Contents

Recent Progress in Ferroelectric Diodes: Explorations in Switchable Diode Effect ................................. 81-87
Chen Ge, Can Wang, Kui-juan Jin*, Hui-bin Lu, Guo-zhen Yang

Nano Brazing of Pt-Ag Nanoparticles under Femtosecond Laser Irradiation ............................................. 88-92
L. Liu*, H. Huang, A. Hu, G. Zou, L. Quintino, Y. Zhou

Synthesis and Growth Mechanism of Net-like Titanate Nanowire Films via Low-temperature and Low-alkali-concentration Route .......................................................... 93-100
Xinwen Huang, Zongjian Liu *

Electrochemical Generation of Cubic Shaped Nano Zn2SnO4 Photocatalysts ........................................... 101-110
Chandrappa K. Govindappa*, Venkatesha T. Venkatarangaiah, Sharifah B. Abd Hamid

Single-step Preparation of Nano-homogeneous NiO/YSZ Composite Anode for Solid Oxide Fuel Cells .......................................................... 111-116
Jung-Hoon Song, Mi-Young Park, Hyung-Tae Lim*

Synthesis and Luminescence Properties of (Y, Gd)(P, V)O4:Eu3+,Bi 3+ Red Nano-phosphors with Enhanced Photoluminescence by Bi3+, Gd3+ Doping .............................................. 117-123
Yong Pu, Ke Tang, Da-Chuan Zhu*, Tao Han, Cong Zhao, Ling-Ling Peng

Growth and Formation Mechanism of Branched Carbon Nanotubes by Pyrolysis of Iron(II) Phthalocyanine .......................................................... 124-128
Qiong Wei, Yunyun Liu, Lijie Zhang, Shaoming Huang *

Surface Texturing of TiO2 Film by Mist Deposition of TiO2 Nanoparticles ............................................... 129-134
Gang Qin, Akira Watanabe *

Thermal Evaporation Deposition of Few-layer MoS2 Films .......................................................... 135-139
Xiying Ma*, Miaoyuan Shi

Giant Magneto-impedance Effect in Composite Wires with Different Core Layer ............................................. 140-144
R. L. Wang, X. Li, X. H. Kong, Y. X. Guo, J. Z. Ruan, Z. J. Zhao *
Recent Progress in Ferroelectric Diodes: Explorations in Switchable Diode Effect

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Abstract: Switchable diode effect in ferroelectric diodes has attracted much attention for its potential applications in novel nonvolatile memories. We briefly review recent investigations on the switchable diode effect in ferroelectric diodes both experimentally and theoretically. Many recent studies demonstrate that the interfacial barrier between the metal-ferroelectrics could be modulated by the polarization charges, and the ferroelectric polarization that can be reversed by an external electric field plays a dominant role in the switchable diode effect. Moreover, we review a self-consistent numerical model, which can well describe the switchable diode effect in ferroelectric diodes. Based on this model, it can be predicted that it is a better choice to select metals with a smaller permittivity, such as noble metals, to obtain a more pronounced switchable diode effect in ferroelectric diodes.

Keywords: Ferroelectric diodes; Switchable diode effect; Metal/ferroelectrics/metal structure; Self-consistent mode

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Introduction

Ferroelectric materials are of characteristics to maintain the polarization state in the absence of a voltage and the possibility to reverse the polarization direction by applying an electric field [1,2]. It is an obvious idea to design robust nonvolatile random access memories based on intrinsic switchable ferroelectric polarization in the ferroelectric materials. Ferroelectric capacitive memories were regarded as a promising candidate for the next generation nonvolatile memories [3,4], but failed to achieve their commercial success mainly because of the scaling limit and the destructive readout that memories must revert to the original polarization state after reading the stored information [5]. It is of great value to explore an alternative route to non-destructively read the polarization in ferroelectric thin films.

A promising solution to these problems is to probe the polarization by measuring resistance states instead of sensing charges in metal/ferroelectrics/metal (MFM) structures [6]. The polarization charges can affect the barrier at the interface between electrodes and ferroelectrics, and the reversal of the polarization produces a change in the band diagram [7,8]. As a result of this, bistable resistance states can be obtained for two opposite polarizations. In other words, the high and low resistance states stem from the interplay of polarization and conduction. Two ferroelectric resistive switching concepts are classified by the conduction mechanism. In the case of ferroelectric ultrathin films, the current transport through ferroelectrics is governed by the tunneling process, which has emerged as an active research topic called as ferroelectric tunnel junctions [9-13]. In the case of ferroelectric thin films, the drift-diffusion or thermionic emission plays a dominant role in transport. The structures in the latter case are called as ferroelectric diodes, which is the focus of this review. For the
General hysteretic resistance concept, please refer to ref. [6].

Ferroelectric diodes have been investigated in the past two decades due to their huge potentials in non-volatile memory applications. Blom et al. first reported bistable resistance states in 1994, showing that in the La_{0.5}Sr_{0.5}CoO_{3}/PbTiO_{3}/Au structure the conducting state exists under one polarization while the insulating state exists under the other polarization [14]. Since then many similar phenomena have been observed in various ferroelectric thin films [15-19]. Most interestingly, the switchable diode effect has been demonstrated recently in various ferroelectric structures ranging from organic films [20,21], inorganic bulks [22-24], and inorganic films [25-29]. The switchable diode effect means that the polarity of the diode can be reproducibly switched by the reversal of the applied electric field in the MFM structures, due to the polarization modulated barrier. In addition, a few theoretical studies on this issue have been presented to reveal the underlying physics in the switchable diode effect [30-32].

In this paper, we will briefly review some recent research progress in the switchable diode effect in ferroelectric diodes, and then discuss the experimental studies on the origin of the switchable diode effect and the role of oxygen vacancies. We will also briefly present a theoretical model, which can well describe the transport property in MFM structures. Before we conclude this article, a short discussion on the effect of electrodes will be presented.

Recent progress in switchable ferroelectric diodes

Up to now, the research on the switchable diode effect is mainly focused on BiFeO_{3} (BFO) materials [22,25-29]. In most cases, the BFO thin films were grown on the bottom electrode covered SrTiO_{3} substrates by pulsed laser deposition, and then the top electrodes were deposited on the BFO films to form MFM structures. SrRuO_{3} (SRO)/BFO/Pt is a most common structure, in which an obvious current hysteresis behavior was observed as shown in Fig. 1(a) [27]. The measurements were repeatedly performed with 25 cycles by sweeping the bias voltage of the top electrode from 8 to −7.5 V and back to 8 V. The numbers in Fig. 1(a) denote the sequence of voltage sweeps. The I-V curves show an obvious hysteresis behavior, and two I-V segments in the range of ±5 V are plotted using solid circle symbols and open circle symbols in the inset of Fig. 1(a) respectively, indicating a switchable diode effect. Figure 1(b) [27] shows the I-V curves plotted on semi-logarithmic coordinates for the 120 and 240 nm BFO films. The switchable diode effect was also observed for the 120 nm film, where the applied voltage range is smaller than that for the 240 nm film (about ±3 V). The resistance switching ratio is 103 at −3 V for the 240 nm films, and it is 79 at −1 V for the 120 nm films.

To further confirm the observed switchable diode effect, Wang et al. used electrical pulses of ±8 V for 200 ms to induce the reversion of the polarization in the 240 nm BFO film, and measured I-V curves with a sweep voltage of ±2 V as shown in Fig. 2 [27,30]. Quite obviously, the structure shows a forward diode-like behavior after the electrical pulse of +8 V, whereas the structure shows a reverse diode-like behavior after the pulse of −8 V. It is worth mentioning that an excellent retention was obtained in this structure ascribed to...
the intrinsic non-volatile nature of spontaneous polarization [26].

An interesting question focuses on what is the origin of the switchable diode. Yang et al. presented the observation of the switchable diode effect in the Ca-doped BFO thin film [25]. It was hypothesized that the mobile oxygen vacancies created to maintain charge neutrality are the key to understand the transport property in this system. For one bias condition, oxygen vacancies can move and pile up near the top surface. Consequently, the donor oxygen vacancies and the acceptor calcium ions are locally unbalanced. Thus the top surface region becomes n-type, whereas the region near the bottom electrode becomes p-type. Then a diode can be formed. For the other bias condition, oxygen vacancies can move and pile up at the bottom surface, resulting in the inversion of the conduction direction in the diode.

However, many recent investigations have demonstrated a dominant role played by the ferroelectric polarization in switchable diode effect [26-29]. Jiang et al. confirmed that the reticent switching curves of the SRO/BFO/Pt structure have identical shapes to the Polarization-Voltage loops. Combined the measurement results of the local polarization and diode current, they concluded that the switchable diode effect in ferroelectric diodes is completely governed by the ferroelectric polarization [26]. Moreover, Wang et al. measured the I-V curves in the virgin 240 nm BFO film capacitance by increasing the sweep range step by step [27], to verify the correlation between the electrical hysteresis and ferroelectric polarization. Obvious hysteresis loops were not observed until the sweep voltages were larger than ±6 V which is close to the coercive voltage of the ferroelectric thin film. The larger the voltage range, the more pronounced the hysteresis will become. It was claimed that the current hysteresis and diode-like behavior can be triggered and switched under a high enough electric field, which can drive the ferroelectric domain switching. Furthermore, Lee et al. also overlapped the response of the J-V curves with the P-V hysteresis loop [28]. Their results showed that the hysteresis behavior of the diode-polarity switching coincides with the ferroelectric switching hysteresis. They claimed that the sharp changes in current values near the coercive voltage exclude the possibility that the switchable diode originated from the migration of oxygen vacancies. The switch-ability between the reverse and forward diodes originates from the band modification and associated change in the barriers at the BFO/metal interfaces, which depends on the ferroelectric polarization direction. By using Conductive-AFM and PFM techniques, Hong et al. observed a switchable diode effect induced by the ferroelectric polarization in BFO nano-islands [29]. In short, most of recent experiments have proved that the polarization dominates the switchable diode effect in ferroelectric diodes. The role of oxygen vacancy should be carefully considered, because the distribution of charged oxygen vacancy could affect charge transport in ferroelectric diodes. Lee et al. observed one-side diode effect in SRO/BFO/Pt, and attributed this phenomenon to the interfacial defective layer possibly induced by the charged oxygen vacancies [28]. During the film deposition process, the downward self-polarization will cause the positively charged oxygen vacancies to migrate toward the top Pt/BFO interface to compensate for the negative polarization charge [33], resulting in a defective layer. The defective layer can seriously affect charge transport at the Pt/BFO interface, especially the carrier injection under a positive bias. In order to obtain a switchable diode effect, the defective layer induced by the oxygen vacancies should be removed from the samples. Lee et al. applied a positive dc bias of +15 V to the as-grown sample for 30 min at room temperature. As a result, the transport behaviors between forward and reverse diodes in BFO thin film capacitors could be switched with the polarization reversal of the ferroelectric layer [28].

Theoretical explanations

For a deeper understanding of the switchable diode effect, it is fundamentally important to carry out a theoretical study on this issue. To that end, a key step is to construct a viable model to quantitatively calculate the band diagram, the charge distribution, and the transport property in MFM structures. One point that must be properly handled is that a ferroelectric thin film cannot be considered in isolation, because the measured property reflects the entire system of films, interfaces, and electrodes [2]. Recently, we have proposed a self-consistent model, particularly taking account of the incomplete screening effect of realistic metal electrodes [34,35], to explain the switchable diode effect in MFM structures [30,31]. The fundamental charge transport equations in this system are as follows:

\[
\frac{d^2 \phi(x)}{dx^2} = - \frac{e}{\varepsilon(x)} \rho(x) \tag{1}
\]

\[
\frac{1}{e} \frac{d}{dx} \left( j(x) - R(x) \right) = 0 \tag{2}
\]

where \(x\) is the spatial coordinate, and \(e\) denotes the elementary charge. \(\phi(x), \varepsilon(x), \rho(x), j(x),\) and \(R(x)\) represent the electrostatic potential, dielectric constant, charge density, current density, recombination rate, respectively. The current density \(j(x)\) and conductivity \(\sigma(x)\) read

\[
\begin{align*}
    j(x) &= \frac{\sigma(x)}{e} \frac{d\varepsilon(x)}{dx} \tag{3} \\
    \sigma(x) &= e\mu(x)n(x) \tag{4}
\end{align*}
\]
where $\kappa(x)$, $\mu(x)$, and $n(x)$ represent the electrochemical potential, mobility, and electron density, respectively. To write the electrochemical potential of metals $\kappa_m(x)$, the free electron model and Thomas-Fermi approximation are employed [36,37]. The semiconductor theory is utilized to calculate the electrochemical potential of ferroelectric films $\kappa_s(x)$. The electrochemical potential $\kappa_m(x)$ and $\kappa_s(x)$ are given by

$$\kappa_m(x) = \frac{h^2}{2m} \left[ 3\pi^2 n_m(x) \right]^{3/2} - e\phi(x) \quad (5)$$

$$\kappa_s(x) = kT \ln \left[ \frac{n_s(x)}{N_c} \right] + E_c - e\phi(x) \quad (6)$$

where $h$, $m$, $k$, $T$, and $E_c$ denote the reduced Planck constant, the effective electron mass, the Boltzmann constant, the temperature, and the bottom of conduction band, respectively. The effective density of states $N_c$ is expressed as $N_c = 2 \left( \frac{m_e kT}{2\pi\hbar^2} \right)^{3/2}$, where $m_s$ represents the effective mass of electrons in ferroelectrics.

A simple approach is employed that the polarization is treated as an infinite thin sheet of charges located at the interfaces. Thus, the boundary condition for the electrostatic potentials can be expressed as [38]:

$$\varepsilon_s \varepsilon_0 \frac{d\phi(x)}{dx} \bigg|_{X_+} - \varepsilon_m \varepsilon_0 \frac{d\phi(x)}{dx} \bigg|_{X_-} = -\sigma(X_l) = P \quad (7)$$

$$\varepsilon_m \varepsilon_0 \frac{d\phi(x)}{dx} \bigg|_{X_+} - \varepsilon_s \varepsilon_0 \frac{d\phi(x)}{dx} \bigg|_{X_-} = -\sigma(X_r) = -P \quad (8)$$

where $\sigma$, $P$, $X_l$, and $X_r$ denote the interface charge density, the ferroelectric polarization, the position of left interface, and the position of right interface, respectively. A simple boundary condition is used to solve the continuity equation [36,37]:

$$\kappa(x) = \text{continuous} \quad (9)$$

These equations (1)-(6) coupled with boundary conditions (7)-(9) can be solved using the iterative method.

The model was applied to the experimental data in SRO/BFO/Pt structures [26,27]. For BFO, the saturation polarization is about 65 µC/cm² [26,27]. Other parameters are listed in Table 1. The theoretical results agree well with experimental data as shown in Fig. 2 [26,28], showing that this model can well describe the switchable diode effect. Based on the model, it was theoretically revealed that the ferroelectric polarization could modulate the barrier at the metal/ferroelectrics interfaces, and the Schottky-to-Ohmic conversion can occur under a large enough electric field [30]. Consequently, the polarity of the ferroelectric diode could be switched with the polarization reversal, giving rise to the switchable diode effect in ferroelectric diodes. Therefore, the ferroelectric polarization dominates the switchable diode effect.

Furthermore, this theoretical model can well explain the effect of the electrodes in ferroelectric diodes. The Schottky barrier for an ideal Schottky diode is determined by the difference of the metal work function and the semiconductor electron affinity, thus the work function of the electrodes can influence charge transport and the switchable diode effect in ferroelectric diodes. In order to further understand the effect of electrodes on the transport characteristics in ferroelectric diodes, we calculated the barrier height variation, defined as the change of the barrier height with and without a polarization, as a function of the polarization in SRO/BFO/Pt. From Fig. 3 [30], $\Delta \phi_{P_{t/BFO}}$ as a function of the polarization deviates away from the linear dependence in the case of a large positive polarization (pointing from SRO to Pt), attributed to a high electron density $2.0 \times 10^{20}$ cm$^{-3}$ under a polarization of 150 µC/cm². However, $\Delta \phi_{SRO/BFO}$ does not show this deviation in the case of a large negative polarization (pointing from Pt to SRO), because the electron density is $2.1 \times 10^{17}$ cm$^{-3}$ under a polarization of $-150$ µC/cm². In addition, $|\Delta \phi_{P_{t/BFO}}|$ is larger than $|\Delta \phi_{SRO/BFO}|$ under the same polarization, mainly due to a smaller permittivity of Pt. Hence, we had better select electrodes with a smaller permittivity besides a suitable work function, such as noble metals rather than oxide electrodes, to obtain a more pronounced switchable diode effect.

Table 1 The parameters used in calculations (Reprinted with permission from Ref. [30]. Copyright 2011, American Institute of Physics)

|                      | SrRuO$_3$ | Pt   | BiFeO$_3$ |
|----------------------|-----------|------|-----------|
| Dielectric constant ($\varepsilon_0$) | 8         | 2    | 100       |
| Mobility (cm$^2$/V·s) | 10        | 60   | 5         |
| Effective mass ($m_0$) | 5         | 1    | 5         |
| Concentration (cm$^{-3}$) | $1.2 \times 10^{22}$ | $1.5 \times 10^{22}$ | $4 \times 10^{16}$ |
| Work function (eV) | 5.0       | 5.55 | 4.7       |
Conclusions

In conclusion, we have reviewed recent progress in the switchable diode effect in both experimental and theoretical aspects. Many recent investigations confirmed that the barrier at the metal/ferroelectrics interfaces could be modulated by the polarization charges and the ferroelectric polarization that can be reversed by an external electric field plays a dominant role in the switchable diode effect. The switchable ferroelectric control of the diode polarity may not be realized if the oxygen vacancies layer is formed at the interfaces in ferroelectric diodes, and the switchable diode effect could be obtained after removing the excess oxygen vacancies. In theoretical aspect, we discuss a self-consistent numerical model that can well describe the switchable diode effect in MFM structures. Calculated results further predict that it is a better choice to select metals with a smaller permittivity, such as noble metals, to obtain a more pronounced switchable diode effect. It is expected that these recent experimental and theoretical works can be of great value for the further progress of the designing in ferroelectric memory devices and a deep understanding of the underlying physics in ferroelectric diodes.

Although considerable progress has been achieved in recent years in the ferroelectric diodes, much more can be expected in future. With the decrease of the ferroelectric film down to tens of nanometers, novel phenomena could emerge due to the competition between the tunneling and the drift-diffusion or thermionic emission in MFM structures. Ferroelectric materials show a rather large photovoltage exceeding several times the band gap, which could be applied in robust optoelectronic devices [22,39-41]. BFO, a typical multiferroic material, offers opportunities for us to control the states of novel devices both electrically and magnetically [42-44]. Besides, the coupling among the ferroelectric, ferromagnetic, and optical properties provides a new route to design multifunctional devices. In terms of the theoretical aspect, it would be a more powerful method to analyze charge transport in MFM structures by considering the multi-domain structure, the hole transport process, the spatial distribution of the polarization charges.

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Nano Brazing of Pt-Ag Nanoparticles under Femtosecond Laser Irradiation

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Abstract: Nano brazing of Pt-Ag nanoparticles with nano Ag filler metal is reported in this letter, which presents an effective way to join nanoobjects by femtosecond laser irradiation. The nano brazed interface between Pt-Ag and Ag showed good lattice matching along $(1\overline{1}1)_{\text{Ag}}//(1\overline{1}1)_{\text{Ag-Pt}}$. Lattice mismatch can hardly be observed at the interface between the filler metal and Pt-Ag nanoparticle, which is important for the joint strength and normally does not occur during joining. The very low mismatch also suggested that melting and solidification occurred during nano brazing by femtosecond laser. The role of Brownian motion on the nano joining process is also discussed in this paper.

Keywords: Femtosecond laser; Nanojoining; Nanoparticles

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Introduction

Further down the road of miniaturization to nanoscale, there is an emerging need to join nanoobjects to form nanoscale devices and systems [1-3]. Nanoparticles are regarded as important parts of nanoscale devices, which make joining nanoparticles necessary as a basic integration process in nanoscale products. It is still challenging to interconnect single nanoobjects with a stable Ohmic contact, which is a key issue for nanoelectronic device manufacturing [1,4]. Direct “fusion” joining of nanoobjects is one way to achieve stable conductive nanojunctions [5,6]. However, most of the “fusion” nanojoining methods are applied for making nanojunctions between nanowires [7,8], because it is hard to control the melting depth of nanoparticles [1]. The consequence is that when two nanoparticles are totally melted, the very high surface tension at nanoscale would merge the two individual nanoparticles into one larger nanoparticle [9].

In this regard, nano brazing/soldering needs to be developed for the purpose of joining nanoparticles with high Ohmic conductivity, since brazing can produce both minimum damage to the base metal and a desired joint morphology. Use of a femtosecond laser can result in an ultrafast and nonthermal melting of solid materials with precisely controlled energy, which is promising for developing nano brazing/soldering junctions for nano- and/or molecular devices [2]. Only a few research works have focused on this area [5], since most of the nanojoining processes were only developed in the past decade and the concept of nanojoining was just proposed very recently [2]. In the present study, an effective and controlled manner of using a femtosecond laser to produce nano brazing joints was demonstrated and the joints were characterized in detail by transmission electron microscope (TEM).

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Experiment

A Ti-sapphire laser system (Coherent Inc) was operated to generate 35 fs laser pulses at repetition rate of 1 kHz and 800 nm. Each laser profile was confirmed to be Gaussian with output energy of 2mJ/pulse. Laser pulses were focused in the middle of a 2-ml-glass quartz vessel by a lens with 13 cm focal length. First, surfactant-free platinum nanoparticles in pure ethanol were prepared by laser ablation of Pt rods for 3 min at the focal point. The laser ablation of Pt in ethanol was accompanied by the presence of a plasma plume on the target surface, easily visible by naked eye. A visible coloration of the solution was observed after the experiment. Ablation of Ag was performed right after Pt in the same solution. The Ag rod was defocused by 5 mm and ablated for 30 min. The nanoparticles’ composition, identification, joint morphology and the nano brazing interface were examined by a field emission transmission electron microscope (TEM, product of JEOL JEM-2010F) operated at both high resolution (HR TEM) and high-angle annular dark field scanning TEM (STEM) mode.

To our knowledge, most laser nanoalloying or nanojoining of nanoparticles using a femtosecond laser is a two step procedure: mixing two prepared pure metal nanocolloid solutions and then irradiating the mixed solution by laser [10, 11]. In our experiment mixing and irradiating occurred at the same time. This not only improves efficiency, but also facilitates the experimental design for three reasons. First, the laser energy density distribution in the glass vessel was significantly non-uniform because of the Gaussian beam and focusing lens. This tended to increase the uncertainty and uncontrollability. With our method the interaction between Ag and Pt-Ag nanoparticles occurred at a controllable place, which was the space in front of the bulk Ag rod. Second, the silver nanoparticles were gradually synthesized during the 30 min. This means the ratio of Ag to Pt increased with irradiation time, suggesting that the number of Pt nanoparticles surrounding the Ag nanoparticles was fairly large at the beginning, which expected to increase the chance of interaction between dissimilar nanoparticles. Third, low energy ablation can generate tiny nanoparticles (less than 10 nm) [12], which can dramatically reduce the melting temperature of the silver nano brazing filler metal [9].

Results and discussion

Figure 1(a) shows STEM image of two typical individual nanoparticles, the left one was Ag and the right one was Pt-Ag nanoalloy, which were confirmed by EDX line scanning as shown in Fig. 1(b). The insert pictures in Fig. 1(a) are HRTEM images of the two nanoparticles in Fig. 1(a). The formation of Pt-Ag nanoparticles was similar to the laser nanoalloying process which can be found elsewhere [10,13]. The STEM image in Fig. 1 indicates that the element distribution of the Pt-Ag nanoparticle was not uniform. However, in HRTEM mode the lattice spacing of the Pt-Ag nanoparticle was the same.

The measured lattice spacing for Ag was (200)$_{Ag}$ = 2.09 Å while Pt-Ag alloy (111)$_{Pt-Ag}$ was 2.33 Å. The lattice parameter of laser induced Pt-Ag nanoalloy was the same as in ref. [14], which was prepared by wet chemical method. The lattice constants calculated based on the measurements were $a = 4.18$ Å for Ag and $a = 4.04$ Å for Pt-Ag. The measured lattice constant of Ag was 3.5% larger than bulk Ag which may be due to the size dependent lattice parameter and apparatus error [4]. The lattice mismatch between the Ag and Pt-Ag can
be calculated by Equation 1

\[ \Delta a = \left| \frac{a_1 - a_2}{\frac{1}{2}(a_1 + a_2)} \right| \]  

in which, \( \Delta a \) is mismatch, \( a_1 \) and \( a_2 \) are lattice parameters of two materials. The calculation shows that the theoretical mismatch between Ag and Pt-Ag nanoalloy was less than 2%.

Typical joined spherical nanoparticles are shown in Fig. 2 in STEM mode. The image clearly shows that the interjunction between spherical Pt-Ag nanoparticles was made by nano-Ag. Due to the low laser fluence, the size of the nano Ag filler metal was less than 10 nm, having the melting temperature in the range of 373-573 K [15], which is much lower than that of Pt. Small radius fillets were found at the braze joint, but not a well-developed wetting over the Pt-Ag surface which can be found in brazing of bulk material. This is due to the ultrafast cooling rate and limited time for the melted Ag to completely wet and spread. Since both Pt and Ag have very low bulk resistance, and the brazed interfaces showed atomic scale bonding and no intermetallic compounds formed, it is believed that the contact (or joint) had good electric conductivity. This structure leads us to conclude that the in-situ synthesized Ag nanoparticles acted as nano filler metal which created ohmic joints among Pt-Ag nanoparticles.

It is believed that the nano brazing process is also related to the Brownian motion. At very small particle size, as in nanofluids, Brownian motion becomes important [16]. The root-mean-square velocity \( (v_N) \) of a Brownian particle can be defined as [16]

\[ v_N = \sqrt{\frac{3k_bT}{m_N}} = \frac{1}{d_N}\sqrt{\frac{18k_bT}{\pi\rho_N d_N}} \]  

where \( k_b \) is the Boltzmann constant, \( T \) the temperature, \( m_N \) the particle mass, \( \rho_N \) the density and \( d_N \) the diameter of the nanoparticle. According to the classic collision theory, the collision frequency is

\[ Z = N_A\sigma_{AB}\sqrt{\frac{8k_bT}{\pi\mu_{AB}}} \]  

where \( N_A \) is the Avogadro constant, \( \sigma_{AB} \) the reaction cross section, \( k_b \) the Boltzmann’s constant, and \( \mu_{AB} \) the reduced mass of the reactants. In the nanofluid theory, an enhanced thermal conductivity of nanoscale colloidal solutions has been found which is primarily due to convection caused by the Brownian movement of these nanoparticles [16]. Collision between nanoparticles is also one of the reasons for the enhanced thermal conductivity but it can be neglected according to order-of-magnitude analysis [17]. In contrary, the role of collision between nanoparticles is very important to a joining process because the two nanoparticles should be in contact before brazing/joining [5] and the contact is believed primarily caused by collision. When collision and laser irradiation occur at the same time, joining tends to occur due to the non-thermal ultrafast melting phenomenon of femtosecond laser. When collision occurs but no laser irradiation, the nanoparticles may also contact because contact can lower the free energy of the system. However, in this case the contacted area would be limited by the free energy reduction value. Following the contact, when laser irradiates, joining also tends to occur and results in well-wetted brazing joint. Therefore, it is believed that both Brownian movement and surface energy played important roles in the nano brazing process.

Figure 3 shows the orientation relationship of the nano brazing interface between Ag and Pt-Ag nanoalloy which were in the same zone axis. The upper-left insert STEM image indicates the interface between Ag and Pt-Ag nanoalloy. HRTEM of the same position shows that \( (111)_{Ag}/(111)_{Ag-Pt} \) and the mismatch between Ag and Pt-Ag can hardly be observed. The lattices at the interface matched very well, as needed to achieve a
good joint strength, especially for a heterophase interface [18]. Usually, this does not occur because lattice defects at the brazing interface occurred in most cases because of either lattice constant mismatch or residual stress induced by the brazing process. We believe that there were two reasons for the very low mismatching. First, the lattice constant of Ag and Pt-Ag was nearly the same, as calculated above based on the lattice image in Fig. 1(a). Second, a melting and epitaxial growth (or solidification) process occurred during femtosecond laser irradiation. For large nanoparticles, only surface melting occurs during femtosecond laser irradiation [19,20]. The Ag nano brazing filler cluster was very small (normally less than 10 nm) due to the lower ablation energy used. If nanoparticles are tiny clusters with limited atoms, they may suddenly display global melting without surface melting, because the effective laser penetration depth was larger than the particle size [19]. After the laser pulse turned off, the Ag nano brazing filler metal solidified and grew epitaxially on the Pt-Ag surface.

Fig. 3 Orientation relationship between Ag-Pt nanoalloy and Ag nano-brazing filler metal, showing the minimum interfacial mismatch.

**Conclusion**

This study presents an effective way to join nanoobjects by femtosecond laser brazing, in which femtosecond laser was used to generate tiny nano-Ag clusters as brazing filler metal and nano brazed Pt-Ag nanoparticles. The nano brazed interface between Pt-Ag and Ag showed good lattice matching along (111)Ag // (111)A g-Pt. It suggests that melting and solidification occurred during femtosecond laser nano brazing. The nano-networks of Pt-Ag produced by femtosecond irradiation make them very attractive for several applications, such as plasmonics, catalysts and nanoscale electronic devices.

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Synthesis and Growth Mechanism of Net-like Titanate Nanowire Films via Low-temperature and Low-alkali-concentration Route

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Abstract: Net-like titanate nanowire films can be grown on Ti substrates by non-hydrothermal treatment of Ti foils in alkali-H2O2 aqueous solutions with a low alkali concentration of 2 M at 60-80°C. The growth mechanism of such films has been investigated by identifying the role of both H2O2 and alkali in the nanowire formation and capturing the film morphology at early growth stages. It is found that the presence of H2O2 is necessary for the nanowire growth, and sufficient amount of H2O2 is needed to produce well-shaped nanowires. The nanowire growth is also strongly dependant on the alkali used, and nanowire films are formed only when metal hydroxides which can react with TiO2 to form layer-structured titanates are chosen. Our results have also revealed that the heterogeneous deposition of titanate on Ti substrate results in the growth of titanate sheets, and the nanowire formation is via a splitting process by which each titanate sheet gradually evolves into nanowire thin layer. Based on the experimental results, a detailed mechanism is proposed for the growth of titanate nanowire films in alkali-H2O2 aqueous solutions at low temperature.

Keywords: Nanostructured materials; Nanowires; Synthesis; Thin films; Titanate

Introduction

Owing to their high length-to-diameter ratio and large specific surface area, one-dimensional (1D) materials, e.g., nanotubes and nanowires, exhibit unique mechanical, physical, or chemical properties and have found applications in many fields, such as electronics, catalysis, and sensors. 1D titanate nanostructures are of great scientific and technical interest because of their photocatalytic activities and interesting ion-exchange/intercalation properties [1-4]. They have shown promising applications in photocatalytic degradation of organic pollutants [1,2], adsorption for radioactive or heavy metal ions [4], solar energy conversion [5], electrochromism [6], and gas sensing [7]. Since the properties of titanate nanostructures are often related to their morphology, the synthesis of titanate nanostructures with desired 1D shape is key to improve their applications. As one of the most effective methods for preparation of 1D titanate nanostructures, the method of hydrothermal treatment of TiO2 in concentrated alkali solutions has gained great attention [8-13] since the pioneering work of Kasuga et al. [14]. In general, under relatively lower temperature (e.g. ≤160°C) and lower alkali concentration (e.g. 5-10 M) nanotubes are formed whereas higher temperature (e.g. 200°C) and higher alkali concentration (e.g. 15 M) or using a rotating autoclave [9] favors the formation of nanowires. In recent years, the extension of such hydrothermal method to treatment of Ti foils...
for fabricating titanate nanotube or nanowire films on Ti substrates has also been aroused increasing interest [15-22] because the formed films can be directly used as photoanodes for photocathodic protection for stainless steel [22] or converted to TiO₂ films for water splitting [20] and decomposition of harmful compounds [21]. For example, Yada et al. have reported that titanate nanotube films can be formed on Ti substrates by hydrothermal treatment of Ti foils in 10 M NaOH solutions at 160°C [16,17]. Similar studies on the formation of titanate nanotube films via hydrothermal treatment method have also been reported by a number of other research groups [15,18-22]. Recently, Hu et al. have treated Ti foils in 10 M NaOH solutions at 180°C in the presence of oxidative organic compounds and found that titanate nanowire films, rather than nanotube films, are formed [21].

While the method of hydrothermal treatment in concentrated alkali solution is routinely used to produce titanate nanotube or nanowire films on Ti substrates, little attention has been paid into another approach, namely non-hydrothermal (or low-temperature) treatment in alkali-H₂O₂ mixed solutions [23,24]. Wu et al. first reported that titanate nanowires could be synthesized by treating Ti foils in a 1:1 (v/v) mixture of 10 M NaOH and 30% (v/v) H₂O₂ at a temperature of 80°C [23]. More recently, we have studied the effect of alkali concentration on the formation of titanate nanowire films by treatment of Ti foils in NaOH-H₂O₂ mixed solutions with a H₂O₂ concentration of 15% (v/v) at 80°C and found that a mixed solution with a much low NaOH concentration (namely 2 M) can be used to produce well-shaped net-like titanate nanowire films [24]. Despite these limited efforts, however, the key issue, namely the formation mechanism of the nanowire film, is still not clear. Wu et al. have assumed that the formation of nanowires is a result of decrease in the surface energy via crystallization of amorphous titanate sheets along one direction [23], but there is no direct evidence for this assumption. In the present work we report the clear observation of the growth of titanate sheets on Ti substrate via heterogeneous deposition and the conversion of each titanate sheet to nanowire layer via a “splitting” process. By identifying the role of both H₂O₂ and alkali in the nanowire formation, a detailed growth mechanism is proposed for low-temperature growth (60-80°C) of titanate nanowire films in alkali-H₂O₂ solutions of low alkali concentration (2 M).

Experiment

Ti pieces of 4.80 × 1.30 × 0.4 mm³ in size were polished with abrasive paper, degreased in a mixed solution of NaOH and Na₂CO₃ (the ratio of NaOH:Na₂CO₃:H₂O by weight is 5:2:100, respectively) at 85°C for 1.5 h, and then washed with deionized water. The degreased Ti piece was etched in a HF aqueous solution at room temperature for about 20 s, followed by washing with deionized water. The pretreated Ti piece was immersed into an aqueous solution containing both H₂O₂ and NaOH in a Teflon-lined autoclave, where the concentration of H₂O₂ was in the range from 0 to 15% (v/v) and that of NaOH is fixed at 2 M. The sealed autoclave was then kept in an oven at a given temperature ranging from 40 to 120°C for a time period of 0.5 to 6 h. In order to investigate the effect of the alkali type on the growth of TiO₂ nanowire thin films, NaOH can be replaced with other alkalis. After treatment, the specimen was removed from the aqueous solution, washed thoroughly with deionized water to remove the alkali, and finally dried in air.

The surface morphology of the films was examined using a scanning electron microscope (SEM, Hitachi S-4700) operating at 15 kV. The chemical composition of the film was characterized by energy-dispersive x-ray spectra (EDS). The energy-dispersive x-ray spectrometer was attached to SEM and operated at a low voltage of 8 kV. The phase composition of the films was analyzed by x-ray diffraction (XRD), which was performed on a Thermo ARL XTRA x-ray diffractometer using Cu Kα X-ray source. The microstructure investigations were performed with a Tecnai G2 F30 S-Twin transmission electron microscopy (TEM) operating at 300 kV.

Results and discussion

Effect of H₂O₂ concentration, temperature, and alkali type on the growth of titanate nanowire films

Figure 1 shows the SEM images of the films formed at 80°C for 6 h in NaOH (2 M)-H₂O₂ solutions with different H₂O₂ concentrations. As shown in Fig. 1(a), in the absence of H₂O₂, chemical etching of Ti by 2 M NaOH only leads to the generation of a porous film. The porous layer contains large amount of oxygen compared to the pretreated Ti substrate (see Fig. 2(a)), but the observation of negligible amount of Na demonstrates that the film is titanium oxide. The atomic ratio of Ti:O calculated is about 2:1, much higher than the value of 1:2 for TiO₂ or 2:3 for Ti₂O₃, suggesting that the film is very thin and the signal of underlying Ti substrate is also collected during EDS measurement. When H₂O₂ (7.5% v/v) is added, one-dimensional nanostructures appear (Fig. 1(b)) although they are not totally separated from each other. With the rise in H₂O₂ concentration, the shape of these one-dimensional nanostructures becomes more defined (Fig. 1(c)), and well-shaped one-dimensional nanostructures are observed when the H₂O₂ concentration reaches 15% v/v (Fig. 1(d)). The investigation by TEM confirms that these
Fig. 1 SEM images of the films formed by treating Ti foils at 80°C for 6 h in H_2O_2-NaOH(2M) mixed solutions with different H_2O_2 concentrations. (a) 0, (b) 7.5% v/v, (c) 11.25% v/v, and (d) 15% v/v. Inset of Fig. 2(d) is the corresponding TEM image of the nanowires.

Fig. 2 (a) EDS spectra of pretreated Ti substrate, porous film formed in NaOH solution, and nanowire film formed in H_2O_2-NaOH mixed solution, and (b) XRD pattern of the nanowire film formed by treating Ti foils in H_2O_2(15%v/v)-NaOH(2M) mixed solutions for 6 h at 80°C.

One-dimensional nanostructures are nanowires (see inset of Fig. 1(d)). In addition, in compared with the film formed in the absence of H_2O_2, the nanowire film contains large amount of Na (see Fig. 2(a)), indicating that the nanowires formed might be mainly in the form of titanate. The atomic ratio of Na:Ti:O calculated from the EDS spectrum is about 0.38:1:2.52. Since the atomic ratios of Na:Ti:O are, respectively, 2:1:3 for Na_2TiO_3, 1:1:3 for NaHTiO_3, 2:1:2.3 for Na_2Ti_3O_7, and 1:1:2.3 for NaHTi_3O_7, we speculate that the nanowires formed are mainly in the form of Na_xH_{2-x}Ti_3O_7 where Na is lacking. The excess of O observed might be related to the contamination of oxygen-containing compounds on the film surface. The formation of titanate nanowire film is also confirmed by XRD measurement (see Fig. 2(b)). Besides the characteristic peaks of Ti substrate, some broad peaks at 2θ of about 9.1°, 24.4°, 28.1°, and 48.2° (indicated by stars), which can be attributed to trititanate [9,11], are also be observed in the XRD pattern of the nanowire film.
The above experimental results suggest that the presence of H$_2$O$_2$ is necessary for the formation of nanowire-like materials and sufficient amount of H$_2$O$_2$ is needed to produce well-shaped nanowires. It is well known that the exposure of Ti foil to H$_2$O$_2$ solution will lead to the formation of titanium peroxide gel Ti(OH)$_2$O$_2$ on Ti substrate [25]. Such a Ti-peroxy gel can be decomposed into amorphous hydrate titania TiO$_2$·nH$_2$O layer [25,26]. In the absence of H$_2$O$_2$, the reaction between Ti and H$_2$O can also lead to the formation of a very thin passivation layer: Ti+3H$_2$O=TiO$_2$·H$_2$O+2H$_2$. Under alkaline environment, the hydrated titania layer may react with NaOH to form NaHTiO$_3$. The formed NaHTiO$_3$ is then expected to be transformed into Na-lacking titanate via the following condensation reaction: 3NaHTiO$_3$+(1-x)H$_2$O=Na$_x$H$_{2-x}$Ti$_3$O$_7$+(3-x)NaOH. Since the solubility of titanate in water is very low, titanate may grow on the Ti surface via heterogeneous deposition. However, the observation of titanium oxide film in the absence of H$_2$O$_2$ demonstrates that the dissolution of the passivation layer by NaOH does not result in the deposition of titanate on the Ti surface. We speculate that the occurrence of the condensation reaction might need a higher concentration of NaHTiO$_3$ in the solution. It is possible that in the absence of H$_2$O$_2$ the dissolution of the very thin passivation layer by NaOH cannot produce a NaHTiO$_3$ solution with its concentration high enough for the formation of Na$_x$H$_{2-x}$Ti$_3$O$_7$. In contrast, the presence of H$_2$O$_2$ can produce sufficient amount of hydrated titania for the formation of Na$_x$H$_{2-x}$Ti$_3$O$_7$. From a kinetic point of view, the rise in H$_2$O$_2$ concentration may increase the formation rate of the hydrated titania layer, and thus for a given time period more hydrated titania can be provided for the formation of titanate. Accordingly, the presence of H$_2$O$_2$ with high concentration favors the formation of titanate films.

Since the treatment temperature may influence all the processes involved in the formation of titanate nanowires, the temperature effect on the formation of nanowire films has also been investigated. Figure 3 shows the SEM images of the films formed in a mixed solution of NaOH (2 M) and H$_2$O$_2$ (15% v/v) for 6 h at different temperatures. At a temperature of 40°C, only a compact layer which is composed of nanoparticles is observed (Fig. 3(a)). When the temperature is raised to 60°C, however, large amount of nanowires are clearly seen (Fig. 3(b)), suggesting that the nanowire growth can occur at a temperature as low as 60°C. With a further rise in temperature, the size of the nanowires increases gradually. For example, the average diameter of the nanowires increases from $\sim$ 30 nm at 60°C to $\sim$ 70 nm at 100°C (see Fig. 3(c)). It should be pointed out that, however, when the temperature reaches 100°C or above, the surface of the nanowires becomes very unsmooth, especially under the hydrothermal conditions (namely 120°C). The shape of the nanostructures formed at 120°C is more similar to short nanobelts than nanowires (Fig. 3(d)), hinting that in NaOH-H$_2$O$_2$ solutions with a low NaOH concentration the hydrothermal

![Fig. 3 SEM images of the films formed by treating Ti foils in H$_2$O$_2$(15%v/v)-NaOH(2M) mixed solutions for 6 h at different temperatures: (a) 40°C, (b) 60°C, (c) 100°C, and (d) 120°C.](image-url)
treatment is not favorable for the formation of nanowire film.

To gain insight into the formation mechanism of titanate nanowires film, we have further clarified the role of NaOH in the formation of nanowire film by replacing NaOH with NaCl, NH₃·H₂O, a mixture of NH₃·H₂O and NaCl, KOH, or Ba(OH)₂. As shown in Fig. 4(a), after treating Ti foil in the NaCl-H₂O₂ solution, we can only find short rod-like materials on the Ti substrate. The observed morphology is a little similar to that of the film obtained in the case where only H₂O₂ aqueous solution is used (see Fig. 4(b)). If the Ti foil is treated in a H₂O₂-NH₃·H₂O mixture, a compact film comprised of nanoparticles will grow (see Fig. 4(c)). These results indicate that only the existence of Na⁺ or OH⁻ in the solution cannot lead to the formation of nanowire film. However, we have found that even though the Ti foil is treated in a NaCl-H₂O₂-NH₃·H₂O mixture, nanoparticle film rather than nanowire film is formed (see Fig. 4(d)), hinting that in order to produce nanowire film the alkali might exist in the form of hydroxide. Further investigation shows that nanowire film can grow in a KOH-H₂O₂ mixed solution (Fig. 4(e)) whereas dense nanoparticle film is produced in a Ba(OH)₂-H₂O₂ mixture (Fig. 4(f)). Since both NaOH and KOH are alkali metal hydroxides which can react with TiO₂ to form a layer-structured alkali metal titanate, it is inferred that the formation of nanowire film is strongly dependent on the structure of the titanate formed, and titanate with a layered structure favors the nanowire growth.

Formation process and growth mechanism of titanate nanowire films

To substantially understand the formation process of titanate nanowire, we have examined the morphology of the films formed at different growth stages. After chemically etched in a HF aqueous solution, the surface of Ti is not flat, but at small scale we can observe a relatively smooth surface (Fig. 5(a)). When the Ti foil is treated in a NaOH-H₂O₂ mixed solution for 0.5 h, an interesting terraces-like morphology appears (Fig. 5(b)). The terraces are obviously built by many sheet-like materials which are actually comprised of nanoparticles (see inset of Fig. 5(b)). We find that the sizes of these sheet-like materials may increase with growth time. As shown in Fig. 5(c), when the treatment duration is prolonged to 1 h, the sizes of the sheet-like materials are much larger than those observed in Fig. 5(b). Furthermore, the sizes of the nanoparticles within the sheets also become larger (see inset of Fig. 5(c)). The observation of these sheet-like materials might be related to the fact that alkali metal titanate has a layered structure and thus favors the formation of sheet-like materials. As the treatment duration is raised to 1.5 h, these titanate sheets begin to evolve into nanowire-like materials (Fig. 5(d)). The high-magnification image (see inset of Fig. 5(d)) where clear boundaries (some boundaries are indicated by arrows) between elongated particles (or nanowire-like materials) are observed provides a clue to the evolution of titanate sheets into nanowires.
Fig. 5  SEM images of the films formed by treating Ti foils in H$_2$O$_2$(15%v/v)-NaOH(2M) mixed solution at 80°C for different durations: (a) 0, (b) 0.5 h, (c) 1 h, (d) 1.5 h, (e) 2 h, and (f) 4 h. Insets of Fig. 5(b), 5(c), 5(d) and 5(e) are the high magnification images of corresponding materials.

Fig. 6  A scheme for the formation of titanate nanowires films in NaOH-H$_2$O$_2$ aqueous solutions. (a) Immersed in NaOH-H$_2$O$_2$ solution, (b) Dissolving hydrated titania layer, (c) Heterogeneous deposition of titanate sheets, (d) Growth of titanate nanowires, (e) Splitting of titanate sheets.

Infer from these images (namely insets of Fig. 5(b), 5(c), and 5(d)) that the nanoparticles within the sheets self-assembly into elongated particles (or nanowire-like materials) and then a “splitting” process along the boundaries between elongated particles (or nanowire-like materials) leads to the formation of nanowires. As the growth time increases to 2 h (see Fig. 5(e) and its inset with some boundaries being indicated by arrows), the splitting process continues and thus the diameter of the nanowire becomes smaller and smaller, with the shape...
of the nanowire being more defined. When the duration is raised to 4 h, well-structured nanowire film is formed (Fig. 5(f)).

Based on our above experimental results, we propose a possible mechanism for growth of titanate nanowire film in NaOH-H$_2$O$_2$ mixture solution at low temperature (Fig. 6). Firstly, when the Ti foil is immersed into NaOH-H$_2$O$_2$ mixture solution, the growth of hydrated titanate layer will occur mainly through the following reactions (step (a) in Fig. 6), namely Ti$+2$H$_2$O$_2+2$H$_2$O$\rightarrow$Ti(OH)$_2$O$_2+H_2$ and Ti(OH)$_3$O$_2$ $\rightarrow$Ti(OH)O $\rightarrow$Ti(OH)$_x$ $\rightarrow$TiO$_2$ $\cdot$ nH$_2$O [25,26]. Secondly, the presence of NaOH in the mixture solution may dissolve the hydrated titanate layer to form NaHTiO$_3$ which is then converted to titanate via a condensation reaction (step (b) in Fig. 6). Thirdly, the low solubility of titanate in water makes it possible for titanate to precipitate on the Ti surface via heterogeneous deposition. Since titanate possesses a layered structure, it tends to form sheet-like structure upon its deposition on the Ti substrate. As the heterogeneous deposition of titanate continues, the successively grown titanate sheets will stack one upon another and thus exhibits a terraces-like morphology (steps (c) and (d) in Fig. 6). Finally, the titanate sheets formed under our experimental conditions do not evolve into nanotubes by rolling up themselves. Instead, each titanate sheet is split into nanowires and thus forms a thin nanowire layer. All these nanowire layers finally construct a nanowire film with net-like structure (step (e) in Fig. 6).

**Conclusion**

We have presented a study on the synthesis and growth mechanism of titanate nanowire films in alkali-H$_2$O$_2$ aqueous solutions with an alkali concentration of 2 M at low temperature. It is shown that the role of H$_2$O$_2$ is to provide sufficient amount of hydrated titanate for the formation of Na$_2$Ti$_3$O$_7$ and the deposition of titanate sheets is through heterogeneous deposition. The nanowire growth is strongly dependent on the alkali used, and its formation is via a splitting mechanism, by which each of the formed titanate sheets is converted into a thin nanowire layer.

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Abstract: In this contribution, an efficient and simple two-step hybrid electrochemical-thermal route was developed for the synthesis of cubic shaped Zn\(_2\)SnO\(_4\) (ZTO) nanoparticles using aqueous sodium bicarbonate (NaHCO\(_3\)) and sodium stannate (Na\(_2\)SnO\(_3\)) electrolyte. The sacrificial Zn was used as anode and cathode in an undivided cell under galvanostatic mode at room temperature. The bath concentration and current density were respectively varied from 30 to 120 mmol and 0.05 to 1.5 A/dm\(^2\). The electrochemically generated precursor was calcined for an hour at different range of temperature from 60 to 600°C. The crystallite sizes in the range of 24-53 nm were calculated based on Debye-Schererrer equation. Scanning electron microscope and transmission electron microscopy results reveal that all the particles have cubic morphology with diameter of 40-50 nm. The as-prepared ZTO samples showed higher catalytic activity towards the degradation of methylene blue (MB) dye, and 90% degradation was found for the sample calcined at 600°C, which is greater than that of commercial TiO\(_2\)-P25 photocatalysts. The photodegradation efficiency of ZTO samples was found to be a function of exposure time and the dye solution pH value. These results indicate that the ZTO nanoparticles may be employed to remove dyes from wastewater.

Keywords: Electrochemistry; Zn\(_2\)SnO\(_4\); Photocatalyst; Cubic; Nanoparticle

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al. used one-step hydrothermal method to prepare ZTO nanocrystal at 200°C and discussed their photocatalytic properties on reactive dyes K-NR, B-RN and B-GFF [11]. Cun et al. have used coprecipitation method for the preparation of nano-sized ZTO and the research of their photocatalytic activities to benzene [12]. Foletto et al. have synthesized ZTO by hydrothermal method at 200°C for 12 hr and investigated their photocatalytic activities on leather dye [14]. Several other literatures reporting synthesis and properties of ZTO nanostructures were also published ever since [15-22].

Large number of methods have been developed for the preparation of ZTO, such as thermal evaporation [23,24], high temperature calcination [12,25], sol-gel synthesis [26,27], mechanical grinding [28] and hydrothermal reaction [6,10,11,18,29-31]. Among these methods, the electrochemical method has aroused a considerable interest in the synthesis of nanosized metal metal-oxide powder and films because of its simplicity, low temperature operation process and viability of commercial production. This method is also a simpler and more effective way to prepare well-crystallized ZTO with pure phase, which is difficult obtained by high-temperature solid state reactions among the evaporated ZnO atmosphere, generally. On the contrary, the electrochemical preparations were usually performed in an aqueous solution using NaHCO₃ as mineralizer.

Increased human population has resulted in the development of large-scale industries such as textile and paper production, whose waste products cause a major environmental hazard to aquatic biota and humans due to their toxicity [32] and the tendency to cause eutrophication [2]. Detection and removal of these toxic chemicals is a major challenge with conventional methods. Thus, there is an urgent need of eco-friendly technologies for the detection and removal of textile effluents from water. It has been shown that dyes can be easily adsorbed and catalyzed on oxide surfaces. However, to the best of our knowledge, there exist only a few reports [33-37] on the direct removal of commonly used industrial dyes. In the present investigation, we focus on the bulk synthesis of cubic shaped ZTO nanoparticles with a hybrid electrochemical-thermal route without using any template or surfactant at room temperature. The effects of electrolyte, current density and reaction media on the shape, size, chemical composition of the generated product, together with the production yield were investigated. FT-IR absorption spectra, SEM and TEM images and power XRD patterns of the products calcined at different temperatures were tested and discussed. It has been found that our method is a simple and feasible electrochemical route for the synthesis of ZTO nanoparticles on commercial scale. As well, the spectroscopic spectra and degradation ratio of commonly used textile dye (Methylene Blue; cationic) in aqueous solution with these ZTO nanoparticles were tested under different UV irradiation time, to characterize ZTO nanoparticles’ photocatalytic properties. The optimum conditions for generation of ZTO nanoparticles were also proposed.

**Experimental Procedure**

**Materials**

High purity Zinc metal plate (99.99%), sodium bicarbonate (AR grade: 99.5%), sodium stannate (AR grade: 98.5 %) purchased from Sisco Research laboratories, Mumbai and Methylene Blue (MB) from S. D. Fine Chemicals Ltd., India, were used as received. Millipore water (specific resistance, 15 MΩ cm at 25°C, Millipore Elix 3 water purification system, France) was used to prepare the electrolyte solution.

**Synthesis of ZTO nanoparticles**

ZTO nanoparticles were synthesized using a standard electrochemical technique mentioned in ref [38]. Prior to electrolysis, the Zn plates were activated by immersing in dilute HCl (1 M) for 30 sec followed by washing with Millipore water. The electrolyte was a 400 ml solution containing 30 mM (1.008 gm) NaHCO₃ and 10 mM Sodium stannate. It was injected in a rectangular undivided cell (5.0 × 6.0 × 0.8 cm³) where Zn plates were used as both cathode and anode. The electrolysis was carried out for about one hour under galvanostatic conditions, the constant current was supplied by a DC power supply (model PS 618 potentiostat/galvanostat 302/2 A supplied by Chem link, Mumbai) with constant stirring at 600 rpm. The schematic diagram of electrolysis process is shown in Fig. 1. The pH of the electrolyte was recorded before and after the electrolysis. A white precipitate was formed and filtered (by whatman filter paper No.41) to isolate from the solution. The final product of solution follows the reaction mechanism,

\[
\begin{align*}
Zn & \rightarrow Zn^{2+} + 2e^- \quad \text{(on anode)} \\
2H^+ + 2e^- & \rightarrow H_2 \uparrow \quad \text{(on cathode)} \\
2NaHCO_3 + 2H_2O & \rightarrow 2Na^+ + 4OH^- + 2CO_2 \uparrow + H_2 \uparrow \quad \text{(in electrolyte solution)} \\
Na_2SnO_3 + 3H_2O & \rightarrow Sn^{4+} + 2Na^+ + 6OH^- \quad \text{(in electrolyte solution)} \\
Zn^{2+} + Sn^{4+} + 6OH^- & \rightarrow ZnSn(OH)_6 \downarrow \quad \text{(precipitate)} \\
Zn^{2+} + 4OH^- & \rightarrow Zn(OH)_4^{2-} \quad \text{(soluble complex)}
\end{align*}
\]

102
The resulting wet precipitate was dried at 60°C in hot air oven for 1 hr and then it was calcined at 300°C or 600°C for 1 hr. The calcined product follows the reaction,

\[
\text{ZnSn(OH)}_6 + \text{Zn(OH)}_2^2- \rightarrow \text{Zn}_2\text{SnO}_4 \downarrow + 4\text{H}_2\text{O} + 2\text{OH}^- \quad (7)
\]

The same procedure was also repeated using 60 and 120 mM of NaHCO₃ and 0.01M Na₂SnO₃.

**Characterization**

The morphology, structure, crystallite size and compositional analysis of the nanoparticles were performed using powder X-ray diffraction (XRD), transmission and scanning electron microscopy and FT-IR spectroscopy. Morphology and compositional analysis were carried out in a scanning electron microscope (SEM, Philips XL 30) in the voltage range of 200-300 kV. Transmission electron microscope (TEM, JEOL 2000 FX-II) images of selected samples were recorded with an acceleration voltage of 200 kV. A 2D or 3D images of selected samples were recorded using powder X-ray diffraction (XRD), transmission and scanning electron microscopy and FT-IR spectroscopy (JCPDS file no. 74-1825). Similar observation was also made by M. J. Kim et al. [21]. The powder XRD patterns for the as-prepared and calcined compounds prepared under the electrolytic concentration of 30 mM NaHCO₃, 10 mM Na₂SnO₃ and the current density of 1 A/dm² were shown in Fig. 2. It can be seen from Fig. 2(a) that the seven peaks appeared at 19.8°, 22.9°, 27.9°, 31.9°, 32.6°, 38.6°, 40.3°, 46.8°, 47.6°, 52.6° and 58.0° correspond to the characteristic peaks of zinc tin hydroxide [Zn-Sn(OH)]₆ phase, (recorded by standard JCPDS file no. 74-1825). Also, the other six peaks appeared at 34.4°, 36.2°, 56.6°, 63.1°, 68.2° and 73.2° correspond to the characteristic peaks of Zn₂SnO₄. The XRD patterns for the calcined samples at 300°C for 1 hr (Fig. 2(b)) could be completely indexed to cubic phase (JCPDS file No. 24-1470). Similar observation was also made by M. J. Kim et al. [21]. The powder XRD pattern for the sample calcined at 600°C is presented in Fig. 2(c). Figure 2(b-c) reveals that an increasing calcination temperature from 300 to 600°C, made the characteristic Zn₂SnO₄ peaks sharper and the crystallinity increased. The crystallite size (d) was found to be 49 nm, estimated from the full width at half

**Photocatalytic degradation of MB dye in aqueous solution**

Photocatalysis experiments were carried out with different sized (24, 35 and 53 nm) ZTO nanoparticles (0.1 g in 100 ml of dye solution) and Methylene blue (MB) dye solution (10 ppm) in Millipore water. The photochemical reactor used in this study was made of a Pyrex glass jacketed quartz tube. A high pressure mercury vapor lamp (HPML) of 125 W (Philips, India) was placed inside the jacketed quartz tube. To avoid fluctuations of the input light intensity, a supply ballast and capacitor were connected in series with the lamp. Water was circulated through the annulus of the quartz tube to avoid overheating of the solution. Synthesized ZTO nanoparticles of varying sizes were added to 100 ml dye solution (10 ppm), with continuous stir for 2 hr for homogeneity. 100 ml of the solution (ZTO and MB) was taken in the beaker under continuous stir to ensure the uniform suspension of the catalyst. The lamp radiated predominantly at 365 nm, corresponding to photon energy of 3.4 eV and photon flux of 5.8×10⁻⁶ mol of photons sec⁻¹. Aliquots were collected from the reaction beaker at regular time intervals, and the concentration of dye in solution and degradation ratio was plotted as a function of time by monitoring the changes of the λ_max line intensity with time.

**Results and discussion**

**X-ray diffraction to study ZTO**

The phase purity and crystalline structure of all synthesized powders were investigated using powder X-ray diffraction technique. The powder XRD patterns for the as-prepared and calcined compounds prepared under the electrolytic concentration of 30 mM NaHCO₃, 10 mM Na₂SnO₃ and the current density of 1 A/dm² were shown in Fig. 2. It can be seen from Fig. 2(a) that the eleven peaks appeared at 19.8°, 22.9°, 27.9°, 31.9°, 32.6°, 38.6°, 40.3°, 46.8°, 47.6°, 52.6° and 58.0° correspond to the characteristic peaks of zinc tin hydroxide [Zn-Sn(OH)]₆ phase, (recorded by standard JCPDS file no. 74-1825). Also, the other six peaks appeared at 34.4°, 36.2°, 56.6°, 63.1°, 68.2° and 73.2° correspond to the characteristic peaks of Zn₂SnO₄. The XRD patterns for the calcined samples at 300°C for 1 hr (Fig. 2(b)) could be completely indexed to cubic phase (JCPDS file No. 24-1470). Similar observation was also made by M. J. Kim et al. [21]. The powder XRD pattern for the sample calcined at 600°C is presented in Fig. 2(c). Figure 2(b-c) reveals that an increasing calcination temperature from 300 to 600°C, made the characteristic Zn₂SnO₄ peaks sharper and the crystallinity increased. The crystallite size (d) was found to be 49 nm, estimated from the full width at half
maximum ($w$) of the dominant (311) peak at diffraction angle $2\theta \approx 34.4^\circ$ using Debye Scherrer’s equation. All the calcined powders of XRD patterns were indexed to the pure cubic structure with a lattice parameter of 8.657(6) Å and its space group: Fd-3m (227). They are matching with the standard JCPDS card No. 24-1470, indicating that the ZTO particles are crystalline with face centered cubic structure. From the XRD data, the average crystallite sizes were found to be 24, 35 and 53 nm, respectively. It clearly indicates that, the non crystalline Zn$_2$Sn(OH)$_6$ phase were gradually converted to cubic crystalline phase of ZTO nanoparticles.

No peaks related to other phases and impurities were found in XRD patterns of calcined compounds, implying the formation of pure ZTO nanoparticles and these particles are fcc Bravias lattice in nature.

**Surface morphological studies**

Scanning and transmission electron micrographs of as-prepared and calcined compounds of ZTO nanopowder are shown in Fig. 3. The as-prepared compound was synthesized from the bath with concentration of 30 mM NaHCO$_3$, 10 mM Na$_2$SnO$_3$ and the current density of 1 A/dm$^2$, and in sequence, it was calcined for 1 hr at 300$^\circ$C or 600$^\circ$C. The SEM images of ZTO nanoparticles show different morphologies. Figure 3(a) presents the SEM image of the starting Zn$_2$Sn(OH)$_6$ compound. It can be seen that the particles exhibit irregular, agglomerated small flower like structure, whereas calcined powder at 300$^\circ$C shows less randomly oriented cubic like morphology (Fig. 3(b)). The small flowers of the starting compound transformed to cubic like ZTO structures, starting at 300$^\circ$C and speeding up at 600$^\circ$C. The as-prepared sample heated at 600$^\circ$C for 1 hr (Fig. 3(c)) produces uniformly oriented cubic structure due to the growth of ZTO particles. As the heat treatment temperature increases, the particles tend to grow as expected. For instance, at 600$^\circ$C, the shape of the nanoparticles is cubic in nature. The TEM images
of ZTO nanoparticles obtained from the electrolyte concentration of 30 mM NaHCO$_3$, 10 mM Na$_2$SnO$_3$ at 1 A/dm$^2$ and calcined at 600°C for 1 hr are given in Fig. 3(d). It can be observed that ZTO nanoparticles are present as granules with clear cubic like shapes and are crystalline in nature. The average particle size ranges from 40-50 nm, which are in good agreement with the values calculated from XRD data by Debye-Scherrer equation.

FT-IR spectroscopy

Infrared spectroscopy was used to detect the presence of functional groups adsorbed on the surface of synthesized nanoparticles during electrochemical process. Figure 4 represents the FT-IR spectra of Zn-Sn(OH)$_6$ and ZTO powder obtained from the bath concentration of 30 mM NaHCO$_3$, 10 mM Na$_2$SnO$_3$ at the current density of 1 A/dm$^2$. The as-prepared sample was heat-treated at different temperatures of 300, and 600°C for 1 hr. Figure 4(a) indicates a strong and broad absorption peaks in the range of 3100-3600 cm$^{-1}$ centered at 3447 cm$^{-1}$, corresponding to the stretching vibration of hydrogen bond (O-H) of surface adsorbed crystalline water and higher amount of hydroxyl group. These vibrations are the evidence for the existence of water in the as-prepared compound. These peaks gradually disappear under increasing calcinations temperature, indicating the removal of water. It is interesting to note that the two bands centered at 1652 and 1522 cm$^{-1}$ are ascribed to the vibration of absorptive water. The weak band at 1040 cm$^{-1}$ appearing in IR spectrum of as-prepared compound may be attributed to the vibrations of M-OH or M-OH-M groups for Zn-Sn(OH)$_6$, and the absorption peak at 502 cm$^{-1}$ is due to the vibration of M-O or M-O-M groups for ZTO nanoparticles. This indicates the presence of ZTO nanoparticles in as-prepared and calcined compounds. The metal oxygen’s frequencies observed for the respective metal oxides are in accordance with literature’s values for Zn-Sn(OH)$_6$ and ZTO [40].

Evaluation of Photocatalytic Activity

Photocatalytic performance of ZTO with MB dye

The successful synthesis of ZTO nanoparticles offers an opportunity to examine their photocatalytic activity. The as-prepared and calcined ZTO nanoparticles were selected for the evaluation of photocatalytic activity with MB dye under the illumination of UV light. In order to study the effect of UV light on degradation of MB dye, a blank experiment was performed under UV light without the addition of photocatalysts (ZTO). The results indicated that MB dye of 10 mg/l was photolyzed up to 5% in 2 hr. This degradation efficiency was negligible when the different sized (24, 35 and 53 nm) nanoparticles were added to the solution under illumination. When there was no UV light, the concentration of MB dye with the addition of ZTO photocatalysts remains unchanged for 2 hr. From these blank experiments, it can be concluded that UV light and photocatalysts are the necessary factors in the photocatalytic process. The chemical structure of MB dye is shown in Fig. 5. MB dye absorbs light in the visible region (550-700 nm) with the absorption maxima at 664 nm. A series of experiments were carried out with different sizes (24, 35 and 53 nm) ZTO nanoparticles in
MB dye solution. The UV-Visible spectra of MB dye (10 mg/l) solution without and with ZTO photocatalysts are shown in Fig. 6. It can be seen that the intensity of absorption peak corresponding to MB molecules at 664 nm decreases and blue-shifted towards 658 nm. This small hypsochromic shift indicates that the photodegradation of MB dye under UV light irradiation experiences a continuous removal of methyl groups. The percentage of decolorization and photodegradation increases with irradiation time.

Influence of calcination temperature on ZTO photocatalysts

The calcination temperature decided particle size (Table 1) and BET surface area affect the photocatalytic efficiency of nano ZTO. The particle size will increase with improved calcination temperature and decreased surface area, accompanied by a drop in photocatalytic activity. This suggests that the morphology of nano ZTO also plays a very important role in deciding the catalyst performance. The degradation efficiencies of different sized ZTO photocatalysts compared with commercially available TiO₂ on MB dye solution are shown in Fig. 7. It can be observed from Fig. 7(a) that there is a small degradation with the as-prepared ZTO nanoparticles. In the initial 60 min, the degradation efficiency reached the highest value of 40%. Afterward, the degradation efficiency ascends tardily up to the maximum of 50%. Figure 7(b) shows the time-dependent UV-Visible spectra of MB dye solution containing calcined (300°C) ZTO nanoparticles. The efficiency of degradation is somewhat higher compared with the as-prepared sample which reaches the highest value of 70%. But in the sample calcined at 600°C (Fig. 7(c)), there is a large degradation observed. In the initial 20 min, the degradation efficiency reached the highest value of 60%. Afterward, the absorbance curve decreases and the efficiency of degradation ascend tardily up to almost 90%. The crucial degradation efficiency after 80 min illumination has changed a little

![Fig. 7 Time-dependent absorption spectra of MB dye during UV light irradiation in presence of ZTO (a) as-prepared, (b) calcined at 300°C, (c) calcined at 600°C and (d) degradation rate of two different catalysts.](http://dx.doi.org/10.5101/nml.v5i2.p101-110)
compared with the efficiency obtained after the initial illumination for 20 min. The relative bigger size and the reduction of the number of surface hydroxyl are the main reasons for the decrease of degradation efficiency of photocatalysts [37]. The increase of particle size with increased calcination temperature to 600°C (Fig. 7(c)) is helpful to increase the photocatalytic activity. However, a higher catalytic activity is observed for calcined ZTO sample only in the early stage of reaction (30 min), the percentage of activity is little increased for longer time degradation.

**Evaluation of photodegradation**

The catalytic activity of ZTO photocatalysts was evaluated by MB dye in aqueous solution and it was compared with that of commercially available TiO$_2$-P25 photocatalysts. Figure 7(d) shows the degradation ratio of calcined (600°C) ZTO photocatalysts compared with that of commercially available TiO$_2$-P25 photocatalysts, which was evaluated by the degradation of MB dye in aqueous solution. The performance of degradation process was defined as % Degradation = $(A_0 - A)/A_0 \times 100\%$, where $A_0$ is the initial absorbance and $A$ is the final absorbance. The degradation of dye molecules by self-direct photolysis was negligible. The activity of ZTO photocatalysts is slightly greater but it is almost equal to commercial TiO$_2$-P25 photocatalysts, which is attributed to its high surface area (41.8 m$^2$/g), higher crystallinity and smaller particle size ($\approx$ 19 nm). The catalytic performance on degradation is a complex function involving several parameters such as morphology, charge density, dye adsorption capacity, and is related to the BET surface area and pore size distribution. Lou et al. [11] observed that ZTO nanocrystals exhibited high photocatalytic activity to various reactive dyes such as K-NR, B-RN and B-GFF because of their large surface area ($\approx$ 62 m$^2$/g). Zhang et al. [25] observed that oxide coupled ZnO-SnO$_2$ nanocrystals had equally excellent photocatalytic activity for the degradation of methyl orange when compared to TiO$_2$-P25. The degradation efficiency of ZTO nanoparticles calcined at different temperature reduced in the order of 600°C > 300°C > 60°C.

**Enhancement of UV activity**

In photocatalytic mechanism, the main oxidative groups (radicals, holes and O$_2^-$) could be detected through trapping experiments of respective scavengers. Large number of enhancement is mainly due to high charge separation induced by surface oxygen-vacancies states. It is advantageous to increase the transport rate of photogeneration carriers, for the improved charge separation efficiency and diminished probability of photogenerated electron-hole pairs' recombination. This leads to an improved photocatalytic activity. A proposed schematic for electron-hole separation together with the energy level diagram for ZTO photocatalysts and TiO$_2$ is shown in Fig. 8. The above results recommend that the photogenerated holes are the main oxidative centers of ZTO system. This suggests that calcined ZTO nanoparticles are highly efficient photocatalysts when compared to commercially available TiO$_2$-P25 photocatalysts for the degradation of MB dye.

**Conclusions**

In the present work, the nanosized ZTO particles were successfully synthesized by hybrid electrochemical-thermal method using NaHCO$_3$ and Na$_2$SnO$_3$ electrolyte, without zinc salts, templates or surfactants. The generated Zn$^{2+}$ ions at Zn electrode combined with Sn$^{2+}$ ions from sodium stannate were
converted into ZTO during electrolysis. The particle size range of the generated ZTO powder was 24-53 nm. The FT-IR spectrum shows the existence of OH−, MOH-M and M-O-M groups in uncalkined sample. After calcinations, the particles morphology was cubic like and is well crystallized in the nanosize of 40-50 nm on nanometer scale. The method could be effectively used to synthesize ZTO on large scale. Also, the evaluations of photocatalytic degradation of MB dye with different sizes ZTO photocatalysts were preformed and compared with commercially available TiO2-P25. The as-prepared ZTO exhibited an efficient catalytic activity in degrading MB dye, and the calcined ZTO has higher photocatalytic activity compared to TiO2-P25 under UV light irradiation. The higher photocatalytic property was probably caused by larger crystallinity and smaller particle size. Thus, synthesized by the simple, fast and eco-friendly electrochemical method, the nano ZTO is a promising candidate for the photodegradation of dyes from wastewaters.

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Single-step Preparation of Nano-homogeneous NiO/YSZ Composite Anode for Solid Oxide Fuel Cells

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Abstract: Homogeneous co-precipitation and hydrothermal treatment were used to prepare nano- and highly dispersed NiO/YSZ (yttria-stabilized zirconia) composite powders. Composite powders of size less than 100 nm were successfully prepared. This process did not require separate sintering of the YSZ and NiO to be used as the raw materials for solid oxide fuel cells. The performance of a cell fabricated using the new powders (max. power density $\sim 0.87 \text{ W/cm}^2$) was higher than that of a cell fabricated using conventional powders (max. power density $\sim 0.73 \text{ W/cm}^2$). Co-precipitation and hydrothermal treatment proved to be very effective processes for reducing cell production costs as well as improving cell performance.

Keywords: Fuel cells; Powder processing; Electrochemistry; Hydrothermal process; NiO/YSZ composite anode

Introduction

Solid oxide fuel cells (SOFCs) are emerging electrochemical energy conversion devices, applicable to small systems of a few watts up to megawatt-sized power plants, with high efficiency and low emissions of pollutants. The SOFC system is generally operated at a temperature between 700 and 800°C. Planar SOFCs are generally classified based on three types of structures, i.e., anode supported, cathode supported, and electrolyte supported. Among these cell structures, anode-supported cells are now recognized as the most desirable in terms of mechanical strength and cell performance. Figure 1 shows a schematic diagram of an anode-supported SOFC. As shown in Fig. 1, the anode support acts as the mechanical layer of the SOFC and the anode acts as the electrochemical reaction layer.

The most important factor in improving the cell performance is therefore controlling the microstructure of the anode. The microstructure of the anode affects gas transport as well as the electrochemical reactions. For these reasons, considerable effort has been made to control the anode microstructure precisely. A fine anode structure with a uniform arrangement of Ni, YSZ (yttria-stabilized zirconia), and a porous phase is known to increase the electrochemical reactivity as well as the connectivity of the porous electrode. It is widely accepted that the preparation of NiO/YSZ composite powders is an effective way of generating better anode microstructures [1-3]. Various preparation methods such as spray pyrolysis, mechanical milling, and gel combustion have been studied for producing composite powders [4-10]. However, these processes have the disadvantage of high production costs.

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In this study, we prepared NiO/YSZ composites using homogeneous co-precipitation and hydrothermal treatment. This process for the preparation of NiO/YSZ composites is low cost because no sintering process is required. Also, the powders prepared using this process are expected to improve the cell performance because they can generate well-organized TPB (three phase boundary) as well as giving effective connectivity of the Ni. In comparison with the previous study by Sato et al. [4], we tried two kinds of precipitator, NH$_3$ and NaOH to investigate their effects on microstructures of NiO/YSZ powder. In addition, we fabricated anode supported cells (the most practical type for commercialization) utilizing our NiO/YSZ nano-composite powder as an anode functional layer, and showed its superior electrochemical properties with measuring I-V characteristics as well as impedance spectra.

**Experimental**

**Co-precipitation with various precipitators**

To select the best the precipitator, several precipitation tests were conducted. Zirconyl oxychloride octahydrate (ZrOCl$_2$·8H$_2$O), yttrium chloride hexahydrate (YCl$_3$·6H$_2$O), and nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) were used as starting materials. These were dissolved in deionized water to prepare source solutions with total cation concentrations of 0.02 M. The source solution was precipitated with various precipitators, i.e., sodium hydroxide (NaOH), ammonia (NH$_3$), urea ((NH$_2$)$_2$CO), and ammonium bicarbonate (NH$_4$HCO$_3$). The precipitation was conducted at pH=5.0-10.0. After precipitation was complete, the supernatant was analyzed using inductively coupled plasma (ICP) spectroscopy to measure the concentration of unreacted metal ions.

**Preparation of NiO/YSZ composite by NH$_3$ precipitation**

The effect of NH$_3$ on the preparation of NiO/YSZ was investigated to understand the metal hydroxide precipitation mechanism. Using NH$_3$ as the precipitator has the advantage that a delicate cleaning process is not required. This is because NH$_3$ is decomposed into N$_2$ and H$_2$O during calcinations. Similar to the co-precipitation test, total cation concentration of source solution was 0.02 M. The NH$_3$ solution was added dropwise to the concentrated source solution to induce precipitation. The precipitation was conducted at pH=2.0-10.0. The solution containing the precipitate was hydrothermally treated for 72 h at 180°C.

**Preparation of NiO/YSZ composite by NaOH precipitation**

To overcome the problems caused by the NH$_3$ precipitator, such as difficulties in controlling the pH and adjusting the concentration, NaOH was used as the precipitator. This has the disadvantage that a delicate cleaning process is required. As in the co-precipitation tests, the concentration of cations in the source solution was 0.02 M. The source solution was added to a 0.5 M NaOH solution to induce precipitation. The precipitation was conducted at pH=7.5-10.0. The solution after precipitation was hydrothermally treated for 48 h at 130°C.

**SOFC fabrication and testing**

The powders prepared in this study were tested as the anode materials in SOFCs. To achieve this goal, SOFCs were fabricated using two different anode powders. One powder was a conventional anode powder fabricated from NiO (J. T. Baker, UK) and YSZ (TZ-8Y, Tosh, Japan), and the other was a composite powder synthesized by the present process. The only difference between the two cells was the powder morphologies. The anode-supported electrolyte was fabricated using a tape-casting and co-firing process. More detailed information on the fabrication process is available in the literature [11, 12]. After fabrication of the anode-supported electrolyte, a La-Sr-Co-Fe-O$_3$ cathode was screen printed on the electrolyte layer at a thickness of about 50 μm; it was then fired at 1040°C for 3 h. The current-voltage characteristics (I-V curve) and impedance spectra were measured using a Solartron 1260/1287 electrochemical system (AC and DC) in order to compare the electrochemical performances of the cells. These measurements were conducted at 750°C with fuel gas in 300 sccm of 97% H$_2$-3% H$_2$O and oxidant gas in 1000 sccm of air. The impedance measurements were conducted in the frequency range ~0.1-100 kHz with a signal amplitude of 100 mV under open-circuit conditions. A detailed description of the cell-testing procedure and method can be found elsewhere [13].
Results and Discussion

Selection of precipitator

Table 1 shows the degree of precipitation of the metal hydroxides (yield) obtained with different precipitators. As shown in Table 1, Zr(OH)$_4$ was generated in high yield, irrespective of the precipitator. However, the yield of Ni(OH)$_2$ was highly affected by the type of precipitator. It can be seen that NaOH and NH$_3$ generated metal hydroxides effectively, with high yields of over 90%. These precipitators were therefore selected for the preparation of the NiO/YSZ composites; the results are discussed in detail later.

Table 1 Maximum yields of metal hydroxides obtained with different precipitators

| Precipitator | pH for maximum precipitation | Zr(OH)$_4$ | Ni(OH)$_2$ |
|--------------|------------------------------|------------|------------|
| NaOH         | > 10                         | ⬤          | ⬤          |
| NH$_3$       | > 8.5                        | ⬤          | ⬤          |
| (NH$_3$)HCO$_3$ | 5.7                         | ⬤          | Δ          |
| (NH$_3$)$_2$CO | 7.4                         | ⬤          | X          |

Yield: ⬤: 99%; ⬤: over 90%; Δ: over 70%; X: less than 50%.

Preparation of NiO/YSZ with NH$_3$ precipitator

The advantage of NH$_3$ as the precipitator is that a delicate cleaning process is not required. As shown in Table 1, NH$_3$ was verified to be a good precipitator of Ni(OH)$_2$ and Zr(OH)$_4$, giving high yields of metal hydroxides. Two influencing parameters, i.e., pH and concentration, were controlled in this study.

Figure 2 shows the results of ICP analysis and the effect of pH on the yields of Y$^{3+}$, Zr$^{4+}$, and Ni$^{2+}$ in the generation of NiO/YSZ composites. It was measured by analyzing the supernatant of the product solution after the hydrothermal treatment. As shown in Fig. 2, YSZ was generated above pH=5 because the reaction extents of Y$^{3+}$ and Zr$^{4+}$ were close to 100% above this pH value. However, it was not possible to obtain complete reaction of Ni$^{2+}$ at all pH values. The maximum reaction extent (~95%) was obtained only at pH=8.5. Above and below this pH value, the reaction extent decreased rapidly. Figure 2 also indicates that the precursor concentration affects the reaction extent. The extent of the reaction of Ni$^{2+}$ decreased, as shown in Fig. 2, when a solution of high-concentration, e.g., 0.05 M, was used. The reaction extent decreased with increasing concentration of source solution. The above findings show that the yield is affected by both factors, i.e., solution pH and concentration. We therefore analyzed the competitive balances based on the solution chemistry. Deng et al. studied the competitive balance of Ni$^{2+}$ and Ni(OH)$_2$ in the presence of NH$_3$ or NH$_4^+$ ions [14]. Equation (1) shows the calculated equilibrium constant based on their study.

$$\text{Ni(OH)}_2(s) + 6\text{NH}_3 = \text{Ni(NH}_3)_6^{2+} + 2\text{OH}^- \quad (1)$$

$$K = 2.2 \times 10^{-7}$$

Fig. 2 Results of ICP analysis: effect of pH and concentration on yield.

This indicates that Ni(OH)$_2$ can form complexes with excess free NH$_3$. They also showed that the complexing acid/alkali competition balance can be expressed as follows [2],

$$\text{Ni(OH)}_2(s) + 6\text{H}_2\text{O} + 2\text{NH}_4^+ = \text{Ni(NH}_3)_6^{2+} + 2\text{NH}_3 \cdot \text{H}_2\text{O} \quad (2)$$

$$K = 6.8 \times 10^2$$

The equilibrium constant in equation (2) is quite large. The solubility of Ni(OH)$_2$ is therefore greatly influenced by the presence of NH$_4^+$. This also indicates that complete conversion of Ni$^{2+}$ into Ni(OH)$_2$ is impossible. Figure 3 shows the competitive balances of Ni$^{2+}$+NH$_3$H$_2$O based on the study by Deng et al. [14]. From the diagram, it can be seen that the region in which Ni(OH)$_2$ exists, i.e., region I, is very narrow (from pH 7.6 to 8.1 for 0.02 M Ni$^{2+}$ solution). Furthermore, this region becomes narrower with increasing Ni$^{2+}$ concentration. The competitive balance can explain why the maximum yield was obtained at pH=8.5 and the reaction decreased with increasing Ni$^{2+}$ concentration, as shown in Fig. 2. The above investigation shows that the preparation of NiO/YSZ using NH$_3$ is unsatisfactory. To use both region I and region II in Fig. 3, the precipitator should not contain NH$_3$-based ions. NaOH was therefore used as the precipitator; this will be discussed in the next section.

Figure 4 shows scanning electron microscopy (SEM) images of NiO/YSZ composites prepared at pH=8.5 with NH$_3$ as the precipitator. As shown in Fig. 4, two types of particle are observed: very large particles and very small particles. The large particles were several microns in size and globular. In contrast, the small particles were of size about 20 nm. To understand the powder compositions, EDS analysis was conducted. It
showed that the large particles were mainly composed of NiO, and small particles of YSZ. Deng et al. studied the effect of the zeta potential on NiO size. They found that the agglomerate size is the biggest near the isoelectric point of NiO. This value is located close to pH=10.59. In our results, the powder sizes obtained by SEM analysis were several microns in size, irrespective of the pH value, and they are too large to determine the effect of surface charge. However, we found that the powder obtained near pH=10 was easier to filter than the powders obtained at other pH values during the cleaning process. This may indicate that the particle sizes are affected by the surface charges of the particles. This indirectly implies that the sizes of the particles can be optimized by the preparation procedure.

**Preparation of NiO/YSZ nanocomposites**

The above results verified that NH$_3$ was not an effective precipitator for obtaining high yields of metal hydroxides. They also showed that complete precipitation of Ni(OH)$_2$ was not possible because of competitive balances. A different precipitator, NaOH, was therefore used. Sato et al. studied NaOH as a precipitator in the preparation of NiO/YSZ composites [4]. Their analysis suggested that it is possible to precipitate all the metal hydroxide over a broad pH range. Figure 5 shows the microstructures of NiO/YSZ composite particles prepared using NaOH as the precipitator. Figure 5 shows that a NiO/YSZ composite of size less than 200 nm was successfully prepared, irrespective of the solution pH. Also, it is expected that smaller nanoparticles can be obtained at high pH values such as pH=13 because NiO has a high negative zeta potential at that point. Sato et al. suggested that high pH values affect the preparation of NiO/YSZ as follows [4].

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![Graph showing competitive balance in reaction of Ni$^{2+}$ + NH$_3$.H$_2$.O](image1.png)

**Fig. 3** Competitive balance in reaction of Ni$^{2+}$ + NH$_3$.H$_2$.O (10).

![SEM images of NiO/YSZ composite powders synthesized with NH$_3$ precipitator](image2.png)

**Fig. 4** SEM images of NiO/YSZ composite powders synthesized with NH$_3$ precipitator (a) 1000×, (b) 200 000× and (c) 7000×.
1. The precipitate size decreases, because the number density of nuclei increases.
2. The differences among hydroxide precipitation extents decrease.
3. Ostwald ripening is suppressed because a higher pH can stabilize finer precipitates and prevent dissolution.

Finer hydroxide phases with a more uniform distribution can therefore be obtained at pH=13 than at lower pH values. Uniformly distributed NiO and YSZ phases suppress grain growth of each other during the subsequent calcination step, resulting in successful synthesis of nanosized NiO (~50 nm)/YSZ (~5 nm) composite particles.

**Electrochemical testing**

Figure 6 shows the current-voltage characteristics ($I - V$ curves) of button cells fabricated using commercial NiO/YSZ composite powder and a nano-YSZ/NiO composite powder prepared using our new method. The new powder showed a better electrochemical performance than the conventional powder. The maximum power density of the cell fabricated using the new powders was \(\sim 0.87\) W/cm\(^2\) while that of a cell fabricated using conventional powders was \(\sim 0.73\) W/cm\(^2\). This may be caused by increased TPBs as a result of the homogeneous and nanosized NiO/YSZ composite anode. Figure 7 compares the impedance spectra between cells with nanocomposite anode and conventional anode; the first semi-circle (corresponding to frequency range \(10^{-1}\) to \(10^{6}\) Hz) significantly decreased in the case of nanocomposite anode. One of the authors in the present work found that this impedance frequency range also responds to the changes of anode composition [15]. Thus, it can be said that the first semi-circle is dominated by activation polarization of anode and the improved electrochemical performance in Fig. 7 is mainly attributed to a reduction in the activation polarization resistance of the anode. Also, a slight decrease in ohmic resistance (the high frequency intercept of the impedance spectra on the real axis) is due to the well-structured connectivity of the NiO/YSZ in the anode layer. The results show that the present process is very effective and promising for the preparation of nanodispersed NiO/YSZ powders, and, eventually, high-
performance SOFCs.

Conclusion

We successfully synthesized nanosized NiO/YSZ composite powders via co-precipitation and hydrothermal treatment. A basic study of NiO/YSZ powder preparation was conducted using different precipitators. A general hydrothermal method using NH$_3$ as the precipitator was not suitable for NiO/YSZ composite production because of the competitive balance of Ni$^{2+}$ with NH$_3$. Agglomeration of the NiO powders was mainly affected by the iso-electric point of NiO. This can be controlled by changing the pH and the precipitation procedure. A different precipitator, NaOH, was used, and the synthesized NiO/YSZ composites had particles sizes of $\sim$50 nm. Electrochemical testing of a cell fabricated form powders produced using the present process showed that the cell performance was much better than that of a cell produced from conventional powders. This may be caused by an increment in the TPB length and well-structured connectivity of the NiO/YSZ in the anode layer.

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Synthesis and Luminescence Properties of (Y, Gd) (P, V)O₄:Eu³⁺, Bi³⁺ Red Nano-phosphors with Enhanced Photoluminescence by Bi³⁺, Gd³⁺ Doping

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Abstract: A series of (Y₁₋₇₡₋₇ₙ, Gd₇ₙ₋₇ₚ)(P₇ₕ₋₇ₙ, V₇ₜ₋₇ₙ)O₄₀.₅₃₊ₓEu³⁺,xBi³⁺ phosphors have been successfully prepared by a subsection method. The crystal structure, surface morphology and luminescence properties were investigated. It was found that the sintered samples crystallized in a tetragonal crystal system with space group I₄₁/amd (a = b = 0.7119 nm, c = 0.6290 nm). The products presented rod-like morphology with length of 100-150 nm and width of 50-100 nm. A maximum peak at 619 nm (⁵D₀ → ⁷F₂) was observed in emission spectrum of the phosphors. It was also found that co-doping of Bi³⁺, P⁵⁺ and Gd³⁺ ions into YVO₄:Eu³⁺ can not only made the right edge of the excitation band shift to the long-wavelength region, but also increased the emission intensity at 619 nm sharply and decreased the lifetime of fluorescence decay. These results may expand the application scope of the phosphors.

Keywords: (Y, Gd)(P, V)O₄:Eu³⁺,Bi³⁺; Rod-like; Red phosphors; Photoluminescence; Doping

Introduction

Over past decades, many efforts have been made to study the rare-earth doped luminescence materials, which have been largely applied in fields of illuminations and displays, such as fluorescent lamps, cathode-ray tubes, field emission displays, plasma display panels, electro-optical polarizers and white light-emitting diodes [1-7]. Yttrium vanadate (YVO₄) has been proved one of the best candidates for doping into rare earth ions [8] since it provides a suitable Y³⁺ site where trivalent rare-earth ions can be replaced without additional charge compensation. In particular, as a typical red-emitting phosphor, europium doped YVO₄ has been explored in many fields [8-11]. Recent years, much attention has been focused on the nanoscale phosphors. It was found that the higher packing density and better paste rheology of smaller-sized phosphors particles led to higher screen resolution and lower screen load [12-16]. Especially, Eu³⁺ doped nanoscaled YVO₄ phosphor has attracted a great deal of attention. Nowadays, a number of methods, such as single crystal growth techniques, the solution combustion process, hydrolyzed colloid reaction (HCR), solution-based sol-gel process and hydrothermal reaction have been used to synthesize the YVO₄:Eu³⁺ nanophosphors. However, due to lower crystallinity and higher surface defect density, most products have lower luminescent intensity compared with their bulk powders. For exam-
ple, compared with commercial PDP red phosphor (Y, Gd)BO₃:Eu³⁺, YVO₄:Eu³⁺ nanoparticles have higher color purity but lower luminescent intensity, especially when the particle size decreased into nanosized scale [15].

Many efforts have been made to improve luminescence properties of YVO₄:Eu³⁺ nanophosphors [17-21]. For example, sensitizer co-doping has been proved to be an efficient way to increase the luminesence efficiency. Till now, many researches are focused on one kind of ions doped into YVO₄:Eu³⁺ nanophosphors. It is relatively less reports on multi-ions co-doping. It was found that high concentration doping of Gd³⁺ and P⁵⁺ into YVO₄:Eu³⁺ would increase the photoluminescence intensity [3,19]. And Bi³⁺ ion can be used as a sensitizer to strengthen and broaden the ultraviolet-vacuum ultraviolet (UV-VUV) excitation bands [10]. In this paper, three kinds of ions (Bi³⁺, P⁵⁺ and Gd³⁺) were co-doped into YVO₄:Eu³⁺ to improve the photoluminescence properties by using a subsection method.

Experimental

Materials and reagents

The materials and reagents used in the experiment were Y₂O₃ (99.99% purity), Gd₂O₃ (99.99% purity), Eu₂O₃ (99.99% purity), Bi(NO₃)₃·5H₂O (A.R.), NH₄VO₃ (A.R.), (NH₄)₂HPO₄ (A.R.), HNO₃ (A.R.), Polyethylene glycol (PEG, molecular weight = 20000, A.R.), Anhydrous ethanol (A.R.), NH₃·H₂O (A.R.), Citric acid (A.R.) and enough distilled water.

Synthesis of (Y, Gd)(P, V)O₄:Eu³⁺, Bi³⁺ samples

All samples were prepared by a two-step subsection method. The YVO₄:Eu³⁺, Bi³⁺ crystal seeds were prepared by a solvothermal method and Gd³⁺, P⁵⁺ were doped into YVO₄:Eu³⁺,Bi³⁺ by a sol-gel process. In a typical solvothermal synthesis process, (Y₀.₅, Gd₀.₅)₀.₉(P₀.₅, V₀.₅)O₄:0.05Eu³⁺,0.05Bi³⁺ was successfully prepared through the following procedures.

Firstly, proper quantity of Y₂O₃ and Eu₂O₃ were dissolved in excess diluted nitric acid to form a mixture. Then, proper quantity of Bi(NO₃)₃·5H₂O and NH₄VO₃ (molar ratio of Y:Eu:Bi)V = 0.90:0.05:0.05:1), 50 ml anhydrous ethanol and distilled water (E:W = 1:1) were mixed and added into the above mixture under ultrasonic mixing for 0.5 h to form a total solution. The initial pH value of the solution was adjusted to 7 using NH₃·H₂O. After that, the solution was transferred into a 100 ml stainless steel Teflon-lined autoclave and heated at 200°C for 12 h. After filtered and washed with distilled water by ethanol several times, the product was dried and white YVO₄:Eu³⁺ nanoparticles was obtained.

In the sol-gel process, proper quantity of Gd₂O₃, Eu₂O₃ and (NH₄)₂HPO₄ (Gd:Eu:P = 0.95:0.05:1) were dissolved in excess diluted nitric acid and evaporated to dryness. The mixture was then dissolved in a 50 ml mixed solution of anhydrous ethanol and distilled water (E:W = 1:1). Proper quantity of citric acid was added as a chelating agent for the metal ions under magnetic stirring (the molar ratio of metal ions to citric acid was 1:2). The proper quantity of polyethylene glycol (molecular weight = 10000, A.R.) was added as a cross-linking agent. Afterwards, a certain quantity of YVO₄:Eu³⁺ nanoparticles, which obtained in the solvothermal method process, were added under stirring. The pH value of the solution was adjusted to 2 by using NH₃·H₂O and the solution was stirred at 60°C for 1 h to form a gel. The gel was dried in an oven at 100°C and ground in an agate mortar for 10-30 min. The porous dried gel was then sintered at 1000°C for 2 h.

Characterization

The structure of the products was analyzed by using a SHIMADZU polycrystalline XRD (Xpert PRD MPD) with Cu-Kα radiation (40 kV, 40 mA, Kα = 0.15418 nm). The surface morphology was observed by a JEOL-JSM5900 and a Quanta 450 scanning electron microscopy (SEM). The excitation spectra, emission spectra and decay curves were recorded on a HITACHI F-7000 fluorescence spectrophotometer. All the measurements were done at room temperature.

Results and discussion

Figure 1 shows the collected XRD patterns of (a) Y₀.₉V₀.₁O₄:0.05Eu³⁺ crystal seeds, (b) Y₀.₉V₀.₁O₄:0.05Eu³⁺,0.05Bi³⁺ crystal seeds, (c) the precursor prepared in the sol-gel process and (d) the final products (Y₀.₅, Gd₀.₅)₀.₉(P₀.₅, V₀.₅)O₄:0.05Eu³⁺,0.05Bi³⁺ crystals sintered at 1000°C for 2 h. In order to explore the phase structure, the diffraction peaks of the samples are indexed on the basis of the single crystal YVO₄ (JCPDS No. 17-0341) in a tetragonal crystal system with space group I₄₁/amd and GdPO₄ (JCPDS No. 32-0386) in a monoclinic system with space group P₂₁/n. All XRD peaks in Fig. 1(a) are in good agreement with the values of standard YVO₄ (JCPDS No. 17-0341). Since Eu³⁺ and Y³⁺ ions have the same valence and similar atomic radius, the doped Eu³⁺ has little effect on the structure of YVO₄. Compared with Fig. 1(a), Fig. 1(b) indicates a pure phase of Y₀.₉V₀.₁O₄:0.05Eu³⁺,0.05Bi³⁺ without obvious impurities. It can be also observed that Bi³⁺ doping will strengthen the peak intensity. In Fig. 1(c),
Fig. 1  XRD patterns of (a) $Y_{0.95}VO_4$: 0.05Eu$^{3+}$; (b) $Y_{0.9}VO_4$: 0.05Eu$^{3+}$, 0.05Bi$^{3+}$; (c) precursor prepared in the sol-gel process; (d) $(Y_{0.5}, Gd_{0.5})_0.9(P_{0.5}, V_{0.5})O_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$ particles annealed at 1000°C for 2 h. a mixture containing YVO$_4$ and GdPO$_4$ was found. However, the peaks for GdPO$_4$ phase were not observed in final product (see Fig. 1(d)). The samples still keep a tetragonal phase with space group I$_{41}$/amd ($a = b = 0.7119$ nm, $c = 0.6290$ nm), which indicates Gd$^{3+}$ and P$^{5+}$ were doped in the sample after sintered at 1000°C for 2 h. In addition, a systematic shifting of diffraction angle $2\theta$ towards larger angle directions was observed, which is due to the different radius of the host ions and the doping ions. Since the radius difference between V$^{5+}$ and P$^{5+}$ is bigger than that between Y$^{3+}$ and Gd$^{3+}$, the cell volumes decreased with increasing the same content rates of Gd$^{3+}$ (Eu$^{3+}$, Bi$^{3+}$) and P$^{5+}$. As a result, the diffraction peaks shifted to the larger angle gradually.

Figure 2 shows SEM images of several representative samples. One can see that the merchant phosphors in Fig. 2(a) are composed of large grains with average size about 1 µm. However, the seeds shown in Fig. 2(b) have spherical or approximately spherical morphology with about 50 nm in size, and the as-prepared particles (see Fig. 2(c), (d)) are short rod-like with average size about 100 nm length and 50 nm width. From Fig. 2(c, d), it was also found that the particles obtained by the solvothermal method are more uniform than those by the hydrothermal method. Figure 3 shows SEM images of $Y_{1-x}, Gd_x)_{0.9}(P_{x}, V_{1-x})O_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$ with different doping content. One can see that the particle sizes increase gradually with the quantity of Gd$^{3+}$ and P$^{5+}$ doping. When doping quantity $x$ is 0.5, the

![Figure 2](image_url)
particles present normal rod-like morphology and the particle size increases obviously. When doping quantity \(x\) is up to 0.75, the sample consists of irregular particles. These results indicate that co-doping Gd\(^{3+}\) and P\(^{5+}\) will increase the particle size and change the particle morphology obviously. This can be understood that YVO\(_4\) particles prepared by the solvothermal method played a role as template to control the shape of the final products due to the template-induced effect of the seed. During the calcine processes, the P\(^{5+}\) and Gd\(^{3+}\) ions were diffused into the YVO\(_4\) particles readily. It will weaken the limit effect of the seeds through increase the concentration of P\(^{5+}\) and Gd\(^{3+}\) ions continuously so that the phosphor particles approach to natural growth. Moreover, the rare earth orthophosphates generally have hexagonal or tetragonal structure and tend to form a wire-like or rod-like morphology [22].

Figure 4 shows the excitation spectra of (a) \(Y_{0.95}VO_4; 0.05\text{Eu}^{3+}\), (b) \(Y_{0.9}VO_4; 0.05\text{Eu}^{3+}, 0.05\text{Bi}^{3+}\), (c) \(Y_{0.9} (P_{0.5}, V_{0.5})O_4; 0.05\text{Eu}^{3+}, 0.05\text{Bi}^{3+}\) and (d) \((Y_{0.5}, \text{Gd}_{0.5})_{0.9}(P_{0.5}, V_{0.5})O_4; 0.05\text{Eu}^{3+}, 0.05\text{Bi}^{3+}\) phosphors. The excitation spectra were measured in the range of 200-500 nm by monitoring the emission of Eu\(^{3+}\) at 619 nm \((^5D_0 \rightarrow ^7F_2)\). As shown in Fig. 4(a), the excitation spectrum of \(Y_{0.95}VO_4; 0.05\text{Eu}^{3+}\) consists of a broad band (210-350 nm) which is owing to the overlap of two peaked at about 275 and 325 nm. The short-wavelength excitation is due to the charge-transfer processes involving the Y-O components, while the long-wavelength excitation is due to the V-O components of the matrix [15]. When Bi\(^{3+}\) is doped into \(Y_{0.95}VO_4; 0.05\text{Eu}^{3+}\) particles, the intensity of the charge transfer (CT) bands (Eu-O and V-O interactions) increased and the right edge of the band shifted to near 400 nm (Fig. 4(b)), which ascribed to the intense absorption of Bi\(^{3+}\) compounds in the band of 250-400 nm. Related reports show that the absorption energy of Bi\(^{3+}\) could transfer to Eu\(^{3+}\), which can
sensitize and enhance the intensity of Eu$^{3+}$ [18]. When P$^{5+}$ is doped into the Y$_{0.9}$VO$_4$:0.05Eu$^{3+}$,0.05Bi$^{3+}$ particles, the intensity of the excitation spectra will increase (Fig. 4(c)), especially the intensity of the band 320 nm-375 nm will enhance obviously. It may be resulted that doping of P$^{5+}$ can enhance the CT band of Bi$^{3+}$-O$^{2-}$ efficiently [19]. Furthermore, the intensity of the excitation spectra increased when Gd$^{3+}$ is doped into the sample (Fig. 4(d)). This is because co-doping Gd$^{3+}$ can produce more efficient excitation of Eu$^{3+}$ in UV region [15].

Figure 5(a) shows emission spectra of $\text{Y}_{0.95}\text{VO}_4$:0.05Eu$^{3+}$, $\text{Y}_{0.9}\text{VO}_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$, $\text{Y}_{0.9}(\text{P}_{0.5}, \text{V}_{0.5})\text{O}_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$ and (Y$_{0.5}$, Gd$_{0.5}$)$_{0.9}$(P$_{0.5}$, V$_{0.5}$)$_{0.9}$O$_4$:0.05Eu$^{3+}$,0.05Bi$^{3+}$ phosphors. For all the phosphors, two typical emission peaks of Eu$^{3+}$ activators are located mainly in the red region (594 nm and 619 nm), which is due to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions when excited under 275 nm. The emission peak near 700 nm is associated with the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition. The strongest emission peak is at 619 nm indicating the final products have fine color purity. It can be obviously seen from Fig. 5(a) that the emission intensity at 619 nm under 275 nm excitation increased after Bi$^{3+}$ doping into YVO$_4$:Eu$^{3+}$. It is also obvious that co-doping of P$^{5+}$ and Gd$^{3+}$ can enhance the emission intensity. This is because the incorporation of P$^{5+}$ and Gd$^{3+}$ into the YVO$_4$:Eu$^{3+}$, Bi$^{3+}$ lattice will increase the absorption of excitation energy and produce more efficient excitation of Eu$^{3+}$, thus enhancing the PL characteristics. The emission spectrum of $\text{Y}_{0.9}\text{VO}_4$:0.05Eu$^{3+}$, 0.05Bi$^{3+}$ excited under 365 nm is shown in the inset of Fig. 5(a). One can find that the emission intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric dipole transition of Eu$^{3+}$ at 619 nm under 365 nm excitation, which has about two-thirds intensity of that under 275 nm excitation, increases sharply with the doping of Bi$^{3+}$ ions. It indicates that Bi$^{3+}$ doping can obviously enhance the emission intensity at 619 nm when excited under 365 nm. Figure 5(b) shows the influence of Bi$^{3+}$ concentration on the relative emission intensity of (Y$_{0.5}$, Gd$_{0.5}$)$_{0.95-x}$(P$_{0.5}$, V$_{0.5}$)$_{0.9}$O$_4$:0.05Eu$^{3+}$,xBi$^{3+}$ at 619 nm under 275 nm excitation. The curve shows that with increase of Bi$^{3+}$ concentration, the emission intensity increased. As Bi$^{3+}$ concentration is more than 5 mol%, the luminous intensity decreases gradually. The sensitization of Bi$^{3+}$ to Eu$^{3+}$ depends on the concentration of Bi$^{3+}$, and the most suitable concentration of Bi$^{3+}$ is 5 mol%.

Figure 6 shows a comparison of the room-temperature luminescence decay curves of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu$^{3+}$ between Y$_{0.95}$(P$_{0.5}$, V$_{0.5}$)$_4$: 0.05Eu$^{3+}$, (Y$_{0.5}$, Gd$_{0.5}$)$_{0.95}$ (P$_{0.5}$, V$_{0.5}$)$_{0.9}$O$_4$: 0.05Eu$^{3+}$ and (Y$_{0.5}$, Gd$_{0.5}$)$_{0.95}$(P$_{0.5}$, V$_{0.5}$)$_{0.9}$O$_4$: 0.05Eu$^{3+}$, 0.05Bi$^{3+}$ under 275 nm excitation. The decay kinetics behavior depends on the number of different luminescent centers, defects, energy transfer and impurities in the host [23]. It is possible to explore the influence of co-doped elements on the decay dynamics of the samples. It can be clearly seen that, the emission of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu$^{3+}$ decays exponentially, which can be well-fitted into the following exponential function:

$$I(t) = I_0 \exp(-t/\tau) + C$$

where $I(t)$ and $I_0$ is the luminescence intensity at time $t$ and initial time, $C$ is a constant which relates to the test equipment, $t$ is the time and $\tau$ is the decay lifetime for the exponential components, respectively. The measurement results of the luminescence lifetime
of the as-synthesized \( Y_{0.95}(P_{0.5}, V_{0.5})O_4:0.05\text{Eu}^{3+}, (Y_{0.5}, \text{Gd}_{0.5})_{0.95}(P_{0.5}, V_{0.5})O_4:0.05\text{Eu}^{3+} \) and \((Y_{0.5}, \text{Gd}_{0.5})_{0.9}(P_{0.5}, V_{0.5})O_4:0.05\text{Eu}^{3+}, 0.05\text{Bi}^{3+}\) samples at 619 nm emission under 275 nm excitation are 862.59, 805.12 and 525.38 µs, respectively. Due to the excitation energy transfer occurs in a very short time in comparison with the relatively long fluorescence decay time, the nature of non-exponential decay cannot be attributed to the excitation energy transfer [25]. It can be noticed that with the doping of \(\text{Bi}^{3+}\), the luminescence lifetime of \((Y_{0.5}, \text{Gd}_{0.5})_{0.9}(P_{0.5}, V_{0.5})O_4:0.05\text{Eu}^{3+}, 0.05\text{Bi}^{3+}\) upon 275 nm decreased a lot. This phenomenon indicates that \(\text{Bi}^{3+}\) can involve the energy transfer rate among \(\text{Eu}^{3+}\) and other ions, correlated to the decay lifetime. Therefore, further researches on the formation of the energy transfer after the introduction of \(\text{Bi}^{3+}\) and other ions into \(\text{Y}(\text{P}, \text{V})O_4:\text{Eu}^{3+}\) become very important.

**Conclusions**

In this paper, series of \((Y_{1-x}, \text{Gd}_x)_{0.95-x}(P_{y}, V_{1-y})O_4:0.05\text{Eu}^{3+}, x\text{Bi}^{3+}\) samples have been synthesized successfully through a subsection method. When doping concentration were \(x = 0.05\), \(y = 0.5\), the samples showed pure phase and present rod-like morphology. The morphology and size of the samples could be controlled by adjusting the ratios between the seeds and the doping ions. The average sizes for the phosphor particles were 100-150 nm length and 50-100 nm width. With the doping of \(\text{Bi}^{3+}, \text{P}^{5+}\) and \(\text{Gd}^{3+}\) ions, the samples showed high red emission at 619 nm \((^5\text{D}_0 \rightarrow ^7\text{F}_2)\), superior color saturation and broad excitation band (210-400 nm). The doping of \(\text{Bi}^{3+}\) and \(\text{Gd}^{3+}\) can increase the emission intensity at 619 nm under 365 nm excitation, and \(\text{Bi}^{3+}\) could decrease the fluorescent lifetime. The advantages may expand the application of the samples.

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Growth and Formation Mechanism of Branched Carbon Nanotubes by Pyrolysis of Iron(II) Phthalocyanine

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Abstract: In this letter, a route for synthesizing vertically aligned multi-walled carbon nanotubes (MWCNTs) with branched nanotubes in large area was reported. The branched MWCNTs up to about 30% can be generated by the pyrolysis of iron(II) phthalocyanine in presence of thiol under Ar/H₂ at 800∼900°C. The growth mechanism of the branched nanotubes was proposed and the possible reason that thiol enhanced branched nanotubes growth is discussed. The as-prepared samples provide a suitable candidate to investigate the special electrical or thermal properties of CNTs with branched structures further.

Keywords: Carbon nanotube; Chemical vapour deposition; Branched; Growth mechanism

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Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991, various CNTs with straight, curved, bamboo-like, planar-spiral, or helical shapes have been identified experimentally either by a carbon-arc-discharge method or by a catalytic pyrolysis of hydrocarbon [1,2]. In addition, other nanoscaled carbonaceous materials including carbon polyhedral [2], graphite onions [3], carbon nanochain [4], carbon "sea urchins" [6], carbon bead with protruding cones [6], fullerene "crop circle" [7], cubic carbon nano-cage [8] and nanohorn [9] have also been reported. Particularly after earlier experimental observation of branched CNT or "Y" junction CNTs [10], controllable fabrication of branched single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) or “Y” junction CNTs were fabricated via template-based chemical vapour deposition (CVD) method [11] as well as pyrolysis of organometallic precursors [12-17]. Theoretical calculations and experimental measurements show that the “Y” junction has interesting electrical properties and potential applications in nanoscaled transistor and amplifiers [18, 19]. The evidence for a dramatic electrical switching behaviour in “Y” junction CNTs has been observed and it is possible as logical gate or other nanoelectronics proposed applications [20]. However “Y” junction CNTs prepared by common templated approaches consist of larger diameter stems with two smaller branches with an acute angle between them resembling “tuning forks” and usually have low graphitisation. Various metal-catalysed CVD methods are usually less controllable for the structures of the Y-junction. It is of particular interest to control the fabrication of the architectures of branched CNTs for the investigation of their properties, especially electrical and thermo-conducting properties [17, 21-23].

We have developed a feasible method to generate free-standing aligned CNT arrays in large scale by pyrolysis of iron(II) phthalocyanine (designated as FePc) which is used as either catalyst and carbon source during 800∼1100°C under H₂/Ar atmosphere [24]. It was
found that a certain percentage branched CNTs can be found in the aligned nanotubes sample when the pyrolysis temperature is over 1000°C, which prompted us to enhance the percentage of the branched CNTs. Here we reported an approach to generate the branched CNTs more efficiently by introducing thiol into the pyrolysis process of FePc at 800∼900°C. Various structures of the branched CNTs were observed and the possible growth mechanism of the branched nanotubes is discussed.

Experimental

Large area aligned CNT arrays on substrate were generated by pyrolysis of iron (II) phthalocyanine (FePc), which is used as catalyst and carbon source, at 800∼1100°C under H₂/Ar atmosphere. The detailed experiment processes was reported in our previous paper [19]. Similar process was applied to fabricate branched aligned CNT arrays in which 2∼5 wt% thiol (octadecanethiol) was added in FePc as a source. Samples were characterized by scanning electron microscopic (SEM, XL-30 FEG SEM, Philips, at 5 kV), EDX attached onto SEM and transition electron microscopy (TEM, JEOL 2010).

Results and discussion

Figure 1(a) and 1(b) shows typical SEM images of aligned CNTs. It can be seen that catalytic metal particles exist both on bottom and top indicated by white arrows in Fig. 1(b), which is different from other CNTs prepared using metal catalysts. The inset in Fig. 1(a) shows the corresponding TEM image (bottom side). It was noted when pyrolysis temperature is over 1000°C (1000∼1150°C), small amount of CNTs (about 5%) were branched and have bamboo-like structure. The bottom parts of the branched CNTs are normally irregular and the diameter is much large than that produced at 800∼900°C. Figure 1c and 1d are the typical SEM and TEM images of the branched MWCNTs arrays (as indicated by white arrows) produced by the pyrolysis of FePc at over 1000°C. This result encouraged us to enhance the yield of the branched CNTs.

![Figure 1](image_url)

As we know that thiol is one of the molecules which can be usually used to adjust the growth activity and the structure of CNTs [25, 26]. In this experiment, 2∼5% (wt%) thiol (e.g. octadecanethiol) was introduced into the reactor where thiol and FePc were simply mixed and the pyrolysis temperature was 800∼900°C. It was very interesting that the yield of the branched nanotubes increased dramatically up to about 30%. The diameter of the nanotubes became smaller and more uniform than that produced over 1000°C. Figure 1e and 1f represent the typical SEM images of the branched (as indicated by arrows) aligned CNTs arrays and individual CNTs produced by pyrolysis of FePc in the presence of thiol. More detailed TEM observations showed that various branched nanotubes with different structural architectures were also produced in the samples as shown in Fig. 2(a)-2(k).
Fig. 2 TEM images of various branched CNTs produced by pyrolysis of FePc with existence of thiol at 850°C. Arrows represent the growth direction of CNTs.

As reported in our early paper [27], growth of aligned CNTs by pyrolysis of FePc involves two metal nanoparticles. As shown in Scheme 1(a) [19], small iron particles at the bottom act catalysts for nucleation of nanotubes, whereas, large iron particles at the top is responsible for growth. However, in most cases the metal particles at the top will drop down upon sonication in acetone for TEM specimen preparation. Therefore in TEM observation images it is usually shown open tip.

Based on the detailed SEM and TEM observation (see Fig. 2), the possible mechanism of formation of various branched CNTs are described in Scheme 1(b)-(g). Like straight CNTs (Scheme 1(a)), two metal particles are hypothetically involved in branched CNTs growth (Scheme 1(b)). The small bottom particles are responsible for nucleation of CNTs and the large particles are for the growth of the nanotubes. As shown in Scheme 1(a), the nanotubes have bamboo-like structures and the inner tube is subdivided by a few graphitic layers. It is believed that the particles on tip of the nanotubes are actually in liquid-like states at high temperature, and carbon sources can diffuse between metal particles. So the particles on tip of nanotubes will easily split into two or more small particles and therefore result in growth of branched nanotubes. Since the split particles are smaller than original ones, the diameter of branched nanotubes is correspondingly smaller than that of original ones. The schematic diagram is shown in Scheme 1(b). This phenomenon was experimentally confirmed by SEM (Fig. 1(f)) and TEM (Fig. 2(a) and 2(b)).
observations.

In another case, the diameter of branched nanotubes is similar or even larger than that of original ones (see Fig. 2(c)). This phenomenon would be understood as follows: during CNTs growth processes, FePc is decomposed continuously and formed Fe atoms are deposited on Fe particles at the top of CNTs. The Fe particles grow larger and result in large-diameter CNTs. It was also observed some Fe particles located inside of nanotubes and “Y” junction of branched nanotubes (Fig. 2(d) and 2(e)). These inside particles may act as nucleation centres, which is similar to those of normal CNTs as described in Scheme 1(c). These particles are generated from the FePc decomposition as shown in Fig. 2(f) and described in Scheme 1(d). If the metal particle is large enough, the branched nanotubes will be branched further (Fig. 2(g)). Most of branched situation is either from middle (Fig. 2(h)) or from bottom (Fig. 2(i)) of nanotubes, which is described in Scheme 1(e) and 1(f). This will lead to tree-like structures (Fig. 2(h) and 2(i)). It is also very interesting to observe two nanotubes joint together at bottom of nanotubes due to high density of metal particles on the substrate (Fig. 2(j), Scheme 1(g) and 1(h)). A nanotube with helical structures was also observed occasionally (Fig. 2(k)).

The reason why thiol can increase the content of branched nanotubes is that sulphur in thiol may reduce the melting point of iron (Fe: 1535°C, FeS: 1193°C) during the pyrolysis process. This will result in the enlargement of iron particles which is responsible for nanotube growth. It is obvious that the metal particle size in bottom as well as the diameter of produced nanotubes is larger with the existence of thiol than those without thiol. As discussed above, since larger particles is responsible for nanotube growth there is more chance to split into smaller ones and therefore benefit branched nanotubes growth.

**Conclusion**

In summary, we have presented a way to generate aligned branched CNTs with high content up to 30% by pyrolyzing FePc with the existence of thiol at 800–900°C. Various branched nanotubes with different structural features were observed and the possible growth mechanism was proposed. The synthesis of branched CNTs provides a candidate to investigate the special corresponding properties, especially electrical and thermo-conductive properties with this kind of nanostructures.

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Surface Texturing of TiO$_2$ Film by Mist Deposition of TiO$_2$ Nanoparticles

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Abstract: Unique and various microstructures of titanium oxide (TiO$_2$) film including macroporous structure, chromatic veins and rings, have been easily fabricated by mist deposition method on silicon substrate with mild preparation conditions. Rutile phase TiO$_2$ nanoparticles were directly used as starting material to prepare film and led to a simple preparation process. It was found that several different microstructures existed in the sample and changed with the varied positions from the center to the edge of the film when the concentration of the TiO$_2$ suspension is 0.06 mol/l, the deposition time is 30 min, the flow rate is 1 l/min and the temperature is 150$^\circ$C. The surface texturing shows apparent distinction as the concentration of the TiO$_2$ suspension decreased to 0.03 mol/l and 0.01 mol/l.

Keywords: Mist deposition; TiO$_2$ film; TiO$_2$ nanoparticle; Surface texturing; Microstructure

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Introduction

There has been great interest in titanium oxide (TiO$_2$) film due to its chemical stability, high transparency in the visible region, photocatalytic activity and great mechanical durability. The main applications of TiO$_2$ films are in solar cells [1], gas sensors [2], optical coatings [3], photo-catalytic systems [4], and other devices. For many applications, porous TiO$_2$ films have attracted considerable attention because of large surface areas [5], highly ordered porous structures [6], and well-defined pore sizes and porosity [7]. There are various preparation methods of porous TiO$_2$ films such as sol-gel method [8], templating assembly method [9], reverse micelle [10], spray-pyrolysis method [11], aerosol deposition [12] and cathodic electrodeposition [13].

Different from these manufacture techniques, mist deposition has outstanding potential for the development of film with some advantages such as easy and atmospheric operation, simple structure, cheapness etc [14]. A film can be efficiently obtained with rapid deposition rate on large area, even rough and diverse substrate such as polymer, silicon, glass and metal. Because of its ability of being used under low temperature, mist deposition method has more practical value to prepare TiO$_2$ film whose crystal form depends on the temperature in a great extent. Up to now, there is no literature report about the preparation of porous TiO$_2$ film by mist deposition method. For an efficient light trapping in the thin-film solar cell, the textured back reflector which will scatter the light backward resulting in an increase in light path in the absorber layer is verified to be an effective technique to enhance photoelectric conversion efficiency. Such TiO$_2$ film can be applied as a textured reflector due to the rough surface and the high reflective index of TiO$_2$. In this paper, we report the novel technique to prepare TiO$_2$ films with unique surface textures possessing not only porous structure but also ring and chromatic veins by mist deposition method using nanoparticles as starting material at a low temperature. The influence of the concentration of TiO$_2$ nanoparticles suspension on thickness and mor-
phology of film was investigated. In comparison with the uniform TiO$_2$ porous films obtained by other methods, the randomly textured TiO$_2$ film prepared by mist deposition is more suitable for our research purpose because its roughness is high and the angular dependence of reflectance is low on random surface and more incident light can be scattered in the solar cell if such kind of textured TiO$_2$ film used as back reflector.

**Experimental**

The mist deposition process was performed in a self-designed apparatus shown in Fig. 1. The deposition apparatus mainly consists of an atomizing system, a tube, and a heater chamber. For deposition of films, TiO$_2$ nanoparticles suspension (TK-535, 23.6 wt% TiO$_2$ unit, rutile crystal form, Tayca Corp., contains 0.7 wt% HNO$_3$ as the stabilizer) was diluted by water to a certain concentration as the precursor. After the chamber and substrate were heated to 150°C, the mist of TiO$_2$ nanoparticles suspension was atomized by ultrasonic power of transducer (frequency: 2.5 MHz) equipped at the bottom of the solution container, transported into the chamber by N$_2$ carrier gas through a tube of 60°C, and then the mist filled in the chamber and deposited on the substrate. When the frequency of the ultrasonic transducer is 2.5 MHz, the diameter of mist droplet is about 3 μm [15]. A p-type (100) silicon substrate and a glass substrate were used in our experiment, and before being used the silicon one was irradiated by deep UV (Photo surface processor, PL16-110, Sen Light Corp.) for 20 min to introduce hydroxyl group on their surface in order to increase the hydrophilicity and to improve the binding force of substrate/TiO$_2$ nanoparticles. The flow rate was controlled by a glass flowmeter. The mist flow was introduced to a cone-shape nozzle through an epoxy tube, both of which have the inner diameter of 4.2 mm. Then mist deposition was carried out from the cone-shape nozzle to a substrate, and the distance between them is 29.5 mm. All the procedures were carried out under 1 atm of pressure.

In contrast, a flat TiO$_2$ film was prepared by spin coating method on the glass substrate. The TK-535 TiO$_2$ nanoparticles suspension was diluted by water to 10 wt%. Spin coating was carried out using a spin coater (MS-A100, Mikasa Co., Ltd) with a rate of 2000 rpm for 30s at RT in air.

The surface morphology and thickness of the film were investigated using a violet laser scanning microscope (VK 9700, Keyence Corp.) and a scanning electron microscope (XL30, Philips Electronic N.V.), and the structure of TiO$_2$ nanoparticles were detected by micro-Raman spectroscopy.

**Results and discussion**

The characteristic of the TiO$_2$ film was investigated by micro-Raman spectroscopy with the measurement area indicated by Fig. 3(b) as the typical case, and no difference in the micro-Raman spectra was observed with the measurement area changing. Figure 2 is the Raman shifts exhibiting dominant peaks at 140.2, 246.1, 449.5, and 615.7 cm$^{-1}$ which can be assigned as the Raman active modes of rutile crystal phase: $B_{1g}$, multi-photon process, $E_g$, and $A_{1g}$, and the numbers and frequencies of the Raman bands coincide with previous studies [16]. The peak of 1060 cm$^{-1}$ is attributed to NO$_3^-$ of the stabilizer HNO$_3$.

![Fig. 2 Micro-Raman spectrum of TiO$_2$ nanoparticles.](image)

A circular white film formed on the substrate when the concentration of suspension based on TiO$_2$ unit is 0.06 mol/l, the deposition time is 30 min and the flow rate is 1 l/min. The morphologies showed a remarkable dependence on the viewing areas of sample, in other words, the morphologies depend on the thickness of the film. The micrographs and 3D images of the TiO$_2$ film observed by laser scanning microscope at varied positions are shown in Fig. 3. In the center of sample (Fig. 3(a)), there is a thick, flat and white film with the thickness of about 11.4 μm and the root mean square roughness ($R_q$) of 0.21 μm. At the site of 843 μm from...
the center (Fig. 3(b)), there are some pores and raised, crossed and white lines like veins on the film, where the depths of the pores are 1.22~1.63 μm and the diameters are estimated to be 2.38~6.21 μm. The thickness of film is approximately 4.73 μm, the width of vein about 2.15 μm and the $R_q$ is 0.5 μm which means that this film is rougher than other textured films previously reported [17]. A little farther away, about 1236 μm from the center (Fig. 3(c)), the bottom of the pore becomes chromatic due to the interference phenomenon of light occurring when the bottom is enough thin. The depth and diameter of the pore are similar to image b, while the thickness of the film decreases to 1.34 μm, the vein width is approximately 1.89 μm, and the $R_q$ is 0.39 μm. When the viewing area continues to move to the edge of the sample and is 1833 μm from center, it can be observed that chromatic veins and bottom appeared (Fig. 3(d)). The thickness of the film is about 160 nm and the bottom is approximately 67 nm. The lines of veins become thinner to 0.88 μm and $R_q$ is 0.14 μm. More close to the edge about 2937 μm from center (Fig. 3(e)), there are many colorized rings with the thickness in 96~138 nm range and the diameter 17.01~23.93 μm on the substrate. On the edge of sample 3672 μm off the center (Fig. 3(f)), only several separated rings can be observed, the thickness of which changes from 71 nm to 136 nm gradually, and the diameter is in the range of 14.35~20.16 μm. Because the diameter of the mist is about 3 μm which is obviously smaller than that of the ring, the extension of it as a result of its flattening must be caused after the deposition on the substrate. TiO$_2$ nanoparticles were transferred to the edge of the flattening droplet from the drop point, and then the nanoparticles were fixed on the edge by the interaction with the substrate accompanying the evaporation of the water. The distribution of the ring size as shown in Fig. 3(f) is narrow due to the homogeneity of the mist size which depends on the frequency of a transducer. The overlapping of the ring structure of TiO$_2$ nanoparticles forms the porous structure as shown in Figs. 3(b), 3(c), and 3(d) with the film thickness increasing. Such roughness remarkably influenced the reflectance properties of the film. The angular dependence of the reflectance of the textured TiO$_2$ film on a glass substrate was compared with a TiO$_2$ nanoparticles film prepared by spin coating method. The decrease of the reflectance of the textured TiO$_2$ at 600 nm was ca. 40% whereas that of a flat TiO$_2$ spin-coated film was 99.48% at 60° between the incident light and perpendicular of film surface. This result means that the textured TiO$_2$ film formed by mist deposition has the potential to be applied as a reflector.

The concentration of TiO$_2$ nanoparticles as the significant affecting factor on the morphology was investigated as shown in Fig. 4. When the concentration of suspension decreased, different surface texturing could
be observed by laser scanning microscope. Figure 4(a) depicts the typical morphology of the sample gotten with the concentration of 0.03 mol/l. It can be seen that some disordered and discontinuous rings appeared and part of the ring is white but the other part is fuscous due to the difference of the thickness. The thickness of white part of the ring is in the range of 70~109 nm while fuscous part is approximately 33~42 nm, and the diameters is about 19.9~20.79 μm. When the concentration was further reduced to 0.01 mol/l, a structure of some connected small chromatic rings was observed as shown in Fig. 4(b), whose thickness is 105 nm, external diameter about 1.13~3.02 μm and width 504 nm. In the case of the droplet with a low concentration of TiO$_2$ nanoparticles, the aggregation of the nanoparticles does not occur remarkably on the edge of the flattening droplet, and then nanoparticles return the drop point with contraction of the flattening droplet. Two connected rings would be formed if a droplet deposited on the substrate adjoining another one previously formed. The morphology as shown in Fig. 4a presents an intermediate case, where there are aggregated and non-aggregated nanoparticles. The aggregated nanoparticles form a ring structure and the non-aggregated nanoparticles form a disordered structure inside the ring.

A close examination of the microstructure has been carried out by SEM. Figure 5(a) and 5(b) were taken from the same position as Fig. 3(b), indicating that there are many blind-holes in the film like lotus seed pod structure. Figure 5(c) and 5(d) exhibit the images of separated ring shown in Fig. 3(f) and it can be observed that the nanoparticles are in short rod-like shape with length of approximately 80~90 nm and width of 25~35 nm. Judging from the SEM images, the shape and size are almost uniform and the nanoparticles are monodisperse particles. If Fig. 4(b) is enlarged by SEM, we can get the images like Fig. 5(e) and 5(f) in which some connected rings exist. Contrast to Fig. 5(c) and 5(d), this kind of ring is not regular and the diameter is smaller.

**Conclusion**

Using rutile phase TiO$_2$ nanoparticles as a starting material, we demonstrated the successful formation of porous TiO$_2$ films by the mist deposition method which is effective, inexpensive, easily-operated and practical at the temperature as low as 150°C and the pressure of 1 atm. Additional advantages of the mist deposition method using nanoparticles as starting material include the controllability of the microstructure and the surface texturing of film. Some unique and various microstructures of TiO$_2$ could be formed, such as macroporous structure, chromatic veins and rings. The significant varying surface morphology including irregular rings and small chromatic rings can be gotten as the concentration of TiO$_2$ nanoparticles suspension decreases.
Fig. 5 SEM images of the surface textures of TiO$_2$ film prepared by mist deposition method.

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Thermal Evaporation Deposition of Few-layer MoS$_2$ Films

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Abstract: We present a study of the fabrication of monolayer MoS$_2$ on n-Si (111) substrates by modified thermal evaporation deposition and the optoelectrical properties of the resulting film. The as-grown MoS$_2$ ultrathin film is about 10 nm thick, or about a few atomic layers of MoS$_2$. The film has a large optical absorption range of 300-700 nm and strong luminescence emission at 682 nm. The optical absorption range covered almost the entire ultraviolet to visible light range, which is very useful for making high-efficiency solar cells. Moreover, the MoS$_2$/Si heterojunction exhibited good rectification characteristics and excellent photovoltaic effects. The power conversion efficiency of the heterojunction device is about 1.79% under white light illumination of 10 mW/cm$^2$. The results show that the monolayer MoS$_2$ film will find many applications in high-efficiency optoelectronic devices.

Keywords: Monolayer MoS$_2$; Thermal evaporation deposition; Absorption spectrum; $I$-$V$ behavior

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Introduction

Two-dimensional materials have attracted much interest for their interesting physics and possible use in electronic devices [1,2]. Molybdenum disulfide (MoS$_2$) is a sandwich-like compound in which a metal atom is bonded to six sulfur atoms, and each layer is linked by a weak Van der Waals force [3]. Analogous to graphene, MoS is easily split into a layered structure. A monolayer MoS$_2$ sheet undergoes a large transformation of the energy band gap from an indirect to a direct one [4,5]. With a large direct energy band of 1.8 eV [3], high electron mobility [6], reduced dimensionality, and favorable mechanical properties [7], single- or few-layer MoS$_2$ has attracted interest for novel nanoscale electronic and optical applications [6,8]. Transistors fabricated with MoS$_2$ atomic thin layers exhibit an excellent on/off current ratio and high carrier mobility, which make them suitable as next-generation transistors [6]. The optical and electronic properties of MoS$_2$ also make it a potential candidate for efficient solar energy cells [9,10] and for use as a cathode in high-density lithium batteries [11,12]. In these devices, the fabrication of a thin MoS$_2$ film and investigation of the electrical properties of the MoS$_2$ heterojunction system are the most commonly encountered processes. Monolayer MoS$_2$ films have been prepared by a variety of techniques such as an adhesive-tape-based micromechanical cleavage technique commonly associated with the production of graphene [6], lithium-based intercalation [13,14], chemical vapor transport [15,16], and metalorganic chemical vapor deposition [17]. The preparation process or equipment used in these approaches is very complex. In this work, the objective of our research was to find a simple method of fabricating a MoS$_2$ film of atomic thickness and study its optical and electronic properties. Thin MoS$_2$ films were prepared by modified thermal evaporation deposition. Then we investigated their morphology and optical and electrical characteristics.

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Experimental

The MoS$_2$ films were fabricated on $n$-Si (111) surfaces by a modified thermal evaporation vapor deposition process. The growth system consists of a large horizontal quartz tube furnace, a vacuum system, a gas meter, and an automatic temperature controller. The $n$-Si substrates 15×15 mm$^2$ in size were cleaned ultrasonically with a sequence of acetone, ethanol, and deionized water, and then they were blown dry with N$_2$ and placed at the center of the furnace. Before deposition, the furnace was pumped to 10$^{-2}$ Pa and heated to 300°C for 10 min to remove any water moisture. In the traditional evaporation technique, the source material is put in an open pot and evaporated by heating. It is hard to control the growth speed and thickness of the deposited film. In our experiment, the source material, analytically pure MoS$_2$ powder, was first pressed into tablets and sintered for 20 min at 300°C. One tablet was placed in a closed cubic iron box with many pinholes on one side, which was positioned at the front end of the quartz furnace. In the MoS$_2$ film deposition process, MoS$_2$ molecules evaporated from the tablet and became MoS$_2$ molecular beams by passing through the pinholes of the closed box; this technique can enable the deposition of a MoS$_2$ film at a very low speed. To obtain uniform growth, Ar gas with a volume ratio of 10~30 sccm was introduced into the reactive chamber at 500°C, and the working pressure was kept at 50 Pa. After MoS$_2$ molecules were absorbed and condensed on the Si substrates, thin MoS$_2$ films were formed by varying the evaporation time between 2 and 10 min. Finally, the samples were removed after the system cooled to room temperature. $Al$ contact electrodes (2×2 mm$^2$, 300 nm) were formed by thermal evaporation through a shadow mask at the corner of the MoS$_2$ and the back side of the Si substrates.

The morphology and structure of the samples were characterized by atomic force microscopy (AFM). The structure was analyzed by X-ray diffraction (XRD) using a RINT2000 vertical goniometer with Cu $K_a$ radiation ($\lambda = 0.1541$ nm). The optical absorption spectrum of the MoS$_2$ films was investigated by ultraviolet-visible (UV-vis) spectroscopy (Shimadzu UV-3600). Finally, the photovoltaic characteristics of the MoS$_2$/Si heterojunction solar cells were evaluated by a Keithley 4200 SCS instrument under white light illumination.

Results and discussion

Figure 1(a) shows an AFM image of the deposited MoS$_2$ film on the $n$-Si substrate. Many MoS$_2$ slices or islands are scattered uniformly at the top of the picture. From the scales of bottom and right of Fig. 1(a), we can estimate the slices are about 50-200 nm in length and 5-6 nm thick, which is about ten layers of MoS$_2$ (a mono layer about 0.65 nm). In the sublayers of the slices, we can see that there is a large, uniform, continuous MoS$_2$ film with a deep yellow color. We confirmed that the MoS$_2$ film grows in layer-island mode. That is, MoS$_2$ islands form on the substrate initially; then the islands gradually combine with each other and become a continuous film, on which new islands are formed continuously over time. This growth mode corresponds to the characteristics of the layered structure of MoS$_2$. Figure 1(b) shows the XRD pattern of the as-grown MoS$_2$ sample. Four strong diffraction peaks are located at 13.4°, 28.3°, 33°, and 36.7°, corresponding to the (002), (004), (100), and (101) crystal planes of MoS$_2$, respectively.

Fig. 1 (a) AFM image of MoS$_2$ film deposited on $n$-Si substrate. MoS$_2$ islands are about 50-200 nm in length and 5-10 nm thick, equaling ten layers of MoS$_2$. (b) XRD pattern of MoS$_2$ film.

The optical absorption properties of the MoS$_2$ film samples were measured at room temperature, as shown in Fig. 2. The deposited MoS$_2$ thin film has strong optical absorption at wavelengths 627 nm and 690 nm, that is, the strong absorption is just in visible light range of 400-700 nm. According to A. Splendiani [3], these two resonances have been well established to be the direct excitonic transitions at the Brillouin zone $K$ point. The observed absorption peaks at 1.79 eV (690 nm) and 1.98 eV (627 nm) correspond to the A1 and B1 direct excitonic transitions with the energy split from valence band spin-orbital coupling. Above 700 nm, the
absorption intensity drops abruptly, and no other absorption peaks are appeared. This can be defined as the absorption edge of MoS$_2$, corresponding to intrinsic absorption by the direct energy band gap of MoS$_2$. For intrinsic semiconductor absorption, the electrons in the valence band absorb optical energy and transmit it to the conduction band. The absorbed optical energy is given by $h\nu = E_c - E_v = E_g$, where $E_c$ is the energy of the conduction band, $E_v$ is that of the valence band, and $E_g$ is the band energy gap. From the absorption edge, we can estimate the energy band gap of MoS$_2$ to be about 1.79 eV, very close to the energy band of 1.8 eV [6], showing that the as-grown MoS$_2$ thin film deposited had a large direct energy band gap. Moreover, the optical absorption covered almost the entire UV-vis wavelength range of 300-700 nm, which is very useful for making high-efficiency solar cells.

![Optical absorption spectrum of MoS$_2$ film samples. Strong absorption covered almost the entire UV-vis wavelength range of 300-700 nm.](image)

Figure 2 shows the absorption spectrum of the MoS$_2$ thin film measured at room temperature. It exhibits strong red emission peaking at 690 nm, which originates from the band-to-band emission of MoS$_2$ [18], where the excited electrons undergo transitions from the conduction band to the valence band. The emission peak of 690 nm corresponds to energy of 1.79 eV, which is quite consistent with the absorption edge of 690 nm in Fig. 2. The position of the PL emission offers more precise measurement of the energy band gap than that of the absorption edge. In addition to the absorption spectrum Fig. 3, no other absorption bands from indirect band gap (1.2 eV) appeared, we can drive that the deposition MoS$_2$ thin film exhibits the characteristics of this direct energy band. Moreover, as-grown MoS$_2$ films prepared using conventional deposition methods usually require additional treatment, such as surface modification and annealing, to obtain prominent PL emission. In our experiment, the MoS$_2$ sample achieved the strong red PL emission through simple thermal evaporation deposition with no additional treatment, showing that the as-grown MoS$_2$ films are of high quality [3].

![Photoluminescence (PL) spectrum of pure MoS$_2$ thin film measured at room temperature. It exhibits strong emission peaking at 690 nm.](image)

Figure 3 shows the photoluminescence (PL) spectrum of the MoS$_2$ thin film measured at room temperature. It exhibits strong red emission peaking at 690 nm, which is very close to the energy band of 1.8 eV [6], showing that the as-grown MoS$_2$ thin film deposited had a large direct energy band gap. The emission peak of 690 nm corresponds to energy of 1.79 eV, which is quite consistent with the absorption edge of 690 nm in Fig. 2. The position of the PL emission offers more precise measurement of the energy band gap than that of the absorption edge. In addition to the absorption spectrum Fig. 3, no other absorption bands from indirect band gap (1.2 eV) appeared, we can drive that the deposition MoS$_2$ thin film exhibits the characteristics of this direct energy band. Moreover, as-grown MoS$_2$ films prepared using conventional deposition methods usually require additional treatment, such as surface modification and annealing, to obtain prominent PL emission. In our experiment, the MoS$_2$ sample achieved the strong red PL emission through simple thermal evaporation deposition with no additional treatment, showing that the as-grown MoS$_2$ films are of high quality [3].

The surface carrier concentration and electron mobility of the MoS$_2$ film were determined by Hall effect measurement. The surface current-voltage ($I$-$V$) plot of the MoS$_2$ film is shown in Fig. 4(a). It shows four perfectly linear $I$-$V$ lines corresponding to four typical measurement points. From the measurement, we determined that the surface carrier concentration of the samples is about $10^9$ cm$^{-2}$. The electron mobility is $5.1 \times 10^2$ cm$^2$/V·s, which is much greater than that of the monolayer MoS$_2$($3.06 \times 10^2$ cm$^2$/V·s) [6]. The current behavior of the MoS$_2$/Si heterojunction is shown in Fig. 4(b), the insert is the structure of the heterojunction. The heterojunction is conducted by on and down Al electrodes. Remarkably, the device shows good rectification characteristics. The current increases exponentially with the applied positive voltage, whereas it is almost zero when a reversed voltage is applied. Figure 4(c) shows the devices’ pronounced photovoltaic effects when they are illuminated by white light with an intensity of 10 mW/cm$^2$. The current density is plotted versus bias voltage for the MoS$_2$/Si heterojunction device. The device shows a much improved open circuit voltage $V_{oc}$ of 0.39 V, and the short-circuit current density ($J_{sc}$) is 0.46 mA/cm. The power conversion efficiency of the MoS$_2$/Si heterojunction device is about 1.79%.

**Conclusions**

We fabricated a MoS$_2$/n-Si heterojunction and studied its optical and electrical properties. The as-grown MoS$_2$ thin film is about 10 nm thick, which equals ten layers of MoS$_2$. The optical absorption covered almost the entire UV-vis wavelength range, which is very useful for making high-efficiency solar cells. Further, the MoS$_2$ thin film produced strong optical luminescence emission at 690 nm. Moreover, the heterojunction exhibited good rectification characteristics and excellent photovoltaic effects. The power conversion efficiency of the MoS$_2$/Si heterojunction device is about 1.79% under white light illumination of 10 mW/cm$^2$. 

![Figure 2](image)
Fig. 4 (a) Surface $I - V$ behavior of MoS$_2$ film obtained by Hall effect measurement; (b) $I$-$V$ characteristics of the MoS$_2$/Si heterojunction, which exhibits good rectification characteristics; (c) Pronounced photovoltaic effects of the MoS$_2$/Si heterojunction illuminated by white light with an intensity of 10 mW/cm$^2$.

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Giant Magneto-impedance Effect in Composite Wires with Different Core Layer

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Introduction

The giant magnetoimpedance (GMI) effect was firstly observed in Co-based amorphous wires by Mohri \textit{et al} in 1992 \cite{1}. It has attracted much interest due to its stability and small size for potential applications in highly sensitive magnetic sensors. Many researchers have investigated GMI effect in different soft magnetic materials including homogeneous and composite materials \cite{2-6}. It was found that GMI origins from classical electrodynamics, which relates to inductive effect, skin effect and ferromagnetic resonance. GMI effect is a preferable way to verify domain structure and saturation magnetostriction coefficient of magnetic materials as a research tool \cite{7}. Simultaneously magnetometer based on GMI effect was developed in practical applications \cite{8}.

GMI effect can be improved by using suitable amorphous or nanocrystalline soft magnetic materials with special geometric structures (microwire, ribbon and thin film) under optimized heat-treatment conditions \cite{9-15}. For composite structures, such as composite wires and sandwiched films, their GMI ratios are much larger than those of homogeneous samples with the same dimensions and of similar ferromagnetic materials. The possible mechanism is enhancement of the skin effect due to electromagnetic interactions. If an insulator layer is added between two layers, composite wires with ferromagnetic core (CWFC) and composite wires with conductive core (CWCC) can be produced \cite{16,17}. The GMI effect may be further enhanced if the thickness of the insulator is suitable for CWCC. The influence of conductive layer for CWFC is not too much. The mechanism is still unclear until now.

Among a variety of techniques for preparation of composite wires, such as electrodeposition \cite{10} and...
magnetic sputtering [12,13], electroless deposition was believed to be the most suitable method due to its ability to provide uniform surface and cost-effectiveness of the fabrication process [14]. In this work, CWFC and CWCC are prepared using an electroless deposition method. Their GMI properties were comparatively studied.

Experimental

The detailed fabrication processes of two kinds of composition wires were reported in our previous work [16]. Firstly, the amorphous microwires of Fe73.0Cu1.0Nb1.5V2.0Si1.5B9.0 were prepared by a glass-coated melt-spinning method [19]. Then, the microwires were annealed at 570°C for 30 min in nitrogen atmosphere to improve their soft magnetic properties. Finally, a layer of copper was deposited onto the microwires by using an electroless deposition method, and the composite wires with ferromagnetic core were obtained.

The composite wire with conductive core, that is, with Cu/insulator/NiCoP structure, was also produced by using an electroless deposition. The Cu wires were carefully cleaned with distilled water and their surface was activated by Pb/Sn particles before being mounted and placed into the electroless deposition bath. The bath composition contains NiSO₄·6H₂O, CoSO₄·7H₂O, Na₂C₂H₄O₂·2H₂O and Na₂C₆H₅O₇·2H₂O. Operating temperature was controlled at 363 K using a water bath and pH value is maintained at ~11. The deposition products were annealed at 200°C to improve their soft magnetic properties.

The surface and the thickness of the plated layer of the samples were observed on scanning electron microscope (SEM, JSM-5610LV). The GMI effect was measured on an impedance analyzer (HP4294A). The constant alternating current \( I_{rms}=5 \) mA flows through the metallic nucleus and the frequency ranges from 40 Hz to 110 MHz. The ratio was defined as,

\[
\frac{\Delta Z}{Z} (%) = 100 \times \frac{Z(H_{ex}) - Z(H_{max})}{Z(H_{max})} \tag{1}
\]

\[
\frac{\Delta R}{R} (%) = 100 \times \frac{R(H_{ex}) - R(H_{max})}{R(H_{max})} \tag{2}
\]

\[
\frac{\Delta X}{X} (%) = 100 \times \frac{X(H_{ex}) - X(H_{max})}{X(H_{max})} \tag{3}
\]

where \( Z, R, X \) are impedance, the real and imaginary component of the impedance, respectively. \( H_{ex} \) and \( H_{max} \) are an arbitrary and maximum intensity of external magnetic field, respectively. The DC external magnetic field was generated by a pair of Helmholtz coils.

Results and discussion

Figure 1 shows a typical SEM view of the two kinds of composite wires. It can be seen that the wires are composed of different layers and the plated surface is smooth. For CWFC wires as shown in Fig. 1(a), the diameter of ferromagnetic core is 7.0 µm. The thickness of coated glass layer and outer conductive layer is respectively 1.0 µm. For CWCC wires as shown in Fig. 1(b), the diameter of copper core is 90 µm. The thickness of coated Polyester ethylene is 5.0 µm and outer ferromagnetic layer is 7.0 µm. Figure 1(c) and 1(d) show the cross-section schematic diagrams of two kinds of composite wires.

The MI effect curves for glass-coated microwires annealed at 570°C tested at different frequencies are shown in Fig. 2. It can be seen that the maximum MI ratio is 118% at 60 MHz. A monotonic decrease of the MI effect curve was observed at low testing frequency. However, at high testing frequency, the MI ratio increases initially with \( H_{ex} \) till it reaches a peak and then falls with further increase of the external field. The MI effect is closely relative to the change in circumferential permeability of the wire with respect to the external field. At low frequencies, the domain wall displacement dominates to the magnetization process [18]. The circumferential permeability decreases with increasing external magnetic field. Along with the increasing of the driving frequency, the domain wall displacement is nearly damped and moment rotation will dominate the magnetization process.

Comparing to the microwires, the MI curves of the CWFC display the similar trend, as shown in Fig. 3. The maximum MI ratio is found to be 114% at 60 MHz.
The dependence of the maximum MI ratio on the driving frequency for the CWFC and the microwires is given in Fig. 4. It can be seen that the GMI magnitude of the CWFC is different from that of the microwires. The MI ratio of the CWFC is higher than that of the microwires when the testing frequency is less than 60 MHz. However, the results are just the opposite when the testing frequency is more than 60 MHz. The circumferential permeability changes due to the electromagnetic interaction between the copper layer and ferromagnetic core [16].

The above mentioned results show that the eddy current in the copper layer is induced by the electromagnetic interactions, though AC current flows only through the ferromagnetic core. The magnetic field induced by the eddy current will in turn magnetize the ferromagnetic core, which will strengthen the dynamic magnetization at low frequencies. With the increase of the driving frequency, the influence of eddy current becomes more obvious. When the frequency is up to 60 MHz, the circumferential permeability is greatly reduced by eddy current loss. Thus the MI ratio decreases. However, the effect of copper layer is not remarkable in such kind of composite wires.

The external field dependence of MI ratio for the CWCC is illustrated in Fig. 5. It can be seen that the samples exhibit a peak MI ratio in variation with the external magnetic field, even at low testing frequencies. The MI ratio increases initially till it reaches a peak and then falls with further increase of the field. As it’s mentioned above, the MI effect is relative to the changes in circumferential permeability with respect to the external field. The circumferential magnetization mainly proceeds via moment rotation for such kind of composite wire even at low frequencies. A maximum MI ratio of 116% was obtained at 600 kHz. The CWCC indicates obvious MI effect at low frequencies.

To study the different influence of electromagnetic interaction on the two kinds of composite wires, the frequency dependences of \( \Delta Z/Z \), \( \Delta R/R \), \( \Delta X/X \) of CWFC and CWCC have been depicted in Fig. 6 and its inset, respectively. It can be found that the maximum GMI ratio for the CWFC is 114% at 60 MHz, and its maximum \( \Delta R/R \) ratio is 111% at 60 MHz. The CWCC reaches its maximum value of 116% at 600 kHz. Its maximum \( \Delta R/R \) ratio achieves 205% at 2 MHz.
According to definition of impedance, \( Z = R + iX \), the GMI ratio can be written as,

\[
\Delta Z/Z = \frac{\sqrt{(R + \Delta R)^2 + (X + \Delta X)^2} - \sqrt{R^2 + X^2}}{\sqrt{R^2 + X^2}}
\]  \hspace{1cm} (4)

Therefore, GMI ratio does not only depend on \( \Delta R/R \) and \( \Delta X/X \), but also on the ratio of \( R \) to \( X \). The resistivity of Cu core (\( \sim 1.75 \times 10^{-8} \Omega \cdot m \)) is very smaller than that of Cu. The values of \( R \) and \( X \) for CWFC are not comparable at low frequencies. Hence the CWCC has better MI properties at low frequencies.

Conclusions

In summary, the difference of the MI effect in two kinds of composite wires was investigated. The maximum MI ratio of 114% was achieved in CWFC at 60 MHz. Comparing to the microwires, the GMI effect of the CWFC strengths at low frequencies due to electromagnetic interaction. However, the effect is not remarkable. The CWCC shows better MI effect at lower frequencies, the maximum MI ratio of 116% was observed at 600 kHz. The results exhibit that the MI ratio reaches the maximum when both \( \Delta R/R \) and \( \Delta X/X \) make the comparative contribution to the total MI ratio. At low frequencies, \( \Delta R/R \) has been obvious for CWCC. Hence the CWCC has better MI properties at low frequencies.

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