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The Prospective Two-Dimensional Graphene Nanosheets: Preparation, Functionalization, and Applications

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(Received 10 December 2011; accepted 20 December 2011; published online 10 January 2012.)

Abstract: Graphene, as an intermediate phase between fullerene and carbon nanotube, has aroused much interests among the scientific community due to its outstanding electronic, mechanical, and thermal properties. With excellent electrical conductivity of 6000 S/cm, which is independent on chirality, graphene is a promising material for high-performance nanoelectronics, transparent conductor, as well as polymer composites. On account of its Young’s Modulus of 1 TPa and ultimate strength of 130 GPa, isolated graphene sheet is considered to be among the strongest materials ever measured. Comparable with the single-walled carbon nanotube bundle, graphene has a thermal conductivity of 5000 W/(m·K), which suggests a potential application of graphene in polymer matrix for improving thermal properties of the graphene/polymer composite. Furthermore, graphene exhibits a very high surface area, up to a value of 2630 m²/g. All of these outstanding properties suggest a wide application for this nanometer-thick, two-dimensional carbon material. This review article presents an overview of the significant advancement in graphene research: preparation, functionalization as well as the properties of graphene will be discussed. In addition, the feasibility and potential applications of graphene in areas, such as sensors, nanoelectronics and nanocomposites materials, will also be reviewed.

Keywords: Graphene; Graphite oxide; Functionalization; Sensors; Transparent conductive films; Nanocomposites

Introduction

Graphene, a nanometer-thick two-dimensional analog of fullerenes and carbon nanotubes, comprises a two dimensional layer of sp²-hybridized carbon atoms, arranged in a hexagonal lattice. Due to its exceptionally outstanding electronic, mechanical, and thermal properties, graphene has aroused much interests among the scientific as well as technology community [1]. More and more publications have emerged focusing on this nanomaterial since 2004 (Fig. 1), not only in the synthesis/production of graphene, but also in its implementation in sensors, field emitters, nanoelectronics, nanocomposite materials, and so on. Therefore, it becomes timely to review and summarize the synthesis and processing of graphene for functional nanostructures and devices [2-9].

In this review, we will discuss the progress of the research on the synthesis of the graphene from the materials chemistry and physics standpoint. An overview of the preparation and properties of graphene will also be discussed. In addition, the feasibility and poten-
tial applications such as sensors, nanoelectronics, and nanocomposite materials will be reviewed as well.

**Preparation of graphene**

Majority of the studies on graphene have been focused on the synthesis of single-layer or few-layer graphene. Table 1 summarizes the main methods used for production of graphene, covering the merits as well as the shortcomings of each method.

From highly ordered pyrolytic graphite (HOPG) to the final products, Geim and his colleagues rubbed lithographically patterned pillars and used Scotch tape to perform the thinning of the graphite stuck to the SiO$_2$/Si sheets [10]. This mechanical exfoliation method is very easy, and the graphite materials can be readily obtained. Furthermore, single graphene sheet with high quality, applicable in the fabrication of electronic devices, can be easily prepared. However, the device fabricated by this method is very complex, and the reproducibility cannot be assured. Despite of this drawback, many unexpected electronic properties of the graphene sheet can be explored by this method.

| Method               | Mechanical exfoliation | Epitaxial growth | graphite oxide-reduced |
|----------------------|------------------------|------------------|------------------------|
| Merits               | Low cost, easy way without any special equipment | Large area of even film can be obtained, amiable for microelectronic application | Suitable for large scale production; Easy control in the solvent for application in various fields. |
| Disadvantages        | Only for laboratory research Very hard to control (hard to obtain uniform film) | High-temperature operation required | The lateral size is limited; The reduction is usually partial. |

Table 1 Main methods for the production of graphene

As micromechanical cleavage of HOPG was first employed to obtain single-layer graphene [10], various methods of graphene synthesis have been reported, including epitaxial growth on an insulator surface such as SiC [11] and chemical vapor deposition (CVD) on surfaces of transition metals such as Ni and Cu [12,13]. Comparing with the mechanical exfoliation method, this method is very suitable for the industrial production of single-layer graphene with large areas, which have great potential application as sensors and transparent conductive films. Although great progress has been achieved by this method, there are still many challenges for us to face, such as the choice of the substrate, how to lower the operation temperature, and so forth.

Chemical reduced graphene (CGR) has aroused much interests due to its relatively easy large-scale production [14]. Through reduction of graphite oxide (GO) suspended in water [15] or organic solvents [16,17], CGR can be easily obtained. Usually, there are three main routes to form GO: Brodie’s method [18], Staudenmaier’s method [19] and Hummers’ method [20]. Hummers’ method is commonly exploited today, and many modified Hummers’ methods have been reported, optimizing the GO production process. The recent review by Dreyer is an excellent, succinct source of further information on preparation, structure, and reactivity of GO [21]. Many kinds of reducing agents, such as hydrazine [22], NaBH$_4$ [23], ethylenediamine [24], Al powder [25], ascorbic acid [26], and p-phenylene diamine [27] have been used to reduce GO and disperse the resultant CGR in the solvent, which is beneficial for further nanocomposite preparation and device fabrication. UV irradiation method [28] has also been reported to reduce GO in aqueous dispersion. TiO$_2$ nanoparticles play an important role in the reduction process. Guo et al. [29] has reported that electrochemical reduction could work very well for the reduction of GO, which is a green approach to obtain CGR in aqueous dispersion. Recently, Li et al. [30] reported a dry microwave synthesis method to obtain CGR, which can be considered to be the most efficient route to date in preparing CGR in the large scale.

**Functionalization of graphene**

Pristine graphene exhibits poor solubility in both water and organic solvents. Therefore, it is necessary to modify this nanomaterial with functional groups, in order to enhance its dispersity in various solvents.

**Covalent functionalization**

Since solution-based chemical reduction of graphite
oxide to graphene is a very easy method for large scale production of graphene, it is a great challenge for this method to be adopted for individual graphene sheets having high dispersity in different solvents in a bulk quantity. Since GO possesses several functionalities such as hydroxyl, carboxyl, and carbonyl, it is rather straight forward to be transformed to other functional groups through acylation or esterification [21,31]. Through chemical reduction of GO by reducing reagents or thermal treatment, the covalently functionalized graphene can be formed, resulting in a much better dispersity in water or organic solvents. In order to enhance the hydrophilicity or lipophilicity of graphene, some small molecules and polymers, can be introduced to the plane of graphene, through radical addition reaction [32], cycloaddition reaction [33], or diazonium salts reaction [34] during the in situ reduction of GO into graphene. As a result, this would lead to a much better dispersity of graphene in water or organic solvents. Molecules, with special functional applications, can also be attached onto the surface of graphene, resulting in new properties for the functionalized materials. For example, porphyrin (5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin) is bonded onto graphene oxide by an amino bond. This new functionalized graphene has better optical limiting properties than C60, which could be used in the field of optical switching and other areas [35]. Graphene nanoribbons are successfully functionalized by aryldiazonium salts, with concentration of the functionalized graphene in N-methyl-2-pyrrolidone and N,N-dimethylformamide up to 1 mg/mL. Thickness of graphene nanoribbons are increased due to the covalent attachment between the functional groups and graphene. Therefore, graphene films, nanotubes and other nanomaterials may be functionalized by this method in the future [36]. Graphene, functionalized by model glucose oxidase and immobilized on the polypyrrole-modified electrode surface, exhibits a high sensitivity (3μM), as well as a stable and steady response. It is utilized for glucose detection and could be applied in the field of electroanalytical chemistry. It is also used in the measurement of the plasma glucose level for diabetes diagnosis [37].

Noncovalent functionalization

The noncovalent functionalization of graphene is achieved by van der Waals forces or π-π stacking. Noncovalent functionalization generally has little effect on the original properties of the graphene. Natural polymers (lignin and cellulose derivatives) are adsorbed on the graphene surface by hydrophobic interaction and π-π stacking. Indeed, functionalized graphene can be kept in stable condition at high concentration (0.6-2 mg/mL) in water [38]. Sulfonated polyaniline (Fig. 2(a)) has good stability, electrochemical properties and water solubility, and is therefore used for the non-covalent functionalization of graphene sheets. This new functionalized graphene is soluble in water at high concentrations (> 1 mg/L) and exhibits good conductivity, with potential application in the field of electrochemistry [39]. Graphene oxide has been functionalized with end-functional polymers which includes polystyrene (-NH2), polystyrene (-COOH) and poly (methyl methacrylate) (-OH). The successive reduction makes sure that the electrical structure of the C atom on the graphene plane does not change, and the new functionalized graphene is soluble in solvents such as N-methyl-2-pyrrolidone, N, N-dimethylformamide, ethanol, and methanol for duration of up to one month [40]. Graphene can be functionalized by a small molecule of methylene green (Fig. 2(b)), with good dispersity in the water. The functionalized graphene is well dispersed on the electrode surface and be readily accessible by redox probes and ions. In addition, this functionalized graphene has high electrochemical and electrocatalytic activity towards nicotinamide adenine dinucleotide [41]. Graphene functionalized with tetrapotassium salt of coronene tetracarboxylic acid (Fig. 2(c)) is a blue fluorescent material as well as an electron-acceptor. From AFM and TEM studies, it has been reported that coronene molecules assist to exfoliate few-layer graphene as well as disperse single-layer and double-layer graphene [42]. The resulting graphene could be used to build electronic devices.

Applications of graphene

Graphene based sensors

Early research shows that graphene possesses excellent electronic and other interesting properties, suggesting that graphene is a promising material for sen-
sors. The operational principle for graphene sensors is based on the change of electrical conductivity in graphene. When gas molecules are adsorbed onto the surface of graphene, charge transfer takes place between gas molecules and graphene [43]. It means that the adsorbed gas molecules are acting as charge donors or acceptors. This charge transfer results in the change in graphene’s carrier concentration. Therefore, the electrical conductivity of graphene would be changed. Meanwhile, some interesting properties of graphene combine synergistically to increase its sensitivity up to single atom or molecular level detection. Firstly, graphene is a practical two-dimensional material with all atoms exposed to the environment [44]. Secondly, graphene is highly conductive (graphene’s electrical conductivity is far better than that of copper), which means a little change in electrical properties would cause a notable signal. Thirdly, graphene has very few crystal defects, which could come up with noise by thermal minimum [45,46]. Finally, large-area ohmic contacts observed in graphene contribute to the reduction of resistance, resulting in making the measurements more convenient [44,47].

Schedin et al. [44] first investigated graphene-based sensors in 2007. Since then, there have been a lot of reports on the sensing by graphene. According to Schedin’s report [44], graphene demonstrates good sensing properties towards NO₂, NH₃, H₂O and CO. Going through vacuum annealing at 150°C or UV illumination for seconds, sensors based on graphene can be fully recovered. Utilizing enzymes and multi-layered graphene, Lu et al. [48] fabricated a sensitive glucose biosensor immobilized in Nafion. Attributing to the high sensitivity and selectivity, the authors suggested that the glucose biosensor based on multi-layered graphene could be an inexpensive alternative to carbon nanotubes for the fabrication of affordable high performance biosensors. By utilizing the four-point electrode system, Fowler et al. [47] suggest that electrode electrical contacts play a minimum role in the sensing mechanism of graphene. The sensing mechanism is primarily due to charge transfer between molecules and graphene. Sundaram et al. [49] chemically modified graphene surface by electrodeposition of Pd nanoparticles. This procedure may be advantageous, as the attached catalyst particles are expected to enhance sensitivity toward certain analytes, which cannot be directly detected by the unmodified material, due to insignificant response. The electro-deposition of Pd on graphene leads to the enhancement of the response of graphene sensors to H₂ detection, as Pd has good affinity towards H₂ detection.

With these key observations and results reported, graphene-based sensors have aroused great interests. However, there are several limitations for these devices. For example, it is absolutely mandatory to improve on the issue of selectivity. A sensor would be useless if it responds in a similar way when exposed to any analyte. Fortunately, the selectivity issue can be overcome by the use of judicious chemistry to modify the graphene surface, which results in selective adsorption and provides specific binding sites. Such an approach would not only provide selective sensitivity to a large variety of chemical species; but also enable the detection of biological agents as well. Great improvements have been made in the selectivity issue for carbon nanotube based gas sensors. The experience from the carbon nanotube-based sensors could most likely accelerate the development of graphene-based gas sensors.

**Transparent conductive films**

Graphene exhibits exceptional electrical conductivity, high carrier mobility, and excellent optical transmittance, comparable with carbon nanotubes. Hence graphene holds potential for transparent conductive films (TCFs) application [50]. Graphene, the fascinating component of TCFs, can be fabricated by several methods: (1) GO-reduced graphene [51-57]; (2) graphene prepared by sonication of graphite in organic solvents, such as N-methyl-2-pyrrolidone and ortho-dichlorobenzene [58,59]; and (3) graphene grown on metal substrate by CVD [60-63]. The large scale productivity and low cost of GO-reduced graphene make it a superior candidate for the fabrication of TCFs. Due to the convenient processing of GO in water, usually GO was used as a precursor to be deposited onto the substrate, followed by chemically (or electrochemical) reduction or thermal annealing, and consequently formed graphene-based TCFs. Several processing of GO precursor, such as spin-coating [51,52], dip-coating [53], vacuum filtration [54], and LB assembly [55,57], have been carried out in order to form TCFs. The process of GO fabrication (oxidation) results in smaller sizes of graphite nanosheets, which affects the final resistance of the films. The resistance can be varied from 10⁴ to 10⁷ Ω/□, due to the quality and connectivity of graphene. The TCFs prepared by sonication of graphite in N-methyl-2-pyrrolidone show a more stable resistance in the order of 10⁵ Ω/□, because the quality of graphene has not been destroyed by sonication treatments. Transferring graphene grown on metal substrate by CVD can lead to much lower resistance of the resultant TCFs, due to the perfect quality and large sizes of graphene nanosheets. The resistance can be reached to the order of 10³ Ω/□, and the values can be slightly varied, depending on the metal substrates used for the growth of graphene. However, the development of this method has been restricted by the preparation process. Since each method has its own advantages and drawbacks, we can judiciously exploit any method in accordance to the requirement. Actually, there is still a large amount of work that needs to
be investigated for TCF applications, in order to reach the intrinsic resistance of graphene (about 30 Ω/□) [60].

Graphene/polymer nanocomposites

Graphene plays a more and more important role in the polymer nanocomposite area, due to its comparable mechanical, thermal, and electrical properties with carbon nanotubes and also having much lower cost, making graphene suitable for industrial production and graphene offers a high potential for a variety of possible applications [3].

As for the preparation of graphene/polymer composites, dispersion of graphene polymer matrix is the most viable, since the properties of the composite materials are generally enhanced in a synergistic way. In order to prepare graphene/polymer nanocomposites, three main routes can be adopted: (1) solution blending method; (2) melt processing method; and (3) in situ polymerization method. Solution blending method is a very simple method for the preparation of polymer composites. The nanosheets, both of GO (with or without functionalization) and graphene, can be dispersed into the common solvents (polymer soluble), and mix with the polymer directly. Poly (vinyl acetate), as a common matrix, has been studied widely due to its water solubility [64-66]. Since GO can be dispersed in water easily, it can be incorporated into aqueous polymer dispersion at different concentrations. Further reduction (chemically or electrochemically) can then be carried out to obtain the graphene/polymer composites [67]. As for the general application of graphene in the nanocomposite fields, it’s necessary to disperse the graphene sheets in most polymers, which are insoluble in water. Therefore, it is necessary to first disperse the graphene or GO nanosheets in an organic solvent, followed by polymer blending in the organic solvent. Therefore, the functionalization of graphene or GO sheets has been carried out in order to change the surface properties of nanosheets, making them more lipophilic and consequently dispersible in organic solvents [24,68-75]. Ruoff et al. [69,70] reported that GO can be chemically functionalized with isocyanate, and dispersed in organic solvents, followed by blending with polystyrene and a chemical reduction step. The results showed that graphene can be dispersed in polystyrene efficiently, and the obtained composite exhibited a high conductivity (Fig. 3). Wu et al. [68] reported that the graphene nanosheets can be grafted with long alkyl chains via simple amidation reaction. Compared with unmodified counterparts, the alkyl attached graphene shows a largely enhanced lipophilicity, and remarkably improvement of dispersion in the nonpolar solvents and polypropylene matrix can be achieved. Other kinds of polymer matrix composites with graphene-based additives, including poly (methyl methacrylate) [71,72], epoxy [73-76], polyester [77], silicone foam [78], polyurethane [79,80], poly (vinyldiene fluoride) [81], and polycarbonate [82] have also been reported. Melting processing method is another route for polymer processing, which is widely applied in industry area and very suitable for nanocomposite preparation through the addition of graphene-based additives into polymer matrix. Du et al. [83] reported the successful reduction of GO with polysulfide ions, leading to the formation of sulfur nanoparticles decorated graphene. Further melt blending of graphene with poly (arylene sulfide) resulted in highly exfoliated platelets in the polymer matrix. In situ polymerization is considered to be a very efficient method dispersing nanomaterials into the polymer matrix [84,85]. Through in situ polymerization, GO or graphene nanosheets have been successfully incorporated into many kinds of polymer matrix, such as poly (methyl methacrylate) [86,87], epoxy [88], and thermoplastic polyurethanes [80].

Fig. 3 The modification of GO (a) and the electrical conductivity of the polystyrene-graphene composites (b). The data are from Refs. 69 and 70.
The mechanical, thermal, and electrical properties of polymer matrix can be significantly improved through the judicious addition of graphene-based additives. Moreover, compared with the conventional fillers, only a small amount of graphene is needed in order to achieve percolation [72,89], due to the large interfacial area and high aspect ratio of graphene nanosheets. As a result, the properties of polymer matrix can be readily enhanced. Incorporating GO into poly (vinyl acetate) matrix, followed by a reduction process, result in a conductive composite with a percolation threshold below 1 wt% [66]. Poly (vinyl acetate) nanocomposites with loading as low as 0.7% showed 76% and 62% increase in tensile strength and Young’s Modulus respectively [90]. The graphene/polymer nanocomposites with excellent thermal properties offer potential applications in electronic packaging and advanced composites. Addition of 25 vol% of graphene into epoxy can lead to the enhancement of the thermal conductivity by more than 3000% [76]. Therefore, graphene/epoxy nanocomposite can be considered as a useful candidate for thermal interface material application.

Graphene resonators and radio frequency switches

The unique properties of graphene have motivated intense work among physicists and engineers, discovering new opportunities to apply graphene in order to improve digital and radio frequency electronics [91], advanced sensors, transparent electronics, low-power switches, solar cells, as well as battery energy storage. In this article we review some of the recent progress made in the use of graphene devices for communication application. Numerous communication systems rely on electromechanical devices, such as filters, resonators, and radio frequency switches. The miniaturization of these devices will strongly affect the development of future communication systems. The ultimate limit to this miniaturization is represented by graphene electromechanical devices, which are only one atom thick. In fact, its enormous stiffness and low density make graphene the ideal material for this kind of devices. The first electromechanical device ever demonstrated in graphene turns out to be nanomechanical resonators. In 2009 Chen et al. [92] fabricated monolayer graphene nanomechanical resonators with operating frequencies in the 50–80 MHz frequency range. These devices show quality factors in the order of $\sim 1 \times 10^4$ at low temperatures (5 K). It has been predicted that the ability of graphene to withstand ultrahigh strains, up to $\sim 25$ percent in nanoindentation experiments, will allow the increase in the resonance frequency of these devices to above the gigahertz range, while maintaining a robust signal level. Graphene electromechanical switches have also been demonstrated recently. Milaninia et al. [93] developed a switch comprising of two polycrystalline graphene films grown by CVD. The top film is pulled into contact with the bottom one by applying a voltage of 5 V between the layers, and the contact is broken after removing the voltage due to restoring mechanical forces. In the ON state, more than 7 kA/cm$^2$ of current can flow through the switch. Although the device performance suffers from a relatively large contact resistance, it is expected that the graphene-graphene contact will be more robust than the traditional metal-metal contact, leading to a significant increase in the reliability of future direct current and radio frequency switches.

Conclusions

In this review, we have discussed the methods related to the preparation, functionalization, and applications of graphene. In the course of the next ten years, it can be expected that there will be an explosion of reports on the new synthesis, functionalization, as well as applications of graphene. Along with the patents and publications, we will witness a revolution in nanoscience in which an entirely new industry and technology will emerge, based on graphene and the chemistry of functionalized graphene.

Acknowledgments

The project was supported by the National Natural Science Foundation of China (No. 50902092 and 51102164), Science and Technology Commission of Shanghai Municipality (No. 1052nm06800 and 1052nm02000), Shanghai Pujiang Program (No. 11PJ0011), and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

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Terahertz Generation Using Implanted InGaAs Photomixers and Multi-wavelength Quantum Dot Lasers

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(Received 6 January 2012; accepted 14 January 2012; published online 20 February 2012.)

Abstract: We report on a study of terahertz (THz) generation using implanted InGaAs photomixers and multi-wavelength quantum dot lasers. We carry out InGaAs materials growth, optical characterization, device design and fabrication, and photomixing experiments. This approach is capable of generating a comb of electromagnetic radiation from microwave to terahertz. For shortening photomixer carrier lifetime, we employ proton implantation into an epitaxial layer of lattice matched InGaAs grown on InP. Under a 1.55 µm multi-mode InGaAs/InGaAsP quantum dot laser excitation, a frequency comb with a constant frequency spacing of 50 GHz generated on the photomixer is measured, which corresponds to the beats of the laser longitudinal modes. The measurement is performed with a Fourier transform infrared spectrometer. This approach affords a convenient method to achieve a broadband multi-peak coherent THz source.

Keywords: Proton implanted InGaAs; Terahertz; Photomixer; Multi-wavelength quantum dot laser; Fourier transform infrared spectroscopy

Citation: Y. Hou, J. R. Liu, M. Buchanan, A. J. Spring Thorpe, P. J. Poole, H. C. Liu, Ke Wu, Sjoerd Roorda and X. P. Zhang, “Terahertz Generation Using Implanted InGaAs Photomixers and Multi-wavelength Quantum Dot Lasers”, Nano-Micro Lett. 4 (1), 10-13 (2012). http://dx.doi.org/10.3786/nml.v4i1.p10-13

Introduction

Convenient sources of terahertz (THz) radiation, 100 GHz~10 THz, fall between the capability of electronics and photonics. Many potential applications exist in this frequency region, for example in sensing, aerospace, medical and biological sciences, information and communication. A key advantage is its low energy, for example, the photon energy is only 4 meV at 1 THz, making it a safer alternative to X-ray in medical imaging. Many rotation and vibration modes of biological and chemical species are in the THz spectrum. Despite of many application prospects, due to the lack of convenient THz radiation sources, a wide spread application is yet to come.

There are mainly four approaches to generate THz radiation. One is the development of THz quantum cascade lasers [1,2], the other is to use femtosecond lasers [3], the third way is by nonlinear optics [4,5], and the fourth is heterodyne photomixing [6]. The quantum cascade laser approach is suited for the upper part of the THz spectrum, for example, greater than about...
2 THz. The femtosecond laser technique provides a broadband THz source, but needs a sophisticated laser and therefore tends to be expensive. The same is true for nonlinear optics. The heterodyne photomixing approach has attracted a lot of interests, and impressive advances have been made notably by Brown et al. [7] Such an approach has the potential of achieving convenient and low-cost THz sources based on semiconductor diode lasers and ultrafast photomixers, albeit more suited for the lower frequency region of about less than 2 THz. Substantial advances have been made based on low-temperature-grown GaAs materials and lasers at wavelengths less than about 0.9 µm, i.e., photon energy at about the GaAs band gap. But it was not convenient to apply it to telecommunication field with lasers working in the 1.3~1.55 µm region.

In this research, we use proton implanted InGaAs THz photomixers and 1.55 µm multi-mode InGaAs/InGaAsP quantum dot (QD) lasers to achieve THz generation. With this method a broadband THz radiation comb with constant frequency spacing and high degree of coherence may be generated. This approach may result in convenient THz sources suitable for applications such as sensing and spectroscopy. Similar work using heavy ions was reported in Refs. [8,9].

Material and device

The InGaAs photomixing material was grown by MOCVD on an InP substrate. The layer structure consists of 0.1 µm InP buffer, 2.0 µm InGaAs, and 10 nm InP top capping layer. Ion implantation is expected to shorten the carrier lifetime. Different fluences of 1 MeV proton implantation are used from 3E10, 9E10, 3E11, 9E11, 3E12, 9E12, to 3E13 cm$^{-2}$.

To characterize the implanted materials photoluminescence (PL) spectroscopy is carried out. Figure 1 is a set of PL spectra taken on an un-implanted reference and implanted samples of various fluencies, all from the same wafer (M1094). With increasing implantation fluence, the PL intensity progressively decreases, implying an increase of non-radiative recombination rate and a decrease of the carrier lifetime. About a 1000-fold decrease is observed on the 3E12 cm$^{-2}$ sample, expecting a decrease of the lifetime to the picosecond region. More heavily implanted samples (PL too weak to measure) are expected to have a lifetime much less than 1 ps, suitable for THz photomixing.

For the device design, factors such as device area, number of interdigitated electrodes, and spiral antenna geometry limit the frequency response. Simulations are carried out to ensure the device performance. In the following we concentrate on 36×36 µm$^2$ area devices with a simulated RC time of 0.62 ps. Figure 2 is a photograph of the completed device.

Experimental and discussion

An optics based THz radiation measurement system was set up. Different from electronic instrument systems based on harmonic mixers, we used an FTIR (Fourier transform infrared) spectrometer. An electronic system would have limitations in reaching high
THz region due to the lack of harmonic mixers. Figure 3 is a schematic of the THz radiation detection system.

In this measurement system, the photomixer was illuminated by the laser beam, which was from the multimode QD InGaAs/InGaAsP laser at around 1.55 µm. An Er-doped amplifier was employed to increase the laser power. A 5 or 6 µm diameter conical lensed fiber was used to focus the laser power onto the photoconductive area. A 1.55 µm multi-mode QD laser spectrum taken on the FTIR is displayed in Fig. 4. From the laser spectrum, a constant frequency spacing between the modes which will create the different optical beats is seen. The minimum spacing is 50 GHz, which means in subsequent measurements the optical beats are at N times 50 GHz, N is a positive integer.

The packaged photomixer is fixed to a stand which is about 1 inch away from the FTIR input-port window. The DC biased device is excited by the 1.55 µm laser beam from the lensed fiber. To couple out the THz emission more efficiently, a 3 mm diameter high resistivity hyperhemispherical silicon lens is affixed to the backside of the photomixer substrate. The laser output power from the Er-doped amplifier is in the range of 30~50 mW. When the multi-mode QD laser output total power is 35 mW, the highest single mode output power is about 8 mW. A black polyethylene film is placed after the photomixer to block the laser from reaching the FTIR detector which is a liquid He cooled Si bolometer. The signal is sent to a lock-in amplifier and then to the FTIR analog to digital converter.

Photomixers with different proton implantation fluences are measured. Figure 5 is an FTIR spectrum of a photomixer with a proton fluence of 9E12 cm$^{-2}$ (Device A). From this spectrum, three peaks with wavenumber values of 1.66, 3.38, 5.32 cm$^{-1}$ are observed. Given the FTIR resolution, this spectrum shows generated radiation at 50, 100, and 150 GHz from the photomixer. The spectrum also shows that the signal intensity decreases with increasing frequency, an effect of the photomixer frequency roll-off. The spectrum from another photomixer (Device B) with a higher fluence (3E13) and the same device area is shown in Fig. 6. Though a calibrated power measurement was not done, in relative terms, signal in Fig. 6 is weaker than that in 5, likely due to a lowering of the responsivity on increasing the
fluence. In the FTIR spectrum of Fig. 6, five peaks at 1.5, 3.4, 5.0, 6.4, and 8.0 cm$^{-1}$ are observed, corresponding to 50, 100, 150, 200, and 250 GHz, respectively. Comparing Figs. 5 and 6, the higher implanted device shows a higher frequency capability, and one could therefore conclude that the carrier lifetime is the limiting factor.

**Conclusion**

We have investigated the approach of using ion-implanted InGaAs photomixer and multi-wavelength QD laser to generate a frequency comb covering from microwave to THz frequencies. The InGaAs materials system is technologically advanced due to its relevance in the telecom applications, and the QD laser works in the telecom wavelength region of 1.55 $\mu$m. For the experimental testing, we used a FTIR spectrometer suitable for measurements extending in the high THz region. With this approach a broadband THz frequency comb may be generated, which would be useful for various applications such as spectroscopy and sensing.

**Acknowledgments**

This work was supported in part by NSERC. HCL thanks the support by the National Major Basic Research Projects (2011CB925603) and Shanghai Municipal Major Basic Research Project (09DJ1400102).

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Electrochemical Synthesis and Photocatalytic Property of Zinc Oxide Nanoparticles

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(Received 5 December 2011; accepted 7 February 2012; published online 29 February 2012.)

Abstract: Zinc oxide (ZnO) nanoparticles of varying sizes (20, 44 and 73 nm) have been successfully synthesized by a hybrid electrochemical-thermal method using aqueous sodium bicarbonate electrolyte and sacrificial Zn anode and cathode in an undivided cell under galvanostatic mode at room temperature. The as-synthesized product was characterized by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), Scanning electron microscopy along with Energy dispersive analysis of X-ray (SEM/EDAX), Transmission electron microscopy (TEM), Ultra Violet - Diffuse reflectance spectroscopic methods (UV-DRS), and UV-DRS spectral methods. The as-synthesized compound were single-crystalline and Rietveld refinement of calcined samples exhibited hexagonal (Wurtzite) structure with space group of $P6_3/mc$ (No.186). The band gaps for synthesized ZnO nanoparticles were 3.07, 3.12 and 3.13 eV, respectively, based on the results of diffuse reflectance spectra (DRS). The electrochemically synthesized ZnO powder was used as photocatalysts for UV-induced degradation of Methylene blue (MB). Photodegradation was also found to be function of exposure time and dye solution pH. It has been found that as-synthesized powder has excellent photocatalytic activity with 92% degradation of MB, indicating ZnO nanoparticles can play an important role as a semiconductor photocatalyst.

Keywords: Zinc Oxide; Methylene Blue; Photocatalytic activity; Semiconductor

Citation: Kodihalli G. Chandrappa and Thimmappa V. Venkatesha, “Electrochemical Synthesis and Photocatalytic Property of Zinc Oxide Nanoparticles”, Nano-Micro Lett. 4 (1), 14-24 (2012). http://dx.doi.org/10.3786/nml.v4i1.p14-24

Introduction

Nanostructured semiconductor oxides are of great importance for several technological applications because of their several interesting optical and electronic properties. The design and fabrication of nanostructured semiconductor metal oxides with a tunable physico–chemical property for advanced catalytic applications have drawn a great deal of attention in the field of catalysis [1-4]. Several semiconductor oxides such as zinc oxide (ZnO), TiO$_2$, SnO$_2$ and ZrO$_2$ have been found to be attractive photocatalysts because they are environmentally sustainable with high catalytic efficiency in the degradation of various environmental pollutants such as pesticides, detergents, dyes and volatile organic compounds into carbon dioxide and water under UV light irradiation [5-8]. Among these semiconductor oxides, use of ZnO as a photocatalyst is preferred because it has a comparable band gap (3.2 eV) with relatively large quantum efficiency [9] in comparison to other commonly used photo-catalysts. Also, it has great potential applications in room-temperature UV lasers [10], sensors [11] and photocatalysis [4, 12] due to its unique electrical and optical properties such as low dielectric constant, high chemical stability, good photoelectric and piezoelectric behaviors [13]. In addition, it has been largely emphasized in the literature that the physico-chemical properties of these semiconductor oxides such as ZnO can be suitably tailored according to our application since there exists a relationship between their size and the catalytic efficiency [14-17]. Gouvea et al. [18] used three methods to prepare nano-ZnO,
and the results indicating that the smaller particle size could lead to higher photocatalytic activity. 

ZnO has received significant importance in the field of photocatalysis because of its large exciton binding energy (60 meV) at room temperature [10], high optical activity, photochemical stability, high surface energy and also cheap and non-toxic in nature [19]. Also, the potential of electron derived from ZnO is more negative than that generated by most-investigated TiO2 for photocatalytic reduction reaction [4]. When ZnO is irradiated under a light with energy equal to or higher than its band gap, it generates electron-hole pair which then participates in the photocatalytic process. In addition, the higher photocatalytic activity of ZnO is also attributed to the large number of defects such as oxygen vacancies, interstitial zinc atom from the donor states, while zinc vacancies and intestinal oxygen atoms from the acceptor states [20].

It has been found that the physico-chemical properties of ZnO and hence its application significantly depends on its synthesis route. In literature, there are large number of reports for the synthesis of nanostructured ZnO such as precipitation/mechanical milling [21], microemulsion [22], ultrasonic radiation [23], microwave irradiation [24], solution combustion, microwave assisted solvothermal [25] and sol-gel method [26]. However, in recent years, the electrochemical method of synthesis of nanosized metal oxide powder and films have acquired a considerable interest because of its simplicity, low operating temperature and viability in commercial production. Recently, ZnO and CuO nanocrystals have been successfully synthesized by electrochemical route [27, 28]. Thus, designing a suitable method for preparing ZnO at ambient temperature with narrow particle size distribution, better properties and less operating cost is a challenge for researchers.

The increase in human population has resulted in the development of large-scale industries such as textile and paper industries whose waste products represent a major environmental hazard to aquatic biota and humans due to their toxicity [29] and the tendency to cause eutrophication [5]. Detection and removal of these toxic chemicals is a major challenge in convention 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 [30-33] which intend to directly remove commonly used industrial dyes. The present investigation is focused on the bulk synthesis and characterization of ZnO nanoparticles by electrochemical route without using any template or surfactant at room temperature. Also, we have discussed in detail spectroscopic detection (and quantification) of commonly used textile dye (Methylene Blue; cationic) in aqueous solution using these ZnO nanoparticles as a function of various parameters.

Experimental Procedure

Starting Materials and Synthesis of ZnO Nanoparticles

Zinc metal plate (99.99%), sodium bicarbonate (AR grade: 99.5%) 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. In a typical synthesis, ZnO nanoparticles are synthesized using a standard electrochemical technique mentioned in ref [27]. 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 consisted of 400 ml, 30 mM (1.008 gm) NaHCO3 solution which was taken in a rectangular undivided cell having dimension 5×6×0.8 cm3 with Zn plates as both cathode and anode. The electrolysis was carried out for about one hour under galvanostatic conditions where the constant current was drawn from a DC power supply (model PS 618 potentiostat/galvanostat 302/2 A supplied by Chem link, Mumbai) with constant stirring at 800 rpm. The pH of the electrolyte was recorded before and after electrolysis. The particles were filtered and isolated from the solution. The same procedure was also repeated using 60 and 120 mM of NaHCO3. The resulting particles were calcined at different temperature ranging from 60°C to 600°C for 1 h.

Catalyst characterization

General morphology, structure, crystallite size, oxidation state, compositional analysis and band gaps of the nanoparticles were performed using powder X-ray diffraction (XRD), transmission and scanning electron microscopy, energy dispersive X-ray analyzer (EDAX), X-ray photoelectron spectra (XPS) and UV-DRS spectroscopy. Morphology and compositional analysis were carried out in a scanning electron microscope (SEM, Philips XL 30) fitted with an EDAX in the voltage range of 200–300 kV. Transmission electron microscope (TEM) images of selected samples were recorded (Model: JEOL 2000 FX-II) with an acceleration voltage of 200 kV. 2 µl of ZnO – ethanol solution was dropped on a Cu grid with a carbon-reinforced plastic film. XRD patterns (X’pert Pro Diffractometer, Phillips, Cu Kα radiation, (λCu=1.5418 Å) working at 30 mA and 40 kV) were recorded in the 2θ range from 10° to 90° at a scanning rate of 1° min−1. For Rietveld refinement analysis, XRD data was refined using
the FullProf Suite-2000 version. The average crystallite sizes were estimated using Scherrer equation [34]. The X-ray photoelectron spectra (XPS) were recorded by Thermo-Scientific Multilab 2000 equipment employing Al Kα X-rays at 150 W. The absorption, reflectance absorption, reflectance and DRS spectra on ZnO nanoparticles were studied using UV–DRS absorption spectroscopy (Speccord S600-212C205 UV Spectrophotometer) and dye adsorption kinetics on ZnO nanoparticles were studied using Spectrum, SP-2102 UVPUC, UV-Vis Spectrophotometer (path length=1 cm). Dye adsorption kinetics were carried out using ZnO nanoparticles (100 mg) of varying sizes which were added to 100 ml (50 ppm, say) of dye solution and stirred continuously for 2 h for homogeneity. Aliquots were collected from the reaction beaker at regular time intervals and concentration of dye in solution and degradation ratio was plotted as a function of time by monitoring the changes in the $A_{\text{max}}$ line intensity with time.

**Photocatalytic Degradation of Dye in Aqueous Solution**

In order to evaluate the photocatalytic activity of the samples, photodegradation of MB dye under UV light irradiation was carried out in presence of ZnO nanoparticles at room temperature. Photocatalysis experiments were carried out with ZnO (100 mg in 100 ml of dye solution) and MB dye (10 ppm, 30ppm and 50 ppm) solution of three different concentrations prepared by dissolving appropriate amount of MB dye 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 in 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 heating of the solution. Reaction suspension was prepared by adding 100 mg of ZnO sample into a 250 ml beaker containing 100 ml of MB (10-50 ppm) dye solution. Prior to illumination, the suspension was magnetically stirred for 2 h in dark to establish an absorption/desorption equilibrium of MB and also to ensure that the suspension of the catalyst was uniform. Subsequently, the dispersion containing MB and photocatalyst (ZnO) was irradiated under UV light. The lamp radiated predominantly at 365 nm corresponding to energy of 3.4 eV and photon flux of $5.8 \times 10^{-6}$ mol of photons sec$^{-1}$. The MB-ZnO solution mixture was repeatedly illuminated for 10 min at 2 min intervals. During the 2 min interval, 3 ml of aliquots were taken from the test mixture. Due to progressive degradation of the dye with consecutive flashes, the color of the solution mixture (as well as aliquots) changed from blue to light blue followed by white. The change in color of the dye solution as a function of time was monitored by using UV-Vis spectroscopy.

**Results and Discussion**

**XRD to Study ZnO Nanostructure**

The powder XRD patterns of as-prepared and calcined compounds of ZnO nanoparticles are shown in Fig. 1. It can be seen from Fig. 1(a) that, the seven peaks appeared at 2θ of 13.1°, 24.1°, 27.9°, 30.9°, 32.9°, 53.9° and 59.6°, corresponding to the characteristic peaks of zinc hydroxy carbonate, and is in accordance with standard JCPDS file no. 72-1100. Similar observation was also made by Siqingaowa et al. [35]. Also, the other small peaks appearing at 2θ of 34.4°, 36.2° and 47.4° values corresponds to characteristic peaks of ZnO. The XRD patterns for the calcined samples at 300°C for 1 h (Fig. 1(b)), could be completely indexed to hexagonal phase (JCPDS file No. 36-1451). The crystallite size (d) estimated from the full width at half maximum (w) of the dominant (101) peak at diffraction angle 2θ=36.2° using Scherrer’s equation was found to be 44 nm. In Fig. 1(a), the diffracted lines were broad, less intense and corresponded to the zinc hydroxy carbonate and ZnO. On increasing calcination temperature from 300 to 600°C, the characteristic ZnO peaks become sharper and the crystallinity increased [35]. The powder XRD pattern for the sample calcined at 600°C is given in Fig. 1(c). From the XRD data, the average crystallite sizes were found to be 20, 44 and 73 nm respectively (Table 1). It clearly indicates that, an increase in calcination temperature brings about a corresponding increase on crystallite sizes of ZnO nanoparticles, leading to sharper diffraction peaks.

![XRD patterns of ZnO](image)

**Fig. 1** XRD patterns of (a) ZnO precursor obtained from the bath concentration at 30 mM NaHCO$_3$ at 1 A/dm$^2$, and calcined for 1 h at different temperature (b) 300 and (c) 600°C.

The preferred orientation of ZnO nanoparticles was estimated from the XRD data according to the methodology developed by Berube and L Esperance [36], where the texture coefficient ($T_c$) is calculated by using the
Table 1  Electrolysis parameter and process efficiency for the preparation of ZnO nanoparticles.

| Temperature (°C) | Crystallite size (nm) | Family of crystallographic planes \{hkl\} |
|-----------------|-----------------------|----------------------------------------|
|                 | \{100\} | \{002\} | \{101\} | \{102\} | \{110\} | \{103\} | \{200\} | \{112\} | \{201\} | Average |
| As-prepared     | 21     | 18     | 10     | 0      | 0      | 0      | 0      | 0      | 31     | 20      |
| 300             | 49     | 71     | 63     | 65     | 34     | 40     | 24     | 24     | 21     | 44      |
| 600             | 49     | 99     | 62     | 103    | 88     | 57     | 77     | 58     | 68     | 73      |

The structural parameters for all the calcined samples were refined using Rietveld refinement method.

The equation below:

\[ T_c = \frac{I_{(hkl)}}{\sum I_{(hkl)}} \times \frac{\sum I_{0(hkl)}}{I_{0(hkl)}} \]  

where, \( I_{(hkl)} \) is the diffraction line intensity of the \( (hkl) \) reflection of ZnO powder, \( \Sigma I_{(hkl)} \) is the sum of the intensities of all the diffraction lines monitored. The \( I_0 \) refers to intensity of the reference ZnO sample (JCPDS file No. 36-1451). Figure 2 shows the texture coefficient of ZnO sample obtained from electrolyte concentration of 30 mM and current density of 1.0 A/dm\(^2\). It can be seen that the majority of the ZnO crystallites are oriented parallel to the (002) plane.

The surface composition and oxidation states of the materials are deciding factors which play very important role in the process of catalytic reaction since they

All the ZnO nanoparticles crystallized in the hexagonal (Wurtzite) structure with space group of P6\(_3\)mc (No. 186). The refined structural parameters for ZnO calcined at 600°C for 1 h is given in Table 2. The observed lattice parameters agreed well with the reported standard JCPDS file No. 36-1451. Observed, calculated XRD patterns and their difference are given in Fig. 3, and there is good agreement between them. Further, we did not see any appreciable change in the lattice parameters on samples calcined to low temperature.

**Surface Composition and Oxidation States**

The surface composition and oxidation states of the materials are deciding factors which play very important role in the process of catalytic reaction since they

![Fig. 2 Texture Coefficient of ZnO nanoparticles obtained from 30 mM NaHCO\(_3\) at 1 A/dm\(^2\), calcined for 1 h at different temperature.](image)

![Fig. 3 Observed, calculated and the difference XRD patterns for the ZnO sample obtained from 30 mM NaHCO\(_3\), 1 A/dm\(^2\), calcined at 600°C for 1 h.](image)

Table 2  Rietveld refined structural parameters for ZnO nanoparticles synthesized by electrochemical method.

| Atoms | Oxidation state | Wyckoff notations | x     | y     | z     | Biso  | Occupancy |
|-------|----------------|-------------------|-------|-------|-------|-------|------------|
| Zn    | 2              | (2b)              | 0.3333| 0.6667| 0.0000| 0.025 | 1          |
| O     | -2             | (2b)              | 0.3333| 0.6667| 0.3820| 0.500 | 1          |

Crystal system=Hexagonal, Lattice parameters; \( a=3.252(2), \ c=5.208(6) \); Space group=P6\(_3\)mc (No. 186); R factors (%), \( R_p=6.86, \ R_{wp}=9.37, \ R_{Bragg}=2.96, \ R_F=1.78. \)
can strongly affect the catalytic activity. The photocatalytic activities of metal oxides are closely related with their surface structures. The surface composition and oxidation states of ZnO (hexagonal) were investigated by X-ray photoelectron spectroscopy (XPS). Figure 4 shows the XPS spectra of ZnO nanoparticles obtained from 30 mM NaHCO$_3$ at 1 A/dm$^2$ and calcined at 600°C for 1 h. It can be seen that the whole region of XPS spectra contains characteristic peaks of Zn (2p) and O (1s) (Fig. 4(a) and 4(b)). The Zn (2p) signal could be deconvoluted into two peaks (Fig. 4(a)). The binding energies obtained in the XPS analysis are corrected for specimen charging by calibrating the C(1s) peak at 285.4 eV and are accurate within ±0.1 eV. The binding energy at about 1022.18 eV is attributed to Zn $^3/2$ and the 1045.37 eV is attributed to Zn $^1/2$, respectively, which are very close to the data for Zn (2p) in ZnO. Also, the Zn 2p$_{3/2}$ peaks are very sharp, this confirms that Zn atom is in the form of Zn$^{2+}$ state in ZnO sample. As shown in Fig. 4(b), the O (1s) core-level spectrum is broad, and these peaks ranging from 527 to 535 eV. The peak area of Zn (2p) and O (1s) cores were measured and it was used to calculate the chemical composition of the sample. Thus, the XPS spectra demonstrate that the synthesized materials are composed of ZnO nanoparticles.

**SEM/EDAX and TEM Analysis**

Scanning electron micrographs and EDAX spectrum of as-prepared and calcined compounds of ZnO nanoparticles are shown in Fig. 5. Figure 5(a) shows the SEM image of as-prepared ZnO powder. It can be seen that the particles are agglomerated producing flower like structure, whereas the ZnO samples calcined at 300°C showed less randomly distributed small spindle shaped particles (Fig. 5(b)). The samples calcined at 600°C showed well defined and randomly oriented spindle like ZnO with somewhat compact structure (Fig. 5(c)). The flower like structure of as-prepared ZnO converted to spindle like structure on heating to 300°C. As the temperature is increased, the particles tend to grow as expected. The EDAX spectrum is shown in Fig. 5(d) indicates the presence of only Zinc and Oxygen, suggesting that the nanoparticles are indeed made up of Zn and O, the inset shows the ratio of zinc and oxygen ion concentration. The spectrum was devoid of any other metal ions indicating the purity of the samples.

The TEM images of ZnO nanoparticles obtained from the electrolyte concentration of (a) 30 mM and (b) 60 mM NaHCO$_3$ at 1 A/dm$^2$ and calcined at 600°C for 1 h are given in Fig. 6. It can be observed that ZnO nanoparticles are present as granules with spindle like shapes and are crystalline in nature. In Fig. 6(a) and 6(b) emphasize the particles have a clear spindle like morphology, and it was found that the average particles size ranging from 30-40 nm and these values are in good agreement with the values obtained from XRD data by Debye-Scherrer equation.

**UV-DRS Spectroscopy**

Figure 7(a) shows the UV–Vis absorption, (b) reflectance and (c) diffuse reflectance spectra (DRS) of as-prepared and calcined ZnO nanoparticles to study their photoabsorption ability which is obtained from the 30 mM NaHCO$_3$ at 1 A/dm$^2$. In Fig. 7(a), the absorption peaks are ascribed in between 330 to 380 nm,
on increasing calcination temperature, the ZnO particles growth will takes place and the corresponding absorption band (λ<sub>max</sub>) increases. The band gap (E<sub>g</sub>) of ZnO nanoparticles were calculated by using E<sub>g</sub> = hc/λ, where h=plank’s constant, c=velocity of light and λ=wavelength. The band gap values were lies in the range 3.34 to 3.42 eV (Table 3). The reflectance peaks (Fig. 7(b)) corresponding to ZnO sample showed the wavelength from 325 to 400 nm. The corresponding band gap was found to be 3.28 to 3.41 eV (Table 3). The optical absorbance properties of the ZnO samples were measured by diffuse reflectance spectroscopy (DRS) at room temperature. As displayed in Fig. 7(c), the absorption edges of ZnO nanoparticles were at about 363, 374 and 380 nm, respectively. Surprisingly, the absorption edge of ZnO nanoparticles shows an obvious blue shift. To obtain the optical band gap (E<sub>g</sub>) of ZnO nanoparticles, the absorbance coefficient (α) was calculated from the corresponding spectrum. The E<sub>g</sub> values were thus determined by extrapolation of the linear portion of the (αhν)<sup>2</sup> curve versus the photon energy hν to (αhν)<sup>2</sup>=0. The corresponding band gap energies were determined and was found to be 3.07, 3.12, 3.13 eV for ZnO nanoparticles (Table 3). Thus, the present electrochemical-thermal method produces ZnO nanoparticles which are in the blue region compared to the bulk ZnO (3.2 eV).

### Table 3  
E<sub>g</sub> values for the different ZnO nanoparticles obtained from UV-Vis absorption, reflectance spectroscopy and DRS.

| Synthesized ZnO material | Abs. peak position (eV) | Rfn. peak position (eV) | E<sub>g</sub> (eV), from DRS |
|--------------------------|--------------------------|--------------------------|-----------------------------|
| As-prepared compound     | 3.42                     | 3.41                     | 3.13                        |
| Calcined at 300°C        | 3.41                     | 3.31                     | 3.07                        |
| Calcined at 600°C        | 3.34                     | 3.28                     | 3.12                        |

### Evaluation of Photocatalytic Activity

#### Photocatalytic performance of ZnO with MB

The successful synthesis of ZnO nanoparticles offers an opportunity to examine their photocatalytic activity. The as-prepared and calcined ZnO 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 the UV light on the degradation of MB dye, a blank experiment was performed...
under UV light without the addition of photocatalysts (ZnO), which verified that MB dye of 10 mg/L was photolyzed up to 5% in 2 h. This degradation efficiency was negligible when the different sized particles were added to the solution. When there was no UV light, the concentration of MB dye with the addition of ZnO photocatalysts remains unchanged for 2 h. From these blank experiments, it can be concluded that UV light and photocatalysts are the necessary factors in the photocatalytic process. MB dye absorbs the light in the visible region (550-700 nm) with the absorption maxima at 664 nm. A series of experiments were carried out with different sized ZnO nanoparticles in MB dye solution. The time-dependent UV-Vis spectra of MB dye solution containing as-prepared ZnO nanoparticles, before and after irradiation interval of 100 min with UV light, are illustrated in Fig. 8. It can be seen that the intensity of absorption peak corresponding to the MB molecules at 664 nm decreases with increase in the exposure time and decreased to <50% at an irradiation time of 40 min. After irradiation under UV light for an hour (t=100 min), the absorption peak shifted towards 635 nm, showing hypsochromic shift of 29 nm. The hypsochromic shift indicated that the photodegradation of MB dye under UV light irradiation proceeded through a continuous removal of methyl groups with extending the irradiation time.

**Effect of Initial dye concentration with ZnO photocatalyst**

Figure 9 shows the effect of initial dye concentration on the rate of exposure time by varying the dye concentration from 10 to 50 ppm with different sizes of ZnO photocatalyst (20-73 nm). The results revealed that
The percentage of photodegradation increases with increase in irradiation time. This suggests that the as-prepared and calcined (600°C) ZnO nanoparticles are exceedingly efficient substrates for degradation of azo-dyes such as MB.

Influence of calcination temperature on the photocatalytic property of ZnO nanoparticles

The particle size and BET surface area affected the efficiency of nano ZnO due to variation in the calcination temperature (Table 4). The particle size will increase with increase in calcination and a drop in surface area; accompanied by a drop in photocatalytic activity; this suggests that, in addition to surface area, the morphology of nano ZnO (the particle size and crystallinity) also plays a crucial role in deciding the catalyst performance. The degradation efficiencies of different ZnO photocatalysts and different MB dye concentrations are shown in Fig. 10. It can be observed from Fig. 10(a), there is a special trend in the as-prepared ZnO nanoparticles. In the initial 70 min, the degradation efficiency reached the highest value of 85%. Afterward, the curve ascends tardily up to 92%. The crucial degradation efficiency after 100 min illumination has changed a little compared to the efficiency obtained after the initial 30 min illumination. The degradation efficiency of ZnO nanoparticles calcined at different temperature reduced in the order, 60°C > 600°C > 300°C. 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.

However, a higher catalytic activity is observed in case of as-prepared ZnO sample only in the early stage of reaction (70 min), while the activity is decreased for longer time degradation. This evidence can be ascribed to the photocorrosion phenomenon in ZnO nanoparticles [37]. The increase of calcination temperature at 600°C (Fig. 10(c)), the increase of particle size and has increase in crystallanity which is helpful to enhance the photocatalytic activity. From this approach, the photocatalysts calcined at 600°C would be a relatively better sample for anti-photocorrosion. This suggests that

Table 4 Comparison of different ZnO photocatalysts.

| Photocatalyst (Synthesized material) | Calcination temperature (°C) | Average particle size (nm) | BET surface area (m² g⁻¹) |
|-------------------------------------|-----------------------------|---------------------------|--------------------------|
| As-prepared ZnO                    | 60                          | 20±2                      | 19                       |
| Calcined ZnO                       | 300                         | 44±2                      | 14                       |
| Calcined ZnO                       | 600                         | 73±2                      | 11                       |
as-prepared and calcined (600°C) ZnO nanoparticles are highly efficient photocatalyst for degradation of MB dye.

Effect of pH on degradation of MB with ZnO photocatalyst

The effect of pH values on the degradation efficiency was studied in the pH values of 5 and 9 at the initial dye concentration of 50 ppm. Figure 11(a) and 11(b) shows the photocatalytic degradation of MB dye as a function of pH and exposure times. The Effect of pH on the photodegradation of MB dye was investigated over the pH range of 5-9, and the reaction pH was altered to study the photodegradation taking place on the surface of photocatalyst, since pH can alter the surface charge properties of the photocatalyst. From Fig. 11(a), in acidic solutions (pH=5.0) the degradation rate becomes slower and degree of degradation was lower in case of as-prepared compound but in calcined samples the degradation rate somewhat higher in the same irradiation time. A steady increase in the degradation of MB dye is observed at pH 9.0 (Fig. 11(b)). Higher the pH value can provide higher concentration of hydroxyl ions to react with holes (h+) to form hydroxyl radicals (OH·), subsequently enhancing the photodegradation rate of MB dye. It indicates that, the smaller particle size, higher crystallanility of photocatalyst and alkalline pH of reaction mixture has good photocatalytic activity for MB dye degradation under UV light irradiation.

Conclusions

In the present work, the nanosized ZnO particles were
successfully generated by hybrid electrochemical-thermal method using NaHCO$_3$ electrolyte without zinc salts, templates or surfactants. The Zn$^{2+}$ ions generated at the sacrificial Zn electrode were converted into ZnO during electrolysis. The size range of the generated ZnO powder was 20-73 nm. The nanoparticles morphology was similar for all the samples obtained at different current densities and the size and shape does not depend on current density. The EDAX spectrum showed 100% ZnO compound in the calcined particles. TEM images confirmed the spindle like shape of ZnO nanoparticles and are well crystallized in the nanosize of 30-40 nm on nanometer scale. The band gap was higher for synthesized ZnO particles than their bulk counterparts. The yield of ZnO at 1 A/dm$^2$ is maximum for 1 h electrolysis in all concentration of NaHCO$_3$. The method could be effectively used to synthesize ZnO on large scale. Also, we have presented here through systematic studies and performance of different sizes of ZnO nanoparticles in quantification and photocatalytic degradation of MB dye in aqueous solution. The higher photocatalytic property was probably caused by the smaller particle size, higher crystallinity and alkalline pH. These results show that the as-prepared and calcined (600°C) ZnO photocatalyst and the alkalline pH have a higher photocatalytic activity against UV light irradiation.

Acknowledgments

The authors thank Kuvempu University, Shimoga, Prof. A. J. Bhattacharyya and S. S. Mandal SSCU, IISc, Bangalore, for providing the lab facilities to bring about this work. KGC and TVV thank, respectively the CSIR, New-Delhi for research grant. DST [No. S.R/S3/ME/014/2007], Government of India (GOI) for research grant.

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Magnetic Tunnel Junction Based on MgO Barrier Prepared by Natural Oxidation and Direct Sputtering Deposition

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(Received 12 December 2011; accepted 15 February 2012; published online 28 February 2012.)

Abstract: Magnetic tunnel junctions (MTJs) based on MgO barrier have been fabricated by sputtering single crystal MgO target and metal Mg target, respectively, using magnetic sputtering system Nordiko 2000. MgO barriers have been formed by a multi-step deposition and natural oxidization of Mg layer. Mg layer thickness, oxygen flow rate and oxidization time were adjusted and the tunnel magnetoresistance (TMR) ratio of optimal MTJs is over 60\% at annealing temperature 385\,°C. The (001) MgO crystal structure was obtained when the separation distance between MgO target and substrate is less than 6 cm. The TMR ratio of most MgO based MTJs are over 100\% at the separation distance of 5 cm and annealing temperature 340\,°C. The TMR ratios of MTJs are almost zero when the separation distance ranges from 6 to 10 cm, due to the amorphous nature of the MgO film.

Keywords: Magnetic tunnel junctions; MgO; Crystal structure; Magnetic sputtering system

Citation: Xiaohong Chen and Paulo. P. Freitas, “Magnetic Tunnel Junction Based on MgO Barrier Prepared by Natural Oxidation and Direct Sputtering Deposition”, Nano-Micro Lett. 4 (1), 25-29 (2012). http://dx.doi.org/10.3786/nml.v4i1.p25-29

Introduction

Since Julliere's research group investigated the first spin-dependent tunneling junctions based on Co and Fe as electrode materials and GeO as insulating barrier in 1974 [1], magnetic tunneling junctions (MTJs) have been extensively studied due to its promising applications in the hard disk read heads, magnetoresistive random access memory and sensors [2,3]. The MTJs based on different tunnel barriers such as NiO [4] and Gd\textsubscript{2}O\textsubscript{3} [5], showed very low tunnel magnetoresistance (TMR) effects. The TMR breakthrough is that Miyazaki et. al. group reported MTJs based on amorphous Al\textsubscript{2}O\textsubscript{3} barriers attained TMR of 18\% at room temperature in 1995 [6]. At the present, the optimal MTJs based on aluminum oxide barrier can reach TMR ratio of 80\% [3]. However, it is difficult for MTJs based on Al\textsubscript{2}O\textsubscript{3} barrier to further improve TMR ratio. According to the first-principle electronic structure calculations, the ordered (001) oriented Fe/MgO/Fe MTJs structure were suggested to reach TMR ratio more than 100\% to even 1000\% [7]. This giant TMR ratio was thought to be caused by an interfacial spin-dependent electronic state with \(\Delta_1\) symmetry at the Fermi energy. Along this theoretical calculation, S. S. P. Parkin group [8] and Shinji Yuasa group [9] reported giant TMR ratio up to 220\% and 180\% at room temperature in 2004, respectively. The higher TMR ratio of 604\% was further reported in CoFeB/MgO(001)/CoFeB MTJs using magnetic sputtering deposition [2]. To realize high TMR in MTJs, it is important to deposit (001) MgO crystallographic orientation. Wang et al reported that an improved crystallinity of the MgO (001) layer is a main reason for increasing TMR ratio at high annealing temperature [10].
The excellent crystalline (001) MgO layer and (200) CoFeB layer are both primary factors for the higher TMR in CoFeB/MgO/CoFeB structure, confirmed by X-ray diffraction [11].

The (001) orientation MgO layer has been fabricated with different methods, such as MBE [9], magnetic sputtering deposition [8,10] and ion beam deposition [12], etc. The deposition parameters, such as Ar pressure [13], sputtering power, deposition rate and the distance between target and substrate would usually affect the crystal structure of MgO layer in magnetic sputtering systems. Therefore, the careful research work that the influence of deposition parameters on the crystal structure of MgO layer and the TMR ratio of MgO based MTJs is important for quickly and successfully fabricating (001) MgO crystal structure and obtaining higher TMR ratio of MgO based MTJs. In this study, we investigated MTJs based on MgO barrier fabricated by magnetic sputtering single crystal MgO target and metal Mg target, respectively. As for MgO barrier deposited with single crystal MgO target, the distance between MgO target and substrate is sensitive to the crystal structure of MgO layer. For MgO barrier prepared by sputtering metal Mg target, the metal Mg layer with several nanometers was naturally oxidized to form MgO barrier. The sputtering parameters of oxygen flow rate and pressure, oxidization time and Mg layer thickness apparently influence TMR ratio and the products of resistance and area (RA).

**Experimental Procedures**

The thin films for the MTJs were deposited onto glass substrate using a magnetron sputtering system (Nordiko 2000), with a base pressure of $5 \times 10^{-8}$ Torr. A magnetic field of 20 Oe was applied to induce parallel easy axis in the bottom and top magnetic electrodes during deposition. The fundamental structure of the MTJ is Ta70/Ru50/Ta50/MnPt200/CoFe25/Ru8/CoFeB30/MgO(tMgO)/CoFeB30/Ta70/TiWN150 (in Å). The $t_{MgO}$ represents the nominal thickness of MgO barriers. For sputtering metal Mg target, MgO barriers were formed by a several-step natural oxidization. First, the Mg layer was deposited on top of bottom magnetic electrode at deposition rate of 0.26 Å/s in the main chamber, and then oxidized by pure oxygen to form MgO layer in the load-lock chamber. To fully oxidize Mg layer and get right thickness of MgO barrier, the process of depositing Mg layer and natural oxidization need to be repeated several times in sequence. For sputtering single crystal MgO target, MgO barriers were deposited by RF sputtering and their nominal thickness was varied from 15 Å to 30 Å. The micro-size junctions were patterned by a self-aligned micro-fabrication process using direct-write laser-lithography, ion-beam milling and lifting off, defining junction areas down to $1 \times 1 \text{ um}^2$. Patterned samples were annealed with different temperature in vacuum pressure of $10^{-6}$ Torr for 1 h, and then moved into a magnetic field of 1 T while cooling down. The TMR transfer curves were measured with a four-contact DC method. The crystalline structure of MgO films was characterized by X-ray diffractometer (XRD, Siemens D-5000, molybdenum source Kα=0.7107 Å) [12].

**Fig. 1** TMR ratios versus RA products for MTJs with different Mg layer thickness.
Results and Discussion

Figure 1 shows TMR ratios versus RA products with different Mg layer thickness. The Mg layer thickness per step deposition was chosen 3.8 Å, 6.24 Å and 7.6 Å, respectively. MTJs were annealed at 370°C for 1 hour. Data are from ∼324 MTJs assemblage. The total nominal thickness of Mg layer was about 30 Å. The first Mg layer was oxidized for 40 seconds and the following several Mg layers were oxidized for 80 seconds at 2 sccm oxygen flow rate. The shortened oxidation time of the first step is to avoid oxidizing the bottom electrode, which can decrease TMR of MTJs [14]. It seems difficult to judge which depositing Mg layer thickness is better for higher TMR ratio, as illustrated in Fig. 1. However, MTJs with 6.24 Å Mg layer are probably worthy further optimization because that the number of MTJs with Mg layer 6.24 Å of more than 40% TMR is more than that of MTJs with Mg layer 7.6 Å and 3.8 Å.

For MTJs with Mg layer 6.24 Å, TMR ratio versus RA products for different oxidation time was shown in Fig. 2. The oxygen flow rate of oxidizing Mg layer was 16 sccm. The MTJs were annealed at 370°C for 1 h. The average RA products of MTJs with oxidation time 80 and 100 seconds are apparently larger than that of MTJs with 60 seconds due to the complete oxidation of these Mg layers [15]. However, the higher TMR ratios of MTJs with oxidation time 60, 80 and 100 seconds are all over 40% at annealing temperature 370°C. The TMR ratio of MTJs was further improved and obtained more than 60% at annealing temperature 385°C, as shown in Fig. 2(d).

For MgO barriers deposited by single crystal MgO target, it is very important for high TMR ratio to obtain (001) MgO crystal structure [7,9]. Here, sputtering parameters, such as RF power, Ar gas flow, gas pressure and the separation distance between MgO target and glass substrate were optimized. However, our experiments indicated that the separation distance between MgO target and substrate is most important parameter in magnetic sputtering system Nordiko 2000. Fig. 3 shows the XRD scan curves of MgO films under different sputtering condition. When the separation distance is between 5 cm and 6 cm, the XRD peak of MgO (002) orientation appears at ∼19.4° [12]. However, the XRD peak of MgO film with separation distance 6 cm is weaker compared to those of separation distance 5 cm. MgO films are almost amorphous at the separation distance ranging from 6 to 10 cm. These results showed that the crystal status of MgO layer is sensitive to the separation distance. When the separation...
distance was set 5 cm, the (002) MgO crystal structure was easily formed in the large range of RF power and Ar gas pressure.

Figure 4 shows the TMR curve of the representative MTJs. MgO barriers were deposited at the separation distance 5 cm. The MTJs were annealed at 340°C for 1 h. The MTJ MgO barrier thickness, RF sputtering power and Ar pressure were 19 Å, 150 W and 12 mTorr (Fig. 4(a)), 15 Å, 150 W and 12 mTorr (Fig. 4(b)), and 15 Å, 100 W and 8 mTorr (Fig. 4(c)), respectively. The TMR ratios of MTJs are about 130% (Fig. 4(a)), 150% (Fig. 4(b)) and 170% (Fig. 4(c)), respectively. One sample with one kind of MgO barrier deposition condition can be fabricated ~324 MTJs. Here, we just chose a representative MTJ to plot a TMR curve under one deposition condition. From a statistical point of view, TMR ratios of most MTJs with above three kinds of MgO barrier deposition conditions are more than 100%. Our results demonstrated that TMR ratios of most MTJs are always more than 100% for MgO barrier deposited with RF sputtering power ranging from 100 W to 200 W, and Ar pressure ranging from 5 mTorr to 20 mTorr at the separation distance of 5 cm. However, TMR ratios of MTJ are almost zero when the separation distance is larger than 6 cm due to amorphous MgO films. Therefore, the separation distance between MgO target and glass substrate is most important parameter to get high TMR ratio of MgO based MTJs in magnetic sputtering system Nordiko 2000.

Conclusions

In summary, MgO barriers were investigated by sputtering single crystal MgO target and natural oxidation, respectively. Mg layer thickness, oxidation time and oxygen flow rate are relative to TMR ratios under natural oxidation method. The TMR ratio of the optimal MTJ is more than 60% at annealing temperature 385°C. The separation distance of MgO target and substrate is more important for depositing (001) MgO crystal structure in magnetic sputtering system Nordiko 2000. The TMR ratios of reasonable MTJs are more than 100% at the separation distance of 5 cm. The MgO film is almost amorphous when the separation distance varies from 6 to 10 cm.

Fig. 3 X-ray diffraction scan curves of MgO films. Solid lines are fitting curves. The deposition conditions of MgO film: (□) RF power 170 W, Ar pressure 12 mTorr, separation distance 5 cm; (■) 170 W, 12 mTorr and 9.5 cm; (▽) 170 W, 5 mTorr and 5 cm; (△) 170 W, 8 mTorr and 5 cm; (⊳) 170 W, 12 mTorr and 6 cm.

Fig. 4 TMR curves of MgO barriers deposited with different deposition parameters.
Acknowledgments

Xiaohong Chen is grateful to the Natural Science Foundation of Shanghai Science and Technology Commission (grant No. 11ZR1411300) and Pujiang Talent Program of Shanghai Science and Technology Commission (grant No. 11PJ1402700) for the financial support.

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The Assembly of C60 in Semicrystalline PLLA Matrix

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(Received 12 October 2011; accepted 01 March 2012; published online 19 March 2012).

Abstract: It has increasingly become a research focus to build higher structure composed of C60. However, there has been very few reports on the influence of polymer addition on the self-assembling behavior of fullerene in organic solvents. In this research, big needle-like C60 assemblings have been obtained in the form of PLLA/C60 composites. The largest C60 needles can be observed by naked eyes. The amount of C60 in the composite influences the length of C60 needles to some extent. DSC results indicate C60 accelerates the crystallization and lift the relative crystallinity of PLLA matrix. the results also imply the addition of semicrystalline PLLA influence the assembling behavior of C60. i.e., the crystallization of PLLA accelerated by C60 also act a driving force for the enriching and the linear assembling of C60 in PLLA matrix via Van der Waals force.

Keywords: C60; Poly (L-lactide acid) (PLLA); Assembling

Citation: Li Chen and Xiujiang Pang, “The Assembly of C60 in Semicrystalline PLLA Matrix”, Nano-Micro Lett. 4 (1), 30-33 (2012).

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Introduction

It has become one research focus to build higher structure composed of C60 fullerene. Novel low-dimensional materials of fullerenes have been extensively investigated up to now. For example, Nakanishi et al. have successfully prepared spherical vesicles, fibers, discs, cones by the self-assembly of fullerene derivatives in mixed solvents [1]. In addition, fullerene nanowiskers, nanowires or nanorods [2-4] have also been fabricated.

The development of aggregates with different morphologies and its aggregation mechanism in solution using well-defined polymeric system are of potential interest to the research community. The self-assembly of polymer-branched C60 have been reported in organic or aqueous solvents [5-8]. However, there are few reports describing the influence of polymer addition on the self-assembling behavior of fullerene in organic solvents [9,10]. Biomass-derived poly (L-lactide acid)(PLLA) has been intensively explored because it is biodegradable, compostable, producible from renewable resources, while at the same time nontoxic to human body and environment. The enhancement of crystallinity with the aid of a nucleating agent is commercially advantageous to improve the mechanical properties and thermal stability of PLLA. It has been found that C60 is effective for accelerating both the cold and melt crystallization of PLLA, and the nucleating effect of C60 is even higher than that of montmorillonite and polysaccharides [11].

In this paper, C60 and PLLA were mixed by solution method, needle-shaped C60 assemblings were found in resultant PLLA composites. The morphology and chemical composition of the C60 needles were studied by optical microscope, scanning electron microscope (SEM) and energy dispersive spectra (EDS). The influence of C60 on the crystallization behavior of PLLA was also investigated through DSC technique. The lin-
ear assembling mechanism of C60 in PLLA during the solvent evaporation was proposed.

Experimental

Materials

Natureworks PLLA 2002D (number-average molecular weight (Mn)=1.8 $\times$ 10$^5$, weight-average molecular weight (Mw)=3.2 $\times$ 10$^5$, Mw/Mn=1.78) was supplied by Cargill Dow LLC, USA. C60 was kindly supplied by NIMS (national institute for materials science) in Japan.

Preparation of PLLA/C60 composites

The PLLA/C60 composites were prepared by the solution mixing method using dichloromethane (H$_2$CCl$_2$) as a solvent at 25°C. The solutions were prepared by dissolving PLLA and C60 in some H$_2$CCl$_2$, respectively. Then, the PLLA solution and C60 solution were mixed in a tube and homogenized by ultrasonication for 2 min. After that, the mixed solution was kept still and let the solvent evaporate very slowly until the composite film was dry. The obtained films were then further dried at room temperature in vacuum oven for 8hrs. PLLA composites containing 0.5 wt %, 1 wt % and 2wt % of C60 were prepared.

Characterizations

The resultant PLLA/C60 composites were put on the sample platform and observed by using a stereoscopic zoom microscopic Nikon SMZ 1500 (Nikon corporation, Japan). In order to study the morphology and composition of the C60 needle, the PLLA in composites were etched by some H$_2$CCl$_2$, one typical C60 needle without PLLA matrix was fixed onto copper grid followed by gilding, the microstructure and chemical composition of the C60 fiber were then studied by JSM7500F and its INCA EDS accessory. Thermal analysis was carried out on a DSC from TA Instruments (model DSC 2920). About 5 mg samples was weighed and sealed in an aluminum pan. The samples were heated to 200°C at 10°C/min and maintained for 5 min, then quenched to 0°C at −50°C/min and maintained for 5min, and then reheated to 200°C at 10°C/min and maintained for 5min and the second heating curves are recorded. The melting enthalpy change was recorded to study the effect of C60 on the crystallinities of PLLA during the evaporation of solvent. The standard melting enthalpy value of fully crystallized PLLA is 93.6 J/g, the relative crystallinity (Xc) of PLLA could be calculated in the following equation:

$$X_c = (\Delta H_m/93.6) \times 100\%$$  (1)

$\Delta H_m$ referred to the melting enthalpy change.

Results and discussions

Morphology of C60 assemblings in PLLA matrix

Stereoscopic microscope image in Fig. 1 showed the assembled C60s in PLLA matrix were like black straight needles. The amount of C60 in PLLA matrix have some influences on the length of assembled C60 needles, e.g., the black needles in PLLA composites with 1wt% C60 was longer than those in PLLA composites containing 0.5wt% or 2wt% C60, and the C60 needles in PLLA composites containing 2wt% C60 were longer than those in PLLA composites containing 0.5wt% C60. The length distribution of black C60 needles in Fig. (a), Fig. (b) and Fig. (c) was 60-110$\mu$m, 300-500$\mu$m, and 200-300$\mu$m, respectively. The longest C60 needle in PLLA composites could reach over 1 cm long and could be easily seen by naked eyes. One typical C60 needle...

Fig. 1 Stereoscopic microscope images of PLLA films with (a) 0.5wt%, (b) 1.0%wt% and (c) 2.0wt% C60, respectively.
separated from the PLLA filled with 1wt% C60 was further studied by SEM and showed a diameter of about 50 µm and a length of 1.6 mm in the SEM image (Fig. 2).

![Fig. 2 SEM image of one C60 needle in PLLA composites containing 1wt% C60.](image)

**EDS analysis**

To make sure whether the black needles were made up of C60, the chemical composition of the C60 needle were further analyzed via EDS. The analysis results of C60 needles in PLLA composites with 1wt% C60 indicated the black needle contained 88.1wt% (95.62atom percent) carbon element and 11.9wt% (4.58atom percent) chlorine element, which implied the needle was mainly assembled by C60 molecules. The chlorine element might come from the residual solvent absorbed or trapped by C60 molecules during evaporating.

**DSC analysis**

C60, as an heterogeneous nucleating agent for PLLA matrix, could induce the PLLA molecules to crystallize during solvent evaporation, in turn, the crystallization of PLLA might also influence the assembling of C60 and the formation of C60 needles. DSC characterization was carried out to study the nucleation action of C60 on PLLA molecules. The melting enthalpy change during the second heating process was recorded to study the effect of C60 on the crystallinity of PLLA matrix. As is shown in Fig. 3 and Table 1, no cold crystallization happened during the second heating process of neat PLLA. The melting peak top temperature of PLLA crystallites formed and the relative crystallinity (X_c) of PLLA was 151.2°C and 0.75%, respectively. In the case of PLLA containing 1.0wt% C60, there is an obvious cold crystallization process that starts at 127.4°C, which indicates the nucleation action of C60. Due to the nucleation effect of C60, the PLLA in composites crystallized faster thus, the melting peak top temperature of PLLA crystallites in composites was about 0.3°C higher than that of neat PLLA, indicating there was a slight increase in the thickness of PLLA crystallites.

![Fig. 3 The DSC 2nd heating curves of (a) neat PLLA and (b) PLLA with 1wt% of C60, respectively.](image)

### Table 1 DSC results of the second heating process for neat PLLA and PLLA/C60(1wt%) composites

| Samples          | T_c(°C)[a] | T_m(°C)[b] | ΔH_c (J/g)[c] | ΔH_m (J/g)[d] | X_c(%)[e] |
|------------------|------------|------------|---------------|---------------|-----------|
| PLLA             | –          | 151.2      | –             | 0.70          | 0.75      |
| PLLA/C60(1wt%)   | 127.4      | 151.5      | −5.61         | 6.61          | 7.06      |

[a] Crystallization temperature of PLLA. [b] Melting temperature of PLLA. [c] Cold crystallization enthalpy change of PLLA. [d] Melting enthalpy change of PLLA. [e] Relative crystallinity of PLLA.

**Assembling mechanism of C60 in PLLA matrix**

Possible assembling mechanism of C60 needles in PLLA matrix was proposed as follows. With the evaporation of H_2CCl_2, the C60 solution became supersaturated, precipitated C60 would crystallize and combine with each other via Van der Waals force. Meanwhile, the molecules of PLLA would condense and crystallize slowly, some C60 could act an effective nucleating agent during solvent evaporation while H_2CCl_2[12] was used as the common solvent for both C60 and PLLA. As indicated by the aforesaid DSC analysis, PLLA could easily crystallize under the nucleating action of C60. The ordered alignment of PLLA molecular chain during crystallization could, in turn, promote the rest of C60 to migrate into the amorphous area or crystal boundary area of PLLA matrix. It is very likely that the C60 needle be assembled by the enriched C60 along PLLA crystal boundaries via Van der Waals force.

**Conclusion**

Needle-like C60 assembling has been obtained in preparing PLLA/C60 composites. The morphology of
the C60 needle studied by optical microscope and scanning electron microscope (SEM) show that the amount of C60 in the mixing system have some influences on the length of C60 needles. The largest C60 needles could have a diameter of 50 µm and a length of 1.6 mm. The energy dispersive spectra (EDS) analysis indicated the C60 needle was mainly composed of C60, DSC analysis indicated C60 accelerated the crystallization and lift the relative crystallinity of PLLA matrix. The results indicate the addition of PLLA influence the assembling behavior of C60. On the one hand, with the evaporation of H2CCl2, C60 precipitated from solution would crystallize and combine with each other via Van der Waals force. On the other hand, PLLA crystallize easily under the nucleating action of C60, the orderly movement of PLLA molecules would drive C60 to migrate into amorphous area and crystal boundary area, the C60 located in the crystal boundary area of PLLA matrix might tend to assemble into C60 needles via Van der Waals force. The assembly of C60 in other semicrystalline polymer matrix will be investigated in our future work.

Acknowledgments

We owe great thanks for the C60 supplied by NIMS and the support from Prof. Guangzhe Piao in Key Lab of Rubber-plastics of Ministry of Education/Shandong Provincial Key Laboratory of Rubber-plastics, Qingdao University of Science & Technology (QUST), Qingdao 266042, China.

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Effect of Biosynthesized Silver Nanoparticles on *Staphylococcus aureus* Biofilm Quenching and Prevention of Biofilm Formation

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(Received 20 November 2011; accepted 02 March 2012; published online 19 March 2012).

**Abstract:** The development of green experimental processes for the synthesis of nanoparticles is a need in the field of nanotechnology. The synthesis of silver nanoparticles was achieved using *Bacillus cereus* supernatant and 1 mM silver nitrate. 100 mM glucose was found to quicken the rate of reaction of silver nanoparticles synthesis. UV-visible spectrophotometric analysis was carried out to assess the synthesis of silver nanoparticles. The synthesized silver nanoparticles were further characterized by using Nanoparticle Tracking Analyzer (NTA), Transmission Electron Microscope and Energy Dispersive X-ray spectra. These silver nanoparticles showed enhanced quorum quenching activity against *Staphylococcus aureus* biofilm and prevention of biofilm formation which can be seen under inverted microscope (40 X). The synergistic effect of silver nanoparticles along with antibiotics in biofilm quenching was found to be effective. In the near future, silver nanoparticles could be used in the treatment of infections caused by highly antibiotic resistant biofilm.

**Keywords:** Silver Nanoparticles; Green Synthesis; *Bacillus cereus*; Biofilm; Quorum Quenching

**Citation:** Pratik R. Chaudhari, Shalaka A. Masurkar, Vrishali B. Shidore and Suresh P. Kamble, “Effect of Biosynthesized Silver Nanoparticles on *Staphylococcus aureus* Biofilm Quenching and Prevention of Biofilm Formation”, Nano-Micro Lett. 4 (1), 34-39 (2012). [http://dx.doi.org/10.3786/nml.v4i1.p34-39](http://dx.doi.org/10.3786/nml.v4i1.p34-39)

1 Introduction

The field of nanotechnology is one of the most active areas of research in modern material science. Nanoparticles are being considered to be the fundamental building blocks of nanotechnology. Nanotechnology is interdisciplinary which includes physics, chemistry, biology, material science and medicine. Instead of using toxic chemicals for the reduction and stabilization of metallic nanoparticles, the use of various biological entities has received considerable attention in the field of nanobiotechnology [1]. Biological methods are regarded as safe, cost-effective, sustainable and environment friendly processes for the synthesis of nanoparticles [2]. Silver nanoparticles have been successfully synthesized using various bacteria [3-5], fungi [6, 7] and plants [8, 9].

The term biofilm has been introduced to designate the thin layered condensations of microbes (e.g. bacteria, fungi, protozoa) that may occur on various surface structures in nature. Free-floating bacteria existing in an aqueous environment, so-called planktonic microorganisms are a prerequisite for biofilm formation. Such films may thus become established on any organic or inorganic surface substrate where planktonic microorganisms prevail in a water-based solution. In dental contexts, a well-known and extensively studied biofilm structure is established during the attachment of bacteria to teeth to form dental plaque. Here, bacteria free in saliva (planktonic organisms) serve as the primary source for the organization of this specific biofilm [10]. The excretion of adhesive substances viz. polysaccha-
rides and proteins is crucial for the initial attachment of organisms as well as for holding the biofilm bacteria together. The structure per se will then provide protection and may allow a better resistance to adverse external influences for the organisms incorporated as compared with the planktonic state [11]. Phenotypically the organisms may also take on a different character. In addition, a growing body of knowledge suggests that organisms in biofilms assume a stronger pathogenic potential than those in a planktonic state. From these aspects, the formation of biofilm carries particular clinical significance because not only host defense mechanisms, but also therapeutic efforts including chemical and mechanical anti-microbial treatment measures, have a most difficult task to deal with organisms that are gathered in a biofilm [12].

In present study, silver nanoparticles are synthesized using \textit{B. cereus} supernatant. The study deals with the effect of biologically synthesized silver nanoparticles on \textit{S. aureus} biofilm quenching and prevention of \textit{S. aureus} biofilm formation. Diseases such as endocarditis, osteomyelitis and medical-device related infections are caused by \textit{S. aureus} biofilms and are not readily treatable with antibiotics. In fact, biofilms are resistant to antibiotic levels 10- to 1,000-fold higher than planktonic, or free-floating, bacteria [13]. Thus, researchers are focusing on silver nanoparticles for the treatment of infections caused by biofilms.

2 Materials and methods

2.1 Collection of \textit{B. cereus} Supernatant

\textit{Bacillus cereus} (ATCC 8640) was obtained from Department of Botany, Government Institute of Science, Aurangabad (MS), India. \textit{Bacillus cereus} was grown on sterile Luria Bertani (LB-Casein enzymatic hydrolysate 10 gm/l, Yeast extract 5 gm/l, Sodium chloride 10 gm/l, Agar 25 gm/l, pH 7.5±0.2) agar plate (at 37°C). The single isolated colony was inoculated in sterile LB broth and incubated at 37°C at 200 rpm in rotary shaker for 24 hours. After incubation, culture was centrifuged at 4500 rpm for 10 minutes, the supernatant was collected.

2.2 Synthesis of silver nanoparticles using culture supernatant of \textit{B. cereus}

Bacterial supernatant was mixed with 1 mM silver nitrate in 1:1 proportion. The pH of solution was adjusted to 9.0-9.5 [14] and then resultant solutions were kept in rotary shaker (200 rpm) at 37°C till the change in the colour of the solution was observed.

2.3 Synthesis of silver nanoparticles using culture supernatant of \textit{B. cereus} along with 100 mM glucose

Bacterial supernatant :1mM silver nitrate :100 mM glucose were mixed in 1:1:1 proportion. The pH of solution was adjusted to 9.0-9.5. The resultant solution was kept in rotary shaker (200 rpm) at 37°C.

2.4 UV-visible spectrophotometer analysis

After observing colour change, the sample was subjected to mild sonication for 10 minutes. The bioreduction of silver ions in aqueous solution was monitored by UV-Vis spectra of the solution between 300 nm–600 nm using Thermo- Biomate 3 UV-visible spectrophotometer. Distilled water was taken to adjust the baseline.

2.5 Nanoparticle Tracking Analyzer (NTA) Measurements

NTA analysis was carried out by using Nanosight-LM20 instrument. 0.3 ml samples were introduced to the viewing unit using a disposable syringe and enhanced by a near perfect black background; particles appear individually as point-scatterers moving under Brownian motion.

2.6 Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectra (EDX) analysis

TEM analysis of the sample was done using PHILIPS- CM 200 instrument operated at an accelerating voltage of 200 kV with resolution of 0.23 nm. A drop of solution was placed on carbon coated copper grid and later exposed to infrared light (45 minutes) for solvent evaporation. The EDX analysis was carried out using JEOL JSM 7600F.

2.7 In vitro synthesis of \textit{Staphylococcus aureus} biofilm

The biofilm related studies have been performed with the modification of protocol suggested by Kaplan-Ragunath-Ramasubbu-Fine [15] and King-Tatum [16]. Tryptone soy broth (TSB: Pancreatic digest of casein 17 gm/l, Papaic digest of Soyabean meal 3 gm/l, Sodium chloride 5 gm/l, Dipotassium hydrogen phosphate 2.5 gm/l, Dextrose 2.5 gm/l, pH 7.3± 2) with 1% of glucose was inoculated with single isolated colony of \textit{S.aureus} (NCIM 5022) and was incubated at 37°C for 24 hrs. After incubation culture was diluted with fresh TSB-1% glucose in 5:100 proportion, then 200 µl of diluted culture was added in 96 well micro titer plate and in-
cubated at 37°C for 48 hrs [15, 16].

2.8 Addition of quenching agent in *Staphylococcus aureus* biofilm

First column of wells was served as positive control in which 25 µl of 20% sodium dodecyl sulphate was added, second column of wells was served as negative control (untreated biofilm). In the third column of wells, 50 µl of concentrated silver nanoparticles were added. About 50 µl of different antibiotics solution, Gentamicin (10 µg/ml) and Chloramphenicol (20 µg/ml) were added in fourth and fifth column of wells respectively. To check synergistic effect of silver nanoparticles along with antibiotics 25 µl of silver nanoparticles along with 25 µl of above antibiotics were added in sixth and seventh column of wells separately. In eighth column of wells 50 µl of 1 mM AgNO₃ was added. The plate was incubated at 37°C for overnight.

After incubation, plate was washed with 200 µl of phosphate buffer saline (pH-7.2) to remove floating bacteria. Micro titer plate was stained with 100 µl of 0.1% crystal violet for 2 minutes then washed with distilled water. Then add 200 µl of 33% acetic acid and incubate for 5 minutes. Then Plate was properly dried in laminar air flow cabinet. Plate was analysed under inverted microscope (40 X) to record the results. The whole experiment has been performed in triplicate to ensure the reproducibility of the results.

2.9 Effect of silver nanoparticles in prevention of *Staphylococcus aureus* biofilm formation

Overnight grown *Staphylococcus aureus* culture was diluted 1:100 in fresh Tryptone soya broth and allowed to grow for 1 hour. About 200 µl of diluted culture was added to micro titer plate. One column of wells was served as positive control (25 µl of 20% sodium dodecyl sulphate); second column of wells was served as negative control (untreated culture). In the third column of wells, 50 µl of concentrated silver nanoparticles were added. In fourth column of well 50 µl of 1 mM AgNO₃ was added. Plate was incubated at 37°C for 3 days [17]. Washing and staining was done by method mentioned above.

3 Results and discussion

3.1 Synthesis of silver nanoparticles using *B. cereus* culture supernatant

Colour change was observed upon mixing the *B. cereus* culture supernatant with aqueous solution of 1 mM silver nitrate in 1:1 (pH 9.0-9.5), which was incubated at 37°C for 24 hours (Fig. 1). Flask containing culture supernatant of *B. cereus* along with 100 mM glucose and silver nitrate showed intense colour change than the method of synthesizing silver nanoparticles using culture supernatant alone. Intense colour change suggested that the synthesis of silver nanoparticles may be more in the case of this method.

3.2 UV-visible spectrophotometer analysis

The synthesis of silver nanoparticles by reduction of aqueous metal ions during exposure of *B. cereus* supernatant can be easily monitored by using UV-visible spectrophotometer. Figure 2 illustrates the absorbance spectra of reaction mixture containing aqueous solution of 1 mM silver nitrate and *B. cereus* culture supernatant after incubation. Reaction mixture showed an absorbance peak at around 425 nm, which is characteristic of silver nanoparticles, due to its surface plasmon resonance absorption band [18]. In case of the synthesis mediated by *B. cereus* supernatant in the presence of 100 mM glucose, the absorbance peak was obtained at around 425 nm.

3.3 NTA measurements

NTA measurements revealed that the mean size of synthesized silver nanoparticles was found to be 39 nm with concentration of 7.8×10¹⁰ particles/ml in case of
Fig. 3  Frequency size distribution graph of silver nanoparticles synthesized using *B. cereus* supernatant. X axis: particle size in nm; Y axis: concentration/ml ×10⁶.

Bacterial supernatant mediated synthesis. The mean size of silver nanoparticles synthesized using bacterial supernatant in presence of glucose was found to be 32 nm with concentration of 10.4×10¹⁰ particles/ml (Fig. 3).

3.4 TEM and EDX analysis

TEM analysis revealed that the silver nanoparticles are prominently spherical (Fig. 4). The silver nanoparticles were found to be well dispersed from each other. The EDX analysis revealed that the silver is present in the solution (Fig. 5). The silver content in the particles was found to be 70.29%.

Fig. 4  TEM micrograph of silver nanoparticles synthesized using (a) *B. cereus* supernatant; (b) and (c) *B. cereus* supernatant and 100 mM glucose.

Fig. 5  EDX spectra of silver nanoparticles solution.

3.5 Quorum quenching Effect of silver nanoparticles on *Staphylococcus aureus* Biofilm

Silver nanoparticles showed quenching of biofilm which can be compared with negative control antibiotics failed to show biofilm quenching alone which can be compared with positive control. But synergistic effect of silver nanoparticles and antibiotic showed the biofilm quenching. 1 mM silver nitrate also did not show any quenching of biofilm. (Fig. 6(a-h))

3.6 Effect of silver nanoparticles in Prevention of *Staphylococcus aureus* biofilm Formation

Silver nanoparticles showed prevention of biofilm formation which can be compared with negative control. Where as positive control showed distinct biofilm formed which indicates that silver nanoparticles prevent formation of bacterial biofilm. (Fig. 6(i)) It is known that the excretion of adhesive substances viz. polysaccharides and proteins is crucial for the initial attachment of organisms as well as for holding the biofilm bacteria together [11]. The silver nanoparticles might be involved in neutralizing these adhesive substances, thus preventing biofilm formation.
4 Conclusion

In the present study, silver nanoparticles have been synthesized using *B. cereus* supernatant alone and *B. cereus* supernatant in the presence of glucose. The increased synthesis of silver nanoparticles was achieved in case of *B. cereus* supernatant in the presence of glucose. The exact role played by glucose in enhancing the rate of synthetic reaction of silver nanoparticles will be the field of research interest.

In the present study, effect of silver nanoparticles in biofilm quenching and prevention of biofilm formation has been demonstrated. From the results it can be concluded that silver nanoparticles can be involved in biofilm quenching or prevention of biofilm formation. However, antibiotics failed to show any quenching of bacterial biofilm. Synergistic effect of silver nanoparticles along with antibiotics in biofilm quenching has also been demonstrated in this study. The exact mechanism of action of silver nanoparticles in biofilm related studies is yet to be demonstrated. In the near future, silver nanoparticles may play a major role in the treatment of infections caused by highly antibiotic resistant biofilm.

Acknowledgments

We are thankful to Dr. Aurobindo Roy, Dr. Suresh Jangle, Dr. Razia Kutty, Mr. Keshav Shinde, Mr. Santosh Suradkar and Mr. Rajesh Raut for their priceless help. We sincerely acknowledge the facilities provided by Institute of Science, Mumbai and SAIF, IIT Mumbai. We are thankful to Pravara Institute of Medical Sciences, Loni (MS), India for the financial support.
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High Potential Columnar Nanocrystalline AlN Films Deposited by RF Reactive Magnetron Sputtering

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(Received 10 February 2012; accepted 12 March 2012; published online 19 March 2012)

Abstract: Columnar nanocrystalline aluminum nitride (cnc-AlN) thin films with (002) orientation and uniform texture have been deposited successfully on large silicon wafers by RF reactive magnetron sputtering. At the optimum sputtering parameters, the deposited cnc-AlN thin films show a c-axis preferred orientation with a crystallite size of about 28 nm and surface roughness (RMS) of about 1.29 nm. The cnc-AlN thin films were well transparent with an optical band gap about 4.8 eV, and the residual compressive stress and the defect density in the film have been revealed by Ramon spectroscopy. Moreover, piezoelectric performances of the cnc-AlN thin films executed effectively in a film bulk acoustic resonator structure.

Keywords: Columnar film; Aluminum nitride; Piezoelectric effect; RF sputtering; Optical property

Citation: Chengzhang Han, Da Chen, Yaozhong Zhang, Dong Xu, Yijian Liu, Eric Siu-Wai Kong and Yafei Zhang, “High Potential Columnar Nanocrystalline AlN Films Deposited by RF Reactive Magnetron Sputtering”, Nano-Micro Lett. 4 (1), 40-44 (2012). http://dx.doi.org/10.3786/nml.v4i1.p40-44

Introduction

AlN has been attracting considerable attentions because of its superior physical properties such as good thermal and chemical stability, high ultrasonic velocity, outstanding thermal conductivity, high electrical resistivity, excellent piezoelectric response, wide optical band gap, etc. Recently, there has been great interest in the excellent properties of AlN thin films for a wide variety of applications [1], such as optoelectronic devices, microelectronic devices and bulk acoustic wave devices [2]. Several methods, such as pulsed laser deposition (PLD), chemical vapor deposition (CVD), molecular beam epitaxy (MBE) and magnetron sputtering [3], have been reported to deposit AlN thin films. However, it is remain to be investigated for obtaining high quality highly oriented cnc-AlN thin films with expected properties, e.g. c-axis perpendicular to the substrate surface, high stiffness, low surface roughness, resistance to solvents, high conductive to heat, etc.

Reactive magnetron sputtering is considered to be a kind of potential deposition technique with advantages of being low temperature, low cost and controllable deposition conditions. Besides, the surface morphology, grain size and band gap energy of AlN films are connected with the deposition conditions [4]. A high degree of c-axis orientation and smooth surface of the AlN films are essential to the bulk acoustic wave devices, since the piezoelectric properties are strongly dependent on the crystallographic orientation of the film [5].

The aim of this work was to develop an advantageous synthesis condition of RF reactive magnetron sputtering-
ing for cnc-AlN thin films with (002) orientation and uniform textured on large silicon wafers for FBAR with effective piezoelectric performances. The characteristic of the cnc-AlN thin films were measured using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), atomic force microscopy (AFM) and spectrum.

**Experimental**

RF reactive magnetron sputtering of an Al (99.999% purity) target in a N₂ (99.999% purity) and Ar (99.999% purity) mixture atmosphere was used for deposition of cnc-AlN thin films. The distance target-to-substrate is about 70 mm and target diameter is 80 mm. All samples were deposited on p-type Si (1 0 0) substrates of 3 inch with 1–10 Ω·cm resistivity. Some controllable deposition parameters in the cnc-AlN films deposition experiments are shown in Table 1.

| Deposition parameters       | Value          |
|----------------------------|----------------|
| Base pressure (Pa)          | 5x10⁻⁵         |
| RF power (W)                | 100~250        |
| N₂ flow rate (sccm)         | 0~20           |
| Ar flow rate (sccm)         | 0~20           |
| Sputtering pressure (Pa)    | 0.5~2.0        |
| Substrate temperature (°C)  | RT~300         |

The crystalline structure of the cnc-AlN films was investigated by XRD using a Cu-Kα radiation (λ=1.54187Å). The surface morphology of the cnc-AlN films was examined using FE-SEM. The crystalline grain size of the cnc-AlN films was observed by TEM. The surface roughness of the cnc-AlN films was determined using AFM. The optical transmission of the film was measured by UV spectrophotometer. The residual stress and defect density of the cnc-AlN films were also evaluated by Raman spectroscopy.

**Results and discussion**

**The effects of deposition parameters on cnc-AlN films**

The deposition parameters, including RF power, pressure, ratio of N₂/Ar, and substrate temperature, have been investigated systematically and demonstrated significant effects on the crystalline structure and properties of AlN films. Figure 1 shows the XRD results of the AlN films deposited on silicon substrates with different RF power with N₂/Ar of 70%, substrate temperature of 300°C, pressure of 1 Pa. When the power was 100 W, there are obvious non-crystalline structure feature as a broad diffraction peak in the XRD curve. With the increase of power, the AlN structure feature are becoming crystalline obvious and the AlN (002) and (100) diffraction peak becomes stronger and sharper. However, the AlN diffraction (100) peak becomes disappeared at the power of 200 W and a sharp AlN (002) peak remains.

![Fig. 1 The XRD results of the cnc-AlN films deposited on silicon substrates for different RF power levels.](image)

The AlN (002) peak is observed at 35.94° with a full width at half-maximum (FWHM) of 0.30°, which indicates that the preferential AlN growth orientation is along the wurtzite c-axis and perpendicular to the surface of substrates. According to the well-known Scherrer formula [6],

\[
D = \frac{0.94 \lambda}{\beta \cos \theta}
\]

where, D is the crystalline grain size, λ is the wavelength of Cu-Kα radiation, β is the FWHM of diffraction peak, and θ is the position of diffraction peak. The crystalline grain size of AlN is estimated to be about 28 nm from the formula, which is similar to the value reported in the paper [7]. But, when the power is high to 250 W, the (002) peak becomes relatively broader, which may due to the high power induced increase of defects in the film nanocrystalline structure.

Figure 2 shows the XRD results of the cnc-AlN films deposited on the silicon substrates at different pressures with the RF power of 200W, N₂/Ar of 70%, substrate temperature of 300°C. It can be seen that as the pressure increased from 0.5 Pa to 2 Pa gradually, the FWHM of the AlN (002) diffraction peak decreases at first and then increases, and the optimum pressure is at 1 Pa. This result may be explained that when the pressure was very low, the Ar⁺ and N⁺ ions with much high momentum were not suitable enough to form well crystallinenature. When the pressure was very high, the ratio of ion collision between each other became more frequent and weaker correspondingly [8], the energy of Ar⁺ and N⁺ ions may be not high enough for the formation of (002) crystal plane, which leads to texture decline in the film.
Figure 2 shows the XRD results of the cnc-AlN films deposited on the silicon substrates for different pressure levels. The XRD results for different pressure levels are shown in Fig. 2. The intensity of the AlN (002) peak increases with increasing pressure, indicating a decrease in the in-plane interatomic distances. The XRD results for different ratios of N₂ to Ar are shown in Fig. 3. The intensity of the AlN (002) peak decreases with increasing N₂ concentration, indicating an increase in the in-plane interatomic distances. The XRD results for different temperatures are shown in Fig. 4. The intensity of the AlN (002) peak decreases with increasing temperature, indicating a decrease in the in-plane interatomic distances.

The structure of (002) oriented cnc-AlN films

The comprehensive features of cnc-AlN films, such as microstructure, grain size, and texture, have been observed intuitionally from TEM micrographs. TEM bright field and dark field images were used to examine the microstructure and grain size of the AlN film, respectively. While the selected area electron diffraction (SAED) was utilized to study the crystalline phase present. Figure 5(a) shows a cross-section bright-filed (BF) TEM micrograph, together with the SAED pattern in Fig. 5(b) and the dark-filed TEM micrograph in Fig. 5(c). The in-plane nanocrystalline grains are columnar with grain size of about 24 nm, which is similar with the value calculated by Scherrer formula. The SAED pattern shown in Fig. 5(c) indicated a crystalline phase of AlN can be obtained. As for AlN, a preferred orientation is already seen from the arcing of the (002) diffraction spots around the growth axis, according to the occurring diffraction rings. In addition, according to the SAED pattern, it is obviously typical of a
polycrystalline film. Moreover, the diffraction spots are very intense, which proved that the film is well crystallite.

Figure 6(a) and (b) show SEM and AFM of the surface morphology of cnc-AlN films deposited on silicon substrates by using the optimal deposition parameters, and Fig. 6(c) shows the cross-sectional image. The cnc-AlN films demonstrate clearly a hummock-like surface morphology with smooth, homogeneous, uncracked, compact and dense. The surface morphology consists of a large number of crystalline grains with compact columnar structure. There are many grain boundaries among columns and the RMS was in an average of 1.29 nm which was measured by the low-high ruggedness in the AFM.

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Figure 7(a) demonstrates the UV transmittance spectrum of cnc-AlN thin films with the thickness of 500 nm deposited on a glass substrate. The optical properties of the cnc-AlN films transparent in appearance with average transmittance of about 92.6% in the wavelength range of 200-800 nm. The fundamental absorption edge for the cnc-AlN films is found to be near 290 nm.

The optical band gap of the cnc-AlN films have been calculated with the Tauc equation [9]:

\[
(\alpha h\nu)^2 = B(h\nu - E_g)
\]

\(\alpha\) is the absorption coefficient, \(B\) is a proportional constant related to the material, \(h\nu\) is the photon energy of incident light and \(E_g\) is the optical band gap, respectively. The optical band gap is obtained by extrapolating the tangential line to the photon energy axis in the plot of \((\alpha h\nu)^2\) as a function of \(h\nu\). Figure 7(b) shows the typical \((\alpha h\nu)^2 \sim h\nu\) curve for the cnc-AlN films. The optical band gap for the cnc-AlN films is estimated about 4.8eV, which is similar to the reported data [10].

Figure 8 shows a typical Raman spectrum of the cnc-AlN films deposited on silicon substrates. Two obvious intense peaks can be observed from the spectrum, one at 519 cm\(^{-1}\) originates from the silicon substrate, another at 660 cm\(^{-1}\) corresponds to the E\(_2\) (high) mode of AlN, of which the frequency is higher than the standard frequency of E\(_2\) at 657.4 cm\(^{-1}\) [11]. This reveals there are small residual compressive stresses in the cnc-AlN films, which is possibly induced by the difference of the thermal expansion coefficient between the film and the Si substrate.
Fig. 8 The typical Raman spectrum of the cnc-AlN films deposited on silicon substrates.

The (002) textured cnc-AlN films have been used crucial for film body acoustic rasonator (FBAR) as the piezoelectric film which is most crucial in quality. Figure 9 shows a schematic of a FBAR sample and the measured frequency response curve. The center frequency of the FBAR is about 2.2 GHz and the insertion loss is about 30 dB. Results showed the devices exhibited excellent performance with the quality factor (Q) about 385 and the effective electromechanical coupling coefficient (k^2eff) about 3.4% [12,13].

Conclusions

Well (002) oriented cnc-AlN films have been deposited on silicon substrates by RF reactive magnetron sputtering with texture. The effect of process parameters on properties of cnc-AlN films has been demonstrated systematically. A hummock-like surface morphology with smooth, homogeneous, uncracked, compact and dense, have been observed by SEM and the crystallite size in the cnc-AlN films is about 24 nm which was measured by TEM observation. The average transmittance is about 92.6% and the optical band gap is estimated to be about 4.8 eV. An intense peak can be observed at 660 cm\(^{-1}\) from the Raman spectrum, which proved the residual compressive stress in the cnc-AlN films. The high quality of the cnc-AlN films have been proved with good performance as a piezoelectric film in the critical structure of film bulk acoustic resonator.

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Assembling ZnO Nanorods into Microflowers through a Facile Solution Strategy: Morphology Control and Cathodoluminescence Properties

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(Received 4 November 2011; accepted 27 February 2012; published online 26 March 2012.)

Abstract: In this work, flowerlike ZnO micro/nanostructures assembled from nanorods are obtained through a facile hydrothermal route. The experimental results indicated that the as-synthesized ZnO microflowers have an average diameter of 2 µm, composed of nanorods of an average diameter of 200 nm and a tapered morphology. ZnO with other morphologies were also obtained by varying the reaction conditions. Systematical condition-dependent experiments were conducted to reveal the growth mechanism of the microflowers. It is suggested that the zinc source types, solution pH value, and reaction temperature, as well as reaction time are responsible for the variations of ZnO morphology. Luminescence properties of ZnO microflowers were investigated through monitoring different parts of nanorods, showing good optical quality.

Keywords: Microflowers; Solution growth; ZnO; Cathodoluminescence

Citation: Ying Lei, Fengyu Qu and Xiang Wu, “Assembling ZnO Nanorods into Microflowers through a Facile Solution Strategy: Morphology Control and Cathodoluminescence Properties”, Nano-Micro Lett. 4 (1), 45-51 (2012). http://dx.doi.org/10.3786/nml.v4i1.p45-51

The size and shape of low dimensional micro/nanoscale materials have a crucial influence on their physical and chemical properties, and on the properties of the integrated nanodevices due to the significant surface effect and quantum size effect [1-3]. In particular, hierarchical assembly of micro/nanoscale building blocks with tunable dimension and structure is essential for the fabrication of micro/nanodevices [4, 5]. Inspired by this, hierarchical and complex micro/nanostructures have been the focus of intensive research in recent years. Fan et al. reported the assembly of ZnO nanorods on SnO$_2$ nanowire backbones through a two-step growth process that combines the vapor transport and deposition process and a hydrothermal method [6]. Dick et al. synthesized heterogeneous GaP-GaAsP nanotrees via a stepwise deposition of gold nanoparticles on GaP nanowires [7]. Ni et al. reported flowerlike ZnO-ZnS heterogeneous microstructures built up by ZnS-particle-strewn on ZnO microrods by a hydrothermal route [8]. Some other flowerlike and hierarchical micro/nanostructures (including metal or ternary compounds) were also reported, such as Au [9], Bi$_2$SiO$_5$ [10], Bi$_2$S$_3$ [11], ZnS [12], InP [13], SnO$_2$ [14] and ZnS-ZnO heterostructures [15].

ZnO, as an important semiconductor material, has a wide variety of applications in pigments [16], field effect transistors [17], field emitters [18], ultraviolet detectors [19], cosmetics [20] and energy storage [21-23]. To date, various splendid morphologies of ZnO nanostructures have been reported by different synthesis approaches including thermal evaporation [24-26], hydrothermal reaction [27-29], electrochemical deposition [30-31]. Among them, the solution approach has been proved to be an efficient way with outstanding advantages, such as simplicity, commercial feasibility and potential for scaling up.
In the literature, there are some reports about ZnO micro/nanostructures. Ogale et al. synthesized ZnO nanoflowers loaded with gold nanoparticles at 180°C and studied the power conversion efficiency of dye-sensitized solar cells based on the ZnO nanoflowers with gold nanoparticles [32]. Tang’s group reported 3D ZnO flowerlike nanostructure and the nanorods assembling flowers possess hexagonal shapes [33]. Prabakar and his coworkers synthesized ZnO nanoflowers through spin coating a film seed layer on FTO substrate [34]. Jiang et al. also reported ZnO nanoflowers through a hydrothermal method [35]. However, in the reports mentioned above, the nanorods composing the flowers are either smooth top or hexagonal shape: none of them investigated the effect of nanorod diameter on the luminescence property. In this study, we reported the fabrication of flowerlike ZnO micro/nanostructures through an assembly of the nanorods with the tapered tops via a simple solution strategy without using any surfactant or template at mild temperature. The morphologies of the ZnO micro/nanostructures can be tunable by adjusting the growth parameters, such as solution basicity, reaction temperature and time. Cathodoluminescence (CL) properties of the as-prepared ZnO products were investigated by comparing the spectra recorded at different parts of the nanorods. Our strategy of assembly of nanorods into microflowers can be extended to some other compounds and even complex micro/nanostructures with ultrahigh surface areas towards the exploration of their unique functional properties.

ZnO microflowers were fabricated via a simple hydrothermal route. All reagents are analytical grade and were used without further purification. In a typical procedure, 0.352 g zinc acetate dehydrate (Zn(Ac)$_2$·2H$_2$O) was first dissolved into 30 ml de-ionized water and 1.12 g KOH was dissolved into 5 ml de-ionized water. The solution of KOH was then added dropwise into the above zinc acetate solution under continuous magnetic stirring for 10 minutes at room temperature. Afterward, the above mixture of solution was transferred into a stainless steel autoclave with a 50 ml PTFE container and maintained at 150°C for 20 h. After the reaction, the autoclave was naturally cooled to room temperature. The resulting products were collected, washed several times with de-ionized water and alcohol in sequence, and finally dried at 60°C for 12 h.

The phase of the as-obtained products were examined using x-ray powder diffraction (XRD, Rigaku Dmax-rB, CuKα radiation, λ=0.1542nm, 40KV, 100mA). The morphology and microstructure of the samples were characterized with scanning electron microscope (SEM, Hitachi-4800) and transmission electron microscope (TEM, JEOL-3010). The samples for TEM were prepared by suspending the synthesized ZnO product in absolute ethanol by ultrasonic treatment for 5 minutes and then transferring onto a carbon-coated copper grid. The copper grid was air-dried under ambient conditions. Cathodoluminescence (CL) properties were investigated using a thermal field emission scanning electron microscope (Hitachi S4200) equipped with a CL system. The CL spectra and images were taken at room temperature at 3 kV and 320 pA.

Figure 1 shows a typical XRD pattern of the as-obtained product. All of the peaks match well with the bulk ZnO, which can be indexed to the hexagonal wurtzite structure of ZnO (JCPDS card No. 05-0664). No peaks were observed from other impurities such as Zn(OH)$_2$, which suggests that as-synthesized product is pure ZnO.

Representative morphologies of the as-synthesized ZnO micro/nanostructures, as revealed by SEM, are shown in Fig. 2(a)-(b). As seen from the low magnification SEM images (Fig. 2(a)), uniform flowerlike nanostructures were obtained with high yield. These flowerlike structures have an average diameter of 2 µm and are composed of nanorods radially branching out from the center (see in Fig. 2(b)). The average diameter of each nanorod is 200 nm and with a sharp tip. It is realized that this kind of tapered nanorod has a different luminescence property, which will be discussed later. Figure 2(c) shows a typical TEM image of a single microflower. The high resolution lattice TEM (HRTEM) image taken in the red square region (shown in Fig. 2(d)) gives a lattice fringe separation of 0.52 nm, corresponding to the (0001) spacing. The corresponding fast Fourier transform (FFT) pattern (the inset in Fig. 2(d)) confirms a single crystal structure with the growth direction along the [0001] direction.

In order to investigate the formation process of the ZnO microflowers, a series of controlled experiments were performed through adjusting several growth parameters, such as reaction temperature, reaction time, dose of the alkali solution and organic solvent. First, SEM images of the products from time-dependent experiments are shown in Fig. 3. When the reaction time...
Fig. 2  SEM and TEM images of the as-synthesized ZnO microflowers: (a) Low magnification SEM images; (b) High magnification SEM images of single microflower; (c) Low magnification TEM image of single microflower; (d) HRTEM image in Fig. 2(c). The inset is the corresponding SAED pattern.

Fig. 3  SEM images of the products from reaction time dependent experiments: (a) 5 h; (b) 20 h; (c) 30 h and (d) 48 h.

is 5 h, only a few microflowers appear while the majorities are incomplete flowers or disperse nanorods (indicated by the blue circle in Fig. 3(a)). With the reaction time increased to 20 h, the as-obtained product is composed of nearly pure microflowers with an average diameter of 2 µm, as shown in Fig. 3(b). With further elongation of the reaction time to 30 h (Fig. 3(c)) and even to 48 h (Fig. 3(d)), the flowerlike morphology still
retains whereas the nanorods tend to bundle together forming a sheet-like structure.

Since the growth of micro/nanostructure undergoes a series of continuous reaction process for nucleation and growth, reaction temperature plays an important role in tailoring the final morphology. The above-shown microflowers were formed from a reaction at 150°C for 20 h. When the temperature was reduced to 100°C with other conditions remain unchanged, the obtained microflowers were not uniform, and more than one microflowers attach each other, as revealed in Fig. 4(a). At the elevated temperature of 180°C, some small particles and rods appeared lying randomly on the microflowers. Further increasing the temperature to 220°C resulted in disappearance of the microflowers and only some microcrystals or nanorods were observed. Hence, the optimum temperature is determined to be 150°C.

Furthermore, the dosage of alkali is expected to have a decisive influence on morphology of the resultant products due to the participation of OH$^-$ ions in the nucleation and formation of the seeds. SEM images of the as-obtained products with different dosage of alkali (0.6 g and 1.0 g) are shown in Fig. 5(a)-(b). One can see that a small amount of alkali (0.6 g) resulted in only some sheets and poor-defined particles. Finally, different zinc salts were also found to induce changes in the morphology of the as-obtained product. The SEM image in Fig. 5(c) shows that only separated nanorods can be seen, without the assembly into microflowers, when Zn(Ac)$_2$ was replaced by ZnSO$_4$ with other growth conditions kept the same as in Fig. 2. Under the condition that Zn(NO$_3$)$_2$ was used, microflowers appeared but the nanorods are connected each other into sheets, as indicated by the rectangle in Fig. 5(d). Finally, as a typical additive in hydrothermal growth of ZnO nanorods, effect of hexamethylenetetramine (HMT) on the morphology of the as-synthesized product was also studied. It is found that addition of HMT also prevents the formation of microflowers (see Fig. 5(e)-(f)). These results reveal that the resultant morphology of the as-obtained product is a result of a delicate interplay of various parameters; On the other hand, such dependence allows one to tune the desired structure of the final product for applications in which either a high aspect ratio or a high structural integrity is desired.

The formation process of crystals involves two stages: nucleation and growth. External parameters may pose dramatic effects on the size and morphology of the final crystal depending on the degree of participation during the nucleation and initial growth. The overall reaction for ZnO micro/nanostructures in an alkaline solution can be proposed as follows:

\[
\begin{align*}
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn(OH)}_2 \\
\text{Zn(OH)}_2 + 2\text{OH}^- & \rightarrow \text{Zn(OH)}_4^{2-} \\
\text{Zn(OH)}_4^{2-} & \rightarrow \text{ZnO} + 2\text{H}_2\text{O} + 2\text{OH}^- 
\end{align*}
\]

In literature, Kim et al. synthesized ZnO nanoflower arrays through using a pre-patterned PMMA mask on the ZnO seed layer deposited on fluorine-doped tin oxide (FTO) glass [36]. Zhang et al. reported flowerlike nanostructures of ZnO by treating Zn(OH)$_4^{2-}$ precursor in water at 180°C, and investigated the shape evolution induced by several growth parameters [37]. Ni et al. proposed the formation of ZnO flower-like structures is
sensitive to the amount of ammonia used in the system [8]. This is also the case in our experiment. When the quantity of alkali is small, only some sheets and particles appear, as shown in Fig. 5(a)-(b). Due to the coordination effect of \( \text{OH}^- \) ions to \( \text{Zn}^{2+} \) ions, it is possible that \( \text{OH}^- \) ions are adsorbed at the circumference of \( \text{Zn} \) ions of the \( \text{ZnO} \) nuclei. Due to the spatial hindrance, \( \text{ZnO} \) grew only along certain directions, which leads the formation of flowerlike structure [8]. Gao et al. believed that the introduction of HMT has an important influence on the formation of \( \text{ZnO} \) flowerlike structures [38]. However, this is not the case in our experiments.

Figure 6 shows a typical CL spectrum obtained at room temperature from the \( \text{ZnO} \) microflowers. The corresponding SEM image is shown in Fig. 6(a). The CL spectra recorded from five spots corresponding to different diameters on a nanorod are recorded. Clearly all spectra have an ultraviolet emission peak at \( \sim 388 \) nm and a broad green emission peak ranging from 521 to 539 nm. It is noted that the emission intensity becomes lower with decreasing diameter. Location of visible emission peaks from spot 1 to spot 5 are 521 nm, 539 nm, 537 nm, 532 nm and 528 nm, respectively. The UV emission peak of the microflowers in this work is 388 nm, which is in good agreement with the typically reported free exciton peak position and could be attributed to UV near-band edge emission [39]. The impurities and structural defects, such as oxygen vacancies and so forth, are responsible for the deep level or trap-state emission in the visible range [40]. For the visible green emission peaks in CL spectrum, it is
generally accepted that the green emission originates from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy [41-42]. Li et al. attributed the green emission to point defects, which can easily form recombination center [43]. In our experiment, when the as-synthesized ZnO nanostructures were dried at 60°C for 12 h in air ambient, the surface of the microflowers would get rougher, revealing that there are abundant surface defects in the product. Taking large surface volume ratio in microflower structures into account, the broadening and enhancement of the green emission peak can be ascribed to abundant surface defects. Abundant defects at the surface of ZnO microflowers can provide new states as visible luminescence centers and broaden the visible emission band.

In summary, we reported an easy and efficient hydrothermal method to synthesize ZnO microflowers through the self-assembly of nanorods at a mild temperature (150°C). A series of control experiments by adjusting several growth parameters were conducted which allows a systematic investigation of the growth process. Optical properties of the as-synthesized ZnO microflowers have been studied, which show both sharp ultraviolet emission peaks and broad green peaks. The emission intensity lowers with decreasing diameter. The ZnO microflowers obtained herein may have potential applications in photocatalyst or photoelectrochemical cells.

Acknowledgement

This work was supported by the Foundation for Key Project of Ministry of Education, China (No. 211046), Open Fund of State Key Laboratory for Modification of Chemical Fibers and Polymeric Materials, Dong Hua University (No. K1012), Open Fund State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University (No. 2012-22) and Program for New Century Excellent Talents in Heilongjiang Provincial University.

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One-Step Synthesis and Photoluminescence Evaluation of Cadmium-containing Quantum Dots

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(Received 8 November 2011; accepted 22 March 2012; publication online 28 March 2012.)

Abstract: We have developed a simple one-step process for synthesis of ternary quantum dots (ZnCdSe, MgCdSe) with photoluminescence wavelengths ranging from the red to the blue region of the visible spectrum. The primary aim of this work was to develop a synthesis for the preparation of Cd-containing quantum dots using a Cd precursor with lower toxicity than those used in common syntheses. This synthesis makes use of Cd(acac)₂ which is significantly less toxic than precursors such as CdO and CdCl₂. We have studied the effect of solvent boiling point, precursors and reaction time on the photoluminescence properties of the ternary quantum dots. Ternary quantum dots synthesized from Cd(acac)₂ in low boiling point solvents have photoluminescence wavelengths in the blue region, while those synthesized in high boiling point solvents have photoluminescence wavelengths in the red region.

Keywords: Quantum dots; ZnCdSe; MgCdSe; Photoluminescence

Introduction

Quantum dots are small semiconductor nanoparticles with electron energy levels that are discrete rather than continuous. The size of the semiconductor nanoparticles determines the spacing of their energy levels and thus, their band gap. The band gap increases as the quantum dots size decreases and thus, the band gaps of quantum dots are tunable. As a result of their high band gaps, smaller quantum dots absorb light at shorter wavelengths than larger quantum dots. The other parameter which controls the band gap of quantum dots is their composition. By controlling both the quantum dot size and composition, it is possible to create quantum dots that absorb light at frequencies spanning the entire solar spectrum. As a result, these materials have great potential for use in photovoltaic applications [1-3].

Knoll et al. [4] reported the synthesis of ZnCdSe quantum dots using a two-step process. In a two-step synthesis process CdSe quantum dots were synthesized first and then used as seeds to make core-shell structures of ZnSe with CdSe inside and ZnSe outside. In this type of two-step process both CdSe and ZnSe are synthesized separately and there is no alloy formation of CdSe and ZnSe until they are annealed. The core-shell structures of CdSe core and ZnSe shell was then heated to form alloy ZnCdSe quantum dots. In that process [4], it was observed that changing the amount of Zn caused a shift in the photoluminescence peak wavelength. The quantum dots of pure CdSe (0% Zn) had photoluminescence peaks in the red region of the solar spectrum while photoluminescence peaks in the blue region of the solar spectrum were observed for Zn₀.₆₇Cd₀.₃₃Se quantum dots. In similar work, other types of three and four component quantum dots have been synthesized using two-step processes that generate core-shell structures [10-12]. The component combinations previously re-

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ported include: CdSe/ZnS, CdSe/ZnSe, CdS/ZnS and CdSe/CdS [10-15]. The core-shell structures are then heated to form alloys. Needless to say, from the point of view of large scale preparation of quantum dots, a one step process would be superior to a two step process. In our method of synthesis we have used one-step synthesis as explained in the experimental section. We have used cadmium and zinc precursors at the same time in the reaction mixture in the presence of selenium and reduced these precursors simultaneously.

A second issue with the reported syntheses of these types of quantum dots is that many of the precursors are highly toxic, which presents another problem in the scale-up of the preparation methods. Typical Cd containing precursors such as CdO, Cd(CH$_3$)$_2$, CdSO$_4$, Cd(C$_{17}$H$_{35}$COO)$_2$ all have Hazardous Materials Identification System (HMIS) and National Fire Protection Association (NFPA) ratings of 4. Chemicals with ratings of 3 and 4 are extremely toxic or hazardous materials. CdCl$_2$ and Cd(NO$_3$)$_2$ have NFPA and HMIS ratings of 3. Another Cd precursor reported in literature is Cd(CH$_2$COO)$_2$ with NFPA and HMIS ratings of 2 (moderately toxic or hazardous). The HMIS and NFPA health ratings for Zn(acac)$_2$ are 2. Again, scale-up of processes for preparation of quantum dots composed of these elements would benefit from the development of syntheses using less toxic and less dangerous precursors.

The objective of the work reported has been to demonstrate a one-step synthesis of ternary quantum dots using low toxicity chemicals and to understand the synthesis parameters that influence the properties of the resulting ternary quantum dots. This understanding will be used to develop ternary quantum dots with improved photoluminescence properties. The ultimate goal is to prepare ternary quantum dots with narrow absorption peaks at any wavelength. In this work we have used two types of solvents (1,2-dichlorobenzene, b.p. 180°C; 1-octadecene, b.p. 315°C), and a variety of Cd precursors (CdO, CdCl$_2$ and Cd(acac)$_2$) and M(acac)$_2$ precursors (M = Zn, Mg) to synthesize ternary alloy quantum dots. The type of Cd precursors did not have any impact on the photoluminescence peaks of the chemically synthesized quantum dots. As a result, we have reported results only from quantum dots prepared using Cd(acac)$_2$ as it is the least hazardous of the three with a HMIS health rating of 1 and a NFPA health rating of 1 (slightly toxic or hazardous material). In this work, several types of ternary quantum dots including ZnCdSe and MgCdSe were synthesized and the effect of solvent on the photoluminescence properties of these quantum dots was studied. We have focused on the photoluminescence properties of these quantum dots prepared using a one-step process starting with low toxicity precursors. Ternary quantum dots synthesized in low boiling point solvents have photoluminescence wavelengths in the blue region, while those synthesized in high boiling point solvents have photoluminescence wavelengths in the red region.

**Experimental**

ZnCdSe quantum dots were synthesized using a one-step process involving reduction of Cd(acac)$_2$ and Zn(acac)$_2$ in a low boiling point polar solvent (1,2-dichlorobenzene, b.p. 180°C) and in the presence of surfactants (oleic acid). The synthesis of ternary alloy quantum dots was conducted in a moisture and oxygen free atmosphere. The Cd(acac)$_2$ (0.15 mmol) and Zn(acac)$_2$ (0.06 mmol) were heated in the 1,2-dichlorobenzene (10 ml) in the presence of oleic acid (0.6 ml) until they dissolved. Then a 1 ml solution of Se in trietylphosphine (TOP) in 1,2-dichlorobenzene (concentration of 0.07 mmol/ml) was added to the reaction mixture (details are in the results section). The reaction mixture was allowed to reflux (180°C) and 0.5 ml aliquots of the reaction mixture were withdrawn after different intervals of time. The aliquots were diluted in 3 ml of toluene in order to obtain photoluminescence spectra. This diluted solution in toluene still had some dichlorobenzene. Similar experiments were also performed using a high boiling point solvent 1-octadecene (b.p. 315°C). In addition to synthesis of ZnCdSe, we have extended our synthesis method to prepare MgCdSe using Mg(acac)$_2$ as a precursor.

The photoluminescence spectra were taken using a PTI Timemaster series spectrofluorometer fitted with a PMT sensor. The excitation source was a Xe lamp emitting at 350 nm. The scan range chosen for each sample was 375-650 nm and spectra were obtained using a 1 nm step and a 0.5 sec integration time. Spectra were captured using the FeliX32 Advanced Fluorescence Analysis Software Package. In our experiments the intensity of photoluminescence peaks is reflective of the concentration of particles which is not controlled in our experiments.

All the solvents and chemicals (Cd(acac)$_2$ (99%), Zn(acac)$_2$, Mg(acac)$_2$, Se powder, hexane, ethanol, 1,2-dichlorobenzene, octadecene, oleic acid, trioctylphosphine, toluene and diocylether) used for the synthesis and washing of the ZnCdSe, MgCdSe quantum dots were obtained from Aldrich Chemical Co. and were used as obtained without further purification. Ethanol was obtained in Sureseal bottles with very low water content (<0.05%). The hexane was 99% pure with low water content.

**Results**

There are a number of parameters that influence the synthesis and final properties of ternary quantum dots. This work focuses on the effects of using M(acac)$_2$ (M
= Cd, Zn, Mg) precursors in the synthesis of ternary quantum dots. The other variable which was explored in the synthesis of ternary alloy quantum dots was the type of solvent used in the synthesis. Solvents with different boiling points and polarity can influence the synthesis of ternary alloy quantum dots. Figure 1 shows the photoluminescence spectra of ZnCdSe quantum dots which were synthesized using 1,2-dichlorobenzene as a solvent. The chemical precursors used in this experiment were Zn(acac)$_2$ (0.06 mmol) and Cd(acac)$_2$ (0.15 mmol) combined in the 10 ml of 1,2-dichlorobenzene. The molar ratio of Cd:Se was 1.8. The molar ratio of Zn:Cd=0.4 was chosen. We wanted to gradually increase the amount of Zn precursor to study the affect of Zn concentration on the photoluminescence properties of the ZnCdSe quantum dots. Increasing the Zn concentration is expected to result in a blue shift of the photoluminescence peak [4]. After heating the reaction mixture of Zn(acac)$_2$ and Cd(acac)$_2$ in 10 ml of 1,2-dichlorobenzene to the boiling point of 180°C, a 1 ml solution of Se powder in trioctylphosphine (TOP) and 1,2-dichlorobenzene was added to the reaction mixture (concentration of 0.07 mmol/ml). The reaction mixture was heated and aliquots (0.5 ml) were withdrawn after 5 min, 10 min, 15 min and 2 h. The aliquots of the reaction mixture (0.1 ml) were diluted in toluene (2.5 ml) before taking photoluminescence measurements. As shown in Fig. 1 (in dotted lines), these CdZnSe quantum dots have narrow photoluminescence peaks (FWHM ~30-35 nm) in the blue to yellow region (494-580 nm). The photoluminescence wavelengths increase with reaction time. This shift in the photoluminescence peaks is caused by the fact that quantum dots grow in size as the reaction proceeds. The photoluminescence spectra of ZnCdSe quantum dots synthesized in 1,2-dichlorobenzene with a Zn:Cd precursor molar ratio of 1.2 is shown in solid line in Fig. 1. The photoluminescence spectra show wavelengths in the range 483-554 nm. The increased Zn content results in a net blue shift of the photoluminescence peaks. This is consistent with a prior report that increasing the Zn content of ZnCdSe quantum dots causes them to absorb at shorter wavelengths [4]. In that work, with increasing the mole fraction of Zn from 0, to 0.28, 0.44, 0.55 and 0.67 the photoluminescence peak shifted from 630 nm to 490 nm. The band gap of CdSe is 1.84 eV while that of ZnSe is 2.82 eV which is consistent with this shift. The molar ratio of Cd:Se in the experiment shown in the Fig. 2 was 1.4. Our previous studies [15] have shown that in the absence of the Zn precursor, with a similar molar ratio of Cd:Se, the photoluminescence peaks were observed at 503 nm (after 4-5 min of reaction time) for CdSe quantum dots. The wavelength of the photoluminescence peak for CdSe quantum dots is almost 20 nm longer than that observed for CdZnSe quantum dots as shown in Fig. 1 (solid lines) (see details in Table 1).

Our next goal was to study the effect of synthesis solvent on the photoluminescence of ternary quantum dots. Figure 2 shows the photoluminescence spectra of ZnCdSe synthesized with a Zn:Cd molar ratio of 0.4 and Cd:Se molar ratio of 1.4 (this ratio of Zn:Cd and Cd:Se is close to that of the experiment shown in Fig. 1) in the reaction mixture but using 1-octadecene as the solvent rather than 1,2-dichlorobenzene. One of the principal differences between these two solvents is that the boiling point of 1-octadecene is 315°C, whereas, the boiling point of 1,2-dichlorobenzene is 180°C. Figure 2 shows that photoluminescence of the quantum dots synthesized at 315°C in 1-octadecene occurs at ~600 nm and there is no shift in the photoluminescence peak wavelength as the reaction proceeds. After 5 min of reaction time in 1-octadecene the photoluminescence peak wavelength is 600 nm, whereas, in 1,2-dichlorobenzene the photoluminescence peak wavelength was 494 nm after 5 min (Fig. 1). This observation suggests that the reaction in 1-octadecene reached completion rather quickly and produced relatively large quantum dots. Another point to note is that the photoluminescence peaks of ZnCdSe quantum dots synthesized in 1-octadecene are broader (FWHM ~50 nm) than those of the ZnCdSe quantum dots synthesized in 1,2-dichlorobenzene (FWHM ~30-35 nm). This suggests that the synthesis at higher temperature yields as a broader distribution of sizes.

One advantage of this one-step synthesis is that it can be performed with numerous types of M(acac)$_2$ precursors (M denotes any metal). Our next experiment attempted to synthesize MgCdSe quantum dots using 0.084 mmol Mg(acac)$_2$ and 0.20 mmol Cd(acac)$_2$ (Mg:Cd precursors = 0.4 and Cd:Se = 2.8) in 1,2 dichlorobenzene. The band gap of MgSe is 5.4 eV which is higher than that of ZnSe (2.82 eV). As result, substitution of Mg for Zn ought to produce quantum dots with higher band gaps and result in a blue shift of the photoluminescence peaks. The photoluminescence spectra shown in Fig. 3 show that after 5 min of

| Cd Precursor | Cd/Se | solvent | b.p°C | Zn/Cd | 2 min | 4 min | 10 min | 15 min | 20 min | 2 h |
|--------------|-------|---------|-------|-------|-------|-------|--------|--------|--------|-----|
| Cd(acac)$_2$ | 1.3   | DCB     | 180   | 0     | 493   | 503   | 506    | 510    |        |     |
| Cd(acac)$_2$ | 1.4   | DCB     | 180   | 1.2   | 483   | 493   | 505    | 554    |        |     |

Table 1 Photoluminescence peak maxima of CdSe and ZnCdSe quantum dots synthesized in 1, 2 dichlorobenzene (DCB).
reaction time the photoluminescence peak for the MgCdSe quantum dots is at 468 nm, whereas, after a similar reaction time the photoluminescence peak for ZnCdSe quantum dots was observed at 494 nm (Fig. 1). The photoluminescence peaks for the MgCdSe quantum dots obtained after 10-15 min of reaction were also observed at shorter wavelengths than those for ZnCdSe quantum dots synthesized for similar periods of time. The results of the synthesis of MgCdSe quantum dots in 1-octadecene were similar to those observed in the case ZnCdSe quantum dots as shown in Fig. 2. The photoluminescence peaks for MgCdSe quantum dots synthesized in 1-octadecene were all located at 630 nm and were quite broad. The high reaction temperature presumably resulted in the synthesis of large quantum dots. This clearly shows that our synthesis method is capable of using Mg(acac)₂ for generating quantum dots to photoluminescence in the blue region.

Fig. 1 Photoluminescence spectra of ZnCdSe quantum dots synthesized in 1,2-dichlorobenzene (b.p. 180°C) for various reaction times and various molar ratio of Zn:Cd precursors used in the synthesis. Photoluminescence peaks shown in dotted lines correspond to Zn:Cd precursor ratio of 0.4. Photoluminescence peaks shown in solid lines correspond to Zn:Cd precursor ratio of 1.2. The photoluminescence peaks for quantum dots synthesized using a molar ratio of Zn:Cd=1.2 occur at shorter wavelengths than for those synthesized using a molar ratio of Zn:Cd=0.4.

Fig. 2 Photoluminescence spectra of ZnCdSe quantum dots synthesized in 1-octadecene (b.p. 315°C) for various reaction times. The molar ratio of Zn:Cd precursors used in the synthesis was 0.4. The higher reaction temperature results in larger particles than those synthesized in 1,2-dichlorobenzene and photoluminescence at longer wavelengths.

Fig. 3 Photoluminescence spectra of MgCdSe quantum dots synthesized in 1,2-dichlorobenzene for various reaction times. The molar ratio of Mg:Cd precursors used in the synthesis is 0.4. The substitution of Mg for Zn results in a shift of photoluminescence peaks towards blue region.

Conclusions

This work demonstrates a one-step synthesis of ternary quantum dots. This synthesis method allows the use of various M(acac)₂ (M = Cd, Mg, Zn) precursors which are less hazardous than many precursors used in similar syntheses of ternary alloy quantum dots. The boiling point of the solvent influences the reaction; the higher the reaction temperature the longer the wavelength at which quantum dots photoluminescence. In addition, the molar ratio of the precursors also dic-
tates the photoluminescence properties. Furthermore, quantum dots with elements that decrease the bandgap of the bulk semiconductor increase the photoluminescence wavelength of the quantum dots.

Acknowledgments:

The authors would like to thank CIT (Carnegie Institute of Technology), and ICES (Institute of Complex Engineered System) for the financial support of this work.

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Application of Modified Silica Coated Magnetite Nanoparticles for Removal of Iodine from Water Samples

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(Received 31 January 2012; accepted 5 April 2012; publication online 6 April 2012.)

Abstract: The adsorption of iodine onto silica coated magnetite nanoparticles (im-SCMNPs) that modified with imidazole was investigated for removal of high concentrations of iodine from wastewater. Modified silica magnetite nanoparticles showed high efficiency in removing iodine from wastewater samples. The optimum pH for iodine removal was 7.0-8.0. The adsorption capacity was evaluated using both the Langmuir and Freundlich adsorption isotherm models. The size of the produced magnetite nanoparticles was determined by X-ray diffraction analysis and scanning electron microscopy. Synthesized magnetite nanoparticles showed the high adsorption capacity and would be a good method to increase adsorption efficiency for the removal of iodine in a wastewater treatment process. The Langmuir adsorption capacity ($q_{\text{max}}$) was found to be 140.84 mg/g of the adsorbent.

Keywords: Modified silica magnetite nanoparticles; Iodine; Imidazole; Water samples

Citation: Tayyebeh Madrakian, Abbas Afkhami, Mohammad Ali Zolfigol, Mazaher Ahmadi and Nadia Koukabi, "Application of Modified Silica Coated Magnetite Nanoparticles for Removal of Iodine from Water Samples", Nano-Micro Lett. 4 (1), 57-63 (2012). http://dx.doi.org/10.3786/nml.v4i1.p57-63

Introduction

It was found that iodine shows low affinity toward subsurface sediment, except illite [1], and iodine is weakly adsorbed on sediment materials [2]. The weak adsorption capabilities of clays for iodine can be enhanced by exchanging the cations in the natural inorganic interlayer with certain organic cations [3]. Activated aerogels impregnated with silver ion can enhance the iodine adsorption due to an increase in electrostatic attraction [4].

Molecular iodine is one of the major species of iodine that may be present in food, drinking water and seawater [5]. Molecular iodine is an important bactericide and is added to drinking water as a disinfectant [6]. Iodine is one of the fission products generated in a nuclear reactor and can enter into the reactor water [7]. The I$_2$ is also an important reactant or product in many chemical reactions that are used for analytical applications [8]. Thus, development of reliable methods for the removal of molecular iodine in different matrices is of considerable importance.

The presence of iodine in environmental samples is relatively low. The main source of contamination of the environment by iodine is thin film transistor liquid crystal displays, TFT-LCD [9]. In the TFT-LCD, wastewater is detrimental to the proper operation of the wastewater treatment facility due to its potential biocidal effect toward microorganisms; and zero-valent iron has been proved effective in removing iodine from the wastewater [10]. Several reports have been published on the removal of iodine from water samples. It was found that iodine shows low affinity toward subsurface sediments, except illite [11]. Um et al. reported that iodine is weakly adsorbed on sediment materials [12]. The weak adsorption capabilities of clays for iodine were en-
hanced by exchanging the cations in the natural inorganic interlayer with certain organic cations [13]. Activated aerogels impregnated with silver ion enhanced the iodine adsorption due to an increase in electrostatic attraction [14]. Curtius and Kattilparampil [15] reported that adsorption of iodine on Mg-Al layered double hydroxide (LDH) is an anion-exchange process. Kentjono et al. used synthesized Mg-Al (NO$_3$) LDH and used to remove boron and iodine from polarizer manufacturing wastewater [9].

Nanometer-sized materials have attracted substantial interest in the scientific community because of their special properties [16]. The size range of nanoparticles is from 1 to almost 100 nm, which falls between the classical fields of chemistry and solid state physics. The relatively large surface area and highly active surface sites of nanoparticles enable them to have a wide range of potential applications, including shape-selective catalysis [17], chromatographic separations [18], sorption of metal ions [19], enzyme encapsulation [20] DNA transfection [21], and drug delivery [22].

The synthesis of magnetite nanoparticles has been intensively developed not only for its great fundamental scientific interest but also for many technological applications in biology [23], medical applications [24], bioseparation [25]; and separation and preconcentration of various anions and cations [26,27], due to their novel structural, electronic, magnetic and catalytic properties.

In the present paper modified magnetite nanoparticles was employed for removal of iodine and used as an effective adsorbent in the wastewater treatment. The technique was found to be very useful and cost-effective for a better removal of iodine.

Experimental

Instrumentation

A Metrohm model 713 pH-meter was used for pH measurements. A single beam UV-mini-WPA spectrophotometer was used for determination of iodine concentration in the solutions. The size, morphology and structure of the nanoparticles were characterized by transmission electronic microscopy (TEM, Philips, CM10, 100 KV) and scanning electron microscope (SEM, SEM-EDX, XL30 Philips Netherland). The crystal structure of synthesized materials was determined by an X-ray diffractometer (XRD, 38066 RIVA, d/G.Via M. Misone, 11/D (TN) ITALY) at ambient temperature. A 40±5% kHz ultrasonic water bath (DSA 100-SKr-Korea) was used as was used.

The mid-infrared spectra of Fe$_3$O$_4$, silica coated and imidazole loaded on silica coated magnetite nanoparticles in the region (4000-400 cm$^{-1}$) were recorded by Perkin-Elmer FT-IR spectrometer (KBr pellets) Model spectrum GX.

Reagents and materials

All the chemicals and reagents used in this work were of analytical grade and purchased from Merck (Merck, Darmstadt, Germany). A stock solution (1000 mg/l) of iodine was prepared in deionized distilled water, and experimental solutions of desired iodine concentrations were obtained by successive dilutions of the stock solution with deionized distilled water. The concentration of iodine in the experimental solution was determined from the calibration curve prepared by measuring absorbance of different predetermined concentrations of iodine solutions at 460 nm ($\lambda_{max}$).

Preparation of nanostructured silica-coated magnetite

The magnetite nanoparticles were synthesized according to a co-precipitation method followed by aeration oxidation proposed elsewhere [28,29]. Then, the magnetite suspension prepared above (20 ml) was placed in a 250 mlround-bottom flask and allowed to settle. The supernatant was removed, and an aqueous solution of tetraethoxysilane (TEOS,10% (v/v), 80 ml) was added, followed by glycerol (60 ml). The pH of the suspension was adjusted at 4.6 using glacial acetic acid, and the mixture was then stirred and heated at 90°C for 2 hunder a nitrogen atmosphere. After cooling to room temperature, the suspension was washed sequentially with deionized distilled water (3×500 ml), methanol (3 × 500 ml), and deionized distilled water (5×500 ml).

Loading of imidazole onto silica coated nanomagnetite with imidazole

The silica coated magnetite nanoparticles derivative moiety was prepared by reaction with 3-chloropropyltrimethoxysilane (CPTS) as silylation agent [30]. A sample of 10.0 g of silica coated magnetite nanoparticles was suspended in 50 mL of dry toluene and 10.66 mmol of CPTS was added to this suspension. The mixture was refluxed for 48 h, and the modified silica was filtered off, washed twice with toluene, and dried under vacuum at room temperature. In order to prepare imidazol modified magnetite nanoparticles (imSCMNPs), 5.0 g silica coated magnetite nanoparticles was added to 50 ml of dry toluene and 5.0 g imidazole. Then a few drops of triethylamine were then added to favor the reaction equilibrium [31]. Triethylamine was used as disprotonant agent to increase the efficiency of the reaction. The reaction mixture was refluxed with stirring for 72 h. The solid phase was filtered, washed with toluene and ethanol, and dried under vacuum at room temperature for 24 h (Fig. 1).
Adsorption behavior of iodine

Adsorption studies were performed by adding 0.05 g im-SCMNPs to the 50 mL solution of different concentrations of iodine in a 250 mL beaker. The pH of the iodine solution was adjusted at 7.0 using 0.1 mol/l HCl and/or 0.1 mol/l NaOH and the solution was stirred for 40 min. Then iodine loaded magnetite nanoparticles were separated with magnetic decantation. The concentration of iodine in the solution was measured spectrophotometrically at 460 nm. The concentration of iodine decreased with time due to its adsorption by magnetite.

Characterization

An infrared spectrum was obtained in the 400-4000 cm$^{-1}$ range, by a Perkin-Elmer FTIR spectrometer. KBr pellets were used for solid samples. The infrared spectroscopy presents a useful tool to initially detect the success of the immobilization process. This proposal can be clarified by comparing the precursor and modified surfaces. The IR spectra of magnetite nanoparticles, $\text{Fe}_3\text{O}_4$, (MNPs), silica coated magnetite nanoparticles (SCMNPs) and imidazole loaded on SCMNPs (im-SCMNPs) are presented in Fig. 2. As can be seen, after silica coated on the $\text{Fe}_3\text{O}_4$, a new peak at 1044 cm$^{-1}$ was appeared that indicated the Si-O band on the $\text{Fe}_3\text{O}_4$. At 2933 and 2864 cm$^{-1}$ wavenumbers the C-H stretching of aliphatic groups and at 3128 cm$^{-1}$ the N-H stretching of imidazole was observed and emphasized the modified silica coated was synthesized.

Results and discussion

The imidazole (1,3-diazole)–diiodine complex has been experimentally investigated in some instances and n–σ complexes were formed, i.e., they involved electron transfer from the N atom at position 3 of the imidazole ring to the antibonding molecular orbital σ$^*$ of $\text{I}_2$. The monomer and charge-transfer complexes of imidazole with $\text{I}_2$ was investigated and clearly revealed that a suitable interaction occurred between the σ$^*$ orbital of $\text{I}_2$ and the N lone pair in the imidazole at position 3 [32-34]. Therefore the chemical reaction of charge-transfer complexation of imidazole and iodine can be written as equation (1) [35,36]:

$$\text{Imidazole} + \text{I}_2^- \rightarrow \text{Imidazole} - \text{I}_2 + \text{I}^- \quad (1)$$

When iodine is added to water, the following reaction takes place:

$$\text{I}_2(1) + \text{H}_2\text{O}(1) \rightarrow \text{OI}^- (\text{aq}) + 2\text{H}^+ (\text{aq}) + \text{I}^- (\text{aq})$$

$$K = 2.0 \times 10^{-13} \quad (2)$$

$I_2$ molecules and water molecules react to substances such as hypoiodite ($\text{OI}^-$) and $\text{I}^-$. The formation of the hypohalite ion ($\text{IO}^-$) in neutral aqueous solutions of iodine is negligible. In basic solutions, iodine converts in
a two stage reaction to iodide and iodate [37].

\[
\begin{align*}
I_2 + 2OH^- & \rightarrow I^- + IO^- + H_2O \quad (K = 30) \quad (3) \\
3OI^- & \rightarrow 2I^- + IO_3^- \quad (K = 10^{20}) \quad (4)
\end{align*}
\]

The reaction can move both ways of the equilibrium, depending on the pH of solution. The following reaction mechanism occurs:

\[
I_2 + I^- \rightarrow I_3^- \quad (5)
\]

Figure 3 shows the spectra of iodine in solution before and after addition of im-SCMNPs to the solution. As the results show, iodine molecule in the solution with pH 7.0 showed three absorption bands at 460, 390 and 290 nm. After 5 min the absorbance of the iodine solution at 460 nm decreased while the absorbance at two wavelengths 360 and 290 nm increased. The decrease and increase in the absorbances is the result of the conversion of iodine to triiodide anion. Triiodide is produced by the reaction of iodine by iodide ion produced from Eq. (2). By addition of im-SCMNPs, the absorbance at all three absorption bands decreased. As Fig. 3 shows, both the \( I_2 \) and \( I_3^- \) species can become adsorbed on im-SCMNPs adsorbent. But the im-SCMNPs adsorbent showed higher affinity towards the \( I_3^- \).

**Characterization of the adsorbent**

The SEM and TEM images of the im-SCMNPs, as shown in Figs. 4 and 5, revealed the diameter of magnetite nanoparticles synthesized were around 38 nm from SEM image. The typical XRD profile of im-SCMNPs is shown in Fig. 6. The crystallite size was obtained around 27 nm from the XRD pattern according to Scherrer equation [26]. As the results show, the particle dimension obtained by SEM is higher than the corresponding crystallite size. This difference may be explained due to the presence of aggregates in SEM grain consisting of several crystallites and/or poor crystallinity [26].

**Effect of contact time**

The effect of contact time on the adsorption of iodine was studied to determine the time taken by im-SCMNPs to remove 254 mg/l iodine solution at pH=7.0. A 0.05 g of im-SCMNPs was added into a 50 ml of iodine solution. Absorbance of the solution at 460 nm with time was determined to monitor the iodine concentration. The decrease in the concentration of iodine in the solution with time is due to its adsorption on magnetite nanoparticles. It can be seen that after about 40 min, almost all the iodine became adsorbed. Agitation time of 40 min was selected for further works.
Effect of pH

The effect of pH in the range 5.0-10.0 on the removal of iodine was investigated using 0.01 mol/l HCl or NaOH solutions for pH adjustment, with the initial iodine concentration fixed at 254 mg/l. As Fig. 7 shows, the percent adsorption increased by increasing pH and reached maximum at pH=7.0, remained nearly constant up to pH=9.0 and decreased at higher pHs. The high negatively charged adsorbent surface sites did not favor the adsorption of iodine at higher pHs due to electrostatic repulsion.

![Fig. 7 Percentage of iodine removal at different pHs. Conditions: 0.05 g adsorbent, 20 ml of 254 mg/l of iodine and agitation time of 40 min.](image)

Effect of the amount of adsorbent

The dependence of the adsorption of iodine to the amount of modified nanoparticles was studied at room temperature and at pH=7.0 by varying the adsorbent amount from 10 to 100 mg in contact with 20 mL solution of the mixture of 254 mg/l of iodine. The results are shown in Fig. 8. The percentage removal of iodine increased by increasing amount of im-SCMNPs due to the greater availability of the adsorbent. The adsorption reached a maximum with 50 mg of adsorbent that maximum percentage removal was about 98%.

![Fig. 8 Percentage removal of iodine at different amounts of adsorbent. Conditions: 20 ml of 254 mg/l of iodine, pH=7.0 and agitation time of 40 min.](image)

Adsorption isotherms

The adsorption isotherm for iodine from water onto im-SCMNPs is shown in Fig. 9. The number of mg adsorbed per gram of adsorbent, $(q_e)$, versus the equilibrium concentration of iodine is illustrated. The initial slope in Fig. 8 for adsorption of iodine on nanoparticles lies very close to the y-axis which shows that the affinity of iodine for this adsorbent is strong.

![Fig. 9 Langmuir adsorption isotherm of iodine for modified im-SCNMPs.](image)

Two models were tested to model the adsorption isotherms: Langmuir [38] and Freundlich [39] models. Langmuir model does not take into account the variation in adsorption energy, but it is the simplest description of the adsorption process. It is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, that there are no interactions between adsorbed molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface.

The general form of the Langmuir isotherm is:

$$\frac{a_L q_e}{K_L} = \frac{K_L C_e}{(1 + K_L C_e)}$$  \hspace{1cm} (6)

where $C_e$ is the equilibrium concentration of the iodine in the solution (mg/l), $q_e$ is the amount of iodine adsorbed per unit mass of adsorbent (mg/g), $K_L$ (l/mg) and $K_L$ (l/g) are the Langmuir constants with $a_L$ related to the adsorption energy and $q_m = K_L / a_L$ signifies the maximum adsorption capacity (mg/g), which depends on the number of adsorption sites. The Langmuir isotherm shows that the amount of anion adsorbed increases as the concentration increases up to a saturation point. As long as there are available sites, adsorption will increase with increasing iodine concentrations, but as soon as all of the sites are occupied, a further increase in concentrations of iodine solutions does not increase the amount of iodine on adsorbents after linearization of the Lang-
muir isotherm, Eq. (6), we obtain:

\[
\frac{C_e}{q_e} = C_L \left( \frac{a_L}{K_L} \right) + \left( \frac{1}{K_L} \right)
\]  

(7)

The parameters of this equation for iodine were calculated and are given in Table 1.

| Table 1 | Adsorption isotherms parameters of iodine onto im-SCMNPs. |
|---------|----------------------------------------------------------|
| Langmuir model | Freundlich model |
| \text{q}_{\text{max}} (mg/g) | \text{K}_L | \text{a}_L | \text{r} | \text{K}_f | \text{1/n} | \text{r} |
| 140.84 | 5.208 | 0.0369 | 0.997 | 5.44 | 0.5546 | 0.704 |

The Freundlich empirical model is represented by:

\[
q_e = K_f C_e^{1/n}
\]  

(8)

where \(C_e\) is the equilibrium concentration (mmol/l), \(q_e\) is the amount adsorbed at equilibrium (mmol/g), and \(K_f\) \((\text{mmol}^{-1/\text{n}} \text{L}^{1/\text{n}}/\text{g})\) and 1/n are Freundlich constants depending on the temperature and the given adsorbent-adsorbate couple. \(n\) is related to the adsorption energy distribution, and \(K_f\) indicates the adsorption capacity.

The linearized form of the Freundlich adsorption isotherm equation is

\[
\ln q_e = \ln K_f + (1/n) \ln C_e
\]  

(9)

The parameters of this equation for iodine were calculated and are given in Table 1. The regression coefficients, \(r\), for fitting the experimental data points to the linear forms of the Langmuir equations can be considered as a measure of goodness of fit and it is seen that Langmuir model is almost better successful in representing experimental isotherm data versus Freundlich model.

**Conclusion**

In this study new modified, nanometer-sized silica-magnetic sorbent has been prepared and indicated that the loaded surface with imidazole after CPTS, as precursor silylating agent, could be used as effective adsorbent material for the removing of iodine from water. The modified nanoparticles are highly monodisperse and magnetically separable, and they have high adsorptive capacities. The nanoparticles can rapidly and quantitatively adsorb iodine from water solutions. In acidic media, at pH <5, no sorption was detected due to the protonation of the functional groups. The imMMNPs may be used as an inexpensive, effective, and alternative sorbent for removal of iodine from water solutions. A comparison between the proposed sorbents with those reported for the adsorption of iodine [9-15] shows that it provides higher adsorption capacity and simpler separation of iodine loaded sorbent from water solutions.

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