawa, Y. Yoshida and L. V. Panina, “Magneto-inductive effect (MI effect) in amorphous wires”, IEEE. Trans. Magn. 28(5), 3150-3152 (1992). http://dx.doi.org/10.1109/20.179741

[2] F. L. A. Machado and B. L. da Silva, “Giant ac magnetoresistance in the soft ferromagnet Co\(_{70.4}\)Fe\(_{4.6}\)Si\(_{15}\)B\(_{10}\)”, J. Appl. Phys. 75, 6363-6365 (1994). http://dx.doi.org/10.1063/1.356919

[3] L. V. Panina and K. Mohri, “Magneto-impedance effect in amorphous wires”, Appl. Phys. Lett. 65, 1189-1191 (1994). http://dx.doi.org/10.1063/1.112104

[4] D. Garcia, V. Raposo, O. Montero and J. I. Inigue, “Influence of magnetostriction constant on magnetoimpedance-requency dependence”, Sens. Acta. A 129(1-2), 277-230 (2006). http://dx.doi.org/10.1016/j.sna.2005.11.046

[5] X. H. Chen and P. P. Freitas, “Magnetic Tunnel Junction Based on MgO Barrier Prepared by Natural Oxidation and Directly Sputtering Depositio”, Nano-Micro Lett. 4(1), 25-29 (2012). http://dx.doi.org/10.3786/nml.v4i1.p25-29
[6] S. Atalay, H. I. Adiguzel and O. Kamer, “Effect of different heat treatments on magnetoelastic properties of Fe-based amorphous wire”, Mater. Sci. Eng A 304, 495-498 (2001). http://dx.doi.org/10.1016/S0921-5093(00)01502-1

[7] M. H. Phan., H. X. Peng and M. R. Wisnom, “Effect of annealing temperature on permeability and giant magneto-impedance of Fe-based amorphous ribbon”, Sen. Act. A. 129(1-2), 62-65 (2006). http://dx.doi.org/10.1016/j.sna.2005.09.050

[8] H. Q. Guo and H. Dragon, “Influence of nanocrystallization on the evolution of domain patterns and the magnetoimpedance effect in amorphous Fe_{73.5}Cu_{11}Nb_{3}Si_{13.5}B_{9} ribbons”, J. Appl. Phys. 89, 514-510 (2001). http://dx.doi.org/10.1063/1.1331649

[9] J. Hu, H. M. Qin and Y. Zhang, “Magnetoimpedance effect in manganite La_{2/3}Ba_{1/3}MnO_{3} at various temperatures”, J. Magn. Magn. Mater. 261(1-2), 105-111 (2003). http://dx.doi.org/10.1016/S0304-8853(02)01430-0

[10] M. H. Phan, S. C. Yu, C. G. Kim and M. Vazquez, “Origin of asymmetrical magnetoimpedance in a Co-based amorphous microwire due to dc bias current”, Appl. Phys. Lett. 83, 2871-2873 (2003). http://dx.doi.org/10.1063/1.1616971

[11] D. P. Wakhnovskiy, L. V. Panina and D. J. Mapps, “Asymmetrical magnetoimpedance in as-cast CoFeSiB amorphous wires due to ac bias”, Appl. Phys. Lett. 77, 121-123 (2000). http://dx.doi.org/10.1063/1.126896

[12] G. V. Kurlyandskaya, J. M. Barandiara and J. L. Munoz, “Frequency dependence of giant magnetoimpedance effect in CuBe/CoFeNi plated wire with different types of magnetic anisotropy”, J. Appl. Phys. 87, 4822-4824 (2000). http://dx.doi.org/10.1063/1.373171

[13] D. X. Chen, L. Pascual and A. Hernando, “Comment on ‘Analysis of asymmetric giant magnetoimpedance in field-annealed Co-based amorphous ribbon’”, Appl. Phys. Lett. 77, 1727-1729 (2000). http://dx.doi.org/10.1063/1.1310202

[14] Z. M. Wu, Z. J. Zhao and L. P. Liu, “Resonance Enhancement of the Giant Magnetoimpedance Effect in Glass-Coated Microwires With Outer Conductive Layer”, IEEE Trans. Magn. 43(7), 3146-3148 (2007). http://dx.doi.org/10.1109/TMAG.2007.895740

[15] A. Shadowitz, “The Electromagnetic Field”, Dover Publications (2010).
Fabrication of Anti-reflecting Si Nano-structures with Low Aspect Ratio by Nano-sphere Lithography Technique

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Abstract: Nano-structured photon management is currently an interesting topic since it can enhance the optical absorption and reduce the surface reflection which will improve the performance of many kinds of optoelectronic devices, such as Si-based solar cells and light emitting diodes. Here, we report the fabrication of periodically nano-patterned Si structures by using polystyrene nano-sphere lithography technique. By changing the diameter of nano-spheres and the dry etching parameters, such as etching time and etching power, the morphologies of formed Si nano-structures can be well controlled as revealed by atomic force microscopy. A good broadband antireflection property has been achieved for the formed periodically nano-patterned Si structures though they have the low aspect ratio (<0.53). The reflection can be significantly reduced compared with that of flat Si substrate in a wavelength range from 400 nm to 1200 nm. The weighted mean reflection under the AM1.5 solar spectrum irradiation can be as low as 3.92% and the corresponding optical absorption is significantly improved, which indicates that the present Si periodic nano-structures can be used in Si-based thin film solar cells.

Keywords: Nano-sphere lithograph; Nano-patterned Si structures; Antireflection

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Introduction

Due to the increased environment problems and the decreased availability of fossil fuel sources, many research efforts has been in developing the clean renewable energy technologies. Among the various energy projects, solar cells which harvest energy directly from sunlight are considered as the most promising candidate for future energy resources [1]. Although a substantial drop of cost and efficiency improvement has been achieved in last decades, significant improvements in both device performance and the manufacturing process are still demanded to keep it economically competitive.

Currently the photovoltaic market is dominated by Si-based materials such as crystalline and polycrystalline Si, of which around half of the cost is from silicon wafers. Therefore, the research work on the development of thin-film solar cells that do not require the use of thick silicon wafers has attracted much attention. Thin film solar cells with a typical thickness of 1~2 μm can be fabricated at a much reduced cost. For the practical application of Si-based thin film solar cells, the development for high throughput processes is required.

For both performance improvement and cost reduc-
tion, photon management is critical in thin film Si-based solar cells, which can not only reduce the optical losses, but also shorten carrier collection length to reduce transport losses. So far, an efficient photon management is still rather challenging because it should work in a broad spectral regime due to the broadband of solar spectrum. The pyramid structure with a feature size of tens of microns is usually applied for the light trapping in crystalline silicon solar cells. However, for thin-film solar cells, the minority-carrier diffusion length is around 300 nm while the light absorption depth is around 1 µm. Hence it is essential to realize an efficient light management which can work in a broad spectral range with a feature size in the sub-wavelength regime. Nano-structures with a scale comparable to the wavelength of most utilized solar spectrum are considered as the promising candidates for the advanced photon management.

Advanced light management by using semiconductor nano-structures, such as nano-wires, nano-columnar, nano-cones etc, is currently proposed to enhance the absorption and reduce the surface reflection in a broad spectral range for high performance solar cells [2-6]. For example, by fabricating Si nano-wires, the peak absorption can be as high as 96% due to the light trapping effect [4]; the optical absorption enhancement has also been observed in Si nano-cones arrays prepared by using SiO$_2$ nano-sphere lithography technique [6]. In many cases, good antireflection characteristics were achieved in Si nano-structures with high aspect ratio, which cannot be used in thin film solar cells due to the thickness limit. Moreover, high aspect ratio may introduce a high level of surface defects to reduce the carrier collection efficiency [7,8]. Recently, the theoretical results suggested that surface feature with low aspect ratio can also enhance the light absorption without or with less reducing the electrical properties [7].

In our previous work, the periodical nano-structures fabricated by polystyrene (PS) nano-sphere lithography technique was introduced to optical devices containing nano-crystalline Si/SiO$_2$ multilayers and an enhanced photon luminescence (PL) and electroluminescence (EL) was observed [9,10]. The nano-structure was also used in hetero-junction thin film solar cells and the enhanced light absorption and significant improvement of cell performance have been achieved [11,12]. However, the influences of formed nano-patterned structures under the various preparation conditions on the reflection and absorption characteristics are still unknown and need further investigation.

In this paper, we reported the fabrication of periodical nano-patterned Si structures using PS nano-sphere lithography technique. By controlling the diameters of PS nano-spheres and the etching parameters, periodically nano-patterned Si structures can be achieved with various periodicities and depths in a large scale. We systematically studied the morphologies and the reflection characteristics of Si nano-patterned structures in order to optimize the fabrication conditions. We found that the reflection can be obviously suppressed and the reflection can be lower than 5% in a broad wavelength regime (400~1200 nm) even with the low aspect ratio. Correspondingly, the optical absorption is significantly enhanced, which indicates the potential applications of the present nano-patterned Si structures prepared by a cheap and easy approach in the thin film solar cells for improving the device performance.

Experiment

Polystyrene nano-sphere lithography technique was used to fabricate the periodically patterned Si nano-structures on (100) p-type Si wafer (1.5~3 Ω·cm). The Si wafers were cut into 2 cm × 2 cm squares and pre-cleaned with standard RCA process and then rinsed in deionized water for several times to get the clean surface. The fabrication process includes the self-assembly of monolayer PS nano-spheres and the subsequent dry etching [13]. First, the cleaned silicon wafers used for transferring were pre-processed by immersing in the 5 wt% Sodium dodecyl sulfate (SDS) solution for more than 24 hours. The blend solution of PS is prepared with the mixture of PS solution and ethanol of a volume ratio 1:4. A drop of the blend solution was dropped on the transfer wafer to form a thin film of PS nano-spheres. Then the thin film of PS nano-spheres was transferred to the water surface which is processed with a few drops of SDS solution and a monolayer of PS nano-spheres was formed on the water surface, the color of which depends on the diameter of PS nano-spheres. The monolayer of PS nano-spheres was transferred to the substrates, and it sticks onto the Si substrates after the water evaporated. Then, the Si wafers covered by the monolayer of PS nano-spheres were set into the conventional reaction ion etching (RIE) system. By using PS nano-spheres as a mask, the patterned structures can be formed on Si wafer after etching. During the etching process, the radio frequency (r.f) power varies from 20 W to 48 W and the reaction chamber pressure is kept at 3.3 Pa by controlling the pumping speed. The CF$_4$ with flow meter of 30 Scm (Standard cubic centimeters per minute) was used as etching gas and etching time varies from 10 min to 15 min. After RIE process, PS nano-spheres were removed in tetrahydrofuran (THF) solution.

We measured the surface morphology by using atomic force microscopy (AFM) with the tapping mode. The etching depths under different r.f power were explored by summarizing the AFM measurement results. The reflection spectra were measured by using
Shimadzu UV-3600 spectrometer without integrating sphere in the wavelength range (400~1200 nm). In our previous work, we found that the reflection spectra are almost the same whether using the integrating sphere or not, which indicates the angle-independent antireflection characteristic of the nano-structures [11]. The reflection spectra of nano-patterned structures etched under different r.f power were measured to investigate the antireflection characteristics of nano-patterned structures and compare with the results of the flat Si substrate without any treatment.

Results and discussion

The morphologies of the nano-patterned Si structures obtained by using PS nano-spheres lithography technique was characterized by AFM measurements. The diameter of used PS nano-spheres is 220 nm and 300 nm, respectively. The scanning area is about 2 µm × 2 µm. As shown in Fig. 1(a) and (b), the ordered and nano-patterned Si structures can be clearly identified for both samples. It is worth pointing out that we measured the various places of the samples and observed the similar surface morphologies which indicates that the periodically nano-patterned Si structures can be formed in a large area (in our case, at least 1 cm²). It is also shown in AFM images that the nearly close-packed Si structures are formed and the periodic length of formed Si nano-structures is consistent with the diameter of used PS nano-spheres, which suggests that one can control the periodicity of Si nano-patterned structures by choosing PS nano-spheres with the suitable sizes.

![AFM image](image)

Fig. 1  AFM image of nano-patterned Si structure prepared by using PS nano-spheres with (a) diameter of 220 nm; (b) diameter of 300 nm. (c) and (d) The cross-sectional AFM images for corresponding AFM images indicated by solid line.

The cross sectional AFM images are also given in Fig. 1(c) and (d). The depth from the top of the nano-structures to the bottom can be roughly estimated from the cross-sectional AFM images. It was found that the average depth is respectively about 94.8 nm and 117.5 nm for 220 nm and 300 nm periodically nano-patterned structures. Figure 2 is the change of etching depth estimated from AFM images with the etching time both for 220 nm and 300 nm periodic structures while the r.f etching power is kept at 20 W. It is shown that the etching depth is gradually increased with the etching time and the etching depth is almost same both for 220 nm and 300 nm periodic structures, especially under the short etching time. After 10 min dry etching, the depth is about 40 nm for both samples and it reaches about 100 nm after 15 min etching for 220 nm periodic nano-structures and exceeds 110 nm for 300 nm periodic one.
It was found that, besides the etching time, the depth of the prepared nano-structures is also strongly depended by the other etching parameters, especially the etching r.f power. Here, we also estimated the etching depths for 300 nm periodic samples under different r.f power by using AFM measurements. Figure 3 is the change of etching depth as a function of etching r.f power. It was found that the etching depth is increased from 41.3 nm for 20 W etched structures to 157.8 nm for 48 W etched structures. Increasing the r.f power can decompose the reactive gas more efficiently, which results in the higher etching rate to get a large etching depth at the same etching time as revealed in our experimental results. We also measured the etching depth by using cross sectional transmission electron microscopy (TEM) for some selected samples. It was also found that the AFM results is slightly under-estimated compared with that that obtained from TEM images [10]. However, the depths obtained from AFM images do reflect the depth increase with the development of etching time and r.f power. Our experiment results demonstrate that PS nano-sphere lithography technique is an effective way to get uniform and periodically nano-patterned Si structures in a large area and the surface morphology of nano-patterned structures can be well controlled by changing the etching parameters such as r.f power and time.

The reflection spectra in the wavelength range from 400 nm to 1200 nm were measured for 220 nm and 300 nm periodically nano-patterned Si structures obtained under the r.f power of 48 W and etching time of 10 min. Figure 4 shows the measurement results. The reflection spectrum of flat Si wafer is also given in the figure for reference. It was found that the reflection for flat Si substrate without patterning is quite high. The reflection is higher than 30% in the whole measurement range and even higher than 40% in the visible light region due to high refractive index of Si material. However, the reflection is obviously reduced for samples with periodically nano-patterned structures. The reflection is less than 20% for 220 nm periodic Si nano-structures and less than 10% for 300 nm periodic one in a whole spectral range. In the visible light region, the reflection of 300 nm periodically nano-patterned structures is even less than 5%. In our previous work, we investigated the reflection spectra for 220 nm periodic Si nano-structures etched under the various etching time [10]. It was found that the reflection can be further reduced by increasing the etching time. The reduced reflection suggests that the present periodically nano-patterned Si structures have the good antireflective characteristics even though they have the low aspect ratio. In the present case, the two kinds of Si nano-structures are obtained under the same etching time (10 min). At the wavelength regime below 800 nm, the two kinds of nano-structures have almost the same antireflection characteristics while at long wavelengths, 300 nm-periodical nano-structures show the better antirefection characteristic. According to the scattering effect theory, when the diameter of nano-structure becomes comparable to the light, the incident light will greatly scattered therefore increase the light path length, which means that 300 nm periodical nano-structure has a broader antireflection wavelength region. As seen in Fig. 1(c) and (d), we can identify that the depth of 300 nm-periodic structures is slightly larger than that of 220 nm-periodic one, which may result in the better antireflection characteristics of 300 nm periodic nano-structures.

In order to further understand the influences of formed nano-structures on the antireflection behaviors, we studied the reflection behaviors of nano-patterned Si
structures obtained under the various r.f etching power. Figure 5 shows the reflection spectra of 300 nm periodically nano-patterned Si structures etched under the various r.f powers (20~48 W). It is clearly shown that the reflection is gradually reduced with increasing the r.f power in a whole spectral range (400~1200 nm). The maximum reflection for 20 W etched sample is about 25%, while for the reflection 48 W etched one is lower than 5% in the whole measurement spectral range. The similar change is also observed for patterned Si nano-structures with periodicity of 220 nm. It is suggested that the present patterned Si nano-structures exhibit the good antireflective characteristics and the reflection can be modulated by controlling the fabrication parameters.

Fig. 4 Reflection spectra of nano-patterned Si structures with periodicities of 220 nm and 300 nm etched at 48 W for 10 min. The reflection spectrum of flat Si substrate is also given as a reference.

Fig. 5 Reflection spectra of 300 nm periodically nano-patterned Si structures prepared under the various r.f etching power.

It is well known that a significant fraction of sunlight (~30%) will be reflected on the Si surface without any treatment and surface roughening is an effective approach to suppress the surface reflection and improve the device performance. The roughening structures are usually prepared by lithography technique or wet etching process and the feature size are around tens of microns [11]. For the application in the film solar cells, it is high desired to develop the technology of photon management in the sub-wavelength regime. Our results demonstrate that PS nano-sphere lithography technique is a simple and low-cost way to provide a sub-wavelength periodically patterned structures with good antireflective properties.

The similar antireflective behaviors have also been reported by other groups. X. Li et al. studied the efficient antireflective properties of periodically aligned Si nano-pillar arrays [14]. They fabricated the periodically nano-patterned Si structures by using silver catalyzed chemical etching process and found that the reflection can be remarkably reduced in the wavelength range of 200~1000 nm. However, the reflection was increased obviously when the wavelength is longer than 1000 nm. M. A. Tsai et al. also reported the reduced reflective behaviors of crystalline Si with frustum nano-rod arrays. They reported that the reflection as low as 10% can be achieved in nano-rod Si arrays, which is lower than that of KOH textured structures in the wavelength range from 400 nm to 1000 nm [15]. In our case, we fabricated the periodically nano-patterned Si structures and the reflection can be lower than 10% in a more wide spectral range (400~1200 nm) under the suitable preparation conditions.

As mentioned before, the reduction of reflection is associated with the morphologies of formed nano-structures [6,16]. The broad band antireflection characteristics can be understood by the effective medium theory [7,17]. According to the effective medium theory, a single layer with sub-wavelength roughness on the surface can be approximated as a set of multi-layers of the “effective medium” with the intermediate refractive index between the substrate and the air. The effective refractive index is a function of the volume fractions of the individual rough layer [17] and gradual reduction of the effective refraction index can be realized which can reduce the reflection in a wide spectral range and incident angles [5,16]. It was also reported that reduced reflection for the long wavelength photons can be attributed to the porous-like layer of nano-structures, which the refractive index discontinuity between air and Si substrate can be effectively buffered [15,18]. In our work, the formed Si nano-patterned structures have the cone-shape which causes the gradually increase of fractional area occupied by Si from top to bottom. The gradually changing of Si filling factor form a gradual effective refractive index from top to bottom which can suppress the reflection in a wide spectral range. Based on the AFM observations, it is found that, with increasing the etching time as well as the r.f etching power, the etching depth is gradually increased while the lat-
eral sizes of formed nano-structure is almost unchanged due to the protection of covered PS nano-spheres. As a result, the aspect ratio becomes larger and the Si filling factor is changed with the etching time and r.f power and in turn, the improved antireflection characteristics are achieved in a wide spectral range.

Considering the application of nano-patterned Si structures in thin film solar cells, we estimated the weighted mean reflection $R_w$ by calculating the reflection ratio of the periodically nano-patterned Si structures to the incident AM (Air Mass) 1.5 light at the each wavelength and averaging the results in the 400~1200 nm. The weighted mean reflection is calculated as follow:

$$R_w = \frac{\int_{\lambda_1}^{\lambda_2} F(\lambda) R(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} F(\lambda) d\lambda}$$

where $F(\lambda)$ and $R(\lambda)$ is the flux of incident light and reflection of nano-patterned structures at wavelength of $\lambda$, and the $\lambda_1$ and $\lambda_2$ is 400 nm and 1200 nm, respectively. Figure 6 shows the weighted mean reflection for 300 nm periodic Si nano-structures as a function of etching r.f power. It shows the trend that the weighted mean reflection is decreased with increasing the r.f power. The weighted mean reflection $R_w$ is decreased from 12.7% to 4.24% with increasing the r.f power from 20 W to 48 W while the lowest reflection is 3.92% for 41 W. This trend is almost consistent with the change of etching depth and a best etching depth exists for the lowest weighted reflection. The lowest reflection around 3.92% is better than the reflection obtained from nano-scale textured Si surface prepared by wet chemical etching technique [19]. Our experimental results indicate that the present nano-patterned Si structures can efficiently reduce the optical reflection loss in 400~1200 nm which covers most of the useful solar spectrum and is a promising candidate for application in the next generation Si-based thin film solar cells.

In order to investigate the optical absorption of nano-patterned Si structures, we measured the reflection ($R$) and transmission ($T$) spectra for nano-patterned Si samples. The optical absorptance ($A$) was calculated by using $A = 1 - R - T$. Figure 7 shows the optical absorption spectra of periodically nano-patterned Si structures with 220 and 300 nm periodicities, respectively. The etching time and r.f power is the same for both two samples. For comparison, the optical absorptance of the flat Si substrate is also given in the same figure. As shown in Fig. 7, the optical absorption of the nano-patterned Si structures is significantly enhanced in a broad wavelength region compared with that of flat Si wafer. It is found that the optical absorptance of nano-patterned Si structures is higher than 80% in the whole measurement wavelength range. For 300 nm periodic nano-patterned Si structures, the optical absorptance is even higher than 90% in a spectral range of 400~1200 nm. The enhanced optical absorption has been reported in Si nano-dome structures [6]. It was found that the optical absorption is obviously improved even in a large incident angles. The enhanced optical absorption can be attributed to the suppressed surface reflection and multiple absorption of the scattering light in the nano-patterned structures.

We also calculated the mean absorption weighted to AM 1.5 (1 sun) solar spectrum and the results are summarized in Fig. 7. The mean weighted optical absorptance of the flat Si wafer is about 62.4% while it is enhanced to 94.5% and 95.7% to 220 nm periodic and 300 nm periodic nano-patterned Si structures, respec-
tively, which is close to the best results reported previously [6,20]. It is implied that the most of the incident sunlight can be utilized by the Si substrates with nano-patterned structures.

The suppressed surface reflection and enhanced optical absorption can be realized by using the present nano-patterned Si structures formed by the nano-sphere lithography technique because they provide the grading refraction index between the air and Si interface as we discussed before. It was also reported that the optical absorption can be enhanced by using periodically sub-wavelength nano-structures. Since the feature size of surface pattern is smaller than wavelength, the incident electromagnetic wave can be coupled with the whole surface sub-wavelength structures which can trap the light to enhance the light harvesting in a wide spectral range [21,22].

Usually, the good antireflective properties and enhanced optical absorption have been achieved by introducing the Si nano-structures with high aspect-ratio. However, in our case, compared with the previous Si nano-structures, such as Si nano-wires (the length is 67 µm in micrometer scale) [4] and Si nano-cones (the length is around 600 nm) prepared by using SiO2 nano-sphere lithography technique [6], the depth of nano-patterned structures is quite low as revealed by AFM observations. The small etching depth indicates the low aspect ratio (<1) of our nano-patterned structures. The aspect ratios of the 300 nm periodically nano-patterned structures etched under the various r.f powers are calculated according to the AFM measurements and the results are also shown in Fig. 3. The aspect ratio is increased from 0.14 to 0.53 with increasing the etching power from 20 W to 48 W. More recently, J. Li et al. theoretically discussed the light-trapping capability of nano-structures with low aspect ratio [7]. They suggested that surface reflection can be reduced especially for the high energy photons (short wavelength region) and the optical absorption can be significantly enhanced even in the nano-patterned structures with low aspect-ratio.

Conclusion

Periodically nano-patterned Si structures have been fabricated by using PS nano-sphere lithography technique. AFM images revealed that the periodic structures can be formed by using PS monolayer as an etching mask. The lateral size and periodicity can be changed by using the PS nano-spheres with various sizes and the depths can be controlled by changing the etching parameters such as etching time and r.f power during the etching process. The formed nano-patterned Si structures exhibit the good antireflection characteristics though they have low aspect ratios. With increasing the diameter of nano-spheres and etching r.f power, the reflection can be significantly suppressed in a broad spectral range (400–1200 nm) compared to the flat Si substrate. The reflection of nano-patterned Si structures can be lower than 10% in the whole measurement range. The mean reflection weighted by AM1.5 sunlight spectrum of the patterned Si nano-structures can be as low as 3.8% and the corresponding weighted mean absorption can be obviously enhanced to 95.7%, which is close to the best values reported previously. Our experimental results indicate that the periodically nano-patterned Si structures can reduce the surface reflection and enhance the optical absorption which can be potentially applied in the new generation Si-based thin film solar cells.

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References

[1] Y. Y. Cao, Z. M. Wu, J. C. Ni, W. A. Bhutto, J. Li, S. P. Li, K. Huang and J. Y. Kang, “Type-II core/shell nanowire heterostructures and their photovoltaic applications”, Nano-Micro Lett, 4(3), 135-141 (2012). http://dx.doi.org/10.13786/nml.v4i3.p135-141
[2] J. Zhu and Y. Cui, “Photovoltaics: More solar cells for less”, Nat. Mater, 9(3), 183-184 (2010). http://dx.doi.org/10.1038/nmat2701
[3] V. V. Iyengar, B. K. Nayak and M. C. Gupta, “Optical properties of silicon light trapping structures for photovoltaics”, Sol. Energy Mater. Sol. Cells 94(12), 2251-2257 (2010). http://dx.doi.org/10.1016/j.solmat.2010.07.020
[4] M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis and H. A. Atwater, “Enhanced absorption and carrier collection in Si wire arrays for photovoltaic applications”, Nat. Mater. 9(3), 239 (2010). http://dx.doi.org/10.1038/nmat2635
[5] S. J. Jang, Y. M. Song, J. S. Yu, C. I. Yeo and Y. T. Lee, “Antireflective properties of porous Si nanocolumnar structures with graded refractive index layers”, Opt. Lett. 36(2), 253-255 (2011). http://dx.doi.org/10.1364/OL.36.000253
[6] J. Zhu, Z. Yu, G. F. Burkhard, C. M. Hsu, S. T. Connor, Y. Xu, Q. Wang, M. McGeehe, S. Fan and Y. Cui, “Optical absorption enhancement in amorphous silicon nanowire and nancone arrays”, Nano Lett. 9(1), 279-282 (2009). http://dx.doi.org/10.1021/nl802886y
[7] J. Li, H. Y. Yu, Y. Li, F. Wang, M. Yang and S. M. Wong, “Low aspect-ratio hemispherical nanopit surface texturing for enhancing light absorption in crys-
talline Si thin film-based solar cells”, Appl. Phys. Lett. 98(2), 021905-021907 (2011). http://dx.doi.org/10.1063/1.3537810

[8] V. Sivakov, G. Andrä, A. Gawlik, A. Berger, J. Plentz, F. Falk and S. H. Christiansen, “Silicon nanowire-based solar cells on glass: Synthesis, optical properties, and cell parameters”, Nano Lett. 9(4), 1549-1554 (2009). http://dx.doi.org/10.1021/nl803641f

[9] D. Chen, Y. Liu, J. Xu, D. Wei, H. Sun, L. Xu, T. Wang, W. Li and K. Chen, “Improved emission efficiency of electroluminescent device containing nc-Si/SiO2 multilayers by using nano-patterned substrate”, Opt. Express 18(2), 917-922 (2010). http://dx.doi.org/10.1364/OE.18.000917

[10] Y. Liu, J. Xu, H.C. Sun, S. H. Sun, W. Xu, L. Xu and K. J. Chen, “Depth-dependent anti-reflection and enhancement of luminescence from Si quantum dots-based multilayer on nano-patterned Si substrates”, Opt. Express 19(4), 3347-3352 (2011). http://dx.doi.org/10.1364/OE.19.003347

[11] Y. Liu, S. H. Sun, J. Xu, L. Zhao, H. C. Sun, J. Li, W. W. Mu, L. Xu and K. J. Chen, “Broadband antireflection and absorption enhancement by forming nanopatterned Si structures for solar cells”, Opt. Express 19(s5), A1051-A1056 (2011). http://dx.doi.org/10.1364/OE.19.0A1051

[12] Y. Wang, J. Rybczynski, D. Z. Wang and Z. F. Ren, “Large-scale triangular lattice arrays of sub-micron islands by microsphere self-assembly”, Nanotechnology 16(6), 819-822 (2005). http://dx.doi.org/10.1088/0957-4484/16/6/033

[13] W. Li, J. Zhou, X. G. Zhang, J. Xu, L. Xu, W. Zhao, P. Sun, F. Song, J. Wan and K. Chen, “Field emission from a periodic amorphous silicon pillar array fabricated by modified nanosphere lithography”, Nanotechnology 19(13), 135308 (2008). http://dx.doi.org/10.1088/0957-4484/19/13/135308

[14] X. C. Li, J. S. Li, T. Chen, B. K. Tay, J. X. Wang and H. Y. Yu, “Periodically aligned Si nanopillar arrays as efficient antireflection layers for solar cell applications”, Nanoscale Res. Lett. 5, 1721-1726 (2010). http://dx.doi.org/10.1007/s11671-010-9701-3

[15] M. A. Tsai, P. C. Tseng, H. C. Chen, H. C. Kuo and P. Yu, “Enhanced conversion efficiency of a crystalline silicon solar cell with frustum nanorod arrays”, Optics Express 19(S1), A28-A34 (2010). http://dx.doi.org/10.1364/OE.19.000A28

[16] N. Wan, J. Xu, G. Chen, X. Gan, S. Guo, L. Xu and K. Chen, “Broadband anti-reflection and enhanced field emission from catalyst-free grown small-sized ITO nanowires at a low temperature”, Acta Mater. 58(8), 3068-3072 (2010). http://dx.doi.org/10.1016/j.actamat.2010.01.041

[17] J. Tang, J. Shi, L. Zhou and Z. Ma, “Fabrication and optical properties of silicon nanowires arrays by electroless Ag-catalyzed etching”, Nano-Micro Lett. 3(2), 129-134 (2011). http://dx.doi.org/10.3786/nmll.v3i2.p129-134

[18] H. Sai, H. Fujii, K. Arafune, Y. Ohshita, M. Yamaguchi, Y. Kanamori and H. Yugami, “Antireflective subwavelength structures on crystalline Si fabricated using directly formed anodic porous alumina masks”, Appl. Phys. Lett. 88(20), 201116-201118 (2006). http://dx.doi.org/10.1063/1.2205173

[19] S. Koynov, M. S. Brandt and M. Stutzmann, “Black nonreflecting silicon surfaces for solar cells”, Appl. Phys. Lett. 88(20), 203107-203109 (2006). http://dx.doi.org/10.1063/1.2204573

[20] R. Biswas and C. Xu, “Nano-crystalline silicon solar cell architecture with absorption at the classical 4n2 limit”, Optics Express 9(S4), A664-A672 (2011). http://dx.doi.org/10.1364/OE.19.000A664

[21] S. Chattopadhyay, Y. F. Huang, Y. J. Jen, A. Ganguy, K. H. Chen and L. C. Chen, “Anti-reflecting and photonic nanostructures”, Mater. Sci. Eng. Rep. 69(1-3), 1-35 (2010). http://dx.doi.org/10.1016/j.mser.2010.04.001

[22] J. S. Li, H. Y. Yu, S. M. Wong, G. Zhang, X. W. Sun, P. G. Lo and D. L. Kwong, “Si nanopillar array optimization on Si thin films for solar energy harvesting”, Appl. Phys. Let. 95(3), 033102-033104 (2009). http://dx.doi.org/10.1063/1.3186046
Synthesis of Nanostructured Copper-doped Titania and Its Properties

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Abstract: Nanostructured pure-TiO$_2$ and Cu3%-TiO$_2$ were successfully synthesized via co-precipitation method. The X-ray diffraction (XRD) result proves that the synthesized sample were predominantly in anatase phase with size in the range of 8∼16 nm, which are in good agreement with the transmission electron microscopy data. Owing to doping of copper, not only did the thermal stability of the TiO$_2$ decrease, but also a significant decrease in its particle size and a shift of the adsorption edge to a higher wavelength region appear. The activity of both pure-TiO$_2$ and Cu3%-doped TiO$_2$ was tested to study their ability to decolorize congo red (CR) dye in aqueous solution. We observed that the CR dye was decolorized faster by Cu3%-TiO$_2$ than pure-TiO$_2$. Results of this study demonstrate a potential application of the synthesized sample for decolorizing dye pollutants from aqueous waste.

Keywords: Nanostructure; Copper; Titania; Decolorization; Congo red

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Introduction

In 1972, titanium dioxide (TiO$_2$) was firstly discovered by Fujishima and Honda as an active photocatalyst [1]. Since then, TiO$_2$ has became one of the most important semiconductor materials in daily life, moreover, it has been widely used in fuel cell, solar energy conversion, photocatalysts/catalyst for environmental remediation processes, white pigment in paints and paper, bone implant material, ultra-violet (UV) absorber in sunscreen cream and other cosmetic products, and additive in food products [2-5]. Such wide range of application is quite reasonable, because TiO$_2$ is an inexpensive, environmentally friendly material with high chemical stability, high mechanical strength and photo activation [6-8]. However, exploring the properties of TiO$_2$ for improving its efficiency is still an emerging area of research. In this regards, modifications of intrinsic properties of TiO$_2$ by doping with other oxide semiconductor such as Al$_2$O$_3$ [9], CeO$_2$ [10], CuO [11], Fe$_2$O$_3$ [12], SnO$_2$ [13], SiO$_2$ [9,14], WO$_3$ [15], ZnO [16] and ZrO$_2$ [9,14] have long been proposed. Specially, copper (Cu) was found to be one of the most considerable element among those oxide semiconductors because of its notable effects on the activity of TiO$_2$. Numerous works on the applications of Cu-TiO$_2$ have been reported in the areas of solar energy [17], environmental remediation for chemical contaminants removal [18-24], and microbial treatment [25,26]. In the area of solar energy, the presence of Cu element significantly extends the light response of TiO$_2$ into the visible region, which further enhance the photoelectochemical properties of the TiO$_2$ [17], and increase the activity of the TiO$_2$ as catalyst for hydrogen generation [22]. The Cu was also found to be a promising dopant to increase the properties of TiO$_2$ for converting carbon dioxide to higher carbon compounds [18-20] and for generating hydrogen from water [21]. In the field of microbial treatment, the Cu species can be used as an impurity material to enhance the TiO$_2$ activity for the treatment of water con-
taining harmful biological contaminants [25,26]. Thus, it is evident that the existence of Cu species at TiO2 matrix plays an important role on the activity, because Cu could influence the particle size [20,23], and optical or electronic properties of TiO2 [17,21], as well as the number of oxygen or intermediate species on the surface of the TiO2 [22,27]. Recently, in the area of environmental remediation for removal of chemical pollutants, materials having nano dimensional structure are still preferred because of the high surface area well-correlated to their small size [28-30], which grant them more adsorption site for better activity [31,32].

Despite the fact that the aims to improve the TiO2 activity by doping with Cu have been pointedly achieved, most of those mentioned studies were conducted with light-assisted method. On the other hand, concerning the environmental remediation process for organic contaminant removal, a direct catalytic application of nanostructured TiO2-based material in the absence of light assistance is still challenging. Therefore, in this study nanostructured pure TiO2 and Cu3%-doped TiO2 were synthesized, characterized and tested for their activity. The nanostructured samples were synthesis by co-precipitation method. The morphology and structure were characterized. The activity of the synthesized samples was evaluated for direct application to decolorize CR dyes, as the model compound, in aqueous solution through microwave-assisted catalytic reaction process in absence of the light assistance.

Experiment

Chemicals

All chemicals were purchased from commercially available sources and were used without further purification. The chemicals include Ammonia solution (NH4OH, Merck, 25%), Cetyltrimethyl Ammonium Bromide (CTAB, Merck, 98%), Zinc chloride (ZnCl2, Merck, 98%), Copper nitrate (Cu(NO3)2·3H2O, Merck, 99.5%), Titanium tetrachloride (TiCl4, Merck, 98%), Congo red dye (Sigma, 97%), and purified water was synthesized, characterized and tested for their activity. The nanostructured samples were synthesis by co-precipitation method. The morphology and structure were characterized. The activity of the synthesized samples was evaluated for direct application to decolorize CR dyes, as the model compound, in aqueous solution through microwave-assisted catalytic reaction process in absence of the light assistance.

Synthesis of Nanostructured Pure-TiO2 and Cu-TiO2

Nanostructured copper-doped titania at 3 wt% level of copper (denoted as Cu3%-TiO2) was synthesized using co-precipitation method with the same procedure as described in our previous study [33], except that copper was used as the metal dopant and a higher calcination temperature (500°C) was applied in present study. The procedure was as follows: A certain amount of copper precursor was dissolved in CTAB solution (0.2 M) under stirring (600 rpm) for 5 min, giving a mixture sol.-A. The mixture sol.-A was stored in a refrigerator at 0°C for further use. Subsequently, a certain amount of concentrated TiCl4 solution was then slowly dropped into freezeed mixture sol.-A, giving a mixture-solution B. After that, the mixture sol.-B was precipitated using NH2OH solution (25%) in 5 ml/min of dropping rate, under stirring, until the pH value of the solution reached 10, then placed the solution at 55~60°C under stirring for 6 h for aging, giving a mixture sol.-C. The wet solid precursor in mixture sol.-C was separated from the solution by centrifugation at 8000 rpm for 10 min. The wet solid precursors were dried at 100°C for 12 h to produce dry solid precursors. The dry solid precursor was calcined at 500°C for 4 h. The pure TiO2 was also synthesized using the same procedure without addition of copper precursor.

Characterization

The thermal curves of thermo gravimetric analyzer (TGA) were obtained from freshly dried solid precursor using a TGA 2050 thermal gravimetry with temperature limit from 20~900°C in air flow. All X-ray diffraction (XRD) patterns of the synthesized samples were recorded on a Rigaku X-ray at 40 kV and 100 mA with CuKα as the radiation source. The 2θ was scanned in the range from 25° to 70° at a speed of 1.2°/min. The average crystallite size of the synthesized samples was calculated from the full-width at half-maximum (FWHM) using Scherrer’s formula [34]. The ultraviolet visible diffuse reflectance (UV-Vis DR) spectra were recorded on a Shimadzu UV2450 spectrophotometer equipped with an integrated sphere. The reflectance spectra of the sample were analyzed under ambient condition in the wavelength range of 300~700 nm. The measured reflectance spectra were transformed into Kubelka-Munk (F(R)) function using \( F(R) = \left(1 - R\right)^2 / 2R \), where \( R \) is the reflectance value of the sample. The Fourier Transform Infrared Spectroscopy (FTIR) spectra of the synthesized samples in potassium bromide (KBr) media were recorded on a Shimadzu IR Prestige DSR-8000 spectrometer in the range of 500 cm\(^{-1}\) to 4000 cm\(^{-1}\) at a scanning rate of 4 cm\(^{-1}\)/min. The surface morphology images and energy dispersive X-ray (EDX) of the synthesized samples was observed from a Tecnai G2 F20 transmission electron microscopy (TEM) at an accelerating voltage 200 kV. The TEM samples were prepared by firstly dispersed in ethanol and then deposited onto a 300 mesh copper grid after sonication.

Activity Testing

The synthesized samples were tested for their activity of decolorizing the congo red (CR) dye in an aqueous solution under microwave irradiation. The catalytic
experiments were carried out using a thermostatic microwave apparatus (Milestone Microwave Laboratory System, MLS 1200). The experimental conditions were as follows: 10 ml of CR solution with known initial concentration (10 ppm) and a certain amount of the synthesized samples were transferred into a teflon vessel, which was put into the microwave apparatus to start the catalytic experiment. The treated CR solution was then centrifuged at 2200 rpm for 5 min to separate the solution from the particles of the synthesized sample. The absorption of the CR in treated solution was measured using a Shimadzu 3501 UV-Vis spectrophotometer at maximum wavelength of 498 nm. The concentration was determined from the particles of the synthesized sample. The absorption of the CR in treated solution was measured using a Shimadzu 3501 UV-Vis spectrophotometer at maximum wavelength of 498 nm. The concentration of the CR in the remaining treated solution was calculated from their calibration curve. The calibration curve \(A=0.0679C+0.0262\) with \(R^2=0.9969\), obtained from the maximal absorbancies of a series of CR solution (0-15 mg/l), abided by Lambert-Beer’s law, was used to determine the CR concentration in the treated solution. The catalytic decolorization percentages of CR (%, Decolorization) is expressed as follows:

\[
\%\text{Decolorization} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

where \(C_0\) (mg/l) and \(C_t\) (mg/l) are the CR initial concentration and concentration after time \(t\) (min), respectively.

Results and discussion

The TGA thermogram of the synthesized samples are presented in Fig. 1. For TGA thermogram of pure TiO\(_2\) samples, it can be seen that the first broad TGA exotherm peak at about 25\,\textdegree\,C to 220\,\textdegree\,C is attributed to the loss of residual organic solvent and physisorbed water. These first two peaks occur concurrently with a mass loss of 11\%. The second broad TGA exotherm peak in the range of 220\,\textdegree\,C to 550\,\textdegree\,C indicates decomposition of hydroxyl groups and organic molecules chemically bonded to the surface of TiO\(_2\) sample, giving a further mass loss of 9\%. In addition, a broad exotherm TGA in the range of 550\,\textdegree\,C to 900\,\textdegree\,C is observed with a mass loss of 3\%. After that, there is no mass loss for the TiO\(_2\) sample and it may be assumed that TiO\(_2\) amorphous phase has changed to TiO\(_2\) crystalline phase. The total mass loss for the pure TiO\(_2\) sample heated to 900\,\textdegree\,C was about 23\%. Similarly, the trend is found for Cu3\%-TiO\(_2\) sample as shown in Fig. 1. Lost of residual organic solvent and physisorbed water from the Cu3\%-TiO\(_2\) sample corresponds to TGA exotherm peak in the range of 50\,\textdegree\,C to 260\,\textdegree\,C, resulting a mass loss of 11\%. A TGA exotherm peak is also observed in the range of 260\,\textdegree\,C to 540\,\textdegree\,C which occur concurrently with a TGA mass loss of 20\%, ascribing to the decomposition of hydroxyl groups and organic molecules. The formation of crystalline phase of Cu3\%-TiO\(_2\) sample is indicated by no TGA exotherm peak in the temperature range of 540\,\textdegree\,C to 900\,\textdegree\,C. From the TGA thermogram properties, it can be concluded that the presence of copper in TiO\(_2\) matrix has obviously influenced the thermal property of the TiO\(_2\). One can notice that, the pure TiO\(_2\) was more stable upon heating with smaller mass loss compared to Cu3\%-TiO\(_2\), giving the following order: pure TiO\(_2\) (23\% mass loss) > Cu3\%-TiO\(_2\) (35\% mass loss). In other words, the thermal stability of TiO\(_2\) has significantly decreased after copper doping.

![Fig. 1 TGA thermograms of the synthesized samples.](image)

Figure 2 presents the XRD pattern of the synthesized samples. The well-defined diffraction peaks with 2\(\theta\) are at about 25\,\textdegree, 38\,\textdegree, 48\,\textdegree, 54\,\textdegree, 55\,\textdegree, 63\,\textdegree, and 69\,\textdegree, which are assigned to the (101), (004), (200), (105), (211), (204) and (116) crystal plane, respectively. This XRD characteristic pattern is consistent with the standard JCPDS values of anatase TiO\(_2\) (JCPDS Card No. 21-1272) [35-37]. No peaks for copper can be observed, which indicates the metal content added during the synthesis process was too low or the metal has been well-dispersed at TiO\(_2\) matrix in the form of small cluster. The average crystallite size of the nanocomposite samples were calculated from the FWHM of anatase (101) reflection plane (Fig. 2(b)) using Scherrer’s formula [38],

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

where \(D\) is the crystallite size, \(k\) is a constant (=0.9, assuming that the particles are spherical), \(\lambda\) is the wavelength of the X-ray diffraction, \(\beta\) is the FWHM and \(\theta\) is the angle of diffraction. From the calculated crystallite size, it was found that the synthesized samples had small crystallite size with an average size of 15 nm and 9 nm for the pure TiO\(_2\) and Cu3\%-TiO\(_2\), respectively. From this point, it can be noticed that the addition of copper decreased the crystallite size of the TiO\(_2\) to some extent. Decrease in the particle size of TiO\(_2\) might be ascribed to a broadening effect due to incorporation of the metal oxides into TiO\(_2\) matrix [39], as can be seen by comparing the (101) reflection plane of pure TiO\(_2\) with Cu3\%-TiO\(_2\) (Fig. 2(a)). Lowering the intensity and broadening the width of the (101) reflection
plane led to a decrease in the calculated crystallite size correspondingly. Moreover, the (101) reflection plane of the Cu3%-TiO\textsubscript{2} samples shifted to higher diffraction angle relative to pure TiO\textsubscript{2} (Fig. 2 (b)), implying an incorporation effect of copper at the TiO\textsubscript{2} lattice as Ti\textsuperscript{4+} position may be substituted by copper due to the similarity of their ionic radii (Ti=0.68 Å and Cu = 0.72 Å) [40].

![Fig. 2 XRD patterns of (a) the synthesized samples; (b) the (101) reflection plane of pure TiO\textsubscript{2} and Cu3%-TiO\textsubscript{2}.](image)

Figure 3 shows the UV-Vis DR spectra of the pure TiO\textsubscript{2} and Cu3%-TiO\textsubscript{2} samples. As can be observed from the spectra, a strong absorption peaks at around 350 nm is ascribed to the TiO\textsubscript{2} system, which decreases after Cu loading. A new strong absorption band between 350~500 nm might be assigned to the presence of Cu species in the Cu3%-TiO\textsubscript{2} sample. In addition, The Cu-species also induced the formation of impurity inside the TiO\textsubscript{2}, resulting in a shift of adsorption edge to higher wavelength region (red shift), which is characteristic for the TiO\textsubscript{2}-system after metal doping.

The FTIR spectra of the synthesized samples were obtained in the scanning range of 500~4000 cm\textsuperscript{-1}. As shown in Fig. 4, the spectra of pure TiO\textsubscript{2} before calcination clearly shows the bands (between 3500 and 3150 cm\textsuperscript{-1}), which correspond to H-bounded hydroxyl groups. It also shows significant peaks at about 2920 and 2850 cm\textsuperscript{-1}, which can be assigned to the C-H symmetrical and C-H asymmetrical stretching vibration from the remaining organic-moiety [41], these peaks would disappear from the surface of all synthesized samples after heating treatment. The bending vibration mode of O-H is marked by peak at about 1628 cm\textsuperscript{-1} for all samples except for Cu3%-TiO\textsubscript{2} [14]. A clear peak at about 1456 cm\textsuperscript{-1} can be ascribed as a bending vibration mode of the N-H band from the CTAB [14]. However, the N-H bending vibration is not marked on the calcined samples.

![Fig. 3 UV-Vis diffuse reflectant spectrum of (a) pure TiO\textsubscript{2}; (b) Cu3%-TiO\textsubscript{2} samples.](image)

![Fig. 4 The FTIR spectra of the synthesized samples.](image)

TEM was used to further examine the particle size, crystallinity and morphology of the synthesized samples as shown in Fig. 5. From this figure, it can be seen that all synthesized samples display similar cluster morphology with estimated average size of the primary particles in the range of 8~16 nm, which is in good agreement with the value determined by XRD data. It was also observed that all synthesized samples were present in pure anatase phase, which is indicated by no shuttle-like morphology for rutile phase. The lattice fringes, as shown in inset of Fig. 5, indicated that the particles are in good crystalline nature. The EDX result demonstrates the present of C, O, and Ti element in the pure TiO\textsubscript{2} sample (Fig. 6(a)), except for Cu which is also present in Cu3%-TiO\textsubscript{2} sample (Fig. 6(b)).
The performance of the synthesized samples were tested for microwave-assisted catalytic decolorization of CR synthetic dye in aqueous solution. Figure 7 shows both the absorption spectra of CR as a function of time during the catalytic decolorization process with pure TiO$_2$ and Cu3%-TiO$_2$. Obviously, the absorbance intensity of CR that were obtained over pure TiO$_2$ (Fig. 7(a)) slowly decreased with passage of time. In contrast, the absorbance intensity of the CR over Cu3%-TiO$_2$ (Fig. 7(b)) rapidly decreased and the absorption band disappeared after the first minute. The absorbance curve indicates that the CR dye was decolorized slower over pure TiO$_2$ than that of Cu3%-TiO$_2$. Inset of Fig. 7 represents the change in color of the dye during the microwave-assisted catalytic decolorization process.

Figure 8 shows a curve of percent decolorization of the CR during the microwave-assisted catalytic process over pure TiO$_2$ and Cu3%-TiO$_2$. As can be seen in the curve, 53% of CR dye was decolorized by the pure TiO$_2$ in the first minute. Furthermore, the decolorization process gradually increases as time prolongs. The CR dye was almost decolorized completely after an interval of 6 min with a maximum decolorization percentage of 97%. In case of decolorization of CR dye over Cu3%-TiO$_2$, the CR dye was decolorized rapidly. It took
only 1 min to decolorize 90% of the CR dye. Furthermore, the decolorization process was completed in 2 min where almost 100% of CR disappeared. Considering the decolorization efficiency of pure TiO$_2$ and Cu3%-TiO$_2$ after being microwave-assisted catalysis for 2 min, it is evident that the Cu3%-TiO$_2$ showed a greater of decolorization ability than that of pure TiO$_2$. This may be due to the Cu3%-TiO$_2$ sample which has smaller particle size compared to that of pure TiO$_2$. As the smaller the crystallite size, the larger the surface area, which further enables the synthesized sample to have more adsorption site and, an increased surface contact of CR-catalyst which, further promote the fast decolorization process under microwave irradiation. However, more detailed study to understand the performance and mechanism of catalytic process over pure TiO$_2$ and Cu3%-TiO$_2$ under microwave assistance is required.

![Decolorization Efficiency Graph](image)

**Fig. 8** Percent decolorization of CR as a function of time (min) (conditions: initial CR concentration = 10 ppm, catalyst dosage = 2.5 g/l, microwave power 300 W).

**Conclusion**

Nanostructured pure-TiO$_2$ and Cu-doped TiO$_2$ have been synthesized by using co-precipitation method. The presence of the copper dopant at TiO$_2$ matrix not only influenced the thermal stability of the TiO$_2$ but also decreased the particle size of the TiO$_2$. The catalytic activity of Cu3%-TiO$_2$ was higher than that of pure TiO$_2$. It can be assumed that the smaller particle size of Cu3%-TiO$_2$ may play an important role for its high activity. The smaller crystallite size which will cause the larger surface area results in the rapid decolorization process over the nanostructured Cu3%-TiO$_2$. However, more detailed study to understand the activity performance of the synthesized sample is essential.

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**References**

[1] A. Fujishima and K. Honda, “Electrochemical photolysis of water at a semiconductor electrode”, Nature 238, 37-38 (1972). [http://dx.doi.org/10.1038/238037a0](http://dx.doi.org/10.1038/238037a0)

[2] O. Carp, C. L. Huisman and A. Reller, “Photoinduced reactivity of titanium dioxide”, Prog. Solid State Ch. 32(1-2), 33-177 (2004). [http://dx.doi.org/10.1016/j.progsolidstchem.2004.08.001](http://dx.doi.org/10.1016/j.progsolidstchem.2004.08.001)

[3] G. R. Dey, “Chemical reduction of CO$_2$ to different products during photo catalytic reaction on TiO$_2$ under diverse conditions: An overview”, J. Nat. Gas Chem. 16(3), 217-226 (2007). [http://dx.doi.org/10.1016/S1003-9953(07)60052-8](http://dx.doi.org/10.1016/S1003-9953(07)60052-8)

[4] K. Kočič, L. Obalová and Z. Lacný “Photocatalytic reduction of CO$_2$ over TiO$_2$ based catalysts”, Chem. Pap. 62(1), 1-9 (2008). [http://dx.doi.org/10.2478/s11696-007-0072-x](http://dx.doi.org/10.2478/s11696-007-0072-x)

[5] A. L. Linsebigler, G. Lu and J. J. T. Yates, “Photocatalysis on TiO$_2$ surfaces: principles, mechanisms, and selected results”, Chem. Rev. 95(3), 735-758 (1995). [http://dx.doi.org/10.1021/cr00035a013](http://dx.doi.org/10.1021/cr00035a013)

[6] J. Cyviene, D. Milcius and G. Laukaitis, “Porosity evaluation of TiO$_2$ thin films deposited using pulsed DC-magnetron sputtering”, Mat. Sci. (Medziagotyra), 15(2), 103-107 (2009).

[7] B. B. F. Mirjalili and A. Akbari, “Nano-TiO$_2$: An eco-friendly alternative for the synthesis of quinoxalines”, Chinese Chem. Lett. 22(6), 753-756 (2011). [http://dx.doi.org/10.1016/j.ccl.2010.12.016](http://dx.doi.org/10.1016/j.ccl.2010.12.016)

[8] M. C. Wü, A. Säpi, A. Avila, M. Szabó J. Hiltunen, M. Huuhhtanen, G. Tóth, A. Kukovecz, A. Kónya, R. Keiski, W. F. Su, H. Jantunen and K. Kordás, “Enhanced photocatalytic activity of TiO$_2$ nanofibers and their flexible composite films: Decomposition of organic dyes and efficient H$_2$ generation from ethanol-water mixtures”, Nano Res. 4(4), 360-369 (2011). [http://dx.doi.org/10.1007/s12274-010-0090-9](http://dx.doi.org/10.1007/s12274-010-0090-9)

[9] B. Reddy, G. Reddy, K. Rao, I. Ganesh and J. Ferreira, “Characterization and photocatalytic activity of TiO$_2$-M$_x$O$_y$ (M=M$_2$O$_3$, Al$_2$O$_3$, and ZrO$_2$) mixed oxides synthesized by microwave-induced solution combustion technique”, Mater. Sci. 44(18), 4874-4882 (2009). [http://dx.doi.org/10.1016/j.matscieng.2009.03.043](http://dx.doi.org/10.1016/j.matscieng.2009.03.043)

[10] S. Yang, W. Zhua, J. Wang and Z. Chen, “Catalytic wet air oxidation of phenol over CeO$_2$-TiO$_2$ catalyst in the batch reactor and the packed-bed reactor”, J. Hazard. Mater. 153(3), 1248-1253 (2008). [http://dx.doi.org/10.1016/j.jhazmat.2007.09.084](http://dx.doi.org/10.1016/j.jhazmat.2007.09.084)

[11] J. Bandara, C. P. K. Udawatta and C. S. K. Rajapakse, “Highly stable CuO incorporated TiO$_2$ catalyst for
photocatalytic hydrogen production from H₂O”, Photochem. & Photobiol.: Sciences 4(11), 857-861 (2005). http://dx.doi.org/10.1038/s507816D

[12] X. Zhang and L. Lei, “Preparation of photocatalytic Fe₂O₃- TiO₂ coatings in one step by metal organic chemical vapor deposition”, Appl. Surf. Sci. 254(8), 2406-2412 (2008). http://dx.doi.org/10.1016/j.apsusc.2007.09.067

[13] L. Shi, C. Li, H. Gu and D. Fang, “Morphology and properties of ultrafine SnO₂-TiO₂ coupled semiconductor particles”, Mater. Chem. Phys. 62(1), 62-67 (2000). http://dx.doi.org/10.1016/S0254-0584(99)00171-6

[14] T. Mishra, J. Hait, N. Aman, M. Gunjan, B. Mahato and R. K. Jana, “Surfactant mediated synthesis of spherical binary oxides photocatalytic with enhanced activity in visible light”, Colloid Interf. Sci. 327(2), 377-383 (2008). http://dx.doi.org/10.1016/j.cis.2008.08.040

[15] J. He, Q. Z. Cai, Q. Luo, D. Q. Zhang, T. T. Tang and Y. F. Jiang, “Photocatalytic removal of methyl orange in an aqueous solution by a WO₃/TiO₂ composite film”, Korean J. Chem. Eng. 27(2), 435-438 (2010). http://dx.doi.org/10.1007/s11814-010-0080-3

[16] Y. Zhao, C. Li, X. Liu, F. Gu, H. L. Du and L. Shi, “Zn-doped TiO₂ nanoparticles with high photocatalytic activity synthesized by hydrogen-oxygen diffusion flame”, Appl. Catal. B:Environ. 79(3), 208-215 (2008). http://dx.doi.org/10.1016/j.apcatb.2007.09.044

[17] Y. Liu, H. Zhou, J. Li, H. Chen, D. Li, B. Zhou and W. Cai, “Enhanced photoelectrochemical properties of Cu₂O-loaded short TiO₂ nanotube array electrode prepared by sonochemical deposition”, Nano-Micro Lett. 2(4), 277-284 (2010). http://dx.doi.org/10.3786/mlv.214.p277-284

[18] I. H. Tseng, W.-C. Chang and J. C. S. Wu, “Photoreduction of CO₂ using sol-gel derived titania and titania-supported copper catalysts”, Appl. Catal. B: Environ. 37(1), 37-48 (2002). http://dx.doi.org/10.1016/S0926-3373(01)00322-8

[19] R. Lopez, R. Goez and M. E. Llanos, “Photophysical and photocatalytic properties of nanosized copper-doped titania sol-gel catalysts”, Catal. Today 148(1-2), 103-108 (2009). http://dx.doi.org/10.1016/j.cattod.2009.04.001

[20] I. H. Tseng, J. C. S. Wu and H.-Y. Chou, “Effects of sol-gel procedures on the photocatalysis of Cu/TiO₂ in CO₂ photoreduction”, J. Catalysis, 221(2), 432-440 (2004). http://dx.doi.org/10.1016/j.jcat.2003.09.002

[21] L. S. Yoong, F. K. Chong and B. K. Dutta, “Development of copper-doped TiO₂ photocatalyst for hydrogen production under visible light”, Energy 34(10), 1652-1661, (2009). http://dx.doi.org/10.1016/j.energy.2009.07.024

[22] F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, V. Ilieva and L. Iadakiev, “Gold, silver and copper catalysts supported on TiO₂ for pure hydrogen production”, Catal. Today 75(1-4), 169-175 (2002). http://dx.doi.org/10.1016/S0920-5861(02)00060-3

[23] B. Zhu, Q. Guo, X. Huang, S. Wang, S. Zhang, S. Wu and W. Huang, “Characterization and catalytic performance of TiO₂ nanotubes-supported gold and copper particles”, Mol. Catal. A: Chem. 219(1-2), 211-217 (2006). http://dx.doi.org/10.1016/j.molcata.2006.01.013

[24] B. Zhu, X. Zhang, S. Wang, S. Zhang, S. Wu and W. Huang, “Synthesis and catalytic performance of TiO₂ nanotubes-supported copper oxide for low-temperature CO oxidation”, Micropor. Mesopor. Mat. 102(1-3), 333-336 (2007). http://dx.doi.org/10.1016/j.micromeso.2006.11.028

[25] T. Sato and M. Taya, “Copper-aided photosterilization of microbial cells on TiO₂ film under irradiation from a white light fluorescent lamp”, Biochem. Eng. 30(2), 199-204 (2006). http://dx.doi.org/10.1016/j.bej.2006.04.002

[26] M. B. Fisher, D. A. Keenan, P. Fernández-Ibáñez, J. Colleavy, S. J. Hinder, K. G. McGuigan and S. C. Pillai, “Nitrogen and copper doped solar light active TiO₂ photocatalysts for water decontamination”, Appl. Catal. B: Environ. 130-131, 8-13 (2013). http://dx.doi.org/10.1016/j.apcatb.2012.10.013

[27] B. Xin, P. Wang, D. Ding, J. Liu, Z. Ren and H. Fu, “Effect of surface species on Cu-TiO₂ photocatalytic activity”, Appl. Surf. Sci. 254(9), 2509-2574 (2008). http://dx.doi.org/10.1016/j.apsusc.2007.09.002

[28] S. Watanabe, X. Ma and C. Song, “Selective sulfur removal from liquid hydrocarbon over regenerable CeO₂-TiO₂ adsorbent for fuel cell application”, ACS: Div. Fuel Chem. 49(2), 511-513 (2004).

[29] B. B. Kefi, L. E. Attracheb, H. Kochkar and F. Ghorbel, “TiO₂ nanotubes as solid-phase extraction adsorbent for the determination of polycyclic aromatic hydrocarbons in environmental water samples”, J. Environ. Sci. 23(5), 860-867 (2011). http://dx.doi.org/10.1016/S1001-0742(10)60481-0

[30] Y. Luo and D. Li, “Experimental study of nanometer TiO₂ for use as an adsorbent for SO₂ removal”, Dev. Chem. Eng. Min. Process 10(3-4), 443-457 (2002). http://dx.doi.org/10.1002/apj.5500100414

[31] S. Deng, Z. Lia, J. Huang and G. Yuan, “Preparation, characterization and application of a Ce-Ti oxide adsorbent for enhanced removal of arsenate from water”, J. Hazard Mater. 179(1-3), 1014-1021 (2010). http://dx.doi.org/10.1016/j.jhazmat.2010.03.106

[32] S. J. Kim, E. G. Lee, S. D. Park, C. J. Jeon, Y. H. Cho, C. K. Rhee and W. W. Kim, “Photocatalytic effects of rutile phase TiO₂ ultrafine powder with high specific surface area obtained by a homogeneous precipitation process at low temperatures”, Sol-Gel Sci. Tech. 22(1-2), 63-74 (2001). http://dx.doi.org/10.1023/A:1011264320138

[33] O. Zuas, H. Budiman and N. Hamim, “Anatase TiO₂ and mixed M-Anatase TiO₂ (M = CeO₂ or ZrO₂) nano powder: synthesis and characterization”, J. J. Nano Dimens. 4(1), 11-18 (2013) In press.
[34] S. Martini and M. Herrera, “X-ray diffraction and crystal size”, J. Am. Oil Chem. Soc. 79(3), 315-316 (2002). http://dx.doi.org/10.1007/s11746-002-0480-z

[35] Y. Masuda and K. Kato, “Synthesis and phase transformation of TiO\textsubscript{2} nano-crystal in aqueous solutions”, Ceram. Soc. Jpn. 117(1363), 373-376 (2009). http://dx.doi.org/10.2109/jcersj2.117.373

[36] N. Sasirekha, S. J. S. Basha and K. Shanthi, “Photocatalytic performance of Ru doped anatase mounted on silica for reduction of carbon dioxide”, Appl. Catal. B: Environ. 62(1), 169-180 (2006). http://dx.doi.org/10.1016/j.apcatb.2005.07.009

[37] L. Ge, M. Xu, M. Sun and H. Fang, “Low-temperature synthesis of photocatalytic TiO\textsubscript{2} thin film from aqueous anatase precursor sols”, J. Sol-Gel Sci. Techn. 38(1), 47-53 (2006). http://dx.doi.org/10.1007/s10971-006-6009-y

[38] S. R. Dhage, S. P. Gaikwad and V. Ravi, “Synthesis of nanocrystalline TiO\textsubscript{2} by tartarate gel method”, B. Mater. Sci. 27(6), 487-489 (2004). http://dx.doi.org/10.1007/BF02707273

[39] O. Vázquez-Cuchillo, A. Cruz-López, L. M. Bautista-Carrillo, A. Bautista-Hernández, L. M. Torres Martínez and S. W. Lee, “Synthesis of TiO\textsubscript{2} using different hydrolysis catalysts and doped with Zn for efficient degradation of aqueous phase pollutants under UV light”, Chem. Intermediat. 36(1), 103-113 (2010). http://dx.doi.org/10.1007/s11164-010-0119-4

[40] R. López, R. Gómez and M. E. Llanos, “Photophysical and photocatalytic properties of nanosized copper-doped titania sol-gel catalysts”, Catal. Today 148(1-2), 103-108 (2009). http://dx.doi.org/10.1016/j.cattod.2009.04.001

[41] M. Sabzi, S. M. Mirabedini, J. Zohuriaan-Mehr and M. Atai, “Surface modification of TiO\textsubscript{2} nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating”, Progr. Org. Coating. 65(2), 222-228 (2009). http://dx.doi.org/10.1016/j.porgcoat.2008.11.006
Semiconductor Type Dependent Comparison of Electrical Characteristics of Pt/InP Structures Fabricated by Magnetron Sputtering Technique in the Range of 20-400 K

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Abstract: The paper describes how electrical properties of Pt/InP Schottky diode were affected by semiconductor type. We fabricated Pt/p-InP and Pt/n-InP Schottky diodes and measured electrical characteristics from 20 K to 400 K. Thicknesses of less than 30 nm of platinum were deposited on the two types of indium phosphide substrates using magnetron sputtering technique after the creation of Zn-Au ohmic back contact. We discussed basic diode parameters of ideality factors, barrier heights and series resistances of the two types of contacts. Additionally, unusual temperature characteristics of the the diodes were highlighted. These results were evaluated in terms of semiconductor type comparison of Pt/InP Schottky structures.

Keywords: Pt/p-InP; Pt/n-InP; Magnetron Sputtering; I-V-T characteristics

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Introduction

The preferred material and technique is mostly effective in the forming of semiconductor devices. InP is an extremely suited substrate since high electron mobility and high speed performance. Platinum is also used in several areas as a gate contact metal in most of devices successfully [1,2]. Magnetron sputtering technique is generally used for controlling the thickness distribution and obtaining high rate of uniform surfaces.

It is of great value to form Schottky diodes that have high barrier heights and good thermal stability in the realization of getting better performance. To achieve fabricating such a diode and obtaining the desired characteristics, it is very important to be careful in all stages from selecting material type, using appropriate technique to physical and chemical cleaning and measurement processes. The successful experimental results in different temperature conditions using platinum and InP separately were published in the literature. Therefore we assess such an option for the material selection. We emphasized the effects of semiconductor type on electrical characteristics in given temperature conditions. Semiconductor type dependent investigations have been done by various researchers. For instance, Yıldız et al. investigated electrical characteristics of Au/SnO$_2$/n-Si and Al/SnO$_2$/p-Si Schottky contacts at 200 and 295 K [3]. Siad et al studied series resistance and diode parameter differences between Al/n-Si and Al/p-Si Schottky contacts [4]. Akkılıç et al., determined correlation between barrier heights and ideality factors of Cd/n-Si and Cd/p-Si Schottky barrier diodes [5]. Arslan et al. published electrical characteristics of Pt/p-InGaN and Pt/n-InGaN Schottky barriers in a wide temperature range [6].

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Experimental Section

In this study, cleaned and polished p-InP and n-InP wafers with respectively $4.8 \times 10^{17}$ cm$^{-3}$ and $2.5 \times 10^{15}$ cm$^{-3}$ carrier concentration and (100) orientation were used. In order to remove undesirable impurities and surface damage layer, wafers were dipped in $5\text{H}_{2}\text{SO}_{4} + \text{H}_{2}\text{O}_{2} + \text{H}_{2}\text{O}$ solution for 1.0 min. After $\text{H}_{2}\text{O} + \text{HCl}$ solution cleaning process, wafers were cleaned in 18 MΩ de-ionized water. High purity nitrogen was used in drying periods. Ohmic contacts were formed by thermal evaporating of Zn-Au alloy on p-InP and n-InP under $10^{-6}$ Torr pressure in a vacuum chamber. The p-InP and n-InP were annealed respectively at 350°C and 300°C for 3 min in flowing $\text{N}_{2}$ to form low resistance ohmic contacts in a quartz tube furnace. DC magnetron sputtering technique was used to form 1.5 mm diameter circular platinum dots in the other face of p-InP and n-InP wafers. Platinum thicknesses were about less than 30 nm as schematically shown in Fig. 1. In fabrication process, while diodes were forming, they were taken under identical conditions to minimize fabrication induced differences. In this context, the main electrical parameters of the diode depending on the semiconductor type will be examined from 20 K to 400 K. $I - V$ measurements were taken under dark conditions by a Keithley 487 Picoammeter/Voltage Source. We can see the basic measurement system schematically in Fig. 2. Temperature was controlled by a Leybold Heraeus closed-cycle helium cryostat enables to measure in the 10-340 K temperature range. A Windaus MD850 electronic thermometer was used for reading temperature. Electronic thermometer sensitivity was better than 0.1 K.

![Schematic diagram of layers of Pt/InP/Zn-Au Schottky contact.](image1)

Results and discussion

Fabrication technique is one of the basic parameters for getting better device quality. We used magnetron sputtering technique in platinum Schottky metal coating process. Figure 2 shows a basic diagram of a coating process using magnetron sputtering technique. This technique permits controlling the thickness distribution and getting high rate of uniform surfaces. So, we can obtain stable contacts. One of the ways of testing contact quality is measuring electrical characteristics.

![Schematic diagram of platinum coating on InP substrate by magnetron sputtering technique.](image2)

Electrical performance of metal-semiconductor contacts are affected by operation temperatures and properties of preferred semiconductor type. Figure 3 displays current voltage characteristics and basic differences between the two types of Schottky diodes depending on temperatures from 20 K to 400 K. Temperature stability of various layered electronic structures containing platinum was emphasized in many studies [1]. Pt/p-InP Schottky contact had high quality rectifying behaviour in all temperature conditions. Reverse saturation currents were changed from about $10^{-9}$ A to $10^{-6}$ A. Ellipse 1 (E1) explains reverse current features of Pt/p-InP Schottky contacts in low temperature region. $I_0$ minimum currents in negative bias region were changed from about $10^{-14}$ A to $10^{-11}$ A in temperature range of 200-300 K. Reverse currents behaviour of Pt/p-InP Schottky diode is very extraordinary as seen in Ellipse (E1). The real reason of this interesting behaviour has not been explained in details. But this fluctuation is mainly attributed to dipole relaxations or reversed carriers passing from the depletion layer to electrode region [7]. The p-type contact reverse currents increase with increasing temperature from just about $10^{-9}$ A to $10^{-6}$ A in respectively from 20 K to 400 K. Pt/p-InP Schottky diode reverse currents have minimums in zero bias in 300-400 K. High performance rectifying capacity of Pt/p-InP in all temperatures can be seen in Fig. 3 explicitly. In all temperatures forward currents, coming up to approximately 0.5 A, were seen very rarely in literature. In forward bias, low temperatures induced coincided current voltage characteristics in consecutive temperatures. This result can be attributed to very low series resistance (nano and micro
ohm) approach of Chand and Bala [8]. Such an intersecting characteristics have not seen in literature up to now in such wide and low temperatures experimentally before. Thus, theoretical approach of Chand and Bala was experimentally verified by this paper. This issue will be discussed again in the course of the results of Norde calculations. In the high temperature region, p-InP based platinum Schottky diode currents were increased with increasing temperatures. In the low temperature region, very low effective barrier height regions were dominant.

Reverse currents of Pt/n-InP varies as seen in literature classically. Reverse currents of Pt/n-InP increase with increasing temperature from about 10⁻⁹ A to 10⁻² A in 20 K to 400 K as can be seen in Fig. 3. High performance rectifying capacity of Pt/n-InP in all temperatures can be seen in Fig. 3 explicitly similar to Pt/p-InP. In all temperatures forward currents pass to approximately 0.5 A values very rarely seen in literature. Coincided current-voltage characteristics as seen p-type contact in low temperature region were attributed to very low series resistance approach of Chand and Bala [8]. In forward bias region of Pt/n-InP, Ellipse 2 (E2) explains that currents were increased with decreasing temperature after a cross point. This unusual result obeys series resistance approach suggested by Oswald and Horwath [9]. They simulated current-voltage characteristics and found temperature independent effects after a cross point. They also explained the result as: “The charge carrier scattering in the depletion region is more effective for the purpose of explanation about current flow mechanism for the lower voltages than the cross-point voltage. Thereby, charge scattering limits current in the quasi-neutral portion of the semiconductor in high voltage region”. This simulated interesting cross point behaviour of Schottky contacts was proved in this paper by experimentally current-voltage characteristics of Pt/n-InP.

$I - V$ characteristics were investigated by thermionic emission (TE) current equation. The TE equation at forward-bias ($V \geq 3 \text{kT}$) can be given as:

$$I = I_0 \left[ \exp \left( \frac{e(V - IR_s)}{nkT} \right) \right]$$

(1)

where $I_0$ is saturation current and it can be defined as:

$$I_0 = AA^*T^2 \exp \left( \frac{-e\Phi_b}{kT} \right)$$

(2)

where $A$ is diode area, $A^*$ is the effective Richardson constants are respectively 60 A·cm⁻²·K⁻² and 9.8 A·cm⁻²·K⁻² for p-type InP and n-type InP. $T$ is temperature in Kelvin, $k$ is Boltzmann constant and $e$ is electronic charge and $\Phi_b$ is the zero bias barrier height (BH). We can write equations for ideality factor and barrier height as follows:

$$n = \frac{e}{kT} \frac{dV}{d(\ln I)}$$

(3)

$$e\Phi_b = kT \ln \left( \frac{AA^*T^2}{I_0} \right)$$

(4)

Figure 4 shows ideality factors ($n$) and barrier heights ($\Phi_b$) depending on given temperatures. Ideality factors were larger than unity for both diodes in all the temperatures. Ideality factors of Pt/n-InP were smaller than Pt/p-InP Schottky diode in 20-220 K. The $n$ values of both diodes were approximately same in 240-400 K. Similar barrier heights were seen in 20-60 K for both contacts. Barrier height differences between two diodes were increased with increasing temperature in range of 80-240 K. After 260 K barrier height difference was remained approximately firm. Generally, high barrier height explains a high quality contact performance. High barrier heights of Pt/p-InP/Zn-Au Schottky diode are mostly attracted attention. Barrier heights were increased with increasing temperature from 20 K to 240 K as can be seen in Fig. 4. This effect means that inhomogeneous barrier height distributions were fastly changed in the effect of temperature differences for each temperature. Approximately unchanged barrier heights show us barrier height distribution was not changed significantly depending on increasing temperature.
Linear correlation between ideality factors and barrier heights was verified in most of studies. Figure 5 shows linear and nonlinear portions of ideality factor-barrier height plot. Linear relationship between $n$ and $\Phi_b$ were seen only 140-400 K and 100-400 K for respectively Pt/p-InP and Pt/n-InP Schottky contacts. Homogeneous barrier heights of Pt/p-InP and Pt/n-InP are respectively 0.891 eV and 0.568 eV in given linear regions. In very low temperatures, nonlinearity is dominant. Nonlinearity behaviour in ideality factor-barrier height is very interesting. Namely, decreases in ideality factors were faster than decreases in barrier heights in the effect of low temperature conditions. So, homogeneous barrier height cannot be calculated from linear relationship between $n$ and $\Phi_b$ for very low temperatures. We can see linearity in BH-$n$ plot in high temperature ranges for both type of diodes. Linear relationship between barrier height and $n$ is attributed to inhomogeneous interfaces and barrier heights. But we cannot say the low temperature region has not uniform interface directly. Perhaps, because of sharp changes in consecutive slopes of the linear regions, linear regions can be brought in a curve similar to the parabola in low temperature regions. This result can be explained by temperature independent inhomogeneities of barrier heights. Very low temperature applications of Schottky diodes are not fully understood due to the experimental difficulties. Investigations under 80 K are very little to enhance a large perspective for a deep explanation of nature of Schottky contacts under this temperature.

Norde proposed a model as follows for series resistance calculations [10]:

$$F(V) = \frac{V}{\gamma} - kT \frac{q}{A^*T^2} \ln \left( \frac{I(V)}{AA^*T^2} \right)$$  \hspace{1cm} (5)

where $\gamma$ is an dimensionless integer greater than ideality factor. $I(V)$ shows current values depending on applied bias obtained from $I-V-T$ measurement results. Norde plot is seen in Fig. 6. $R_S$ is series resistance and calculated from Eq. 6.

$$R_S = \frac{kT(\gamma-n)}{qI}$$  \hspace{1cm} (6)

Series resistances were seen in Table 1. Mclean explained Norde plot as: function approaches a line with a gradient of +1/2 if there is only one series resistance [11]. Therefore, two types of Pt/InP contacts have unique series resistances at low temperatures in accordance with the approach of Chand and Bala as can be seen in Fig. 6 [8]. The +1/2 gradient of lines can be seen clearly in Fig. 6 from about 20 K to 140 K. Norde curves tend from parabolas to linear plots after a critical temperature in high temperature range for both types of contacts as a result of series resistance values. Figure 6 and Table 1 show us relationship between linearity in
Norde plots and only one series resistance approach of Norde clearly. For respectively Pt/n-InP and Pt/p-InP diode 20-100 K and 20-140 K temperature regions were seen as one series resistance regions. Norde functions did not have explicit minimums in these regions. This result is compatible with the overlapping  $I - V$ curves in low temperatures and very low series resistance approach of Chand and Bala in a perfect way as can be seen in Fig. 3 [8]. Series resistances of both types of contacts depending on temperature were seen in Table 1.

### Table 1  Series Resistances of Pt/p-InP and Pt/n-InP Schottky diodes

| T (K) | Series Resistances (R<sub>S</sub>, Ω) Pt/n-InP | Series Resistances (R<sub>S</sub>, Ω) Pt/p-InP |
|-------|---------------------------------------------|---------------------------------------------|
| 20    | only one series resistance                   | only one series resistance                   |
| 40    | only one series resistance                   | only one series resistance                   |
| 60    | only one series resistance                   | only one series resistance                   |
| 80    | only one series resistance                   | only one series resistance                   |
| 100   | only one series resistance                   | only one series resistance                   |
| 120   | 18.34 only one series resistance             |                                             |
| 140   | 21.22 only one series resistance             |                                             |
| 160   | 15.77 12.67 only one series resistance       |                                             |
| 180   | 29.95 15.00 only one series resistance       |                                             |
| 200   | 20.50 26.84 only one series resistance       |                                             |
| 220   | 29.68 35.33 only one series resistance       |                                             |
| 240   | 23.23 42.44 only one series resistance       |                                             |
| 260   | 22.42 41.14 only one series resistance       |                                             |
| 280   | 24.53 37.00 only one series resistance       |                                             |
| 300   | 21.36 19.97 only one series resistance       |                                             |
| 320   | 12.55 22.33 only one series resistance       |                                             |
| 340   | 7.27 24.63 only one series resistance        |                                             |
| 360   | 1.40 26.85 only one series resistance        |                                             |
| 380   | 0.88 18.41 only one series resistance        |                                             |
| 400   | 1.14 18.95 only one series resistance        |                                             |

### Conclusion

We fabricated Pt Schottky diodes based on n and p-types of InP semiconductor substrates by magnetron sputtering technique and compared their electrical performance. The stable temperature dependent electrical characteristics showed both two type of DC magnetron sputtered contacts showed excellent performance. The theoretical approaches of Chand and Bala and Oswald and Horwath were proved experimentally by the characteristics of p-type and n-type InP Schottky contact characteristics [8,10]. This result is supported by Norde calculations. Barrier heights and ideality factors graph show an interesting unexpected nonlinear behaviour in low temperature region. Pt/n and p-type InP Schottky diodes demonstrated high rate of electrical response from 20 K to 400 K.

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### References

[1] A. Akbay, H. Korkut, K. Ejderha, T. Korkut and A. Türüüt, “Responses of Pt/n-InP Schottky diode to electron irradiation in different temperature conditions”, J. Radioanal. Nucl. Chem. 289(1), 145-148 (2011). http://dx.doi.org/10.1007/s10967-011-1041-y

[2] P. Veeramani, M. Haris and S. M. Babu, “Investigation of CdTe<sub>x</sub> and Cd<sub>1-x</sub>Zn<sub>x</sub>Te Schottky barrier diode structure based γ-ray detectors”, Mater. Manuf. Proc, 22(3), 375-378 (2007). http://dx.doi.org/10.1080/10426910701190873

[3] D. E. Yıldız, Ş. Altundal, Z. Tekeli and M. Özer, “The effects of surface states and series resistance on the performance of Au/SnO<sub>2</sub>/n-Si and Al/SnO<sub>2</sub>/p-Si (MIS) Schottky barrier diodes”, Mat. Sci. Semonic. Proc. 13(1), 34-40 (2010). http://dx.doi.org/10.1016/j.mssp.2010.02.004

[4] M. Siad, A. Keffous, S. Mamma, Y. Belkacem and H. Menari, “Correlation between series resistance and parameters of Al/n-Si and Al/p-Si Schottky barrier diodes”, Appl. Surf. Sci. 236(1-4), 366-376 (2004). http://dx.doi.org/10.1016/j.apsusc.2004.05.009

[5] K. Akkiliç, A. Türüüt, G. Çankaya and T. Kiliçoğlu, “Correlation between barrier heights and ideality factors of Cd/n-Si and Cd/p-Si Schottky barrier diodes” Solid State Commun. 125(10), 551-556 (2003). http://dx.doi.org/10.1016/S0038-1098(02)00829-3

[6] E. Arslan, H. Çakmak and E. Özbay, “Forward tunneling current in Pt/p-InGaN and Pt/n-InGaN Schottky barriers in a wide temperature range” Microelectron. Eng. 100, 51-56 (2012). http://dx.doi.org/10.1016/j.mee.2012.07.103

[7] K. Kaneto and W. Takashima, “Fabrication and characteristics of Schottky diodes based on regioregular poly(3-hexylthiophene)/Al junction”, Curr. Appl. Phys. 1(4-5), 355-361 (2001). http://dx.doi.org/10.1016/S1567-1739(01)00035-9

[8] S. Chand and S. Bala, “Analysis of current–voltage characteristics of inhomogeneous Schottky diodes at low temperatures”, Appl. Surf. Sci. 252(2), 358-363 (2005). http://dx.doi.org/10.1016/j.apsusc.2005.01.009
[9] J. Osvald and Zs. Horvath, “Theoretical study of the temperature dependence of electrical characteristics of Schottky diodes with an inverse near-surface layer”, J. Appl. Surf. Sci. 234(1-4), 349-354 (2004). http://dx.doi.org/10.1016/j.apsusc.2004.05.046

[10] H. Norde, “A modified forward I-V plot for Schottky diodes with high series resistance”, J. Appl. Phys. 50, 5052-5053 (1979). http://dx.doi.org/10.1063/1.325607

[11] A. B. Mcleon, “Limitations to the Norde I-V plot”, Semicond. Sci. Technol. 1, 177-179 (1986). http://dx.doi.org/10.1088/0268-1242/1/3/003
Vapor Phase Polymerization Deposition Conducting Polymer Nanocomposites on Porous Dielectric Surface as High Performance Electrode Materials

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Abstract: We report chemical vapor phase polymerization (VPP) deposition of poly(3,4-ethylenedioxythiophene) (PEDOT) and PEDOT/graphene on porous dielectric tantalum pentoxide (Ta2O5) surface as cathode films for solid tantalum electrolyte capacitors. The modified oxidant/oxidant-graphene films were first deposited on Ta2O5 by dip-coating, and VPP process was subsequently utilized to transfer oxidant/oxidant-graphene into PEDOT/PEDOT-graphene films. The SEM images showed PEDOT/PEDOT-graphene films was successfully constructed on porous Ta2O5 surface through VPP deposition, and a solid tantalum electrolyte capacitor with conducting polymer-graphene nano-composites as cathode films was constructed. The high conductivity nature of PEDOT-graphene leads to resistance decrease of cathode films and lower contact resistance between PEDOT/graphene and carbon paste. This nano-composite cathode films based capacitor showed ultralow equivalent series resistance (ESR) ca. 12 mΩ and exhibited excellent capacitance-frequency performance, which can keep 82% of initial capacitance at 500 KHz. The investigation on leakage current revealed that the device encapsulation process has no influence on capacitor leakage current, indicating the excellent mechanical strength of PEDOT/PEDOT-graphene films. This high conductivity and mechanical strength of graphene-based polymer films shows promising future for electrode materials such as capacitors, organic solar cells and electrochemical energy storage devices.

Keywords: Vapor-phase polymerization; Conducting polymers; Graphene; Nanocomposites; Solid tantalum electrolyte capacitor

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Introduction

Conducting polymers (CPs) and its nanostructures has been a subject of growing interest in recent years for their promising application in microelectronics, capacitor, sensor, solar cell, et al [1-4]. As for capacitor and solar cell, it can offer high conductivity and optical transparency for the application of electrode materials, and optimized device performance has been reported after construction of CPs and its nanostructure for electrode materials and electrode surface modifying [5-7].

Solid tantalum electrolyte capacitors (STEC) based on sintered tantalum powder structure makes them volumetrically efficient, which has compact porous con-
struction and large capacitance. CPs, such as poly (3,4-ethylenedioxythiophene) (PEDOT) has been used as STEC cathode films due to its higher conductivity and reliability, which produces high performance STEC with low equivalent series resistance (ESR) [8]. However, one of the drawbacks for PEDOT as STEC electrodes is their brittleness and low mechanical strengths. Coupling CPs to carbon nanomaterials has been shown to be an effective approach to improving the mechanical strengths and conductive performance of the CPs.

Most of conducting polymers are insoluble and infusible due to the stiffness of their all-conjugated aromatic backbone structures and processing uniform conducting polymer and its nanostructures on special substrate, especially on a porous structure, to build electrode films has always represented a challenge [9-13]. The common deposition process of CPs cathode films on porous tantalum pentoxide to fabricate STEC is based on an in situ polymerization method, which is a solution based deposition process. However, this deposition process represents challenge with the decrease of tantalum particle size, which can afford larger capacitance with smaller size. With decrease of tantalum particle size, the solution based deposition method is getting difficult and uncontrollable to prepare uniform CPs films onto the tantalum pentoxide surface containing micro/nano porous structure.

Among the different techniques used to obtain micro/nano structure CPs, the vapor-phase polymerization (VPP) has attracted more attention because of its simplicity and controllability [14,15]. VPP process is a solvent-free process and polymers are synthesized by delivering monomers to a surface through the vapor phase. VPP method can also form chemically well-defined films directly on the different morphology surface or template, and represents a facile way to prepare conducting polymer and its nanocomposites on special substrate, such as porous structure substrate [16]. In the VPP process, the oxidant is thought to play a templating role that leads to particularly ordered polymers and sometimes crystalline ones, which would result in formation of polymer nanostructures with significantly higher charge conductivities because of better interchain π-π stacking in the obtained polymers. This conducting polymer nanocomposites with excellent electrical and thermal stability would be suitable as high performance capacitor electrode materials. Moreover, the simple and controllable preparation method of VPP would also give a convenience to fabricate high performance capacitors and nanocapacitors [17,18].

VPP self-assembly deposition of PEDOT has been reported by some research teams, and theses VPP conducting polymer films show promising applications in solar cells and supercapacitors [19,20]. However, to our best knowledge, there is a lack of reported work to build PEDOT and PEDOT nanocomposites as SETC electrode films through VPP process. In this work, we report VPP deposition of PEDOT and PEDOT-graphene on porous Ta2O5 as tantalum electrolyte capacitor cathode films. In the first step, oxidant and oxidant-graphene nanocomposite for polymerization were successively prepared on porous tantalum pentoxide surface by dip-coating. In the second step, the exposure of oxidant films on 3,4-ethylenedioxythiophene (EDOT) monomer vapor was used to convert the oxidant/oxidant-graphene films into PEDOT/PEDOT-graphene composite films. The inner PEDOT layer constructed on Ta2O5 is for entire capacitance extraction, and the outer PEDOT-graphene layer constructed on PEDOT is for improving conductive ability and mechanical strength of cathode films. A VPP film based Ta/Ta2O5/PEDOT/PEDOT-graphene/carbon/Ag electrolyte capacitor is constructed, and electrical performance of this capacitor is measured.

Experiment

Materials

A solution of oxidant iron (III) p-toluenesulfonate (FeTos) 40 wt% in butanol and 3, 4-ethylenedioxythiophene (EDOT) were obtained from HC Starck (under the respective trade names Clevios CB40 and Clevios M). Graphene dispersion and other reagents were purchased from Sigma-Aldrich and used without further purification. A porous tantalum sintering pellet (tantalum powder specific volume=100000 µm3/µF) for capacitor construction was purchased from Xinyun electronic company.

Construction of tantalum capacitor

Ta/Ta2O5 anodes of 68 µF used in the experiments were regular anodes, sintered in vacuo and subsequently anodized in 2.5% (wt%) phosphoric acid at 65°C. Then the Ta2O5 covered porous anodes pellet was dipped in FeTos solution and the FeTos solution was dip-coated on Ta2O5 surface. This process was carried out in KSV dip-coating instrument with a 0.5 mm/min dipping speed, which can ensure a well soaking of oxidant solution into the porous Ta2O5 structure. Then, the FeTos covered pellet was put in a 60°C vacuum oven for solvent evaporation. Oxidant layer was increased by a repeated dip-coating and drying process. After the construction of FeTos layer as inner layer, a FeTos/graphene outer layer was introduced on FeTos films by dip-coating and drying process. The thickness of this outer layer was also increased by repeated process. Following the construction of FeTos and FeTos/graphene films, tantalum sintering pellet was transferred into a small vial full of EDOT monomer vapor. The FeTos and
FeTos/graphene films were exposed on EDOT monomer vapor for 1 h to ensure complete polymerization. After the polymerization, the PEDOT/PEDOT-graphene films were then soaked in ethanol for 10-15 min and dried under vacuum oven at 40 °C for 30 min. For a complete tantalum capacitor construction, graphite and Ag pastes were deposited on PEDOT/graphene in sequence to form the electrical contact. The schematic VPP deposition and capacitor structure are shown in Fig. 1.

![Figure 1](image)

Fig. 1 Schematic of (a) VPP deposition of PEDOT/ PEDOT-graphene on Ta$_2$O$_5$ as cathode films and (b) structure of VPP film based capacitor.

Characterization

XRD patterns were recorded on Brucker AXS D8 using scanning speed of 0.02°/s and an accelerating voltage of 40 kV. Film surface morphology was investigated by using scanning electron microscopy (SEM) model S-2400 from Hitachi. The conductivity of VPP PEDOT and PEDOT/graphene was characterized by a homemade four-point probe instrument. The characterization of the capacitors was carried out using an HP 4263A LCR meter measuring capacitance, dissipation factor (DF), and equivalent series resistance (ESR). The leakage current (LC) was measured by using Tonghui LC testing instrument with model TH4321.

Results and discussion

One key issue in manufacturing vacuum sintered anodes based solid tantalum electrolyte capacitors is to build up a robust cathode layer to protect dielectric layer from possible mechanical damage. We find out the drawback of the Ta/Ta$_2$O$_5$/PEDOT capacitors made using the VPP process is the fragility of the parts due to the powdery nature of chemically synthesized PEDOT. In order to overcome this problem, we develop a VPP deposited PEDOT/graphene outer layer to improve the mechanical strength of the whole cathode films. This PEDOT/graphene outer layer can not only improve the mechanical strength ability of the whole cathode, but also reduce the cathode resistance due to the high conductive ability of graphene. The PEDOT/graphene may also result in lower contact resistance between PEDOT/graphene and latter formed carbon paste due to its suitable conductivity, and therefore, further reduces the capacitor’s ESR effectively.

Figure 2(a) shows typical sintered anode Ta porous structure, and this body shows high specific surface for the fabrication of capacitors with large capacitance. Figure 2(b) shows porous sintered anode covered by a continuous tantalum pentoxide dielectric layer. The extremely porous nature of the pellet structure requires that the cathode plate is prepared with some type of liquid or vapor preparation process. These processes will allow penetration into the depths of the structure to facilitate the deposition of cathode films through the pore structure, covering the entire surface area of the dielectric Ta$_2$O$_5$. It is essential that the solid electrolyte, in this case PEDOT, covers the whole dielectric layer in order to achieve full capacitance. It should be noted that low dipping and raising speed for sintered anode body from the FeTos solution is critical to achieve full capacitance, which will ensure a complete coverage of FeTos films on tantalum pentoxide surface. After the exposure of FeTos and FeTos/graphene covered sintered anode body in EDOT vapor, the anode body changes from yellow (shown in Fig. 2(b)) to deep violet (as shown in Fig. 2(d)) corresponding to the polymerization of EDOT into PEDOT. It should be noted that sufficient polymerization time is required for this VPP process because of the low EDOT vapor pressure in the reactor, and the enough time for EDOT vapor to pervade into films and be adsorbed on oxidant spot is needed. A reaction time at least 30-60 min appeared to be necessary to reach complete EDOT polymerization under ambient temperature or shorter at higher temperature. Figure 2(c) shows close package of VPP PEDOT on tantalum pentoxide, and it also presents particle morphology due to coverage of ultrathin PEDOT layer. After the VPP deposition of PEDOT/graphene, the particle morphology disappears and the entire tantalum pentoxide surface was covered by PEDOT/PEDOT-graphene films (as shown in Fig. 2(d)). However, we did not introduce the FeTos/graphene as inner layer in order to avoid the blocking of graphene on pore structure, which may result in incomplete coverage of PEDOT/graphene on Ta$_2$O$_5$ and incomplete capacitance extraction.
Fig. 2 SEM images of (a) high specific surface area sinter anode tantalum body, (b) Ta₂O₅ covered anode, (c) PEDOT covered tantalum body and (d) PEDOT/graphene covered tantalum body.

The VPP PEDOT films deposited on Ta₂O₅ exhibits a better uniform molecular structure because of the template effect, which results from self-assembly of EDOT in crystalline FeTos films. The XRD analysis (as shown in Fig. 3) presents diffraction peaks at 2θ = 10.8°, 12.3°, 16.5°, and 23.7°, and these peaks have been attributed to the crystalline lattice of PEDOT chains doped by tosylate anions [21]. The XRD spectrum of PEDOT/graphene almost exhibits same diffraction peaks with relative weak peak intensity, indicating the close package of PEDOT on graphene also results in formation crystalline PEDOT structure in nanocomposites.

Fig. 3 XRD analysis of VPP PEDOT/graphene (red line) and VPP PEDOT (black line) deposited on sintered tantalum anode body.

The VPP deposition of PEDOT films on tantalum pentoxide is time dependent on deposition process, enough polymerization time is needed to ensure the complete coverage of PEDOT on dielectric layer to achieve full capacitance. Figure 4 shows capacitance evolution of capacitor with increasing polymerization time. The PEDOT/PEDOT-graphene device shows satisfactory capacitance with extraction at 1 h, which is attributed to making homogeneous PEDOT coating inside the tantalum oxide pores. However, the PEDOT-graphene device shows inferior capacitance extraction performance. As we mentioned above, due to the larger size of graphene, the FeTos/graphene solution may block the pore structure, and prevent the latter oxidant solution from soaking into pore structure to form a complete coverage on inside tantalum pentoxide.

Fig. 4 Capacitance dependence of capacitor on polymerization time of VPP process.

For the conductive performance investigation, the VPP PEDOT and PEDOT/graphene deposited on SiO₂ substrate show conductivity ca. 250±20 and 320±20 s/cm respectively, measured by four probe method. The VPP PEDOT/PEDOT-graphene nanocomposite shows conductivity ca. 310±20 s/cm,
which exhibits higher conductivity than pure VPP PEDOT. The higher conductivity leads to lower resistance of cathode films and ESR of capacitors. Figure 5 shows ESR-frequency characteristics of capacitors with different VPP films as cathode films. The PEDOT/PEDOT-graphene based capacitor exhibits ultralow ESR about 12 mΩ and excellent ESR-frequency performance. Although the PEDOT-graphene films exhibits highest conductivity, the capacitor with pure PEDOT-graphene as cathode films shows high ESR. We conclude that graphene may block the pore structure during FeTos/graphene dip-coating process and latter FeTos/graphene solution cannot penetrate into the depths of the pore structure to facilitate the deposition of PEDOT onto the inside Ta_2O_5. Incomplete coverage of PEDOT on Ta_2O_5 would lead to extremely enhancement of contact resistance between dielectric layer and carbon paste, which would also result in higher ESR of capacitor.

The advantage of lower ESR of tantalum capacitor means the device may exhibit excellent capacitance-frequency characteristic. Tantalum electrolyte capacitor based on sintered porous structure likes a parallel connection structure of abundant particle capacitors (as shown in Fig. 1(b)). There is additional resistance added to the capacitor element from its location to the termination points of the capacitor. With the increase of working frequency, the deep particle capacitor will show up as decaying capacitance with increasing frequency, which results in a “roll-off” effect of capacitance. As shown in Fig. 6, all VPP films based capacitor show decaying capacitance with increasing frequency, and higher ESR would lead to an enhancement of decaying capacitance. The PEDOT/PEDOT-graphene based capacitor exhibits best capacitance-frequency performance, and it can keep 82% of initial capacitance at 500 KHz. These results indicate that the PEDOT/PEDOT-graphene nanocomposite layer constructed on Ta_2O_5 lead to substantial decrease of capacitor ESR, and is suitable as ultralow ESR tantalum capacitor cathode films.

As practical electrical applications, the tantalum electrolyte capacitors need to be encapsulated, and this encapsulation process gives a mechanical force on anode Ta_2O_5 films, which would result in leakage current resulted performance degradation of devices. In this

![Graph](image-url)

**Fig. 5** ESR versus frequency performance of tantalum capacitor with different VPP films as cathode films.

![Graph](image-url)

**Fig. 6** Capacitance versus frequency performance of different VPP film based tantalum capacitors.

![Graph](image-url)

**Fig. 7** Influence of device encapsulation process on leakage current of VPP (a) PEDOT/PEDOT-graphene films and (b) PEDOT films based capacitor.
work, the advantage to introduce PEDOT/graphene into cathode films is not only to improve the conductive ability of cathode films, but also to improve the mechanical strength of cathode films to protect dielectric layer from possible mechanical force damage. Figure 7 shows the leakage current performance comparison of VPP films based capacitors before and after encapsulation. As shown in Fig. 7(a), the encapsulation process shows no influence on leakage current of PEDOT/PEDOT-graphene based capacitor, indicating the excellent mechanical strength of PEDOT/PEDOT-graphene to protect Ta$_2$O$_5$ dielectric layer. However, an obvious leakage current enhancement is observed in VPP PEDOT based capacitors (as shown in Fig. 7(b)). We conclude the fragile nature of PEDOT can not form an effective buffer layer to absorb or reduce the mechanical force during the encapsulation, which lead to mechanical destroy of Ta$_2$O$_5$ and the increase of leakage current. In addition, we did not found any influence of encapsulation process on other parameters of PEDOT/PEDOT-graphene based capacitor, and this capacitor shows stable electrical performance for practical electronic applications. We also give a capacitor performance comparison between our work and the polypyrrole (PPy) based tantalum capacitor, which is shown in Table 1. It can be seen that PEDOT/graphene based capacitor exhibit lower ESR and better leakage current-temperature characteristic, indicating high performance of this nanocomposite as electrode materials. Furthermore, comparing with noxious PPy, the innoxious characteristics of PEDOT/graphene also gives it promising future as environment-friendly electrode materials.

Conclusions

We developed PEDOT/PEDOT-graphene nanocomposite films as cathode films for solid tantalum electrolyte capacitor. The PEDOT inner layer and PEDOT-graphene outer layer were constructed on porous Ta$_2$O$_5$ anode surface through VPP process. The incorporation of graphene into PEDOT resulted in an enhancement of conductivity and mechanical strength than pure PEDOT films, and the high conductivity of PEDOT-graphene also resulted in lower contact resistance between PEDOT and carbon paste. The VPP PEDOT/PEDOT-graphene based tantalum capacitor showed ultralow ESR ca. 12 mΩ and exhibited excellent capacitance vs frequency characteristic. The device encapsulation process showed no influence on leakage current of PEDOT/PEDOT-graphene based capacitor, indicating the excellent mechanical strength of PEDOT/PEDOT-graphene’s protecting the Ta$_2$O$_5$ dielectric film from being destroyed during encapsulation. In conclusion, this highly conductive and mechanically strong graphene-based polymer films shows promising future for high performance electrode materials such as capacitors, organic solar cells and energy storage device applications.

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References

[1] A. J. Heeger, “Semiconducting and metallic polymers: the fourth generation of polymeric materials (nobel lecture)”, Angew. Chem. Int. Ed. 40(14), 2591-261 (2001). http://dx.doi.org/10.1002/1521-3773(20010716)40:14<2591::AID-ANIE2591>3.0.CO;2-0
[2] E. E. Tannverdi, A. T. Uzumeu, H. Kavas, A. Demir, A. Baykal, “Conductivity study of polyaniline-cobalt ferrite (PANI-CoFe$_2$O$_4$) nanocomposite”, Nano-Micro Lett. 3(2), 99-107 (2011). http://dx.doi.org/10.3786/nml.v3i2.p99-107
[3] S. Guenes, H. Neugebauer and N. S. Sariciftci, “Conjugated polymer-based organic solar cells”, Chem. Rev. 107(4), 1324-1338 (2007). http://dx.doi.org/10.1021/cr050149z
[4] I. S. Chronakis, S. Grapenson and A. Jakob, “Conductive polypyrrole nanofibers via electrospinning: electrical and morphological properties”, Polymer 47(5), 1597-1603 (2006). http://dx.doi.org/10.1016/j.polymer.2006.01.032
[5] V. Khomenko, E. Frackowiak and F. F. Béguin, “Determination of the specific capacitance of conducting polymer/nanotubes composite electrodes using different cell configurations”, Electrochim. Acta

Table 1 Performance comparison of capacitors with PEDOT/graphene and PPy as cathode electrode materials (capacitor model 16 V68 μF)

| Electrode materials | Capacitance (µF) | Loss (%) | ESR (mΩ) | Leakage current (µA) |
|---------------------|-----------------|----------|----------|----------------------|
| PEDOT/graphene      | 67.3            | 1.7      | 12       | 6.8, 7.2             |
| PPy                 | 67.1            | 2.5      | 35       | 7.1, 20.3            |

(20°C 65°C)
50(12), 2499-2506 (2005). http://dx.doi.org/10.1016/j.electacta.2004.10.078

[6] A. Graeme, P. K. Snook and S. B. Adam, “Conducting-polymer-based supercapacitor devices and electrodes”, J. Power Sources 196(1), 1-12 (2011). http://dx.doi.org/10.1016/j.jpowsour.2010.06.084

[7] H. W. Gerhard and J. Friedrich, “Poly(alkylenedioxythiophene)s—new, very stable conducting polymers”, Adv. Mater. 4(2), 116-118 (1992). http://dx.doi.org/10.1002/adma.19920040213

[8] Y. Kudoh, K. Akami and Y. Matsuya, “Solid electrolytic capacitor with highly stable conducting polymer as a counter electrode”, Synth. Met. 102(1), 973-974 (1999). http://dx.doi.org/10.1016/S0379-6779(98)01012-1

[9] L. Ci, J. Suhr, V. Pushparaj, X. Zhang and P. M. Ajayan, “Continuous carbon nanotube reinforced composites”, Nano Lett. 8(12), 2762-2766 (2008). http://dx.doi.org/10.1021/nl8012715

[10] T. L. Kelly, K. Yano and M. O. Wolf, “Supercapacitive properties of PEDOT and carbon colloidal microspheres”, ACS Appl. Mater. Interfaces 1(11), 2536-2543 (2009). http://dx.doi.org/10.1021/am900575v

[11] O. Fichet, T. V. Francois, T. Dominique and C. Chevrot, “Interfacial polymerization of a 3,4-ethylenedioxythiophene derivative using Langmuir-Blodgett technique. Spectroscopic and electrochemical characterizations”, Thin Solid Films 411(2), 280-288 (2002). http://dx.doi.org/10.1016/S0040-6090(02)00271-7

[12] M. H. Jung and H. Y. Lee, “Patterning of conducting polymers using charged self-assembled monolayers”, Langmuir 24(17), 9825-9831 (2008). http://dx.doi.org/10.1021/la8014207

[13] Y. Wang, H. D. Tran and R. B. Kaner, “Template-free growth of highly aligned conducting polymer nanowires”, J. Phys. Chem. C 113(24), 10346-10349 (2009). http://dx.doi.org/10.1021/jp903583e

[14] W. E. Tenhaeff and K. K. Gleason, “Initiated and oxidative chemical vapor deposition of polymeric thin films: ICVD and OCVD”, Adv. Funct. Mater. 18(7), 979-992 (2008). http://dx.doi.org/10.1002/adfm.200701479

[15] L. D. Acqua, C. Tonina, A. Varesano, M. Canettib, W. Porziob and M. Catellani, “Vapour phase polymerisation of pyrrole on cellulose-based textile substrates”, Synth. Met. 156(5), 379-386 (2006). http://dx.doi.org/10.1016/j.synthmet.2005.12.021

[16] R. Sreenivasan and K. K. Gleason, “Overview of strategies for the CVD of organic films and functional polymer layers”, Chem. Vap. Deposition 15(4), 77-90 (2009). http://dx.doi.org/10.1002/cvde.200800040

[17] B. W. Jensen, J. Chen, K. West and G. Wallace, “Vapour phase polymerization of pyrrole and thiophene using iron(III) sulfonates as oxidizing agents”, Macromolecules 37(16), 5930-5935 (2004). http://dx.doi.org/10.1021/ma049365k

[18] A. Malinauskas, “Chemical deposition of conducting polymers”, Polymer 42(9), 3957-3972 (2001). http://dx.doi.org/10.1016/S0032-3861(00)00800-4

[19] B. W. Jensen and K. West, “Vapor-phase polymerization of 3,4-ethylenedioxythiophene: a route to highly conducting polymer surface layers”, Macromolecules 37(12), 4538-4543 (2004). http://dx.doi.org/10.1021/ma0498641

[20] J. Y. Kim, M. H. Kwon, Y. K. Min, S. Kwon and D. W. Ihm, “Self-assembly and crystalline growth of poly(3,4-ethylenedioxythiophene) nanofilms”, Adv. Mater. 19(21), 3501-3506 (2007). http://dx.doi.org/10.1002/adma.200602163

[21] L. Alexis and R. Lucie, “Production of conductive PEDOT nanofibers by the combination of electrospinning and vapor-phase polymerization”, Macromolecules 43(9), 4194-4200 (2010). http://dx.doi.org/10.1021/ma9027678
Acetylcholinesterase Biosensor Based on Poly (diallyldimethylammonium chloride)-multi-walled Carbon Nanotubes-graphene Hybrid Film

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Abstract: In this paper, an amperometric acetylcholinesterase (AChE) biosensor for quantitative determination of carbaryl was developed. Firstly, the poly (diallyldimethylammonium chloride)-multi-walled carbon nanotubes-graphene hybrid film was modified onto the glassy carbon electrode (GCE) surface, then AChE was immobilized onto the modified GCE to fabricate the AChE biosensor. The morphologies and electrochemistry properties of the prepared AChE biosensor were investigated by using scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. All variables involved in the preparation process and analytical performance of the biosensor were optimized. Based on the inhibition of pesticides on the AChE activity, using carbaryl as model compounds, the biosensor exhibited low detection limit, good reproducibility and high stability in a wide range. Moreover, the biosensor can also be used for direct analysis of practical samples, which would provide a new promising tool for pesticide residues analysis.

Keywords: Biosensor; Acetylcholinesterase; Multi-walled carbon nanotubes; Graphene; Poly (diallyldimethylammonium chloride)

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Introduction

Carbaryl, one of the carbamate pesticides, has been widely used in agriculture because of its high effectiveness for insect control [1,2]. However, long-term accumulations in environment, carbaryl will present a serious risk to human health due to its high toxicity to acetylcholinesterase, a key enzyme for the function of the central nervous system in humans [3-7]. Traditional analytical methods, such as liquid chromatographic [8,9], gas chromatography [10] and high performance liquid chromatography (HPLC) [11] are rationally selective and have low limits of detection. However, these methods require extensive sample preparation, specialized analytical equipment, and technical expertise, which are all unsuitable for rapid, immediate and large-scale sample analysis. Thus, the development of efficient, sensitive and simple analytical method for the determination of pesticide residues in food has become increasingly important.

Enzymatic methods have some advantages such as rapid response, time saving, low cost and high sensitivity [12,13]. Among these, amperometric acetylcholinesterase (AChE) biosensors based on the inhibition action of pesticides on AChE have shown satisfactory results, in which the enzymatic activity is employed as an indicator of quantitative measurement of insecticides [14-16]. The performance of the biosensors depends on the effective immobilization of enzyme onto the surface of electrode. To maintain the inherent nature of enzyme, it is necessary to choose adequate supporting materials and immobilization methods [17-20].

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Recently, the use of multi-walled carbon nanotubes (MWCNTs) and graphene (GR) for the fabrication of electrochemical biosensors has attracted considerable attention [21-24]. MWCNTs and GR have advantages in the biosensor field because of their unique physicochemical properties including high surface area, excellent electric conductivity, strong mechanical strength, good adsorptive ability and excellent biocompatibility [25-27]. Moreover, studies have revealed that nanohybrid can often combine the merits of each component and exhibit enhanced properties [28-30]. Previous literatures have proved that MWCNTs-GR hybrid can generate synergy effect, which can greatly accelerate electron-transfer processes and provide a promising electrochemical sensing platform [31-33]. However, both MWCNTs and GR are hydrophobic and tend to form agglomerates, limiting their further biological applications [34,35]. So we need to find effective dispersants to solve this problem.

Poly (diallyldimethylammonium chloride) (PDDA), a water soluble cationic polyelectrolyte, can improve the dispersibility of MWCNTs in water and form the thin films of MWCNTs for various applications [36-40]. Additionally, PDDA has excellent binding capability with graphene and increase the solubility of graphene [41,42]. Therefore, PDDA can be used for dispersing MWCNTs-GR hybrid to fabricate biosensor. However, to the best of our knowledge, there is no report based on PDDA-MWCNTs-GR hybrid modified electrodes for the quantitative determination of carbaryl. AChE/PDDA-MWCNTs-GR/GCE without carbaryl. The performance of the biosensor was tested by its DPV measurement in the same condition. The inhibition rate of of carbaryl was calculated as follows:

\[
\text{Inhibition} = \left( \frac{I_{P, \text{control}} - I_{P, \text{exp}}}{I_{P, \text{control}}} \right) \times 100\%
\]

Where, \(I_{P, \text{control}}\) was the peak current of ATCl on AChE/PDDA-MWCNTs-GR/GCE without carbaryl

**Apparatus**

A three-electrode system was employed with the modified GCE (d = 3 mm) as the working electrode, a platinum electrode as the auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode. Electrochemical measurements were performed with CHI660D electrochemical workstation (Shanghai Chenua Co., China).

**Preparation of PDDA-MWCNTs-GR hybrid**

PDDA-MWCNTs-GR hybrid was prepared according to the literatures with minor modifications [33,43]. 2 mg of MWCNTs and GR (3:1, MWCNTs:GR) were dispersed into 4 ml of 0.25% PDDA aqueous solution (containing 0.5 M NaCl) by sonication. The resulting suspension was centrifuged at 14000 rpm and washed three times with water. Finally, the obtained hybrid was dispersed into some water to form a concentration of 1 mg/ml and the resulting solution was sonicated for 5 min before use.

**Configuration of the biosensor**

First, the bare GCE was polished to a mirror-like surface with 0.3 μm and 0.05 μm alumina powder, respectively, and washed through sonication with doubly distilled water, ethanol and doubly distilled water for 3 min and dried with nitrogen stream. Then the clean GCE was coated with 7.0 µl PDDA-MWCNTs-GR suspension and dried at room temperature. Finally, the PDDA-MWCNTs-GR/GCE was coated with 5.0 µl AChE solution (100 mU) to obtain the AChE/PDDA-MWCNTs-GR/GCE. The obtained biosensor was stored at 4°C when not in use. The stepwise fabrication process of the biosensor was shown in Fig. 1.

**Measurement procedure**

The AChE/PDDA-MWCNTs-GR/GCE biosensor was employed for the determination of carbaryl using differential pulse voltammetry (DPV) method. The performance of the biosensor was tested by its DPV response in pH 7.0 PBS solution containing 1.0 mM ATCl. Then the electrode was rinsed with water and incubated in pH 7.0 PBS solution containing desired concentration of carbaryl for 12 min. Finally, it was transferred into the 1.0 mM ATCl solution for DPV measurement in the same condition. The inhibition rate of carbaryl was calculated as follows:

\[
\text{Inhibition} = \left( \frac{I_{P, \text{control}} - I_{P, \text{exp}}}{I_{P, \text{control}}} \right) \times 100\%
\]

Where, \(I_{P, \text{control}}\) was the peak current of ATCl on AChE/PDDA-MWCNTs-GR/GCE without carbaryl.
inhibition and $I_p,\text{exp}$ was the peak current of ATCl on AChE/PDDA-MWCNTs-GR/GCE with carbaryl inhibition.

After inhibited by carbaryl, the AChE/PDDA-MWCNTs-GR/GCE was reactivated by immersing into 5.0 mM pralidoxime iodide for 12 min, then transferred into pH 7.0 PBS containing 1 mM ATCl for DPV analysis of the electrochemical response. The reactivation efficiency was calculated as follows:

$$R(\%) = \frac{(I_r - I_p,\exp)}{(I_p,\text{control} - I_p,\exp)} \times 100\%$$

Where, $I_r$ was the peak current of 1 mM ATCl on AChE/PDDA-MWCNTs-GR/GCE after 5.0 mM pralidoxime iodide reactivation.

**Preparation and determination of real samples**

For the analysis of carbaryl in real samples, cleaned cabbage, garland chrysanthemum, leek and pakchoi were washed three times with double-distilled water and chopped. Then 5 g of each sample was sprayed with different concentrations of carbaryl and stored at 4°C for 24 h, then mixed with 10 ml mixed solution of acetone/pH 7.0 PBS (1:9, v:v). After that, the mixture was sonicated for 15 min and centrifuged (10 min, 10,000 rpm). The DPV analysis was performed directly in the acquired supernatants without extraction or preconcentration. The concentration of carbaryl in the samples can be obtained from the calibration curve.

**Results and discussion**

**Characterization of MWCNTs, GR and PDDA-MWCNTs-GR hybrid**

The morphologies of only MWCNTs and GR film together with PDDA-MWCNTs-GR hybrid film were characterized with scanning electron microscope (SEM). As seen from Fig. 2(a), PDDA-MWCNTs presented a large number of filamentous structure. Figure 2(b) showed a general view of PDDA-GR which clearly illustrated the flake-like shapes of graphene. Figure 2(c) showed a typical SEM image of PDDA-MWCNTs-GR hybrid film in which MWCNTs were uniformly dispersed throughout GR film. We can found that the number of junctions and extent of stacking between MWCNTs in the hybrid film were clearly reduced compared to the only MWCNTs film (Fig. 2(a)). The usual aggregation and stacking between individual GR were significantly inhibited in the PDDA-MWCNTs-GR hybrid film due to the introduction of MWCNTs. These interesting properties could enhance the surface area and porosity of PDDA-MWCNTs-GR hybrid film, which are very beneficial to the further application in biosensor field [44,45].

**Electrochemical impedance analysis**

The stepwise assembly of the biosensor was characterized by electrochemical impedance spectroscopy (EIS), and the results were shown in Fig. 3. The
electron transfer resistance (Rct) of the bare GCE was 486 Ω (curve a), by contrast, the Rct of PDDA-GR/GCE (curve b) and PDDA-MWCNTs/GCE (curve c) decreased dramatically to about 180 Ω and 120 Ω, respectively. This phenomenon suggested that PDDA-GR and PDDA-MWCNTs hybrid greatly improved the conductivity of the modified electrode due to their high surface area and excellent electric conductivity. For PDDA-MWCNTs-GR/GCE (curve d), the Rct was 50 Ω, further decreased compared with curve b and curve c. The reason might be that the nano-hybrid of MWCNTs and GR could significantly reduce the aggregation and stacking between MWCNTs or GR, which resulted in enhanced surface area and wide porous structure of PDDA-MWCNTs-GR hybrid. When AChE was immobilized onto the surface of PDDA-MWCNTs-GR/GCE (curve e), the Rct remarkably increased to 1100 Ω due to the increase of the thickness of the interface, which insulated the conductive support and reduced the electron transfer between anionic [Fe(CN)]$_6^{3−/4−}$ and GCE [46-48].

Cyclic voltammetric behavior of ATCl

Figure 4(A) showed the cyclic voltammograms (CVs) of different fabricated electrodes in absence and presence of ATCl in pH 7.0 PBS. No peak was observed at bare GCE (curve a) and AChE/PDDA-MWCNTs-GR/GCE (curve b) in PBS without ATCl. CV of AChE/PDDA-MWCNTs-GR/GCE (curve d) showed an irreversible oxidation peak in the presence of 1.0 mM ATCl, whereas no detectable signal was observed for PDDA-MWCNTs-GR/GCE (curve c). Conspicuously, this peak is ascribed to the oxidation of thiocholine, hydrolysis product of ATCl, catalyzed by immobilized AChE. The peak current produced by the oxidation of thiocholine was used as an indicator for quantitative measurement of the enzyme activity.

To further study the different modified materials of electrode, the CVs of AChE/GCE (curve a), AChE/PDDA-GR/GCE (curve b), AChE/PDDA-MWCNTs/GCE (curve c) and AChE/PDDA-MWCNTs-GR/GCE (curve d) in the presence of 1.0 M ATCl in pH 7.0 were showed in Fig. 4(B). AChE/GCE (curve a) showed a small peak current, which may be due to the low enzyme loading arising from the weak combination between AChE and GCE. Compared with AChE/GCE, the peak currents increased sharply of the electrode with PDDA-GR or PDDA-MWCNTs. It was estimated that PDDA-GR and PDDA-MWCNTs had the ability to promote the electron transfer. A significant increase of peak current was obtained at AChE/PDDA-MWCNTs-GR/GCE (curve d), which was attributed to the synergistic effect between PDDA-GR and PDDA-MWCNTs.

![Fig. 3 EIS of (a) bare GCE; (b) PDDA-GR/GCE; (c) PDDA-MWCNTs/GCE; (d) PDDA-MWCNTs-GR/GCE; (e) AChE/PDDA-MWCNTs-GR/GCE recorded in pH 7.0 PBS containing 5.0 mM [Fe(CN)]$_6^{3−/4−}$ and 0.1 M KCl.](image)

![Fig. 4 (A) CVs of (a) bare GCE; (b) AChE/PDDA-MWCNTs-GR/GCE in the blank PBS (0.1 M, pH 7.0); and (c) PDDA-MWCNTs-GR/GCE; (d) AChE/PDDA-MWCNTs-GR/GCE in 0.1 M PBS (pH 7.0) containing 1.0 mM ATCl. (B) CVs of (a) AChE/GCE; (b) AChE/PDDA-GR/GCE; (c) AChE/PDDA-MWCNTs /GCE; (d) AChE/PDDA-MWCNTs-GR/GCE in the presence of 1.0 mM ATCl in 0.1 M PBS (pH 7.0).](image)
Fig. 5 (a) Effect of the PDDA-MWCNTs-GR concentration on the amperometric response; (b) Effect of enzyme amount on the amperometric response; (c) Relationship between inhibition rate and inhibition time; (d) Effect of the detection solution pH on the amperometric response.

Optimization of experimental parameters

Influence of PDDA-MWCNTs-GR concentration

The concentration of PDDA-MWCNTs-GR hybrid played an important role in achieving good analytical performance. The response currents of the enzyme electrode were investigated in 0.1 M pH 7.0 PBS containing 1.0 mM ATCl. As shown in Fig. 5(a), the signal current increased gradually with the increase of PDDA-MWCNTs-GR concentration, and when it increased to 1 mg/ml, no obvious enhancement of current was observed. Thus, 1 mg/ml PDDA-MWCNTs-GR was selected to prepare the biosensor.

Influence of enzyme amount

Figure 5(b) showed the influence of enzyme amount on the response of biosensor. With the increasing of AChE loading amount, the peak current increased sharply and reached the maximal value at 0.1 U. After that, the amperometric response decreased gradually as the amount of AChE further increased. Therefore, 0.1 U of AChE was used in the subsequent experiment.

Influence of detection solution pH

The sensitivity and stability of the biosensor depended greatly on the pH of electrolyte solution. Figure 5(c) showed the plot of peak current of the biosensor versus different pH in 0.1 M PBS in the presence of 1.0 mM ATCl. The maximum peak current appeared at pH 7.0, which was closed to that previous report for free AChE [49], suggesting the immobilization did not change the fundamental microenvironment of AChE. Thus, pH 7.0 was chosen for the subsequent experiment.

Influence of incubation time on inhibition

The incubation time was an important factor for capturing carbaryl. As shown in Fig. 5(d), the steady-state current decreased greatly with the increase of incubation time. When the immersing time was longer than 12 min, the inhibition curve trended to a stable value. However, the inhibition of carbaryl could not reach 100%, which indicated that the binding sites between pesticides and enzymes could reach an equilibration...
Fig. 6 (a) The DPVs of AChE/PDDA-MWCNTs-GR/GCE after inhibition by carbaryl of different concentrations (from a to k): 0, 0.1, 0.5, 20, 35, 50, 100, 500, 800, 1000, 1200 ng/ml under the optimal conditions; (b) Relationship between inhibition rates and carbaryl concentrations. Inset: linear relationship between low inhibitions and low concentrations.

Table 1 Comparison of analytical characteristics with other reported biosensors for the detection of carbaryl

| Electrode                   | Liner range               | Detection limit | References |
|-----------------------------|---------------------------|-----------------|------------|
| AChE-CdS-G-CHIT/GCE         | 2-2000 ng/ml              | 0.7 ng/ml       | [51]       |
| AChE/PB-CHIT/GCE            | 2-80 ng/ml, 200-1000 ng/ml| 0.6 ng/ml       | [52]       |
| AChE/carbon paste electrodes| 1-15 µg/ml                | 0.4 µg/ml       | [53]       |
| AChE-CHIT/Au                | 0.005-0.1 µg/ml, 0.5-5 µg/ml| 0.003 µg/ml     | [54]       |
| GC/MWCNT/CoPc               | 66-1322 ng/ml             | 1.1 ng/ml       | [55]       |
| GC/PANI/MWCNT/AChE          | 1.98-9.92 µg/ml           | 0.28 µg/ml      | [56]       |
| AChE/PDDA-MWCNTs-GR/GCE     | 0.8-50 ng/ml, 50-3000 ng/ml| 0.13 ng/ml     | This work  |

state [50]. Thus, the time of 12 min was selected as the optimum inhibition time.

Detection of carbaryl

Figure 6(a) showed the DPVs of the biosensor before and after incubation with carbaryl of different concentrations under the optimal conditions. It was evident that the peak current decreased drastically with the increasing concentration of carbaryl. It might be due to the fact that carbaryl exhibited fairly high toxicity and performed irreversible inhibition action on AChE, which reduced the enzymatic activity to its substrate. Under the optimal conditions, the inhibition of carbaryl on AChE/PDDA-MWCNTs-GR/GCE was proportional to its concentrations in two ranges, from 0.5 to 50 ng/ml and from 50 to 3000 ng/ml (Fig. 6(b)). The regression equations were $I\% = 0.313c$ (ng/ml) + 20.228 ($R = 0.9971$) and $I\% = 0.0128c$ (ng/ml) + 36.185 ($R = 0.9968$). The detection limit was calculated to be 0.13 ng/ml ($S/N = 3$).

A comparison of analytical characteristics of AChE/PDDA-MWCNTs-GR/GCE with other reported biosensors for the detection of carbaryl was summarized in Table 1.

Precision, stability and reactivation

The inter-assay precision was estimated by comparing the responses of 5 different electrodes to 1.0 mM ATCl after being treated with 10 ng/ml carbaryl solutions for 12 min. Similarly, the intra-assay precision of the biosensor was evaluated by analyzing carbaryl levels for 5 replicate measurements at one enzyme electrode. The RSD values of inter-assay and intra-assay were found to be 4.1% and 4.7%, respectively, indicating acceptable precision and replicability. The enzyme electrode was stored at 4°C in dry condition for 7 days, and no obvious decrease in the response of ATCl was observed. After a 30-day storage period, the biosensor still retained 87% of its initial current response, indicating satisfactory stability.

According to previous reports, the inhibited AChE could be reactivated by oximes, such as pralidoxime iodide [57,58]. After reactivation with 5.0 mM pralidoxime iodide solution for 12 min, the activity of regenerated AChE could reach to 93% of its original value, indicating acceptable reproducibility.
Real samples analysis

In order to evaluate the practicality of the proposed biosensor, the recovery tests were studied by adding different amounts of carbaryl into real samples, cabbage, garland chrysanthemum, leek and pakchoi. Results were summarized in Table 2. The recoveries were from 92.3% to 107%, suggesting that the proposed biosensor could be used for direct analysis of practical samples.

Table 2 Recovery studies of carbaryl in real samples

| Sample                  | Taken (ng/ml) | Found (ng/ml) | Recovery (%) |
|-------------------------|---------------|---------------|--------------|
| cabbage                 | 10            | 9.31          | 93.1         |
|                         | 100           | 97.1          | 97.1         |
| garland chrysanthemum   | 10            | 10.5          | 105          |
|                         | 100           | 92.3          | 92.3         |
| leek                    | 10            | 10.7          | 107          |
|                         | 100           | 106           | 106          |
| pakchoi                 | 10            | 9.53          | 95.3         |
|                         | 100           | 106           | 106          |

Conclusion

In this work, the AChE/PDDA-MWCNTs-GR/GCE biosensor had been successfully fabricated for the detection of carbaryl. The nano-hybrid of MWCNTs-GR could significantly reduce the aggregation and stacking between MWCNTs and GR, which resulted in enhanced surface area and wide porous structure of the hybrid. At the same time, PDDA increased the solubility of MWCNTs-GR hybrid. Based on these good properties, the AChE/PDDA-MWCNTs-GR/GCE exhibited excellent performances for the detection of carbaryl, such as wide linear detection range, low detection limit, high sensitivity, good stability and acceptable reproducibility. In addition, the biosensor could be applied for direct analysis of practical samples. Therefore, we believe the PDDA-MWCNTs-GR hybrid biocompatible film will pave the way to the new AChE-based inhibitor biosensor for carbamate pesticides’ determination.

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References

[1] D. W. Miwa, G. R. P. Malpass, S. A. S. Machado and A. J. Motheo, “Electrochemical degradation of carbaryl on oxide electrodes”, Water Res. 40(17), 3281-3289 (2006). http://dx.doi.org/10.1016/j.watres.2006.06.033
[2] F. Arduini, F. Ricci, C. S. Tuta, D. Moscone, A. Amine and G. Palleschi, “Detection of carbamic and organophosphorous pesticides in water samples using a cholinesterase biosensor based on Prussian Blue-modified screen-printed electrode”, Anal. Chim. Acta. 580(2), 155-162 (2006). http://dx.doi.org/10.1016/j.aca.2006.07.052
[3] J. M. Abad, F. Pariente, L. Hernández, H. D. Abruna and E. Lorenzo, “Determination of organophosphorus and carbamate pesticides using a piezoelectric biosensor”, Anal. Chem. 70(14), 2848-2855 (1998). http://dx.doi.org/10.1021/ac971374m
[4] D. Du, M. H. Wang, J. Cai, Y. Tao, H. Y. Tu and A. D. Zhang, “Immolization of acetylcholinesterase based on the controllable adsorption of carbon nanotubes onto an alkanethiol monolayer for carbaryl sensing”, Analyst 133(12), 1790-1795 (2008). http://dx.doi.org/10.1039/b803851a
[5] A. Vakurov, C. E. Simpson, C. L. Daly, T. D. Gibson and P. A. MIlller, “Acetylcholinesterase-based biosensor electrodes for organophosphate pesticide detection: II. Immobilization and stabilization of acetylcholinesterase”, Biosens. Bioelectron. 20(11), 2324-2329 (2005). http://dx.doi.org/10.1016/j.bios.2004.07.022
[6] D. Du, S. Z. Chen, J. Cai and A. D. Zhang, “Electrochemical pesticide sensitivity test using acetylcholinesterase biosensor based on colloidal gold nanoparticle modified sol-gel interface”, Talanta 74(4), 766-772 (2008). http://dx.doi.org/10.1016/j.talanta.2007.07.014
[7] N. Sattarahmady, H. Heli and A. A. Moosavi-Movahedi, “An electrochemical acetylcholine biosensor based on nanoshells of hollow nickel microspheres-carbon microparticles-Nafion nanocomposite”, Biosens. Bioelectron. 25(10), 2329-2335 (2010). http://dx.doi.org/10.1016/j.bios.2010.03.031
[8] M. C. Pietrogrande, G. Blo and C. Bighi, “High-performance liquid chromatographic determination of naphthols as 4-aminoantipyrine derivatives: Application to carbaryl”, J. Chromatogr. 349(1), 63-68 (1985). http://dx.doi.org/10.1016/S0021-9673(00)90633-2
[9] B. D. McGarvey, “High-performance liquid chromatographic methods for the deter- mination of N-methylcarbamate pesticides in water, soil, plants and air”, J. Chromatogr. 642(1-2), 89-105 (1993). http://dx.doi.org/10.1016/0021-9673(93)80079-N
[10] E. P. Syrago-Styliani, T. Anthony and A. S. Panayotis. “Determination of carbofuran, carbaryl and their main metabolites in plasma samples of...
agricultural populations using gas chromatography-tandem mass spectrometry”, Anal. Bioanal. Chem. 385(8), 1444-1456 (2006). http://dx.doi.org/10.1007/s00216-006-0569-0

[11] C. Mohan, Y. Kumar, J. Madan and N. Saxena, “Multiresidue analysis of neonicotinoids by solid-phase extraction technique using high-performance liquid chromatography”, Environ. Monit. Assess. 165(1-4), 573-576 (2010). http://dx.doi.org/10.1007/s10661-009-0968-8

[12] X. Sun and X. Y. Wang, “Acetylcholinesterase biosensor based on prussian blue-modified electrode for detecting organophosphorous pesticides”, Biosens. Bioelectron. 25(12), 2611-2614 (2010). http://dx.doi.org/10.1016/j.bios.2010.04.028

[13] D. Du, W. J. Chen, W. Y. Zhang, D. L. Liu, H. B. Li and Y. H. Lin, “Covalent coupling of organophosphorous hydrolase loaded quantum dots to carbon nanotube/Au nanocomposite for enhanced detection of methyl parathion”, Biosens. Bioelectron. 25(6), 1370-1375 (2010). http://dx.doi.org/10.1016/j.bios.2009.10.032

[14] M. Shi, J. J. Xu, S. Zhang, B. H. Liu and J. L. Kong, “A mediator-free screen-printed amperometric biosensor for screening of organophosphorous pesticides with flow-injection analysis (FIA) system”, Talanta 68(4), 1089-1095 (2006). http://dx.doi.org/10.1016/j.talanta.2005.07.007

[15] F. N. Kok and V. Hasirci, “Determination of binary pesticide mixtures by an acetylcholinesterase-choline oxidase biosensor”, Biosens. Bioelectron. 19(7), 661-665 (2004). http://dx.doi.org/10.1016/j.bios.2003.07.002

[16] A. Amine, H. Mohammadi, I. Bourais and G. Palleschi, “Enzyme inhibition-based biosensors for food safety and environmental monitoring”, Biosens. Bioelectron. 21(8), 1405-1423 (2006). http://dx.doi.org/10.1016/j.bios.2005.07.012

[17] D. Du, S. Z. Chen, J. Cai and A. D. Zhang, “Immobilization of acetylcholinesterase on gold nanoparticles embedded in sol-gel film for amperometric detection of organophosphorous insecticide”, Biosens. Bioelectron. 23(1), 130-134 (2007). http://dx.doi.org/10.1016/j.bios.2007.03.008

[18] S. Sotiropoulou and N. A. Chaniotakis, “Lowering the detection limit of the acetylcholinesterase biosensor using a nanoporous carbon matrix”, Anal. Chim. Acta. 530(2), 199-204 (2005). http://dx.doi.org/10.1016/j.aca.2004.09.007

[19] D. Shan, E. Han, H. G. Xue and S. Cosnier, “Self-assembled films of hemoglobin/laponite/chitosan: application for the direct electrochemistry and catalysis to hydrogen peroxide”, Biomacromolecules 8(10), 3041-3046 (2007). http://dx.doi.org/10.1021/bm070329d

[20] W. Zhao, P. Y. Ge, J. J. Xu and H. Y. Chen, “Selective detection of hypotonic organophosphates pesticides via PDMS composite based acetylcholinesterase-inhibition biosensor”, Environ. Sci. Technol. 43(17), 6724-6729 (2009). http://dx.doi.org/10.1021/es900841n

[21] L. Q. Rong, C. Yang, Q. Y. Qian and X. H. Xia, “Study of the nonenzymatic glucose sensor based on highly dispersed Pt nanoparticles supported on carbon nanotubes”, Talanta 72(2), 819-824 (2007). http://dx.doi.org/10.1016/j.talanta.2006.12.037

[22] Y. Wang, Y. M. Li, L. H. Tang, J. Lu and J. H. Li, “Application of graphene-modified electrode for selective detection of dopamine”, Electrochem. Commun. 11(4), 889-892 (2009). http://dx.doi.org/10.1016/j.electacta.2009.02.013

[23] C. S. Shan, H. F. Yang, J. F. Song, D. X. Han, A. Ivaska and L. Niu, “Direct electrochemistry of glucose oxidase and biosensing for glucose based on graphite”, Anal. Chem. 81(6), 2378-2382 (2009). http://dx.doi.org/10.1021/ac802193c

[24] X. H. Kang, J. Wang, H. Wu, I. A. Aksay, J. Liu and Y. H. Lin, “Glucose oxidase-graphene-chitosan modified electrode for direct electrochemistry and glucose sensing”, Biosens. Bioelectron. 25(4), 901-905 (2009). http://dx.doi.org/10.1016/j.bios.2009.09.004

[25] Y. Li, R. Yuan, Y. Q. Chai and Z. J. Song, “Electrodeposition of gold-platinum alloy nanoparticles on carbon nanotubes as electrochemical sensing interface for sensitive detection of tumor marker”, Electrochim. Acta. 56(19), 6715-6721. http://dx.doi.org/10.1016/j.electacta.2011.05.066

[26] J. D. Huang, X. R. Xing, X. M. Zhang, X. R. He, Q. Lin, W. J. Lian and H. Zhu, “A molecularly imprinted electrochemical sensor based on multiwalled carbon nanotube-gold nanoparticle composites and chitosan for the detection of tyramine”, Food Res. Int. 44(1), 276-281 (2011). http://dx.doi.org/10.1016/j.foodres.2010.10.020

[27] Z. Yang, R. G. Gao, N. T. Hu, J. Chai, Y. W. Cheng, L. Y. Zhang, H. Wei, E. S. Kong and Y. F. Zhang, “The prospective two-dimensional graphene nanosheets: preparation, functionalization, and applications”, Nano-Micro Lett. 4(1), 1-9 (2012). http://dx.doi.org/10.1007/s13299-012-0014-0

[28] R. Y. Zhang and X. M. Wang, “One step synthesis of multiwalled carbon nanotube/gold nanocomposites for enhancing electrochemical response”, Chem. Mater. 19(5), 976-978 (2007). http://dx.doi.org/10.1021/cm062791v

[29] T. Yang, N. Zhou, Y. C. Zhang, W. Zhang, K. Jiao and G. C. Li, “Synergistically improved sensitivity for the detection of specific DNA sequences using polyaniline nanofibers and multi-walled carbon nanotubes composites and chitosan modified electrode for direct electrochemistry and glucose sensing”, Biosens. Bioelectron. 24(7), 2165-2170 (2009). http://dx.doi.org/10.1016/j.bios.2008.11.011

[30] Y. H. Xiao and C. M. Li, “Nanocomposites: from fabrications to electrochemical bioapplications”, Electroanal. 20(6), 648-662 (2008). http://dx.doi.org/10.1002/eela.200704125

[31] H. Zhang, L. Z. Fan and S. H. Yang, “Significantly accelerated direct electron-transfer kinetics of hemoglobin in a C60-MWCNT nanocomposite film”, Nano-Micro Lett. 5(1), 47-56 (2013). http://dx.doi.org/10.3786/nml.v5i1.p47-56
[32] M. Zhou, J. D. Guo, L. P. Guo and J. Bai, “Electrochemical sensing platform based on the highly ordered mesoporous carbon-fullerene system”, Anal. Chem. 80(12), 4642-4650 (2008). http://dx.doi.org/10.1021/ac702496k

[33] X. Chen, J. Zhu, Q. Xi and W. S. Yang, “A high performance electrochemical sensor for acetaminophen based on single-walled carbon nanotube-graphene nanosheet hybrid films”, Sens. Actuators B 161(1), 648-654 (2012). http://dx.doi.org/10.1016/j.snb.2011.10.085

[34] Y. Y. Wang, X. S. Wang, B. Y. Wu, Z. X. Zhao, F. Yin, S. Li, X. Qin and Q. Chen, “Dispersion of single-walled carbon nanotubes in poly(diallyldimethylammonium chloride) for preparation of a glucose biosensor”, Sens. Actuators B 130(2), 809-815 (2008). http://dx.doi.org/10.1016/j.snb.2007.10.054

[35] J. Manso, M. L. Mena, P. Yáñez-Sedeño and J. M. Pingarrón, “Alcohol dehydrogenase amperometric biosensor based on a colloidal gold-carbon nanotubes composite electrode”, Electrochim. Acta 53(11), 4007-4012 (2008). http://dx.doi.org/10.1016/j.electacta.2007.10.003

[36] B. Kim, H. Park and W. M. Sigmund, “Electrostatic interactions between shortened multiwall carbon nanotubes and polyelectrolytes”, Langmuir 19(6), 2525-2527 (2003). http://dx.doi.org/10.1021/la026746n

[37] B. Kim and W. M. Sigmund, “Self-alignment of shortened multiwall carbon nanotubes on polyelectrolyte layers”, Langmuir 19(11), 4848-4851 (2003). http://dx.doi.org/10.1021/la026679x

[38] J. J. Rouse and P. T. Lillehei, “Electrostatic assembly of polymer/single walled carbon nanotube multilayer films”, Nano Lett. 3(1), 59-62 (2003). http://dx.doi.org/10.1021/nl025780j

[39] R. Z. Ma, T. Sasaki and Y. Bando, “Layer-by-layer assembled multilayer films of titanate nanotubes, Ag- or Au-loaded nanotubes, and nanotubes/nanospheres with polycations”, J. Am. Chem. Soc. 126(33), 10382-10388 (2004). http://dx.doi.org/10.1021/ja048855p

[40] A. B. Artyukhin, O. Bakajin, P. Stroeve and A. Noy, “Layer-by-layer electrostatic self-assembly of polyelectrolyte nanoshells on individual carbon nanotube templates”, Langmuir 20(4), 1442-1448 (2004). http://dx.doi.org/10.1021/la035699b

[41] K. P. Liu, J. J. Zhang, G. H. Yang, C. M. Wang and J. J. Zhu, “Direct electrochemistry and electrocatalysis of hemoglobin based on poly (diallyldimethylammonium chloride) functionalized graphene sheets/room temperature ionic liquid composite film”, Electrochem. Commun. 12(3), 402-405 (2010). http://dx.doi.org/10.1016/j.elecom.2010.01.004

[42] Q. L. Feng, K. P. Liu, J. J. Fu, Y. Z. Zhang, Z. X. Zheng, C. M. Wang, Y. L. Du and W. C. Ye, “Direct electrochemistry of hemoglobin based on nano-composite film of gold nanoparticles and poly (diallyldimethylammonium chloride) functionalized graphene”, Electrochim. Acta. 60, 304-308 (2012). http://dx.doi.org/10.1016/j.electacta.2011.11.048

[43] M. Eguilaz, R. Villalonga, P. Yanez-Sedeno and J. M. Pingarron, “Designing electrochemical interfaces with functionalized magnetic nanoparticles and wrapped carbon nanotubes as platforms for the construction of high-performance biocatalyst biosensors”, Anal. Chem. 83(20), 7807-7814 (2011). http://dx.doi.org/10.1021/ac201466m

[44] D. W. Wang, F. Li, M. Liu, G. Q. Lu and H. M. Cheng, “3D periodic hierarchical porous graffitic carbon material for high rate electrochemical capacitive energy storage”, Angew. Chem. Int. Ed. 47(2), 373-376 (2008). http://dx.doi.org/10.1002/anie.200702721

[45] A. Walcarius and A. Kuhn, “Ordered porous thin films in electrochemical analysis”, Trends Anal. Chem. 27(7), 593-603 (2008). http://dx.doi.org/10.1016/j.tacl.2008.03.011

[46] J. Zhang, J. Lia, F. Yang, B. L. Zhang and X. R. Yang, “Preparation of prussian blue@Pt nanoparticles/carbon nanotubes composite material for efficient determination of H2O2”, Sens. Actuators B 143(1), 373-380 (2009). http://dx.doi.org/10.1016/j.snb.2009.08.018

[47] D. Du, S. Z. Chen, D. D. Song, H. L. Li and X. Chen, “Development of acetylcholinesterase biosensor based on CdTe quantum dots/gold nanoparticles modified chitosan microspheres interface”, Biosens. Bioelectron. 24(3), 475-479 (2008). http://dx.doi.org/10.1016/j.bios.2008.05.005

[48] N. Chauhan and C. S. Pundir, “An amperometric biosensor based on acetylcholinesterase immobilized onto iron oxide nanoparticles/multi-walled carbon nanotubes modified gold electrode for measurement of organophosphorus insecticides”, Anal. Chim. Acta. 701(1), 66-74 (2011). http://dx.doi.org/10.1016/j.aca.2011.06.014

[49] M. Bernabei, S. Chiavarri, C. Cremisini and G. Palleschi, “Anticholinesterase activity measurement by a choline biosensor: application in water analysis”, Biosens. Bioelectron. 8(5), 265-271 (1993). http://dx.doi.org/10.1016/0956-5663(93)80014-G

[50] D. Du, X. X. Ye, J. Cai, J. Liu and A. D. Zhang, “Acetylcholinesterase biosensor design based on carbon nanotube-encapsulated polypryro and polyaniline copolymer for amperometric detection of organophosphates”, Biosens. Bioelectron. 25(11), 2503-2508 (2010). http://dx.doi.org/10.1016/j.bios.2010.04.018

[51] K. Wang, Q. Liu, L. Dai, J. J. Yan, C. Ju, B. J. Qiu and X. Y. Wu, “A highly sensitive and rapid organophosphate biosensor based on enhancement of CdS-decorated graphene nanocomposite”, Anal. Chim. Acta 695(1-2), 84-88 (2011). http://dx.doi.org/10.1016/j.aca.2011.03.042

[52] Y. H. Song, M. Zhang, L. Wang, L. L. Wan, X. P. Xiao, S. H. Ye and J. R. Wang, “A novel biosensor based on...
[53] J. Caetano and S. A. S. Machado, “Determination of carbaryl in tomato “in natura” using an amperometric biosensor based on the inhibition of acetylcholinesterase activity”, Sens. Actuators B 129(1), 40-46 (2008). http://dx.doi.org/10.1016/j.snb.2007.07.098

[54] D. Du, J. W. Ding, J. Cai and A. D. Zhang, “Determination of carbaryl pesticide using amperometric acetylcholinesterase sensor formed by electrochemically deposited chitosan”, Colloids Surf. B 58(2), 145-150 (2007). http://dx.doi.org/10.1016/j.colsurfb.2007.03.006

[55] F. C. Moraes, L. H. Mascaro, S. A. S. Machado and C. M. A. Brett, “Direct electrochemical determination of carbaryl using a multi-walled carbon nanotube/cobalt phthalocyanine modified electrode”, Talanta 79(5), 1406-1411 (2009). http://dx.doi.org/10.1016/j.talanta.2009.06.013

[56] I. Cesarino, F. C. Moraes, M. R. V. Lanza and S. A. S. Machado, “Electrochemical detection of carbamate pesticides in fruit and vegetables with a biosensor based on acetylcholinesterase immobilised on a composite of polyaniline-carbon nanotubes”, Food Chem. 135(3), 873-879 (2012). http://dx.doi.org/10.1016/j.foodchem.2012.04.147

[57] D. Du, S. Z. Chen, J. Cai and D. D. Song, “Comparison of drug sensitivity using acetylcholinesterase biosensor based on nanoparticles-chitosan sol-gel composite”, J. Electroanal. Chem. 611(1-2), 60-66 (2007). http://dx.doi.org/10.1016/j.jelechem.2007.08.007

[58] H. S. Yin, S. Y. Ai, J. Xu, W. J. Shi and L. S. Zhu, “Amperometric biosensor based on immobilized acetylcholinesterase on gold nanoparticles and silk fibroin modified platinum electrode for detection of methyl paraoxon, carbofuran and phoxim”, J. Electroanal. Chem. 637(1-2), 21-27 (2009). http://dx.doi.org/10.1016/j.jelechem.2009.09.025
Hydrothermal Synthesis and Characterization of Europium-doped Barium Titanate Nanocrystallites

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Abstract: Barium titanate nanocrystallites were synthesized by a hydrothermal technique from barium chloride and tetrabutyl titanate. Single-crystalline cubic perovskite BaTiO3 consisting of spherical particles with diameters ranging from 10 to 30 nm was easily achieved by this route. In order to study the influence of the synthesis process on the morphology and the optical properties, barium titanate was also prepared by a solid-state reaction. In this case, only the tetragonal phase which crystallizes above 900°C was observed. High-temperature X-ray diffraction measurements were performed to investigate the crystallization temperatures as well as the particle sizes via the Scherrer formula. The lattice vibrations were evidenced by infrared spectroscopy. Eu3+ was used as a structural probe, and the luminescence properties recorded from BaTiO3:Eu3+ and elaborated by a solid-state reaction and hydrothermal process were compared. The reddish emission of the europium is increased by the nanometric particles.

Keywords: BaTiO3; Europium; Nanocrystallites; Hydrothermal technique

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Introduction

BaTiO₃ is one of the most widely used ferroelectric materials, especially for the manufacture of thermistors, electro-optics devices and multilayered capacitors (MLCCs) [1,2]. Many researches are devoted to diminishing the size of BaTiO₃ crystals in order to fulfill the requirements of nanoelectronic devices. When they are doped with lanthanide ions, insulating materials exhibit optical properties, which are greatly dependent on the crystals’ size [3]. As a consequence the studies related on the luminescence properties of newly doped nanostructured systems with rare earth elements have been increased as an efficient tool to investigate the insulating materials’ size [4]. In particular, barium titanate has been studied regarding its luminescent properties when doped with rare earth elements such as Eu3+ [3], Yb3+ [4,5] and Er3+ [6]. Its perovskite structure allows hosting ions of a different size, and a high concen-

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tronization of doping ions can be accommodated without major difficulties. Therefore, recently there has been a tremendous interest to prepare such materials.

The conventional solid-state reaction to synthesizing ceramics requires a calcination step at high temperature for enhancing the diffusivity between raw solid materials, whereby resulting in the increase of grain size. To overcome such a drawback, wet chemical routes have been intensively investigated because they allow a better control of the granulometric distribution and lead to highly pure BaTiO$_3$ nanocrystals, e.g., by using a hydrothermal method [7-11], sol-gel process [12-16], oxalate route [17], micro-emulsion process [18], microwave heating [19], polymeric precursor method [20] and homogeneous coprecipitation [21]. The hydrothermal synthesis of ceramic powders is of great interest because of the possibility to prepare pure and ultrafine particles with narrow size distribution from inexpensive and easily accessible precursors in a single step [22]. Hence, the synthesis can be performed at moderate temperature and pressure using a simple autoclave. Varying the chemical process parameters, such as reagent concentrations, temperature, pressure, and pH, can optimize the conditions of a hydrothermal reaction. Several polymorphic varieties of BaTiO$_3$ have already been isolated: rhombohedral, orthorhombic, tetragonal, cubic, and hexagonal [23].

It is well known that the ferroelectricity degree of BaTiO$_3$ decreases when decreasing the particle size, and disappears below a certain critical size because of the crystallographic phase transition from tetragonal to cubic [24]. A limit size of 50 nm has been postulated by Ishikawa et al. [25] and Schlag et al. [26] as being critical for ferroelectric properties of BaTiO$_3$. Few studies have already described the preparation of Eu$^{3+}$-doped BaTiO$_3$ using the hydrothermal method [27,28]. In the present work, nanocrystallites of BaTiO$_3$:Eu$^{3+}$ (5 mol %) were obtained by an original synthesis procedure using a hydrothermal method (hm). BaTiO$_3$:Eu$^{3+}$ (5 mol%) powders were also synthesized by using the solid-state reaction (ssr) for comparison. The samples were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), FTIR and Raman spectroscopies as well as scanning and transmission electron microscopies (SEM and TEM). Furthermore, the photoluminescence properties were recorded for both samples.

**Experimental Section**

**Preparation of barium titanate powders by hydrothermal synthesis**

Barium titanate was prepared via a hydrothermal route according to the following procedure. All experiments were carried out at room temperature under an inert atmosphere. BaCl$_2$ (0.95 eq) and EuCl$_3$ (0.05 eq) were dissolved in a round flask with the appropriate amount of MeOH under vigorous magnetic stirring for 2 h. Then, metallic potassium (2.05 eq.) was added to the reaction mixture, leading to an exothermic reaction and the precipitation of potassium chloride. After 2 h, 1 eq. of titanium (IV) butoxide was introduced drop by drop, with a milky solution being obtained. Thereafter, the suspension obtained above was transferred into a cylindrical autoclave (Teflon-lined stainless steel) filled at 2/3 of its volume. The autoclave was put inside the oven, and the reaction was performed for 24 h at 200°C. After cooling down to room temperature, the insoluble reaction products were washed several times using a solution of 0.1 M HCl and water for removing the excess ions arising from starting materials. Finally, the resulting BaTiO$_3$:Eu$^{3+}$ powders were oven-dried at 90°C for 24 h.

**Preparation of barium titanate powders by solid-state reaction**

The detail of sample preparation has been reported in the literature [17]. BaTiO$_3$ was obtained by firing at high temperature a mixture of BaCO$_3$ and TiO$_2$ powders. Two steps were involved: ball milling for 2 h at 300 rpm and then a sintering at 1150°C for 4 h.

**Characterization techniques**

The structures of BaTiO$_3$: Eu$^{3+}$ (5 mol%) powders were determined by an automated powder diffractometer (Philips Xpert Pro) using Cu-K$_\alpha$ radiation at 40 kV and 30 mA. The powder’s High-Temperature X-ray diffraction (HT-XRD) data were collected at 25°C and every 100°C during the heating/cooling steps between 100 and 1200°C. After putting the sample on a platinum ribbon and reaching the given temperature at 10°C/min, the diffractrometer was held at each temperature for 1 h prior to the data collection, and then XRD data were collected for 50 min over the 2θ range 10-70°. The powders were analyzed by DTA and thermo gravimetry (TG) using a Mettler Toledo TGA/SDTA 851e. The thermal cycle applied to collect DTA and TG data consisted of heating θm- and ssr-derived powders, respectively, from room temperature at 800°C and 1000°C at 2°C/min upon a nitrogen atmosphere.

The IR transmittance spectra were recorded from powders heat-treated at 1150°C for 4 h using an FTIR 2000 Perkin-Elmer in the range of 4000-200 cm$^{-1}$. The samples were analyzed using the KBr and polyethylene pelleting technique for the ranges of 4000-400 cm$^{-1}$ and 400-200 cm$^{-1}$ respectively. The Raman spectra of powders were recorded using a T64000 Jobin-Yvon confocal micro-Raman Spectrometer with a 514 nm wavelength line green laser excitation source (Coherent model 70C5 Ar$^+$) operating at 800 mW with approximately 1 cm$^{-1}$
resolution. SEM images of BaTiO$_3$:Eu$^{3+}$ (5 mol%) powders were obtained using a scanning electron microscope (Zeiss Model Supra-55 VP) equipped with an Everhardt Thornley secondary electron (SE) detector operating at 2.5 kV at high-vacuum mode. Conventional Transmission Electron Microscopy (CTEM) was performed on a Hitachi H-7650 at an acceleration voltage of 120 kV. BaTiO$_3$:Eu$^{3+}$ (5% mol) powders were dispersed in water using an ultrasonic bath, with the solution being directly deposited onto a carbon grid.

The luminescence spectra were recorded with a monochromator Jobin-Yvon HR 1000 spectrometer, using a dye laser (continuum ND62) pumped by a frequency-doubled pulsed YAG:Nd$^{3+}$ laser (continuum surelite I). The dye solution was prepared by mixing Rhodamines 610 and 640. To achieve a resonant pumping in the blue wavelength range, the output of the dye laser was up-shifted to 4155 cm$^{-1}$ by stimulated Raman scattering in a high-pressure gaseous H$_2$ cell.

![HTXRD patterns](image_url)

Fig. 1 HTXRD patterns of (a) ssr; (b) hm BaTiO$_3$:Eu$^{3+}$ (5 mol%) powders.
Result and discussion

XRD analysis

To investigate the structural characteristics of the BaTiO$_3$:Eu$^{3+}$ synthesized by a solid-state reaction, the samples were put directly in the HTXRD chamber just after the ball milling without 4h heat treatment at 1150°C. Figure 1(a) shows the HTXRD diffraction patterns. The first scan corresponds to the pattern for the as-synthesized BaTiO$_3$:Eu$^{3+}$ powder at room temperature, and reveals the presence of BaCO$_3$ and TiO$_2$ starting materials which are observed until 700°C, as can be seen in this figure. In the following scans, between 600 and 1100°C, BaTiO$_3$ starts to crystallize on the basis of the appearance of the diffraction peak at 32°. The complete crystallization of BaTiO$_3$ powder occurs above 1100°C. On the other hand, the XRD patterns of BaTiO$_3$:Eu$^{3+}$ powders heat-treated at 1150°C were recorded at room temperature (Fig. 2). Figure 3(a) ascribed to the ssr sample reveals a fully crystallized BaTiO$_3$ with two diffraction peaks for (0 0 2) and (2 0 0) planes between 45 and 46°, as shown in the top inset. This splitting is characteristic of tetragonal BaTiO$_3$ [29].

To evaluate the phase transformation of the barium titanate at high temperatures, the sample after hydrothermal treatment was heat-treated from room temperature to 1200°C in the HT-XRD chamber, and the different recorded XRD patterns are gathered in Fig. 1(b).

It can be noticed that the cubic structure formed after the hydrothermal treatment at 200°C for 24 hours is stable up to 800°C. At higher temperatures from 800°C to 1200°C, the patterns reveal a mixture of cubic and hexagonal BaTiO$_3$ in addition to BaTi$_2$O$_5$.

The phases present in BaTiO$_3$ powders after hydrothermal treatment were investigated by recording the XRD pattern at room temperature. Figure 2(b) shows well-crystallized BaTiO$_3$ with wider diffraction peaks in comparison with those observed for ssr powders. Figure 2(b) also displays the magnified peak situated at 2θ = 45°; in this case, no splitting of the peak was observed, which is characteristic of a cubic perovskite structure of BaTiO$_3$. The mean size of crystallites (D) was calculated from the full-width at half maximum (FWHM) of the XRD peaks using Scherrer’s equation [30]:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where \( \lambda \) (nm) represents the wavelength of the Cu Kα radiation (1.54056 Å), \( \theta \) is Bragg’s angle of the selected diffraction peak, \( \beta \) is the corrected half-width of the selected diffraction peak, and \( K \) is a geometric factor (\( K = 0.9 \) for spherical particles). Analyses of diffraction peaks for various samples showed that crystallite size is approximately 20 nm.

![Fig. 2 XRD pattern of (a) ssr; (b) hm BaTiO$_3$:Eu$^{3+}$ (5 mol%) powders recorded after respectively annealing for 4 h at 1150°C and hydrothermal treatment for 24 h at 200°C.](image)

Thermal analysis

In order to understand the synthesis process for BaTiO$_3$, TGA/DTA measurements were firstly performed for the ssr powders and exhibit decomposition in two steps (Fig. 3(a)). The first endothermic phenomenon appearing in the range of 20-450°C is accompanied by a minimal loss of mass (3.5%) and can be attributed to the decomposition of BaCO$_3$. The next important event from 600 to 1000°C reveals a larger loss of mass (12.8%) associated with an endothermic phenomenon, and can be ascribed to the following reaction: BaCO$_3$+TiO$_2$ →BaTiO$_3$+CO$_2$. Figure 3(b) shows the TG curve of the hm sample, which reveals a total loss of mass (11.9%) in two steps, which is lower than that of the ssr powder (16.3%). The first loss (4.6%) below 200°C was attributed to the release of adsorbed water and removing of remaining MeOH solvent. Between 200 and 800°C, the loss of mass can result from the decomposition of remaining alkoxy groups of butoxide precursor. Several defects, such as hydroxyl ions (OH$^-$), protons (H$^+$) or carbonates (CO$_3^{2-}$), are incorporated into the lattice during the hydrothermal process at high water pressure [31,32]. These defects stabilize the cubic phase, and hence decrease the tetragonality of the powder [33,34].

FT-IR characterization

The FT-IR spectrum of BaTiO$_3$ ssr powder is presented in Fig. 4(a). Two weak bands situated at 1430 cm$^{-1}$ and 860 cm$^{-1}$ are assigned to asymmetric stretching vibrations and out-of-plane bending vibrations of carboxylic groups respectively [35]. Besides, a weak
Solid state reaction \( \text{BaTiO}_3: \text{Eu}^{5\%} \): 

| Temperature (°C) | Weigth loss (mg·g\(^{-1}\)) | Deriv. differential temperature (°C−1) |
|------------------|-------------------------------|--------------------------------------|
| 200              | 50                           | 2                                    |
| 400              | 50                           | 2                                    |
| 600              | 50                           | 2                                    |
| 800              | 50                           | 2                                    |
| 1000             | 50                           | 2                                    |

Fig. 3 DTA and TGA curves of (a) ssr; (b) hm \( \text{BaTiO}_3: \text{Eu}^{5\%} \) powders.

Hydrothermal method \( \text{BaTiO}_3: \text{Eu}^{5\%} \):

| Temperature (°C) | Weigth loss (mg·g\(^{-1}\)) | Deriv. differential temperature (°C−1) |
|------------------|-------------------------------|--------------------------------------|
| 30               | 19.0                          | 0                                    |
| 160              | 19.5                          | 0                                    |
| 420              | 20.0                          | 0                                    |
| 410              | 20.5                          | 0                                    |
| 160              | 21.0                          | 0                                    |

Fig. 4 IR spectra of (a) ssr; (b) hm \( \text{BaTiO}_3: \text{Eu}^{3+} \) (5 mol%) powders.

\( \text{BaTiO}_3: \text{Eu}^{3+} \) powders.

**Raman Study**

The Raman spectrum of ssr \( \text{BaTiO}_3 \) samples was collected at room temperature and is shown in Fig. 5(a). From this Fig. 5(a) the Raman fundamental modes (P4 mm) expected for tetragonal \( \text{BaTiO}_3 \) powders were observed [41,42]. According to Kaiser et al. [43] and Asieie et al. [2], the weak shoulder below 300 cm\(^{-1}\) belongs to an \( A_1 \) (TO) phonon mode. The peak at \( \sim 307 \) cm\(^{-1}\) corresponds to an \( E(TO+LO) \) phonon mode of tetragonal \( \text{BaTiO}_3 \) [44], and the strong band peaking at \( \sim 515 \) cm\(^{-1}\) is attributed to an \( A_1 \) (TO) phonon mode of the tetragonal or cubic phase [45]. The weak peak at \( \sim 718 \) cm\(^{-1}\) has been associated with the highest-frequency longitudinal optical mode (LO) of \( A_1 \) symmetry. The Raman spectrum reported in Fig. 5(b) for hm \( \text{BaTiO}_3 \) powders reveals the same spectral features as the ssr \( \text{BaTiO}_3 \) sample with vibration modes at 718, 515, 306, and 260 cm\(^{-1}\), which are also observed in the case of cubic structure. The only difference comes from the phonon mode \( A1(LO) \) at 185 cm\(^{-1}\), which is unambiguously ascribed to the presence of the cubic \( \text{BaTiO}_3 \) phase.

**SEM and TEM observations**

Figure 6(a) shows the SEM micrograph recorded from ssr \( \text{BaTiO}_3: \text{Eu}^{3+} \) powder annealed for 4 h at bending normal vibrations [37], while the one situated at 565 cm\(^{-1}\) is assigned to the TiO\(_6\) stretching vibrations connected to the barium [38]. Figure 4(b) shows the FT-IR spectrum of \( \text{BaTiO}_3 \) hm powder. This sample is characterized by a stretching band of hydroxyl (free and bonded) groups, respectively, in the range of 3600-3100 cm\(^{-1}\) and at 1632 cm\(^{-1}\) arising from bending vibrations of coordinated H\(_2\)O [39]. The two strong bands related to Ti-O bonds which are observed in the vicinity of 600-480 and 480-350 cm\(^{-1}\) are associated with Ti-O\(_6\) stretching vibrations to the vertical and the O\(_{1}\)-Ti-O\(_{1}\) bending vibrations [40] of a TiO\(_6\) octahedron in the crystalline \( \text{BaTiO}_3 \) hm powder.
1150°C. The morphology consists of parallelogram-like particles exhibiting a noticeable agglomeration as well as a regular shape with an average length of about 200 nm.

The particle size and morphology of hm BaTiO$_3$:Eu$^{3+}$ samples were firstly analyzed by SEM just after the product was washed and dried in an oven at 90°C during 24 h. As shown in Fig. 6(b), the particle size is too low to be determined by this technique of electron microscopy. Thus, this sample was observed by TEM (Fig. 7(a)), and exhibited nanoparticles of a cubic shape. The average particle size distributions measured by image analyzer software (Fig. 7(b)) were statistically estimated to be 20 nm, as calculated from XRD patterns by the Scherrer formula.

**Photoluminescence analysis**

Figure 8 reports the $^7$F$_0 \rightarrow ^5$D$_2$ excitation spectra recorded at 300 K for the hm and ssr BaTiO$_3$:Eu$^{3+}$ (5 mol%) samples by monitoring the overall $^5$D$_0 \rightarrow ^7$F$_2$ emission bands at 615.6 nm. Eu$^{3+}$ ions are distributed in the Ba$^{2+}$ site, i.e., one site of Oh symmetry and one site of C4v symmetry, respectively, in cubic and tetragonal phases. As a result, on the basis of the site symmetry, five and four Stark components are expected for the $^7$F$_0 \rightarrow ^5$D$_2$ transition, respectively, for the ssr and hm samples. This result is confirmed for ssr BaTiO$_3$:Eu$^{3+}$ (5 mol%), whereas in the case of the hm sample, the $^7$F$_0 \rightarrow ^5$D$_2$ transition consists of a unique broad band which has been blue-shifted.
This peculiar spectral shape can be attributed to the embedding of Eu$^{3+}$ ions in nano-size particles, which implies the same optical behavior as Eu$^{3+}$ ions in amorphous powders [46]. Such an assumption is confirmed by the emission spectra recorded at 300 K upon excitation at 465.3 nm in the blue region (Fig. 9). Both spectra exhibit the typical $^5D_0 \rightarrow ^7F_{j=0-4}$ transitions of Eu$^{3+}$ ions, but on the emission spectrum recorded from the ssr sample we can distinguish several Stark components for each transition, whereas this is not possible for the spectrum related to the hm sample.

In this latter case, the spectrum is typical of Eu$^{3+}$ ions embedded in an amorphous compound or in nanosized crystallites. As a result, each peak of $^5D_0 \rightarrow ^7F_{j=0-4}$ transitions is broadened and the intensity ratio $^5D_0 \rightarrow ^7F_2$ / $^5D_0 \rightarrow ^7F_1$ is dramatically increased, indicating a lowering of symmetry atonanom-local order.

**Conclusion**

BaTiO$_3$:Eu$^{3+}$ (5 mol%) with a predominant cubic phase was successfully prepared by an original hydrothermal process using a titanium alkoxide as starting material. The formation of nanocrystallites was evidenced by XRD and MET analyses. Such a feature was confirmed by the photoluminescence investigation, which has demonstrated that the Eu$^{3+}$ ions are embedded in nanosized powders in comparison with BaTiO$_3$:Eu$^{3+}$ (5 mol%) samples prepared by the conventional solid-state reaction. Accordingly, the intensity of the $^5D_0 \rightarrow ^7F_2$ transition becomes much stronger than the one of the $^5D_0 \rightarrow ^7F_1$ transition, leading to a strong red fluorescence. Based on the theory of thermodynamic nucleation and growth, a short synthesizing process and low reaction temperature, compared with a solid-state reaction, reduce the possibility of particle growth. Besides, by using a hydrothermal method, it was possible to produce monozided distribution equiaxed BaTiO$_3$ powders with a predominant cubic phase of 20 nm, therefore facilitating the production of high-performance ceramic.

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**References**

[1] H. Xu, L. Gao and J. Guo, “Hydrothermal synthesis of tetragonal barium titanate from barium chloride and titanium tetrachloride under moderate conditions”, J. Am. Ceram. Soc. 85(3), 727-729 (2002). [http://dx.doi.org/10.1111/j.1151-2916.2002.tb00163.x](http://dx.doi.org/10.1111/j.1151-2916.2002.tb00163.x)

[2] Mohammed A. Alam, Leonard Zuga and Michael G. Pecht, “Economics of rare earth elements in ceramic capacitors”, Ceram. Inter. 38(8), 6091-6098 (2012). [http://dx.doi.org/10.1016/j.ceramint.2012.05.068](http://dx.doi.org/10.1016/j.ceramint.2012.05.068)

[3] R. Pazik, D. Hreniak, W. Strek, V. G. Kessler and G. A. Seisenbaeva, “Photoluminescence investigations of Eu$^{3+}$ doped BaTiO$_3$ nanopowders fabricated using heterometallic tetranuclear alkoxide complexes”, J. Alloys Comp. 451(1-2), 557-562 (2008). [http://dx.doi.org/10.1016/j.jallcom.2007.04.232](http://dx.doi.org/10.1016/j.jallcom.2007.04.232)

[4] J. Amami, D. Hreniak, Y. Guyot, R. Pazik, C. Goutaudier, G. Boulon, M. Ayadi and W. Strek, “Second harmonic generation and Yb$^{3+}$ cooperative emission used as structural probes in size-driven cubic-tetragonal phase transition in BaTiO$_3$ nanogel nanocrystals”, J. Lumina. 119-120, 383-387 (2006). [http://dx.doi.org/10.1016/j.jlumin.2006.01.021](http://dx.doi.org/10.1016/j.jlumin.2006.01.021)

[5] J. Amami, D. Hreniak, Y. Guyot, R. Pazik, W. Strek, C. Goutaudier and G. Boulon, “New optical tools used for characterization of phase transitions in nonlinear nanocrystals. Example of Yb$^{3+}$-doped BaTiO$_3$”, J. Phys. Condens. Matter. 19(9), 1 (2007). [http://dx.doi.org/10.1088/0953-8984/19/9/096204](http://dx.doi.org/10.1088/0953-8984/19/9/096204)

[6] L. Chen, X. Wei and X. Fu, “Effect of Er substituting sites on upconversion luminescence of Er$^{3+}$-doped BaTiO$_3$ films”, T. Nonferr. Metal. Soc. 22(5), 1156-1160 (2012). [http://dx.doi.org/10.1016/S1003-6326(11)61299-5](http://dx.doi.org/10.1016/S1003-6326(11)61299-5)

[7] D. Hennings, G. Rosenstein and H. Schreinemacher, “Hydrothermal preparation of barium titanate from barium-titanium acetate gel precursors”, J. Eur. Ceram. Soc. 8(2), 107-115 (1991). [http://dx.doi.org/10.1016/0955-2219(91)90116-H](http://dx.doi.org/10.1016/0955-2219(91)90116-H)

[8] T. Kimura, Q. Dong, S. Yin, T. Hashimoto and A. Sasaki, T. Sato. “Synthesis and piezoelectric properties of Li-doped BaTiO$_3$ by a solvothermal approach”,

![Fig. 9 Emission spectra of (a) ssr; (b) hm (dashed line) BaTiO$_3$:Eu$^{3+}$ (5 mol%) powders recorded at 300 K upon excitation at 465.3 nm.](http://dx.doi.org/10.3786/nml.v5i1.p57-65)
J. Eur. Ceram. Soc. 33(5), 1009-1015 (2013). http://dx.doi.org/10.1016/j.jeurceramsoc.2012.11.007

[9] W. W. Lee, W.-H. Chung, W-S. Huang, W.-C. Lin, W.-Y. Lin, Y.-R. Jiang and C.-C. Chen, “Photocatalytic activity and mechanism of nano-cubic barium titanate prepared by a hydrothermal method”, J. Taiwan Inst. Chem. Eng. (2013). http://dx.doi.org/10.1016/j.jtice.2013.01.005

[10] X. Zhu, J. Zhu, S. Zhou, Z. Liu and N. Ming, “Photocatalytic activity and mechanism of nano-cubic barium titanate prepared by a hydrothermal method”, J. Crystal Growth 310(2), 434-444 (2008). http://dx.doi.org/10.1016/j.jcrysgro.2007.10.076

[11] E. Çifçi, M. N. Rahaman and M. Shumsky, “Hydrothermal precipitation and characterization of nanocrystalline BaTiO₃ particles”, J. Mater. Sci. 36(20), 4875-4882 (2001). http://dx.doi.org/10.1023/A:1011828018247

[12] J. Yuh, L. Perez, W. M. Sigmund and J. C. Nino, “Sol-gel based synthesis of complex oxide nanofibers”, J. Sol-Gel Sci. Technol. 42(3), 323-329 (2007). http://dx.doi.org/10.1007/s10971-007-0736-6

[13] Z. Xinle, M. Zhimei, X. Zuojiang and C. Guang, “Preparation and characterization on nano-sized barium titanate powder doped with lanthanum by sol-gel process”, J. Rare Earths 24(1), 82-85 (2006). http://dx.doi.org/10.1016/S1097-0274(06)60329-9

[14] M. Cernea, O. Monneron, P. Llewellyn, L. Tortet and Carmen Galassi, “Sol-gel synthesis and characterization of Ce doped-BaTiO₃”, J. Eur. Ceram. Soc. 26(15), 3241-3246 (2006). http://dx.doi.org/10.1016/j.jeurceramsoc.2005.09.039

[15] D. Hreniak, W. Strek, J. Chmielowiec, G. Pasciak, R. Pazik, S. Gierlotka and W. Lojkowski, “Preparation and conductivity measurement of Eu doped BaTiO₃ nanocrystalline”, J. Alloys Comp. 405-412, 637-640 (2006). http://dx.doi.org/10.1016/j.jallcom.2004.12.098

[16] M. A. Meneses-Nava, O. Barbosa-García, J. L. Maldonado, G. Ramos-Ortiz, J. L. Pichardo, M. Torres-Cisneros, M. García-Hernández, A. García-Murillo and F. J. Carrillo-Romo, “Yb⁵⁺ quenching effects in co-doped polycrystalline BaTiO₃:Erb³⁺, Yb⁵⁺”, Opt. Mater. 31(2), 252-260 (2008). http://dx.doi.org/10.1016/j.optmat.2008.04.002

[17] L. Simon-Seveyrat, A. Hajjaji, Y. Emziane, B. Guiffard and D. Guyomar, “Re-investigation of synthesis of BaTiO₃ by conventional solid-state reaction and oxalate coprecipitation route for piezoelectric applications”, Ceram. Inter. 33(1), 35-40 (2007). http://dx.doi.org/10.1016/j.jceraltec.2005.07.019

[18] Y. Sakabe, Y. Yamashita and H. Yamamoto, “Dielectric properties of nano-crystalline BaTiO₃ synthesized by micro-encapsulation method”, J. Eur. Ceram. Soc. 25(12), 2739-2742 (2005). http://dx.doi.org/10.1016/j.jeurceramsoc.2005.03.226

[19] K. H. Felner, T. Muller, H. T. Langhammer and H. P. Abicht, “On the formation of BaTiO₃ from BaCO₃ and TiO₂ by microwave and conventional heating”, Mater. Lett. 58(12-13), 1943-1947 (2004). http://dx.doi.org/10.1016/j.matlet.2003.11.037

[20] V. Vinodhini, P. Singh and M. Balasubramanian, “Synthesis of barium titanate nanopowder using polymeric precursor method”, Ceram. Inter. 32(2), 99-103 (2006). http://dx.doi.org/10.1016/j.ceramint.2004.12.012

[21] Z. C. Hu, G. A. Miller, E. A. Payzant and C. J. Rawn, “Homogeneous (co)precipitation of inorganic salts for synthesis of monodispersed barium titanate particles”, J. Mater. Sci. 35(12), 2927-2936 (2000). http://dx.doi.org/10.1023/A:1004718508280

[22] M. Yoshimura and K. Byrappa, “Hydrothermal processing of materials: past, present and future”, J. Mater. Sci. 43(7), 2085-2103 (2008). http://dx.doi.org/10.1007/s10971-007-0853-x

[23] D. E. Rase and R. Roy, “Phase equilibria in the system BaO-TiO₂”, J. Am. Ceram. Soc. 38(3), 102–113. (1955). http://dx.doi.org/10.1111/j.1511-2916.1955.tb14585.x

[24] J.-H. Kim, W.-S. Jung, H.-T. Kim and D.-H. Yoon, “Properties of BaTiO₃ synthesized from barium titanyl oxalate”, Ceram. Inter. 35(6), 2337-2342 (2009). http://dx.doi.org/10.1016/j.jceramic.2009.01.006

[25] K. Ishikawa, K. Yoshikawa and N. Okada, “Size effect on the ferroelectric phase transition in PbTiO₃ ultra-fine particles”, Phys. Rev. B 37(10), 5852-5855 (1988). http://dx.doi.org/10.1103/PhysRevB.37.5852

[26] S. Schlag and H. F. Eicke, “Size driven phase transition in nanocrystalline BaTiO₃”, Solid State Commun. 91(11), 883-887 (1994). http://dx.doi.org/10.1016/0038-1098(94)90007-8

[27] M. K. Rath, G. K. Pradhans, B. Pandey, H. C. Verma, B. K. Roul and S. Anand, “Synthesis, characterization and dielectric properties of europium-doped barium titanate nanopowders”, Mater. Lett. 62(14), 2136-2139 (2008). http://dx.doi.org/10.1016/j.matlet.2007.11.033

[28] R. Pazik, R. J. Wiglusz and W. Strek, “Luminescence properties of BaTiO₃:Eu³⁺ obtained via microwave stimulated hydrothermal method”, Mater. Res. Bull. 44(6), 1328-1333 (2009). http://dx.doi.org/10.1016/j.materresbull.2008.12.010

[29] S. Zhang, F. Jiang, Gang Qu and C. Lin, “Synthesis of single-crystalline perovskite barium titanate nanorods by a combined route based on sol-gel and surfactant-templated methods”, Mater. Lett. 62(15), 2225-2228 (2008). http://dx.doi.org/10.1016/j.matlet.2007.11.085

[30] A. L. Patterson, “The scherrer formula for X-ray particle size determination”, Phys. Rev. 56(10), 978-982 (1939). http://dx.doi.org/10.1103/PhysRev.56.978

[31] F. K. Detlev Hennings, C. Metzmacher and B. Seriyati Schreinemacher, “Defect chemistry and microstructure of hydrothermal barium titanate”, J. Am. Ceram. Soc. 84(1), 179-182 (2001). http://dx.doi.org/10.1111/j.1551-2916.2001.tb00627.x
[32] S.-W. Kwon and D.-H. Yoon. “Tetragonality of nano-sized barium titanate powder prepared with growth inhibitors upon heat treatment”, J. Eur. Ceram. Soc. 27(1), 247-252 (2007). http://dx.doi.org/10.1016/j.jeurceramsoc.2006.02.031

[33] G. Arlt, D. Hennings and G. de With. “Dielectric properties of fine-grained barium titanate ceramics”, J. Appl. Phys. 58(4), 1619-1625 (1985). http://dx.doi.org/10.1063/1.336051

[34] J. Nowotny and M. Rekas. “Defect chemistry of BaTiO$_3$”, Solid State Ionics 49, 135-154 (1991). http://dx.doi.org/10.1016/0167-2738(91)90079-Q

[35] L. Li, Y. Chu, Y. Liu, L. Dong, L. Huo and F. Yang. “Microemulsion-based synthesis of BaCO$_3$ nanobelts and nanorods”, Mater. Lett. 60(17-18), 2138-2142 (2006). http://dx.doi.org/10.1016/j.matlet.2005.12.087

[36] P. Yu, B. Cui and Q. Shi. “Preparation and characterization of BaTiO$_3$ powders and ceramics by sol-gel process using oleic acid as surfactant”, Mater. Sci. Eng. A 473(1-2), 34-41 (2008). http://dx.doi.org/10.1016/j.msea.2007.03.051

[37] S. Ghosh, S. Dasgupta, A. Sen and H. S. Maiti. “Synthesis of barium titanate nanopowder by a soft chemical process”, Mater. Lett. 61(2), 538-541 (2007). http://dx.doi.org/10.1016/j.matlet.2006.05.006

[38] A. García Murillo, F. J. Carrillo Romo, M. García Hernández, J. Ramírez Salgado, M. A. Domínguez Crespo, S. A. Palomares Sánchez and H. Terrones. “Structural and morphological characteristics of polycrystalline BaTiO$_3$:Er$^{3+}$, Yb$^{3+}$ ceramics synthesized by the sol-gel route: influence of chelating agents”, J Sol-Gel Sci. Technol. 53(1), 121 (2010). http://dx.doi.org/10.1007/s10971-009-2069-0

[39] Y. Gao, Y. Masuda, Z. Peng, T. Yonezawa and K. Koumoto. “Room temperature deposition of a TiO$_2$ thin film from aqueous peroxotitanate solution”, J. Mater. Chem. 13, 608-613 (2003). http://dx.doi.org/10.1039/b208681f

[40] K. Sadhana, T. Krishnaveni, K. Praveena, S. Bharadwaj and S. R. Murthy. “Microwave sintering of nanobarium titanate”, Scripta Materialia 59(5), 495-498 (2008). http://dx.doi.org/10.1016/j.scriptamat.2008.04.036

[41] R. Cho, S. H. Kwun, T. W. Noh and M. S. Jang. “Electrical properties of sol-gel deposited BaTiO$_3$ thin films on Si(100) substrates”, Jpn. J. Appl. Phys. 36, 2196-2199 (1997). http://dx.doi.org/10.1143/JJAP.36.2196

[42] W. K. Kuo and Y. C. Ling. “Effects of monosubstituting chelating agents on BaTiO$_3$ prepared by the sol-gel process”, J. Mater. Sci. 29(21), 5625-5630 (1994). http://dx.doi.org/10.1007/BF00349957

[43] L. Kaiser, M. D. Vaudin, G. Gillen, C. S. Hwang, L. H. Robins and L. D. Rotter. “Growth and characterization of barium titanate thin films prepared by metalorganic chemical vapor deposition”, J. Crystal Growth 137(1-2), 136-140 (1994). http://dx.doi.org/10.1016/0022-0248(94)91261-0

[44] C. J. Xiao, C. Q. Jin and X. H. Wang. “Crystal structure of dense nanocrystalline BaTiO$_3$ ceramics”, Mater. Chem. Phys., 111(2-3), 209-212 (2008). http://dx.doi.org/10.1016/j.matchemphys.2008.01.020

[45] H. X. Zhang, C. H. Kam, Y. Zhou, X. Q. Han, Y. L. Lam, Y. C. Chan and K. Pita. “Optical and electrical properties of sol-gel derived BaTiO$_3$ films on ITO coated glass”, Mater. Chem. Phys., 63(2), 174-177 (2000). http://dx.doi.org/10.1016/S0254-0584(99)00222-9

[46] C. H. Yan, L. D. Sun, C. S. Liao, Y. X. Zhang, Y. Q. Lu, S. H. Huang and S. Z. Lü. “Er$^{3+}$ ion as fluorescent probe for detecting the surface effect in nanocrystals”, Appl. Phys. Lett. 82(20), 3511-3513 (2003). http://dx.doi.org/10.1063/1.1575504

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Progress of Microfluidics for Biology and Medicine

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Abstract: Microfluidics has been considered as a potential technology to miniaturize the conventional equipments and technologies. It offers advantages in terms of small volume, low cost, short reaction time and high-throughput. The applications in biology and medicine research and related areas are almost the most extensive and profound. With the appropriate scale that matches the scales of cells, microfluidics is well positioned to contribute significantly to cell biology. Cell culture, fusion and apoptosis were successfully performed in microfluidics. Microfluidics provides unique opportunities for rare circulating tumor cells isolation and detection from the blood of patients, which furthers the discovery of cancer stem cell biomarkers and expands the understanding of the biology of metastasis. Nucleic acid amplification in microfluidics has extended to single-molecule, high-throughput and integration treatment in one chip. DNA computer which is based on the computational model of DNA biochemical reaction will come into practice from concept in the future. In addition, microfluidics offers a versatile platform for protein-protein interactions, protein crystallization and high-throughput screening. Although microfluidics is still in its infancy, its great potential has already been demonstrated and will provide novel solutions to the high-throughput applications.

Keywords: Microfluidics; Lab-on-a-chip; Droplet; High-throughput; Cell; Nucleic acid amplification

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Introduction

Microfluidics is a science and technology system that processes or manipulates small amounts of fluids, using channels with dimensions of tens to hundreds of microns [1]. It offers advantages in terms of small volume, low cost, short reaction time and high-throughput. Since micro total analysis system (µ-TAS), also known as “lab-on-a-chip” was proposed in the early 1990s [2], microfluidics has been considered as a potential technology to miniaturize the conventional equipments and technologies. The early microfluidics was served as a simple means to deliver small amount of analytes to the sensor [3]. Quake et al. [4] proposed the concept of large-scale integration in microfluidics based on micropump and microvalve in 2002. It offered the potential of microfluidics in academia and industry. With the development of microelectromechanical system (MEMS) technology, some integrated and multifunction microfluidic chips were proposed. They are significantly changing the way of processing chemical and biological analysis [5,6], cell and gene analysis [7,8], drug discovery and clinical diagnostics [9,10], material synthesis [11,12] and environmental monitoring [13,14]. Among them, the applications in biology and medicine research and related areas are almost the most extensive and profound.

In this review, we first provide the physics of microfluidics to understand the physical phenomena at the microscale. Then we introduce a summary of droplet microfluidics technology with droplet generation and manipulation and an ingenious SlipChip. Finally, we discuss recent advances of microfluidics in biology and medicine, such as cell analysis, nucleic acid analysis,
protein engineering and high-throughput screening.

Physics of microfluidics

The fluid flow in microfluidics shows different properties due to small scaling. Generally, the characteristic scale is from 0.1 \( \mu \text{m} \) to 1 mm and it agrees well with the scale range of microhydrodynamics. Stone et al. [15] provided an overview of fluid flow in microfluidics with focus on electrokinetics, mixing and dispersion, and multiphase flows.

Laminar Flow

Laminar flow indicates the velocity of a particle in a fluid stream is not a random function of time [16]. The flow in microfluidics is almost always laminar due to the small size of microchannels. The flow regime -laminar or turbulent can be described by Reynolds number \( Re \). The Reynolds number \( Re \) indicates the importance of inertia compared with viscous stresses, and is defined as [17]

\[
Re = \frac{\rho u D_h}{\eta}
\]

where \( \rho \), \( u \) and \( D_h \) are density, flow velocity and hydraulic diameter of the microchannel, respectively.

Diffusion

The different streams flowing in contact with each other can not mix except by diffusion due to laminar flow in microfluidics. Diffusion can be modeled by the equation [16]:

\[
t = \frac{l^2}{2D}
\]

where \( t \) is the diffusion time of a molecule to diffuse over a distance \( l \) and \( D \) is the diffusion coefficient of the molecule in solution. Some recent excellent reviews on mixing in microfluidics [18,19] can also be referred for further understandings.

Capillary number

Droplet microfluidics has become an increasingly popular platform for fluid flow at the microscale, since its advent in the early 2000s [20-22]. Several key dimensionless parameters can be used to analyze droplet dynamics. The capillary number \( Ca \) plays a key role in microfluidic droplet’s formation. The capillary number is defined in terms of the continuous phase flow field that acts to deform the droplet [23],

\[
Ca = \frac{\eta_c u_c}{\gamma}
\]

where \( \eta_c \) is the viscosity of the continuous phase, \( u_c \) is the velocity of the continuous phase, and \( \gamma \) is the interfacial tension between the oil and water phases. The capillary number is characterized by the relative importance of viscous stresses and capillary pressure. Droplet breaks off when the capillary number is beyond a certain critical value.

Weber number

The Weber number \( We \), which compares inertia to interfacial tension, is used frequently to parametrize droplet breakup processes. The result of multiplying the Reynolds number and the capillary number gives the Weber number,

\[
We = Re \times Ca
\]

The interface effect has a significant influence on flow in microfluidics due to small Weber number, comparing with flow in macroscale.

Bond number

Finally, the Bond number \( Bo \) characterizes the relative importance of gravity and interfacial tension, and is given by

\[
Bo = \frac{\Delta \rho g w^2}{\gamma}
\]

where \( \Delta \rho \) is the density difference between the two immiscible fluids, \( g \) is the acceleration of gravity, and \( w \) is the characteristic length scale. Gravity is typically negligible in droplet formation in microfluidics due to small density difference for water droplets in oil.

Types of microfluidics

Microfluidics can be divided into continuous-flow microfluidics and droplet microfluidics.

Continuous-flow microfluidics

Continuous-flow microfluidics refers to only a single phase fluid in the chip. It reduces consumption of sample and reagent, enhances analysis speed and improves reproducibility, comparing with traditional experiment. However, there are some problems to be solved. (1) In continuous-flow microfluidics, some of sample and reagent is wasted caused by the channel filled with reagent for continuous flow. So it is important to further reduce consumption of the precious sample and reagent. (2) It need more time to achieve rapid and uniform mixing due to laminar flow [18,19]. (3) The sample and reagent is easy to be contaminated by the channel. (4) Scaling up is a challenge as the size of devices scales almost linearly with the number of parallel experiments [24].
Droplet microfluidics

Droplet microfluidics deals with generation, manipulation, and applications of droplets in microfluidic devices. Unlike continuous-flow microfluidics, droplet microfluidics focuses on creating discrete droplets using immiscible phases. The droplets serve as discrete microreactors, so the reaction in each droplet can be carried out without cross-talk between samples or reagents. Droplet microfluidics also provides a platform to perform many reactions and offers greater potential in high-throughput applications.

In general, droplets are typically generated using three main generation strategies: co-flowing [20, 25], T-junction [21] and flow focusing [22], as shown in Fig. 1 [26]. Droplet microfluidics is capable of generating over 1-million, monodisperse, picolitre droplets in several minutes [27], so parallel processing and experimentation can be easily achieved, and large data can be acquired efficiently. Therefore, droplet microfluidics provides a platform to perform many reactions and offers greater potential in high-throughput applications.

Aside from passive methods, active droplet fusion methods based on electric field, heating and optical tweezers have also been proposed [30, 31].

It is desirable not only to fuse droplets but also to fragment a droplet into two or more droplets for some microfluidic processing steps to increase the droplet production frequency, as shown in Fig. 2(b). It can be used for incubation or screening to enhance the effectiveness of droplet [32-35].

Mixing of reagents is necessary to accurately determine the starting time of a reaction. In continuous flow microfluidic systems, mixing is achieved by diffusion because of laminar flow. It is commonly a very slow process even inside droplets. Basically, there are also passive and active methods in droplet mixing like droplet fusion. A classic passive way is using turns and bends in a channel to introduce chaotic advection and enhance the internal mixing within droplets [18, 36-38]. In a straight channel, two equal recirculation flows are generated in each half of the droplet. As the droplet moves along a winding channel, the two halves of the droplet experience unequal recirculating flows due to the shear interaction of the channel wall, as shown in Fig. 2(c). Active mixing is categorized with respect to the type of external perturbation energy: electrokinetic, dielectrophoretic, electrowetting and ultrasound. A detailed review can be seen in the paper by Capretto et al. [19].

In order to store droplets for up to several hours or even days or maximize the number of drops in the microscope field of view, it is necessary to position droplets in an array. Huebner et al. [39] presented a device that enables local storage and release of picoliter-sized water-in-oil droplets without using electrical or optical actuators, as shown in Fig. 2(d). The device consists of hydrodynamic droplet trapping structures array. The trapped droplets can be recovered from the microfluidic array for further processing. Then they proposed a microfluidic chip for the efficient trapping of droplet pairs [40]. The trapping structure can trap droplets from two directions. So a surfactant bilayer is formed between the trapped droplets. It provides a high throughput and effective platform for the observation and detection of diffusion across such bilayer. Multiple-droplet clustering in a controlled manner has been realized with the guiding tracks [41].

Some researchers also proposed other methods to generate droplets. Recently, the team in the University of Chicago pioneered an ingenious method (SlipChip) to perform microfluidic chip without external pumps, valves and other equipment for operation [42-44]. The working principle of the SlipChip is illustrated in Fig. 3. The system consists of two glass plates with arrays of wells (reservoirs) and ducts (fluidic pathways) on its surface. The wells and ducts of one plate are complementary in pattern to that of other plate. So they can

![Fig. 1. Illustrations of the three main microfluidic strategies used for droplets generation: (a) Co-flowing in a capillary format, (b) T-junction in a planar chip format, (c) Flow focusing in a planar chip format [26].](image-url)
Fig. 2  Droplet manipulation (a) Passive fusion by Bremond et al. [28]. (b) T-junctions droplets splitting by Link et al [32]. (c) Mixing in microdroplets flowing in a winding microchannel [37]. (d) Principle and Results of droplet trapping arrays [39].

Fig. 3  The working principle of the SlipChip. (a) The preloaded wells and ducts of the bottom plate, and the wells of the top plate. (b) Creating continuous fluidic paths by moving the plates relative to one another. (c) and (d) Loading of a single sample through the fluidic path provided by the ducts and wells. (e) Slipping of the top plate relative to the bottom plate to make the sample contact, (f) A reaction taking place after mixing and incubation [42].
create continuous fluidic paths used for reagent delivery by moving the plates relative to one another. This approach can be utilized to generate many droplets with different reaction environment in parallel. The SlipChip requires no bonding during fabrication of chips and no valves for operation and become a valuable tool in both resource-poor and resource-rich settings in high-throughput PCR (polymerase chain reaction) [45-47], immunoassays [48,49], protein crystallization [50] and screening [44].

**Applications in biology and medicine**

**Cell analysis**

Cell is the basic unit of biological morphology and life activities. So the focus has now been shifting more toward addressing the need for cell studies [16,51,52]. With the appropriate scale that matches the scales of cells, microfluidics is well positioned to contribute significantly to cell biology [52]. Rapid analysis of cells is critical in the biological, medical, and pharmaceutical communities. The first important step is to isolate and characterize single cells from a heterogeneous population. Recently, various separation techniques have been successfully applied to separate cells based on different methods, such as optical [53], dielectrophoretic [54], magnetic [55], acoustic [56] and hydrodynamic [57,58].

The team of Yu-Chong Tai in California Institute of Technology made great progress in the microminiaturization of hematology analyzer and developed a point-of-care test for the leukocyte count by using a microflow cytometer and a fluorescent dye assay as shown in Fig. 4 [59]. They demonstrated a four-part leukocyte differential count including lymphocyte, monocyte, neutrophil and eosinophil using a small amount of blood (5 ml) and reagents (68 ml in total). This method is optimal for point-of-care applications due to minimal sample volume, long reagent shelf life and portable instrument.

It is easy to provide an accurate extracellular microenvironmental in an array microfluidics due to laminar fluid flow, diffusion-based fluid mixing and closed culture volumes [2]. So it can provide an unprecedented understanding of the molecular and cellular events and thus generate successful regenerative medicine outcomes [60].

Leclerc et al. [61] developed a microfluidic chip for cell culture. The chip was composed of two stacked layers of PDMS (polydimethylsiloxane). They completed human hepatocellular carcinoma (HepG2) cell culture and succeeded in this chip.

A fully automated screening system based on a microfluidic chip that provides unattended stimulation of the cells using complex time-varying was proposed [62]. The quantitative measurements of the effect of osteogenic differentiation media and motility of primary human mesenchymal stem cells were first performed through this device. The team of Lin developed an integrated microfluidic device to characterize doxorubicin induced apoptosis in HepG2 cells [63]. It offers a unique platform to characterize various cellular responses in a high-throughput fashion by integrating the cell culture, stimulation, staining, and washing steps into a single device. In order to enhance the efficiency of pairing, a microfluidic device to trap and properly pair thousands of cells was proposed. The device contains a dense array of weir-based passive hydrodynamic cell traps. The fibroblasts, mouse embryonic stem cells and myeloma cells were tested, pairing efficiencies up to 70% were achieved, as shown in Fig. 5 [7].

Srisa-Art et al. [64] proposed droplet microfluidics as a platform technology for the identification and quantification of distinct single cells encapsulated within picoliter-sized aqueous droplets. The result was verified using conventional flow cytometry and found that both results were comparable. Bogojevic et al. [65]...
presented the first droplet microfluidic platform to implement parallel-scale cell-based apoptosis assays. The platform was found to be superior to pipetting and aspiration for retaining weakly adhered apoptotic cells for analysis and a 33-fold reduction in reagent consumption relative to the conventional technique. An automated and multifunctional platform to perform flexible generation and complex manipulation of picoliter-scale droplets was developed [66]. This provides a powerful platform for achieving high efficiency research on the single cell level.

Artificial cells as simplified models of living cells which provide valuable model platforms are designed to reveal the functions of biological systems [67,68]. Microfluidics has attracted much attention as biophysical tools for investigations of the molecular basis of life [68-70].

Microfluidics is also used for cancer cell detection, separation and capture [71]. It is a technical challenge to circulating tumor cells (CTCs) isolation because they are rare in the blood of patients. Microfluidics provides unique opportunities for cell sorting and rare-cell detection. The microfluidic chip, which can capture large numbers of viable CTCs in a single step from whole blood without pre-dilution, pre-labeling, pre-fixation or any other processing steps [72] had been proposed. It could further the discovery of cancer stem cell biomarkers and expand the understanding towards the biology of metastasis.

Gong et al. [73] demonstrated the drug effect analysis on cells using a high throughput droplet microfluidic chip. The result is similar to that of conventional petri dish technique, which indicates its great potential in drug effect analysis and for high throughput drug screening and discovery.

Nucleic acid analysis

Handling and characterizing samples of DNA is the key to a wide range of applications, especially molecular biology [74]. The PCR technique was first developed in 1985 [75], and has been widely used as a molecular biological tool to replicate DNA by cycling through three temperature steps. After the first PCR chip to amplify DNA was introduced by Northrup et al. [76], many research groups began to study microfluidic PCR chips and developments of microfluidic PCR chips were accelerated. Currently, the microfluidic PCR chips can be classified into three distinct types: chamber stationary PCR chips [75,77], flow-through PCR chips [78,79] and thermal convection-driven PCR chips [80,81].

The working principle of this type of PCR chip is that the PCR solution is kept stationary and the temperature of the reaction chamber is cycled between three different temperatures. The stationary PCR chips can reduce the time for analysis and increase the PCR throughput because it can perform different sequential PCR tests concurrently. However, it is crucial to ensure temperature uniformity between chambers. The whole chip, including the sample, is heated and cooled through specific thermal-cycling temperatures. Therefore, chamber stationary PCR chips have high thermal inertia and long thermal-cycling time.

The working principle of this type of PCR chip is that the PCR solution is continuously flowing through three different temperature zones necessary for DNA amplification. It has advantage in rapid heat transfer and high potential for further integration. Kopp et al. [78] successfully performed the PCR in continuous flow at high speed using a micromachined chemical amplifier.

The working principle of convection PCR chip is Rayleigh-Bénard convection, which is caused by buoyancy-driven instability in a confined heated fluid layer. This convection PCR chips consist of two fixed different temperature zones. Buoyancy force is the only force to drive PCR solution flow through the temperature zones.

The PCR chip has undergone the transition from simple microfluidic components to highly integrated systems. An ideal integrated PCR chip can integrate individual microfluidic components, such as cell isolation and capture, cell lysis, DNA/RNA extraction and purification, DNA/RNA amplification, and product
detection components into a single automated, portable chip with sample-to-answer capability. Hong et al. [82] developed microfluidic chips for automated nucleic acid purification from small numbers of bacterial or mammalian cells, as shown in Fig. 6. The chip has 26 access holes, 1 waste hole and 54 valves within $20 \times 20 \text{ mm}^2$, as shown in Fig. 5. The chip involves all processes in terms of cell isolation, cell lysis, DNA or mRNA purification, and recovery, so any pre- or post-sample treatment is not needed. In addition, the chips are capable of processing different samples in parallel, thereby performing high-throughput characteristics.

Some researchers used surface modification methods to prevent PCR inhibition and contamination [83-85]. Schneegass et al. [83] modified the channel surface with hexamethyldisilazane (HMDS) before the injection of the PCR solution, so the hydrophobic material surface of the silicon/glass was changed to enhance surface biocompatibility. However, this method is not easy to manipulating in the sealed chip. Fortunately, the PCR inhibition and contamination can be overcome by using droplet PCR chip.

The PCR droplet microfluidics provides a solution to the limitations of throughput and cost, is able to detect single-copy target nucleic acids from a complex environment [86] associated with millions of reactions. Srisa-Art et al. [87] proposed a droplet microfluidic system to solve the problems of surface contamination, rapid mixing, and rapid detection in conventional laminar microfluidics. They demonstrated a high-throughput biological assay by generating droplets in a rapid and reproducible manner and monitoring them in real time. Then the temperature ramp rate has also been improved to directly increase the throughput of PCRs by allowing a faster transition between the different temperatures of each PCR cycle [88]. The bulk sample preparation ‘averaging’ phenomena in multi-cell PCR decrease the precision of the result. So it is necessary to create single cell high-throughput PCR. Recently, a novel high-speed droplet-PCR assay was fabricated with the ability to detect human influenza virus in less than 30 min [89]. Compared with screening using microtiter plate-based systems, a completely in vitro ultrahigh-throughput screening platform using droplet-based microfluidics can reduce the cost by almost 105-fold, allowing the screening of 106 genes using only 150 nL of reagents [90]. Specially, droplet microfluidics provides the ability to perform and quantify multiple amplifications simultaneously within the same reaction volume (multiplexing) for both PCR and real-time PCR [90]. Massively parallel multiplex PCR on the single-cell level in droplets had been successfully developed. Zhu et al. [91] had developed the sensitive and quantitative analysis of a single E. coli O157:H7 cell in the high background of 100 000 excess normal K12 cells and demonstrated rare pathogen detection through agarose droplet PCR microfluidic, as shown in Fig. 7(a).

Isothermal amplification methods have been
proposed because PCR generally requires a highly precise thermal cycler. Nucleic acid can be amplified under a single working temperature in isothermal amplification methods.

The first high-throughput, on-chip analysis droplet microfluidic system using isothermal hyperbranched rolling circle amplification (HRCA) was achieved by Mazutis et al. Then Konry et al. proposed a highly sensitive labeling method to translate antigen-antibody recognition processes into DNA detection using miniaturized nanoliter reaction droplets rolling circle amplification (RCA) [93]. This method can enhance the sensitivities and specificities for various applications, including early diagnosis of cancer.

A sample self-digitization (SD) chip with automated, lossless digitization of sample volumes on-chip was described. They demonstrated accurate quantification of relative and absolute DNA concentrations using digital loop-mediated DNA amplification (dLAMP) [94]. It is an inexpensive and easy-to-operate device for DNA amplification.

This SlipChip can also be applied to perform high-throughput PCRs. Ismagilov et al. [45] first proposed a very simple and inexpensive SlipChip to perform droplet PCR. Then they described high-throughput nanoliter multiplex PCR using SlipChip platform with robust performance and lack of false negatives, false positives, and cross-contamination [46]. They used up to 384 nanoliter-scale reactions for multiplex PCR with a preloaded array of primer pairs. Recently, they designed a microfluidic rotational multivolume droplet real-time PCR SlipChip to performance viral HIV and HCV RNA for high-performance diagnostics, as shown in Fig. 7(b) [47].

Mathies developed high-throughput DNA sequencing by using a microfabricated 96-channel radial capillary array electrophoresis microchannel plate [95]. The system can produce sequencing data at a rate of 1.7 kbp/min, a 5-fold increase at lower reagent volumes and lower sample concentrations. It presents great potential for high performance DNA sequencing platform with integrated sample preparation and handling.

DNA computer is based on the computational model of DNA biochemical reaction [96]. And they experimentally demonstrated that DNA molecules could be used to solve hard combinatorial problems. Then hairpin formation by single-stranded DNA molecules was exploited to explore the feasibility of autonomous molecular computing, which sheds a new light on the potentials of DNA [97]. Gehani and Rief [98] first proposed a bio-molecular computation model with the recombinant DNA technology and micro-flow technology. The DNA computer model must integrate MEMS pumps, valves, sensors, actuators, flow control systems and digital to analog conversion. Grover and Mathies [99] developed an integrated microfluidic processor to performs molecular computations using single nucleotide polymorphisms (SNPs) as binary bits, as shown in Fig. 8.
Fig. 8  (a) Photograph and (b) mask design of the microfluidic processor. (c) Oblique view of a single capture chamber [99].

Fig. 9  Schematic illustration of the “hybrid” droplet microfluidics for protein crystallization and a plot quantifying a hybrid screen, performed in a separate experiment [103].

It suited for performing larger-scale DNA computations well and offered a valuable platform for many types of next-generation molecular computations.

Protein engineering

Protein engineering is becoming increasingly important in industrial biotechnology-based manufacturing of commodities related to bioenergy and biosustainability [100]. A rapid screening method has been developed to determine binding affinities for protein-protein interactions in a microfluidic platform [101]. The method reduced the experimental duration by more than 10-fold comparing with the conventional ki-
nentic exclusion assay method.

In droplet microfluidics, many droplets, each containing different crystallization conditions, can be generated in a single experiment by systematically changing the flow rates of the streams of aqueous reagent, protein, buffer, and precipitants. Zheng et al. [102] proposed a microfluidic system for screening hundreds of protein crystallization conditions using less than 4 nL of protein solution for each crystallization trial. This chip has the ability to handle 5-10 solutions and provides multidimensional phase diagrams for protein crystallization. So this system offers the potential to serve as the basis of high-throughput, automated crystallization systems. High-throughput screening and optimization experiments are critical to biology. Then Li et al. [103] reported a “hybrid” droplet microfluidics approach to combines high-throughput screening and optimization into one simple experiment, as shown in Fig. 9. In addition, this approach uses nanoliter-sized plugs to minimize sample consumption. Recently, droplet microfluidics is also used to perform high-throughput analysis of protein-protein interactions [104]. Compared with equivalent bulk assays, this method only using 14 nL of sample in per experiment represents a reduction of 4 orders of magnitude.

Ismagilov et al. [50] provided a convenient and high-throughput SlipChip-based approach for protein crystallization. The composite SlipChip was designed to screen multiple reagents, each at multiple mixing ratios and multiple equilibration times.

High-throughput screening

High-throughput screening can provide an enormous amount of information and is considered as a new technology for the 21st century [105]. Recently, microfluidic-based high-throughput screening is becoming an attractive alternative to conventional laboratory-based screening. However, it is challenging to control and vary the concentration of the analytical sample under investigation [106]. Niu et al. [106] developed a dilution module for high-throughput screening using droplet microfluidics. They generated a sequence of output droplets with droplet concentration gradient through a process of droplet merging, mixing and re-splitting. It is an inexpensive chip-level screening technology for high-throughput and high-efficiency experimentation.

Granieri et al. [107] reported a microfluidic approach for the high-throughput screening of structurally complex enzyme variants. The droplet microfluidic system allows a throughput over 100 times higher and reduces cost almost one million-fold lower than conventional screening formats such as microtiter plates. Brouzes et al. [108] developed a fully integrated droplet microfluidic workflow that enables high-throughput screening of single mammalian cells, as shown in Fig. 10. It is a generic, fast, and robust tool that can be used large-scale screen and analysis of small samples. Recently, a modular approach to droplet-based screening was proposed, which included droplets library generation, storage, mixing, and optical detection [109].

![Fig. 10 Droplet microfluidic workflow for single-cell high-throughput screening](http://dx.doi.org/10.3786/nml.v5i1.p66-80)

Conclusions

In summary, we provided a comprehensive review of the technologies for microfluidics and its applications in biology and medicine. Microfluidics has been considered as a potential technology to miniaturize the conventional equipments and technologies. It offers advantages such as small volume, low cost, short reaction time and high-throughput. We provide the physics of microfluidics to understand the physical phenomena at the microscale. Then we introduce a summary of droplet microfluidics technology with droplet generation and manipulation and an ingenious SlipChip. Finally, we discuss these recent advances of microfluidics in biology and medicine, such as cell analysis, nucleic acid analysis, protein engineering and high-throughput screening. Cell culture, fusion and apoptosis were successfully performed in microfluidics due to the appropriate scale matching the scales of cells. Microfluidics provides unique opportunities for rare circulating tumor cells isolation and detection from the blood of patients, which furthers the discovery of cancer stem cell biomarkers and expands the understanding of the biol-
ology of metastasis. Nucleic acid analysis in microfluidics has been extended to single-molecule, high-throughput and integration treatment in one chip. DNA computer which is based on the computational model of DNA biochemical reaction will become practice from concept in the future. In addition, microfluidics offers a versatile platform for protein-protein interactions, protein crystallization and high-throughput screening. Although microfluidics is still in its infancy, its great potential has already been demonstrated and will provide novel solutions to the high-throughput applications. Even though microfluidics is still in the early stages, we believe that the potentials of microfluidics for high-throughput applications have yet to be fully investigated and exploited. Moreover, we anticipate that microfluidics will be increasingly used in science and technology.

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References

[1] G. M. Whitesides, “The origins and the future of microfluidics”, Nature 442, 368-373 (2006). http://dx.doi.org/10.1038/nature05058
[2] A. Manz, N. Graber and H.M. Widmer, “Miniaturized total chemical analysis systems: a novel concept for chemical sensing”, Sens. Actuators B 1, 244-248 (1990). http://dx.doi.org/10.1016/0925-4005(90)80209-I
[3] D. Lombardi and P. S. Dittrich, “Advances in microfluidics for drug discovery”, Expert Opin. Drug Dis. 5, 1081-1094 (2010). http://dx.doi.org/10.1517/17460441.2010.521149
[4] T. Thorsen, S. J. Maerkl and S. R. Quake, “Microfluidic large-scale integration”, Science 298, 580-584 (2002). http://dx.doi.org/10.1126/science.1076996
[5] A. J. Demello, “Control and detection of chemical reactions in microfluidic systems”, Nature 442, 394-402 (2006). http://dx.doi.org/10.1038/nature05062
[6] X. D. Fan and I. M. White, “Optofluidic microsystems for chemical and biological analysis”, Nature Photon. 5, 591-597 (2011). http://dx.doi.org/10.1038/nphoton.2011.206
[7] A. M. Skelley, O. Kirak, H. Suh, R. Jaenisch, and J. Voldman, “Microfluidic control of cell pairing and fusion”, Nat. Methods 6, 147-152 (2009). http://dx.doi.org/10.1038/nmeth.1290
[8] J. D. Chen, D. Chen, T. Yuan and X. Chen, “Microfluidic PCR chips”, Nano Biomed. Eng. 3, 203-210 (2011). http://dx.doi.org/10.5101/nbe.v3i4.p203-210
[9] P. S. Dittrich and A. Manz, “Lab-on-a-chip: microfluidics in drug discovery”, Nat. Rev. Drug Discov. 5, 210-218 (2006). http://dx.doi.org/10.1038/nrd1985
[10] H. X. Du, Z. G. Wang, Z. L. Yang, D. Chen, J. D. Chen and R. J. Hu, “Separation of circulating cancer cells by unique microfluidic chip in colorectal cancer” Oncology Research 19, 487-500 (2012). http://dx.doi.org/10.3727/096504012x3286534482476
[11] Y. J. Song, J. Hormes and C. S. S. R. Kumar, “Microfluidic synthesis of nanomaterials”, Small 4, 698-711 (2008). http://dx.doi.org/10.1002/smll.200701029
[12] I. Doh, E. Y. Erdem and A. P. Pisano, “Trapping and collection of uniform size droplets for nanoparticle synthesis”, Appl. Phys. Lett. 100, 074106-074108 (2012) http://dx.doi.org/10.1063/1.3685695
[13] N. Yanaguchi, M. Torii, Y. Uebayashi and M. Nasu, “Rapid, semiautomated quantification of bacterial cells in freshwater by using a microfluidic device for on-chip staining and counting”, Appl. Environ. Microbiol. 77, 1536-1539 (2011). http://dx.doi.org/10.1128/aem.01765-10
[14] S. Neethirajan, I. Kobayashi, M. Nakajima, D. Wu, S. Nandagopal and F. Lin, “Microfluidics for food, agriculture and biosystems industries”, Lab Chip 11, 1574-1586 (2011). http://dx.doi.org/10.1039/c0lc00230e
[15] H. A. Stone, A. D. Stroock and A. Ajdari, “Engineering flows in small devices microfluidics toward a lab-on-a-chip”, Annu. Rev. Fluid Mech., 36, 381-411 (2004). http://dx.doi.org/10.1146/annurev.fluid.36.050802.122124
[16] D. J. Beebe, G. A. Mensing and G. M. Walker, “Physics and applications of microfluidics in biology”, Annu. Rev. Biomed. Eng. 4, 261-286 (2002). http://dx.doi.org/10.1146/annurev.bioeng.4.112601.125916
[17] G. F. Christopher and S. L. Anna, “Microfluidic methods for generating continuous droplet streams”, J. Phys. D: Appl. Phys. 40, R319-R336 (2007). http://dx.doi.org/10.1088/0022-3727/40/19/R01
[18] V. Hessel, H. Löwe and F. Schönfeld, “Micromixers—a review on passive and active mixing principles”, Chem. Eng. Sci. 60, 2479-2501 (2005). http://dx.doi.org/10.1016/j.ces.2004.11.033
[19] L. Capretto, W. Cheng, M. Hill and X. Zhang, “Micromixing within microfluidic devices”, Top. Curr. Chem. 304, 27-68 (2011). http://dx.doi.org/10.1007/128_2011_150
[20] P. B. Umbanhowar, V. Prasad and D. A. Weitz, “Monodisperse emulsion generation via drop break off in a coflowing stream”, Langmuir 16, 347-351 (2000). http://dx.doi.org/10.1021/la990101e
[21] T. Thorsen, R. W. Roberts, F. H. Arnold and S. R. Quake, “Dynamic pattern formation in a vesicle-generating microfluidic device”, Phys. Rev. Lett. 86, 4163-4166 (2001). http://dx.doi.org/10.1103/physrevlett.86.4163
[22] S. L. Anna, N. Bontoux and H. A. Stone, “Formation of dispersions using “flow focusing” in microchannels”, Appl. Phys. Lett. 82, 364-366 (2003). http://dx.doi.org/10.1063/1.1537519

[23] C. N. Baroud, F. Gallaire and R. Dangla, “Dynamics of microfluidic droplets”, Lab Chip 10, 2032-2045 (2010). http://dx.doi.org/10.1039/c001191f

[24] S. Y. Teh, R. Lin, L. H. Hung and A. P. Lee, “Droplet microfluidics” Lab Chip 8, 198-220 (2008). http://dx.doi.org/10.1039/b715524g

[25] A. S. Utada, A. Fernandez-Nieves, H. A. Stone and D. A. Weitz, “Dripping to jetting transitions in coflowing liquid streams”, Phys. Rev. Lett. 99, 94502-94505 (2007). http://dx.doi.org/10.1103/PhysRevLett.99.094502

[26] X. C. I. Solvas and A. deMello, “Droplet microfluidics: recent developments and future application”, Chem. Commun. 47, 1936-1942 (2011). http://dx.doi.org/10.1039/c0cc02474k

[27] A. C. Hatch, J. S. Fisher, A. R. Tovar, A. T. Hsieh, R. Lin, S. L. Pentoney, D. L. Yang and A. P. Lee, “1-million droplet array with wide-field fluorescence imaging for digital PCR”, Lab Chip 11, 3838-3845 (2011). http://dx.doi.org/10.1039/c1lc20561g

[28] N. Bremond, A. R. Thiam and J. Bibette, “Decompression emulsion droplets favors coalescence”, Phys. Rev. Lett. 100, 24501-24504 (2008). http://dx.doi.org/10.1103/PhysRevLett.100.24501

[29] L. Mazutis, J. C. Baret and A. D. Griffiths, “A fast and efficient microfluidic system for highly selective one-to-one droplet fusion”, Lab Chip 9, 2665-2672 (2009). http://dx.doi.org/10.1039/b903608c

[30] M. Chabert, K. D. Dorfman and J. L. Viovy, “Droplet fusion by alternating current (AC) field electrocoalescence in microchannels”, Electrophoresis 26, 3706-3715 (2005). http://dx.doi.org/10.1002/elps.200500109

[31] R. M. Lorenz, J. S. Edgar, G. D. M. Jeffries and D.T. Chiu, “Microfluidic and optical systems for the on-demand generation and manipulation of single femtoliter-volume aqueous droplets”, Anal. Chem. 78, 6433-6439 (2006). http://dx.doi.org/10.1021/ac0607481

[32] D. Link, S. L. Anna, D. A. Weitz and H. Stone, “Geometrically mediated breakup of drops in microfluidic devices”, Phys. Rev. Lett. 92, 54503-54506 (2004). http://dx.doi.org/10.1103/PhysRevLett.92.054503

[33] A. M. Leshansky and L. M. Pismen, “Breakup of droplets in a microfluidic T junction”, Phys. Fluids 21, 023303 (2009). http://dx.doi.org/10.1063/1.3078515

[34] J. H. Choi, S. K. Lee, J. M. Lim, S. M. Yang and G. R. Yi, “Designed pneumatic valve actuators for controlled droplet breakup and generation”, Lab Chip 10, 456-461 (2010). http://dx.doi.org/10.1039/b915596a

[35] A. R. Abate and D. A. Weitz, “Faster multiple emulsification with drop splitting”, Lab Chip 11, 1911-1915 (2011). http://dx.doi.org/10.1039/c00706d

[36] H. Song, M. R. Bringer, J. D. Tice, C. J. Gerdts and R. F. Ismagilov, “Experimental test of scaling of mixing by chaotic advection in droplets moving through microfluidic channels”, Appl. Phys. Lett. 83, 4664-4666 (2003). http://dx.doi.org/10.1063/1.1630378

[37] M. R. Bringer, C. J. Gerds, H. Song, J. D. Tice and R. F. Ismagilov, “Microfluidic systems for chemical kinetics that rely on chaotic mixing in droplets”, Phil. Trans. R. Soc. Lond. A 362, 1087-1104 (2004). http://dx.doi.org/10.1098/rsta.2003.1364

[38] N. T. Nguyen and Z. Wu, Microm, “Micromixers—a review”, J. Micromech. Microeng. 15, R1-R16 (2005). http://dx.doi.org/10.1088/0960-1317/15/2/R01

[39] A. Huebner, D. Bratton, G. Whyte, M. Yang, C. Abell and F. Hollfelder, “Static microdroplet arrays: a microfluidic device for droplet trapping, incubation and release for enzymatic and cell-based assays”, Lab Chip 9, 692-698 (2009). http://dx.doi.org/10.1039/b813709a

[40] Y. P. Bai, X. M. He, D. S. Liu, S. N. Patil, D. Bratton, A. Huebner, F. Hollfelder, C. Abell and W. T. S. Huck, “A double droplet trap system for studying mass transport across a droplet-droplet interface”, Lab Chip 10, 1281-1285 (2010). http://dx.doi.org/10.1039/b025133b

[41] J. Xu, B. Ahn, H. Lee, L. F. Xu, K. Lee, R. Panchapakesan and K. W. Oh, “Droplet-based microfluidic device for multiple-droplet clustering”, Lab Chip 12, 725-730 (2012). http://dx.doi.org/10.1039/c2lc20883x

[42] W. B. Du, L. Li, K. P. Nichols and R. F. Ismagilov, “SlipChip”, Lab Chip 9, 2286-2292 (2009). http://dx.doi.org/10.1039/b908978k

[43] L. Li, W. B. Du and R. F. Ismagilov, “User-loaded SlipChip for equipment-free multiplexed nanoliter-scale experiments”, J. Am. Chem. Soc. 132, 106-111 (2009). http://dx.doi.org/10.1021/ja908555n

[44] D. Belder, “Screening in one sweep using the SlipChip”, Angew. Chem. Int. Ed. 49, 6484-6486 (2010). http://dx.doi.org/10.1002/anie.201002059

[45] F. Shen, W. B. Du, J. E. Kreutz, A. Fok and R. F. Ismagilov, “Digital PCR on a SlipChip”, Lab Chip 10, 2666-2672 (2010). http://dx.doi.org/10.1039/c004521g

[46] F. Shen, W. B. Du, E. K. Davydova, M. A. Karymov, J. Pandey and R. F. Ismagilov, “Nanoliter multiplex PCR arrays on a SlipChip”, Anal. Chem. 82, 4606-4612 (2010). http://dx.doi.org/10.1021/ja1007249

[47] F. Shen, B. Sun, J. E. Kreutz, E. K. Davydova, W. B. Du, P. L. Reddy, L. J. Joseph, and R. F. Ismagilov, “Multiplexed quantification of nucleic acids with large dynamic range using multivolume digital RT-PCR on a rotational SlipChip tested with HIV and Hepatitis C viral load”, J. Am. Chem. Soc. 133, 17705-17712 (2011). http://dx.doi.org/10.1021/ja106111b

[48] W. S. Liu, D. L. Chen, W. B. Du, K. P. Nichols and R. F. Ismagilov, “SlipChip for immunosassays in nanoliter volumes”, Anal. Chem. 82, 3272-3282 (2010). http://dx.doi.org/10.1021/ac100044c
[101] H. Salimi-Moosavi, P. Rathana-swami, S. Rajendran, M. Toupikov and J. Hill, “Rapid affinity measurement of protein–protein interactions in a microfluidic platform”, Anal. Biochem. 401, 134-141 (2012). http://dx.doi.org/10.1016/j.ab.2012.04.023

[102] B. Zheng, L. S. Roach and R. F. Ismagilov, “Screening of protein crystallization conditions on a microfluidic chip using nanoliter-size droplets”, J. Am. Chem. Soc. 125, 11170-11171 (2003). http://dx.doi.org/10.1021/ja037166v

[103] L. Li, D. Mustafi, Q. Fu, V. Tereshko, D. L. Chen, J. D. Tice and R. F. Ismagilov, “Nanoliter microfluidic hybrid method for simultaneous screening and optimization validated with crystallization of membrane proteins”, Proc. Natl. Acad. Sci. USA 103, 19243-19248 (2006). http://dx.doi.org/10.1073/pnas.0607502103

[104] J. W. Choi, D. K. Kang, H. Park, A. J. deMello and S. I. Chang, “High-throughput analysis of protein–protein interactions in picoliter-volume droplets using fluorescence polarization”, Anal. Chem. 84, 3849-3854 (2012). http://dx.doi.org/10.1021/ac300414g

[105] R. P. Hertzberg and A. J. Pope, “High-throughput screening: new technology for the 21st century”, Curr. Opin. Chem. Biol. 4, 445-451 (2000). http://dx.doi.org/10.1016/S1367-5931(00)00110-1

[106] X. Z. Niu, F. Gielen, J. B. Edel and A. J. deMello, “A microdroplet dilutor for high-throughput screening”, Nature Chem. 3, 437-442 (2011). http://dx.doi.org/10.1038/nchem.1046

[107] L. Granieri, J. C. Baret, A. D. Griffiths and C. A. Merten, “High-throughput screening of enzymes by retroviral display using droplet-based microfluidics”, Chem. Biol. 17, 229-235 (2010). http://dx.doi.org/10.1016/j.chembiol.2010.02.011

[108] E. Brouzes, M. Medkova, N. Savenelli, D. Marran, M. Twardowski, J. B. Hutchison, J. M. Rothberg, D. R. Link, N. Perrimon and M. L. Samuels, “Droplet microfluidic technology for single-cell high-throughput screening”, Proc. Natl. Acad. Sci. USA 106, 14195-14200 (2009). http://dx.doi.org/10.1073/pnas.0903542106

[109] V. Trivedi, A. Doshi, G. Kurup, E. Ereifej, P. Vandervord and A. S. Basu, “A modular approach for the generation, storage, mixing, and detection of droplet libraries for high throughput screening”, Lab Chip 10, 2433-2442 (2010). http://dx.doi.org/10.1039/c004768f