

Ronald W. Buckley

Editor

# Solid State Chemistry Research Trends

## Contributors

P. Benito

E. Beyers

N. Bilba

A. M. Busuioc

Wallace C. H. Choy

P. Cool

Konstantinos D. Demadis

Wen-Ya Huang

F. M. Labajos

O. I. Lebedev

Jia-Lin Li

Li-Li Ma

M. Mertens

V. Meynen

V. Rives

DongLiang Tao

Vo Van Hoang

G. Van Tendeloo

E. F. Vansant

Ying Yu

NOVA

# **SOLID STATE CHEMISTRY RESEARCH TRENDS**

**RONALD W. BUCKLEY**  
**EDITOR**

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## PREFACE

The new book on solid state chemistry presents studies of chemical, structural, thermodynamic, electronic, magnetic, and optical properties and processes in solids. Research areas include: bonding in solids, crystal chemistry, crystal growth mechanisms, diffusion epitaxy, high-pressure processes, magnetic properties of materials, optical characterization of materials, order-disorder, phase equilibria and transformation mechanisms, reactions at surfaces, statistical mechanics of defect interactions, structural studies and transport phenomena.

In chapter one, carbon nanotubes (CNTs) have been the focus of current research due to their unique structure and special mechanical and electronic properties. Cylindrically layered and hollow tubule nanostructures with their high thermal and chemical stabilities make it possible for CNTs to function as supports for nanosized metal and metal oxide particle catalysts. Many catalysts such as Pt, Ru,  $\text{TiO}_2$  were deposited on CNTs in order to improve their catalytic activity. Meanwhile, the ZnO nanostructure is one of the most promising materials for optoelectronic application due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV. ZnO has been extensively investigated as heterogeneous semiconductor photocatalyst because it offers low cost, mild reaction condition, high photochemical reactivity and low environment toxicity. It is possible that ZnO deposited on the surface of CNTs will have better photocatalytic activity due to the properties of transporting electron and high surface area for multiwall carbon nanotubes (MWCNTs).

The present work deals with the coating of ZnO onto the outer surface of MWCNTs using polyol sol-gel method and the photocatalytic property of the prepared composites. The effects of preparation parameters such as the experimental procedure, purification of MWCNTs, deposition reaction time and temperature, and the ratio of ZnO to MWCNTs, on the morphology of the composites were investigated in detail. In addition, the degradation efficiency of the dye methyl orange using the prepared composites as photocatalysts was explored. The results show that the polyol sol-gel method can be used to synthesize ZnO/MWCNTs composites with MWCNTs covered by pure hexagonal wurtzite ZnO. TEM and SEM reveals that the nanosized ZnO is evenly and densely coated onto the outer surface, while the morphology of ZnO can be controlled from nanoparticle, with the diameter of about 10 nm, to nanorods with the diameter of 15 nm and the length of 20 ~ 25 nm. The initial ratio of ZnO to MWCNTs does not affect the morphology of ZnO on the surface of MWCNTs. The presence of the extra ZnO after the formation of the mixture of MWCNTs and ZnO sol leads to the thick coverage of ZnO on the surface of MWCNTs. Thus, the amount of ZnO on

the surface can be controlled. Nevertheless, different pretreatment processes of MWCNTs result in the morphology difference of the ZnO in the composite and lead to changes in their photocatalytic activity as catalysts. For methyl orange solution, degradation efficiency under UV light by using ZnO/MWCNTs composites prepared with highly purified MWCNTs is better than that with pure ZnO. Moreover, MWCNTs can inhibit the photocorrosion of ZnO. A mechanism for the growth of nanosized ZnO on the surface of MWCNTs and the enhancement of photocatalytic activity of ZnO by MWCNTs is proposed.

Chapter two states that Rare Earth (RE) organic complexes are composed of lanthanide ions and organic ligands, which combine with each other by electrovalent bond or coordinate band. RE organic complexes include RE organic small molecule complexes and RE polymer complexes. The complexes possess some outstanding features such as the narrow spectral width with a typical value less than 10nm and theoretical 100% internal quantum yield, which are much better than that of the conventional light emitting polymers, organic small molecules and other metal complexes. Besides, RE complexes can emit red, green, blue and white color. As a consequence, RE complexes have been extensively investigated in organic light emitting diodes (OLEDs). The performance including the luminescence efficiency and brightness of OLEDs using RE complexes as the light emitting layer is continuously improving. In this chapter, the research work on the RE organic complexes used in OLEDs, the luminescent principle of RE organic complexes, methods of synthesizing RE complexes, structures of OLED, the principle excitation mechanisms of the RE complexes in OLED and the recent progress of RE complexes to enhance the performance of RE-OLEDs. Finally, the outlook of RE complexes research is addressed.

Chapter three informs us that Plugged Hexagonal Templated Silica (PHTS) materials, resembling SBA-15 materials, will be discussed. PHTS is a combined micro- and mesoporous material in a hexagonal ordering containing large tailorable uniform pores (3-15 nm) and thick pore walls (3-6 nm). In addition, PHTS materials contain a tuneable amount of extra amorphous microporous nanoparticles within the mesopores. Similar to SBA-15, PHTS has a high thermal and hydrothermal stability due to the thick pore walls. Moreover, the pillaring effect of the amorphous microporous nanoparticles in the mesoporous channels is responsible for the improved high mechanical stability of PHTS compared to other mesoporous materials. Furthermore, these nanoparticles were found to influence the adsorption and diffusion process of molecules in the mesopores. Due to its enhanced properties, PHTS is a promising candidate for adsorption, encapsulation, catalysis etc. Nevertheless, their practical use is limited since the amorphous nature of the nanoparticles causes restrictions compared to other materials like zeolites in adsorption capacity, selectivity and activity of the PHTS materials. Therefore, a new synthesis method was developed to simultaneously synthesize and activate PHTS materials. Preformed zeolite (vanadium silicalite-1) nanoparticles or metal oxide (anatase) particles were impregnated in the mesoporous channels of SBA-15. By using this post-synthesis deposition method, catalytically active plugs are formed within the mesopores creating both open and narrowed (inkbottle-like) mesoporous channels similar to the PHTS material. By changing the synthesis/deposition conditions, the structural characteristics, diffusion, adsorption capacity and catalytic activity can be controlled. Changing parameters such as the nanoparticle concentration and pH will allow a wide variation in the ratio of open/narrowed pores, micropore and mesopore volume, the amount of catalytically active materials, crystal form and the size of the deposited nanoparticles. Therefore, by choosing the

appropriate synthesis conditions, the final properties and applicability of the material can be tuned.

In chapter four, dynamical heterogeneities in liquid  $\text{GeO}_2$  have been investigated by Molecular Dynamics (MD) method. Simulations were done in the basic cube under periodic boundary conditions containing 3000 particles with the pair interatomic potentials, which have a weak electrostatic interaction and a Morse type short range interaction. The system was cooled down from 5000 K to 0 K by the cooling rate of  $5.0 \times 10^{13}$  K/s. We have evaluated the non-Gaussian parameter for the self part of the van Hove correlation function, partial radial distribution functions (PRDFs) of 5% most mobile and immobile particles compared with the mean ones in the model obtained at the temperature of 3000 K, and we found a clear evidence of the existence of dynamical heterogeneities in liquid  $\text{GeO}_2$ . Calculations showed that particles of extremely low or fast mobility have a tendency to form a cluster and mean cluster size of most mobile particles increases with decreasing temperature. We found the temperature dependence of mean cluster size of the most mobile or immobile particles. Further, the evolution of PRDFs of 5% most mobile and immobile particles upon cooling was found and presented. It is essential to notice that for the first time such interatomic potentials for the liquid and amorphous  $\text{GeO}_2$  have been proposed and therefore, structural characteristics of models obtained at the temperatures of 2000 K and 300 K have been analyzed in details through PRDFs, coordination number distributions and bond-angle distributions. Calculations show that proposed interatomic potentials describe well both structure and atomization energy of the liquid and amorphous  $\text{GeO}_2$ .

Chapter five shows that metal phosphonate chemistry is going through a renaissance in the last decade. Synthetic chemists, chemical engineers, pharmacists, medical doctors, water technologists, and other application scientists have been involved in this exciting area of chemistry and technology from different perspectives. Metal phosphonate chemistry has found numerous applications in the areas of chemical water treatment, pharmaceutical science, ion exchange, catalysis, medicine, agronomy, etc. In this contribution the chemistry and applications of metal phosphonates are reviewed with emphasis on alkaline earth metal phosphonates and research progress that has originated from our laboratory. In particular synthetic methodologies will be presented for M-phosphonates ( $M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$  and  $\text{Zn}$ ). Methods of structural characterization will also be reviewed. Lastly, the role of these metal phosphonates in modern, ground breaking application areas will be presented. These include chemical water treatment, oilfield drilling, desalination, scale inhibition, dispersion, ion exchange, catalysis, treatment of osteoporosis, treatment of osteoarthritis and related pathological conditions, and others. This review will be useful for chemists, chemical engineers, biochemists, medical doctors and graduate students who are involved in modern inorganic and organic synthesis and in biochemical sciences.

In chapter six, one of the main current topics in solid state chemistry is the development of new, environmentally friendly, economic, well-established synthesis methods or post-synthesis treatments which permit to control the properties of materials. One of them is the use of microwave energy as a source of heating in the synthesis of solids, which represents an attractive alternative to the conventional heating sources. In the present work the microwave-hydrothermal treatment, a modification of the conventional hydrothermal one, has been used during the post-treatment of different Layered Double Hydroxides (LDHs). These are lamellar compounds whose chemical formulae can be written as  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2](\text{X}^{n-})_{n/2}$ .

$n\text{H}_2\text{O}$ ; modifying both the nature of the cations and of the anions a wide variety of materials can be prepared. Although they are easily synthesized by coprecipitation, sometimes it is necessary to age them in order to obtain well crystallised materials, usually by hydrothermal treatment. The main advantages of replacing the conventional furnaces by microwave ovens are not only the notably reduction of the required time to complete the process to obtain well crystallised materials, but also the modification of their particle size distribution, textural and thermal properties. It has also been found that the properties of the products prepared by calcination are also influenced by the microwave irradiation time of the precursors. These features might have important consequences on their application as catalysts, adsorbents and polymer fillers.

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*Chapter 1*

## **PREPARATION AND PHOTOCATALYTIC PROPERTY OF ZnO/MWCNTs COMPOSITES**

***Ying Yu\*, Wen-Ya Huang, Jia-Lin Li and Li-Li Ma***

Nano Institute of Science and Technology, HuaZhong Normal University,  
Wuhan 430079, P.R. China

### **ABSTRACT**

Since carbon nanotubes (CNTs) were discovered, they have been the focus of current research due to their unique structure and special mechanical and electronic properties. Cylindrically layered and hollow tubule nanostructures with their high thermal and chemical stabilities make it possible for CNTs to function as supports for nanosized metal and metal oxide particle catalysts. Many catalysts such as Pt, Ru, TiO<sub>2</sub> were deposited on CNTs in order to improve their catalytic activity. Meanwhile, the ZnO nanostructure is one of the most promising materials for optoelectronic application due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV. ZnO has been extensively investigated as heterogeneous semiconductor photocatalyst because it offers low cost, mild reaction condition, high photochemical reactivity and low environment toxicity. It is possible that ZnO deposited on the surface of CNTs will have better photocatalytic activity due to the properties of transporting electron and high surface area for multiwall carbon nanotubes (MWCNTs).

The present work deals with the coating of ZnO onto the outer surface of MWCNTs using polyol sol-gel method and the photocatalytic property of the prepared composites. The effects of preparation parameters such as the experimental procedure, purification of MWCNTs, deposition reaction time and temperature, and the ratio of ZnO to MWCNTs, on the morphology of the composites were investigated in detail. In addition, the degradation efficiency of the dye methyl orange using the prepared composites as photocatalysts was explored. The results show that the polyol sol-gel method can be used to synthesize ZnO/MWCNTs composites with MWCNTs covered by pure hexagonal wurtzite ZnO. TEM and SEM reveals that the nanosized ZnO is evenly and densely coated onto the outer surface, while the morphology of ZnO can be controlled from

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\* Corresponding author, tel: 86-27-67861185, email: yuying@phy.ccnu.edu.cn

nanoparticle, with the diameter of about 10 nm, to nanorods with the diameter of 15 nm and the length of 20 ~ 25 nm. The initial ratio of ZnO to MWCNTs does not affect the morphology of ZnO on the surface of MWCNTs. The presence of the extra ZnO after the formation of the mixture of MWCNTs and ZnO sol leads to the thick coverage of ZnO on the surface of MWCNTs. Thus, the amount of ZnO on the surface can be controlled. Nevertheless, different pretreatment processes of MWCNTs result in the morphology difference of the ZnO in the composite and lead to changes in their photocatalytic activity as catalysts. For methyl orange solution, degradation efficiency under UV light by using ZnO/MWCNTs composites prepared with highly purified MWCNTs is better than that with pure ZnO. Moreover, MWCNTs can inhibit the photocorrosion of ZnO. A mechanism for the growth of nanosized ZnO on the surface of MWCNTs and the enhancement of photocatalytic activity of ZnO by MWCNTs is proposed.

## INTRODUCTION

Since their discovery carbon nanotubes (CNTs) have attracted considerable attention due to their special 1D structure and extraordinary mechanical and electronic properties. Their high mechanical strength makes them good candidates for advanced composites [1]. They can be either semi-conducting, semi-metallic or metallic, depending on the tube helicity and diameter [2], which opens opportunities for nanoscale electrodevice applications. Their large specific surface area, hollow and layered structures indicate that they can be an ideal hydrogen storage material [3] and function as supports for preparing nanosized particle catalysts [4, 5]. Recently, it was found that CNTs are an efficient adsorbent for dioxin, fluoride (F<sup>-</sup>), lead (Pb<sup>2+</sup>) and cadmium (Cd<sup>2+</sup>) [6-9], and are promising materials for use in environment cleaning. Owing to cost reductions for preparation, the price of CNTs has reduced significantly and it is possible for CNTs to be used in large-scale operations. In our previous works [10-12], we reported CNTs can enhance the photocatalytic activity of TiO<sub>2</sub> and Cu<sub>2</sub>O due to their properties of conducting e<sup>-</sup> and a high adsorption capacity. Additionally, deposition of Pt [13] and Ru [14] on CNTs has been reported to improve their catalytic activity.

Nanoscale semiconductor materials are currently the focus of considerable interest due to their great potential for fundamental studies in physical properties as well as for the application in optoelectronic nanodevices and functional materials. The ZnO nanomaterials are one of the most promising materials for optoelectronic application due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV [15]. ZnO has also great potential in applications in solar cell [16], sensors [17], photocatalysis [18], nanolaser [19], and so on. There are various methods for producing nanoscale ZnO such as MOVPE [20], infrared irradiation [21], thermal evaporation [22], thermal deposition [23], electrochemical deposition [24], gas reaction [25], catalytic growth [26], catalyst-free CVD [27], and solution deposition [28]. Additionally, ZnO nanoparticles [29, 30], nanowires [31] and nanorods [32] are reported to be formed on the outer surface of CNTs by using the methods shown above. So far, there is no report describing the sol-gel method for the preparation of ZnO deposited on the surface of CNTs. Polyol sol-gel process is a synthetic technique for material preparation with the advantage of simplicity, convenience, less demanding energy consumption and less consuming material. Additionally, this method enables accurate control of the size distribution and shape of the particles from the micrometric to colloidal scale [33]. Over the

past two decades, this method has been widely used to synthesis inorganic materials, such as metals and alloys, metal oxides, binary sulfides [34, 35], in which the reducing and dissolving properties of a high-temperature boiling alcohol towards a suitable precursor are utilized. The polyol method has been successfully used to prepare Cu<sub>2</sub>O/multiwall carbon nanotubes (MWCNTs) composites [36, 37]. In this study, this method was used to synthesize ZnO/MWCNTs composites.

Heterogeneous photocatalysis is a technique used for environment cleaning and remediation. The most effective functional materials for photocatalytic applications are the nano-sized semiconductor oxides. ZnO has been extensively investigated as heterogeneous semiconductor photocatalyst [38-40] because it offers low cost, use of sunlight, mild reaction condition, high photochemical reactivity and low environment toxicity [41]. However, photocorrosion frequently occurs with UV illumination and this phenomenon is considered as a main reason limiting photocatalytic activity in aqueous phase [42, 43]. But this disadvantage does not exist for the application in the gas phase [44]. It also shows other advantages such as the use of oxygen as the only required oxidant and its capability to make oxidative and reductive reactions happen simultaneously. It is estimated that ZnO may be a suitable alternative to TiO<sub>2</sub> since its photodegradation mechanism has been proven to be similar to that of TiO<sub>2</sub> [45, 46]. Moreover, some studies have confirmed that ZnO exhibits a better efficiency than TiO<sub>2</sub> in photocatalytic degradation of some dyes, even in aqueous solution [45, 47].

The present work deals with the deposition of ZnO onto the outer surface of MWCNTs using the polyol sol-gel method and then, examines the photocatalytic property of the prepared ZnO/MWCNTs composites. This study tries to experimentally relate the photocatalytic activity of ZnO/MWCNTs composites with the morphology of the components in the nanocomposites.

## EXPERIMENTAL

**Materials** All of the reagents and chemicals except those mentioned separately are reagent grade and purchased from Beijing Chemical Company. MWCNTs used in current work were synthesized by the chemical vapor deposition of propylene in a fixed-bed flow reactor at 750°C using Fe and Al catalyst. TEM image shows the average diameter of these carbon nanotubes is about 20 nm, and it contains impurities, such as carbon fiber, carbon particles and catalyst particles (Fig. 1a). For purification and functionalization, as-prepared MWCNTs were treated with two processes. First, they were dispersed in concentrated nitric acid (65% HNO<sub>3</sub>) and refluxed for 4 h at 140°C. Second, 10 g MWCNTs were refluxed in 150 mL concentrated HNO<sub>3</sub> and 250 mL concentrated sulfuric acid (mixed acid) for 2 h at 140°C. The treated MWCNTs were washed repeatedly using hot distilled water until pH of the solution reached 7, and then dried at 120°C overnight. It can be seen from TEM images (Figs. 1 b and c) that after strong acid treatment, impurities are removed. The FTIR spectrum displays hydroxyl groups (3425 cm<sup>-1</sup> and 1408 cm<sup>-1</sup>) on the MWCNTs that were treated with HNO<sub>3</sub> (MWCNTs-A) (Fig. 2) and there is no carboxyl group. MWCNTs treated with the mixed acid (MWCNTs-B) have a similar spectrum. Nevertheless, the quality for the obtained MWCNTs-A (Fig. 1b) is better than that for MWCNTs-B (Fig. 1c) since the surface for the

sample in Fig. 1c is rougher than that in Fig. 1b and the tubes treated by  $\text{HNO}_3$  are more uniform than those treated by the mixed acid.

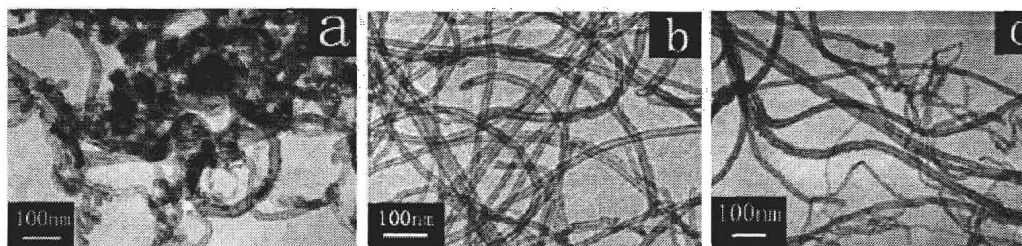


Figure 1. TEM images of (a) raw MWCNTs sample produced by CVD method, (b) MWCNTs purified with concentrated  $\text{HNO}_3$ , (c) MWCNTs purified with concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .

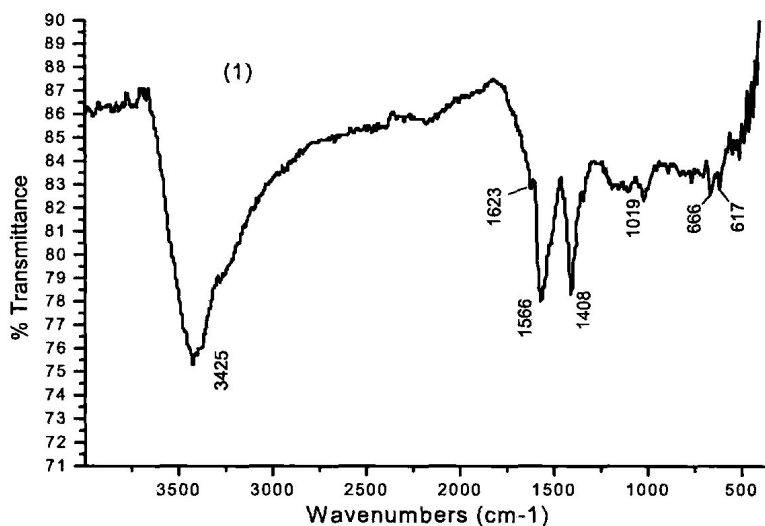


Figure 2. IR spectrum of the MWCNTs treated with  $\text{HNO}_3$ .

Methyl Orange (MO) is a small azo dye and often used as a degradation model for the evaluation of photocatalysts. Its structure is shown in Fig. 3. MO was purchased from Guangzhou Chemical Company and was used without further purification.

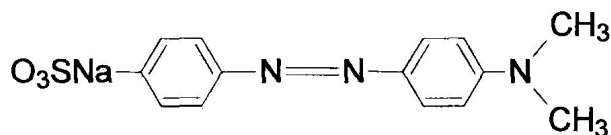


Figure 3. Structure of methyl orange (MO).

**Preparation of ZnO/MWCNTs composites** In a typical synthesis with the polyol sol-gel method [33-35], 219 mg of zinc acetate  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and 2 mL of distilled water were added to 50 mL of diethylene glycol (DEG) under vigorous stirring and the solution was directly heated to  $180^\circ\text{C}$ . A white precipitate was formed after a few minutes. The mixture

was cooled to room temperature and transparent ZnO sol was obtained after 30 min. Then, purified MWCNTs were mixed with the ZnO sol and directly heated to 180°C again. After the deposition reaction proceeded for many minutes, MWCNTs coated by ZnO were separated by centrifugation, washed with absolute ethanol and dried in air for 5 h. For comparison, the effects of experimental procedure, deposition reaction time and temperature, and the ratio of ZnO to MWCNTs were also conducted. The preparation process was typically based on the above and there was a little change according to different experimental requirements. For the synthesis of pure ZnO, a similar polyol sol-gel process was used. After the solution of zinc acetate in DEG was heated to high temperature, white ZnO precipitates appeared. The precipitates were immediately collected for further use.

**Characterization of MWCNTs and ZnO/MWCNTs composites** The composites were characterized by powder X-ray diffraction (XRD) using a Rigaku (Japan) D<sub>max</sub> X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at a scan rate of 0.03 °/s. The Fourier transform infrared (FTIR) spectrum of MWCNTs was detected by a Shimadzu IR-400 spectrometer as KBr disks. TEM images were obtained on a JEM-100CX and JEM-2010HT transmission electron microscope, using an accelerating voltage of 80 kV and 200 kV, respectively. SEM images were obtained on a JEOL JSM-6700F scanning electron microscope, using an accelerating voltage of 5 kV. The photoluminescence (PL) emission spectra of the samples were measured at -261°C. A 325 nm He-Cd laser was used as an excitation light source and the light from the sample was focused into a spectrometer (Spex500) and detected by photo multiplier tube (PMT); finally, the signal from the PMT was input into a photon counter (SR400) before being recorded by a computer.

**Photocatalysis of ZnO/MWCNTs composites for the degradation of methyl orange (MO)** The laboratory-scale photoreactor is shown in Fig. 4, which includes 6 parts and was made of quartz glass.

Since the temperature of the reactor, illuminated by 375 W high-pressure mercury lamp, will increase with the irradiation time, cooling water is necessary for preventing the system from overheating. Aeration was performed by putting air into the system with a AC9602 pump (China) and O<sub>2</sub> was saturated during photocatalytic reaction.

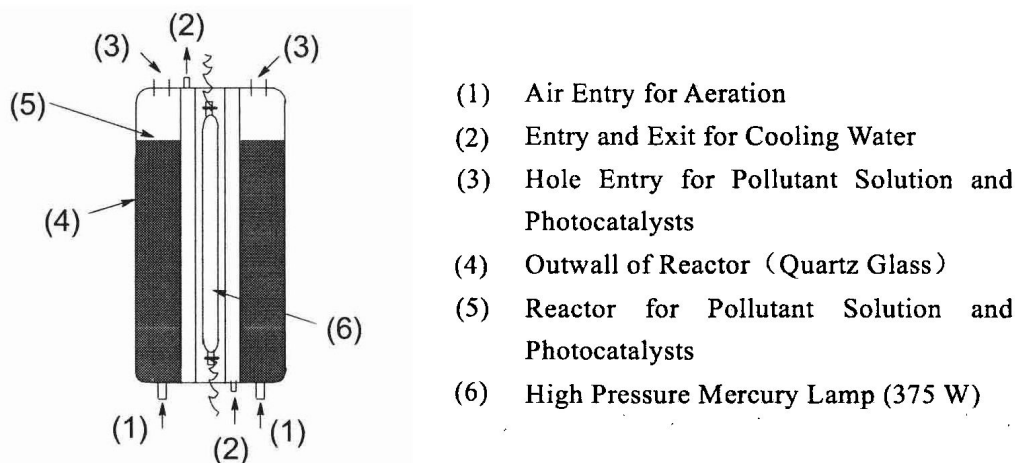


Figure 4. Diagram of the photoreactor for the degradation of MO with the presence of photocatalysts.

The photocatalytic activity of the prepared ZnO/MWCNTs composites was determined by adding 30 mg of different photocatalysts to a 500 mL solution of 20 mg/L MO. Before the UV light lamp was turned on, the above aqueous dispersions were sonicated for 40 min to reach the equilibrium of the adsorption and desorption for MO onto the surface of photocatalysts. The procedure was carried out according to a previous study [48] at 25°C. During the photocatalytic process, at given time intervals such as 5, 10, 15, 20, 25 and 30 min, respectively, 2 mL of solution was collected and centrifuged for the colorimetric analysis of dye concentration. Analysis of the dye solutions was conducted with a UV-7501 spectrophotometer (Technol, China). The dye concentration was measured colorimetrically at the maximum absorbance wavelength of the dye MO, 467 nm. Under optimized conditions, 30 min is enough to decolorize 30 mg/L MO solution completely.

## RESULTS AND DISCUSSIONS

*Characterization of ZnO/MWCNTs composites* TEM images of the as-prepared ZnO/MWCNTs composites are shown in Figs. 5a and c. It is obvious that almost the entire outer surface of MWCNTs is covered uniformly and densely with ZnO nanoparticles. The size of the nanoparticles is about 20 nm. SEM images (Figs. 5b and d) present a relatively big range and confirm that the coating of ZnO on MWCNTs is uniform. Since the resolution of the obtained images is not high enough, it is difficult to observe the shape of the nanoparticles. However, it can be distinctly seen that there are short ZnO nanorods on the surface of MWCNTs (arrows in Fig. 5c). In fact, the binding of the ZnO nanoparticle to the outer surface of MWCNTs is quite strong because extensive washing and sonication can not remove the particles from the surface of MWCNTs, which indicates that interaction between ZnO and MWCNTs is a result of strong rather than weak (Van der Waals) forces.

XRD is used to analyze the crystal structure of the as-prepared ZnO/MWCNTs composites. Fig. 6 shows XRD pattern of the same materials as presented in Fig. 5. The diffraction peak at  $26.07^\circ$  is attributed to the  $\langle 002 \rangle$  plane of carbon nanotubes [49].  $2\theta$  values for the other peaks are 32.08, 34.66, 36.55, 47.78, 56.80, 63.07, 68.01 and  $69.37^\circ$ , which correspond to  $\langle 100 \rangle$ ,  $\langle 002 \rangle$ ,  $\langle 101 \rangle$ ,  $\langle 102 \rangle$ ,  $\langle 110 \rangle$ ,  $\langle 103 \rangle$ ,  $\langle 112 \rangle$  and  $\langle 201 \rangle$  planes of ZnO, respectively. Compared with the literature values (JCPDS No.36-1451), it is known that the as-prepared ZnO on the surface of MWCNTs is hexagonal Wurtzite ZnO, with unit cell parameters of  $a = 3.258 \text{ \AA}$  and  $c = 5.214 \text{ \AA}$ . Thus, the obtained composite is mainly composed of MWCNTs and hexagonal wurtzite ZnO. Furthermore, the diffraction peak of carbon nanotubes ( $2\theta = 26.07^\circ$ ) are weak and broad while the characteristic peaks attributed to  $\langle 100 \rangle$ ,  $\langle 002 \rangle$  and  $\langle 101 \rangle$  crystal planes of pure ZnO are much stronger and sharper than that of carbon nanotubes, revealing the high crystallinity of ZnO. The average size of ZnO can be calculated from the half-width of the strongest diffraction peak corresponding to  $\langle 101 \rangle$  plane of ZnO by using the Scherrer equation [50]. The calculated size is 21.76 nm for ZnO crystalline, which is comparable to that estimated from the TEM image shown in Fig. 5.

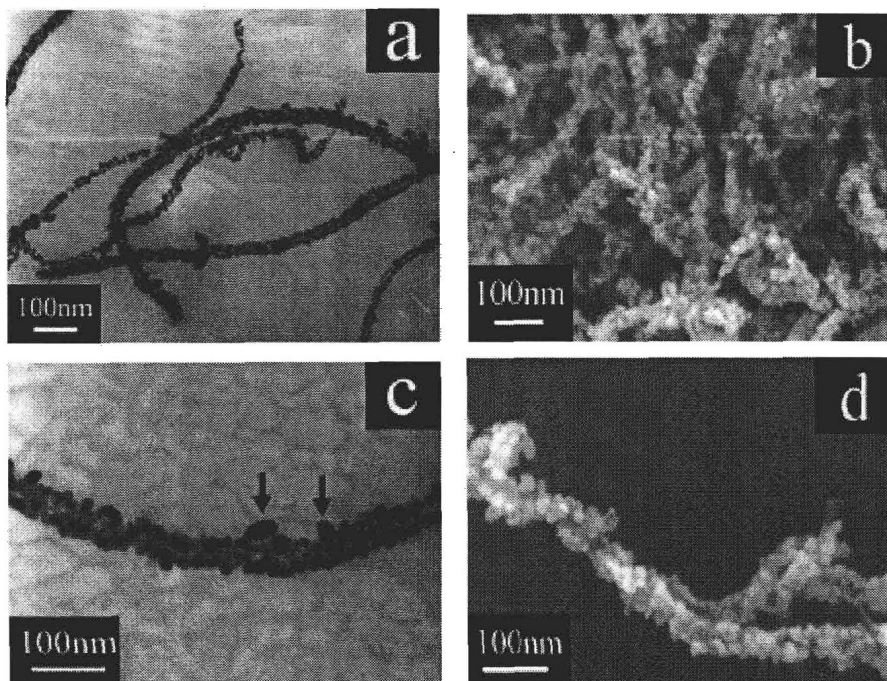


Figure 5. TEM and SEM images of ZnO/MWCNTs composites with the ratio of ZnO to MWCNTs 1:3, with the reaction time of 40 min and prepared at 180°C: (a) and (c) TEM images, (b) and (d) SEM images.

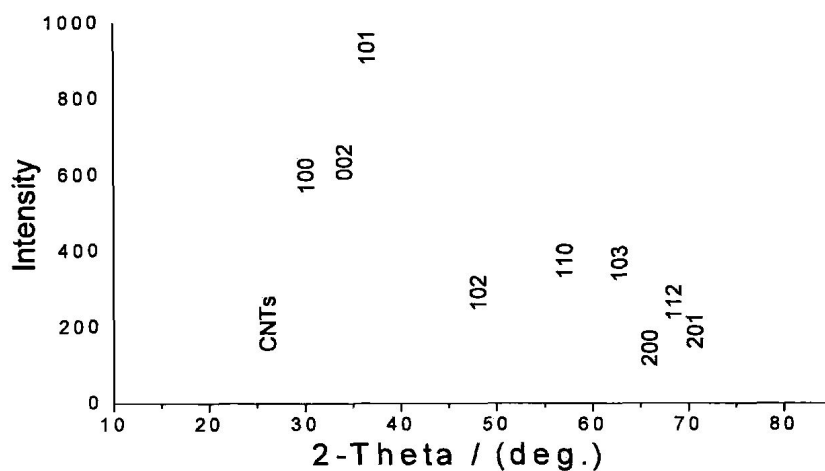


Figure 6 XRD pattern of the ZnO/MWCNTs composites corresponding to the materials shown in Fig. 5.

*Effect of experimental conditions on the morphology of ZnO/MWCNTs composites.* After MWCNTs are mixed with ZnO sol solution and the system is heated to high temperature, the deposition reaction starts. The deposition reaction time is important in determining the shape of the ZnO on the surface of MWCNTs. Fig. 7 shows the comparison of TEM images for the composites prepared with different deposition reaction time. When the

reaction time is only 20 min, the size for the ZnO deposited on the surface of MWCNTs is very small, about 10 nm, and the nanoparticles are spherical. In this case, almost all of the nanoparticles in the image (Fig. 7a) have a similar size. When the reaction time extends to 40 min, the spherical ZnO nanoparticles on MWCNTs grow to short nanorods with length of 20 ~ 25 nm and diameter 10 ~ 12 nm (Fig. 7b). It may be related to the space effect of MWCNTs and the high viscosity of solvent DEG, which inhibits the growth of ZnO crystal in any direction. Thus, ZnO nuclei grow along a preferred direction with the extension of reaction time [51]. XRD patterns of the two samples prepared with different deposition reaction times are shown in Fig. 8. Comparing the intensity and the peak width of ZnO for the reaction time of 40 min and that for the reaction time of 20 min, it is obvious that the crystallinity increases and the peak width becomes narrower with an increase in reaction time. Thus, the longer reaction time leads to much better crystallization and the size of ZnO crystalline becomes larger correspondingly. The average size of the as-synthesized crystalline ZnO, calculated from the half-width of the  $\langle 101 \rangle$  diffraction peak using the Scherrer equation, is 21.76 nm for ZnO crystalline with the reaction time of 40 min and 9.85 nm with reaction time of 20 min, which is consistent with the size shown in TEM images.

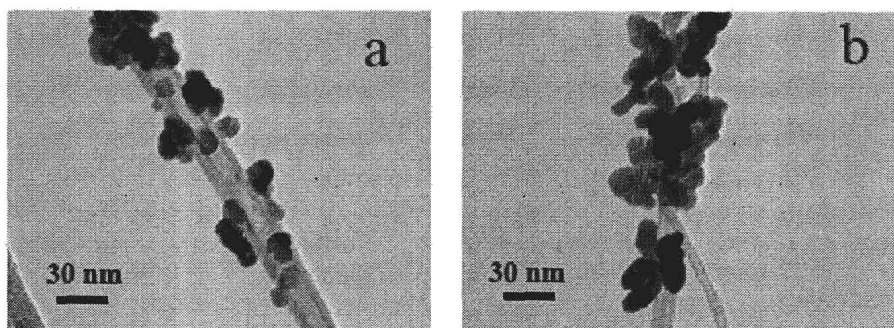


Figure 7. TEM images of ZnO/MWCNTs composites with the ratio of ZnO to MWCNTs 1:3, prepared at 180°C and with different deposition reaction time: (a) 20 min, (b) 40 min.

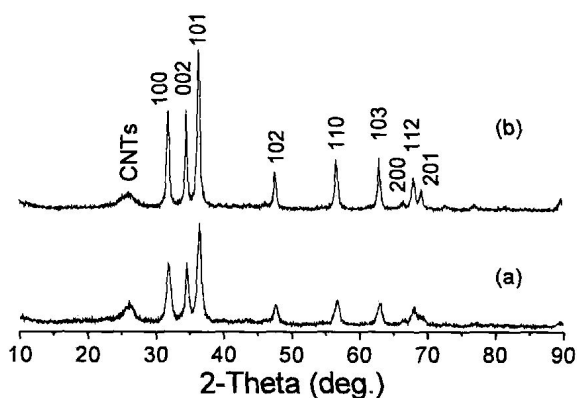


Figure 8. XRD patterns of ZnO/MWCNTs composites prepared with different reaction time: (a) 20 min, (b) 40 min.



After the deposition reaction gets started, the reaction temperature is crucial to the uniform coating of ZnO onto MWCNTs. If the system of the ZnO sol mixed with MWCNTs is not heated and is kept stirring at room temperature for 6 h, there is little ZnO deposited on the surface of MWCNTs (Fig. 9a). The background of the image is clean and no ZnO is dispersed. Since the size of ZnO sol is quite small and can be easily dissolved into water, it is reasonable that there are no particles on the surface of MWCNTs. When the same system is heated to 90°C for 1.5 h, most of MWCNTs is naked (Fig. 9b). Although there are some ZnO particles on the surface of MWCNTs, the coating is not uniform. Meanwhile, most of ZnO particles aggregate together and surround MWCNTs. When the system is heated to 180°C for only tens of minutes, the uniform coating of ZnO onto the surface of MWCNTs is obtained (Figs. 5 and 7). Thus, the reaction temperature is important for the formation of ZnO/MWCNTs composites with a good dispersion of ZnO on the outer surface. The reason may be due to the existence of electrical double layers composed of  $\text{Zn}^{2+}$  on the surface of ZnO sol particles and acetate anion. Since the ZnO sol particles are isolated by the electrical double layers from MWCNTs, enough energy must be provided to overcome the energy barrier. When the temperature for the reaction is not high, there is not enough energy for the ZnO sol to attach to the surface of MWCNTs. With an increase of the reaction temperature, the average energy for ZnO sol increases, which make it possible for the interaction between MWCNTs and ZnO sol. The high temperature is necessary also for ZnO sol to form the ZnO crystal phase.

The effect of experimental procedure on the morphology of ZnO on the surface of MWCNTs is greater than any other parameters. At the beginning of this study, a very simple mixing procedure was conducted, which zinc acetate, MWCNTs and a little distilled water was dispersed into DEG with continuously stirring and then heated directly to 180°C for 1 h. From the TEM image of the obtained sample shown in Fig. 10, it can be seen that with this mixing procedure, only part of MWCNTs is coated by ZnO spherical aggregates with the diameter of 100 nm, which are assembled by small nanorods. It seems that these spherical aggregates assembled through strong interaction since ultrasonic treatment can not separate them to single nanorods. Comparing the data shown in Fig. 10 with those in Figs. 5 and 7, one can see that the formation of ZnO sol is very important for the uniform deposition of ZnO onto the surface of MWCNTs. When ZnO sol is formed in the presence of MWCNTs, part of ZnO sol can reach the surface of MWCNTs before the uniform sol solution is obtained.

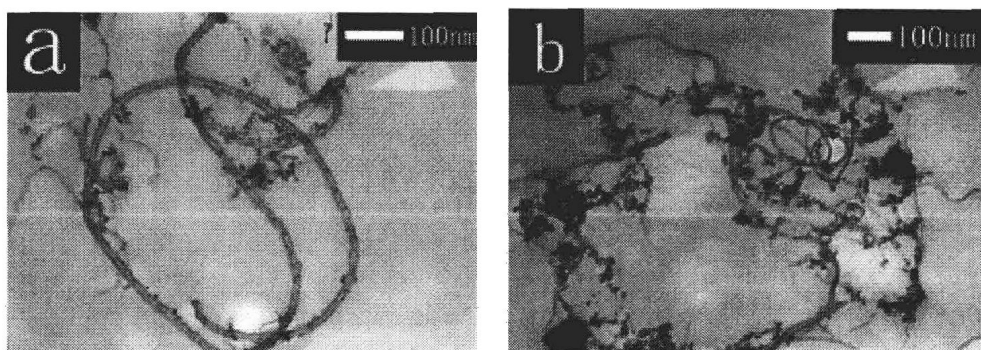


Figure 9. TEM images of ZnO/MWCNTs composites with the ratio of ZnO to MWCNTs 1:3 and prepared at different deposition reaction temperature: (a) 25°C and (b) 90°C.