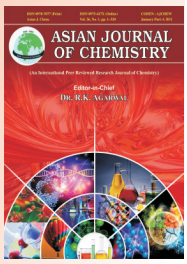
Asian Journal of Chemistry; Vol. 26, No. 5 (2014), 1497-1500

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17270



Photocatalytic Degradation using MWCNTs Modified with Fe(III)-Doped ZnO for Water Treatment†

XIAO-JIE SONG[1], ZHONG-QIONG QIN[1], FAN YANG[2,*], QUN-LING FANG[3], HAN-MEI HU[1] and ZHI-JUN SONG[1]

[1]School of Materials and Chemical Engineering, Anhui Jianzhu University, Hefei 230026, P.R. China
[2]Department of Chemistry, Anhui Medical University, Hefei 230026, P.R. China
[3]School of Medical Engineering, Hefei University of Technology, Hefei 230009, P.R. China

*Corresponding author: Tel: +86 551 65161138; E-mail: fyang99@mail.ustc.edu.cn

Published online: 1 March 2014; AJC-14811

Fe(III) doped ZnO nanoparticles were introduced onto the surface of multi-walled carbon nanotubes (MWCNTs) *via in situ* chemical precipitation method. The products MWCNTs modified with Fe(III)-doped ZnO nanocomposites (MWCNTs/Fe(III)/ZnO) were characterized by X-ray diffraction, transmission electron microscopy and energy dispersive X-ray spectroscopy. The effects of the ratio of reactants on its dispersion in aqueous solution were analyzed. The nanocomposites with 0.5 mol % Fe(III) showed satisfactory photocatalytic activity in the removal of methyl orange from aqueous solution. Moreover, existence of MWCNTs and doped Fe(III) enhanced the photocatalytic activity of ZnO.

Keywords: Carbon nanotubes, ZnO, Fe(III) doped, Photocatalytic activity, Methyl orange.

INTRODUCTION

As an important wide-bandgap semiconductor (3.37 eV) with a large exciton binding energy (60 meV), ZnO has received widespread attention because of its excellent performance in electronics, optics and photonics systems[1]. A range of 1D ZnO nanostructures have been fabricated[2], ZnO nanoparticles and quantum dots have been synthesized by different methods[3,4] and can also be assembled into 1D structures[5]. Due to their tubular morphology and unique electronic properties, multi-walled carbon nanotubes (MWCNTs) are the best candidates for the preparation of photocatalytic composites. Kim[6], Park and co-workers[7] have reported the coating of ZnO nanorods on carbon nanotubes (CNTs) by chemical vapor deposition (CVD) in a tube furnace. Gao and co-workers[8,9] have reported the deposition of ZnO particles on MWCNTs and their enhanced photocatalytic activity.

However, some modifications are needed for the sake in photocatalytic degradation of organic dyes. Thus, particular efforts have been dedicated to modify MWCNTs/ZnO with Fe(III) ions. MWCNTs/Fe(III)/ZnO is observed as a catalyst with high efficiency because of its large surface area, pore volume and porous channel[10] as well as effectiveness in enhancing the rate of the reaction. The amount of Fe(III) used is one of critical parameters in catalyst preparation as excessive amount could negatively affect the rate of reaction.

Wang *et al.*[11] did a preliminary study on the roles of Fe(III)/TiO_2 in combination with the ultrasound for the degradation of azo fuchsine. They reported that synergistic effect of Fe(III) ions as dopants was achieved when used in combination with ultrasonic irradiation.

Taking the above consideration into account, a new nanocomposites material consisting of Fe(III) doped ZnO nanoparticles (NPs) and MWCNTs was prepared by a facile and versatile approach. In this work, Fe(III) doped ZnO nanoparticles were introduced onto the surface of MWCNTs by *in situ* chemical precipitation method. The specific aim was to investigate the effect of MWCNTs/Fe(III)/ZnO on photocatalytic behaviours.

EXPERIMENTAL

Multi-walled carbon nanotubes (MWCNTs, > 90 % purity) were purchased from Shengzhen Nanotech Port Co., Ltd. The average outer diameter of MWCNTs was between 20 and 40 nm the length was up to a dozen micrometer. The MWCNTs were prepared by the catalytic decomposition of CH_4 before

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

use. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, AR), sodium dodecyl sulfacte (SDS, AR), ammonium bicarbonate (NH_4HCO_3, AR), zinc nitrate ($Zn(NO_3)_2$, AR) and methyl orange (AR) were all purchased from Sinopharm Chemical Reagent Co., Ltd. These reagents were used directly without any further purification.

Synthesis of MWCNTs/Fe(III)/ZnO: 2.02 g MWCNTs were added into 150 mL nitric acid solution. The mixture was refluxed with stirring for 4 h at 80 ºC. The acid-treated MWCNTs were collected by filtration, washed with deionized water for several times until neutral and dried at 70 ºC overnight. The purified MWCNTs were dispersed in 80 mL SDS (1 wt %) aqueous solution by ultrasonication for 2 h to modify the MWCNTs surface.

50 mL NH_4HCO_3 (0.4 mol/L) solution, MWCNTs adsorbed SDS and $FeCl_3 \cdot 6H_2O$ were mixed into a flask, then 50 mL $Zn(NO_3)_3$ (0.4 mol/L) solution was added into the reaction mixture slowly. The mixture was stirred at 80 ºC for 0.5 h, cooled to room temperature and sonicated for 10 min. The product was filtrated and washed with deionized water repeatedly, then dried in oven at 120 ºC for 1 h and calcined at 500 ºC for 2 h.

Synthesis of ZnO nanoparticles: Was put into a flask with mixing temperature of 80 ºC, 50 mL Zn $(NO_3)_3$ (0.4 mol/L) solution was added into 50 mL NH_4HCO_3 (0.4 mol/L) solution slowly. The mixed solution was stirred at 80 ºC for 0.5 h and cooled to room temperature. The product was filtrated and washed with deionized water repeatedly, then dried in oven at 120 ºC for 1 h and calcined at 500 ºC for 2 h.

Synthesis of Fe(III) doped ZnO nanoparticles: 50 mL NH_4HCO_3 (0.4 mol/L) solution and $FeCl_3 \cdot 6H_2O$ were mixed into a flask and 50 mL Zn $(NO_3)_3$ (0.4 mol/L) solution was slowly added into the reaction mixture. The mixed solution was stirred at 80 ºC for 0.5 h, cooled to room temperature and sonicated for 10 min. The product was filtrated and washed with deionized water repeatedly, then dried in oven at 120 ºC for 1 h and calcined at 500 ºC for 2 h.

Photocatalytic properties research of MWCNTs/Fe(III)/ZnO: The photocatalytic experiment was carried out at 25 ºC pure ZnO NPsMWCNTs/ZnO composites and MWCNTs/Fe(III)/ZnO were used as photocatalysts, respectively. 75 mg photocatalyst and 50 mL methyl orange solution (initial concentration c_0 = 50 mg/L) were added into a beaker. The mixture was stirred in the dark for 3 h to reach adsorption equilibrium[12]. The photocatalytic experiments were carried out under UV light (365 nm, 80 W) with stirring. 1 mL solution at regular intervals was taken out, diluted to 10 mL and centrifuged at 16000 rpm/min for 5 min. The supernatant liquid was analysed by UV-visible spectroscopy for the methyl orange concentrationThe characteristic absorption wavelength of methyl orange was 472 nm which was chosen as the monitored parameter in the process of photocatalytic degradation.

RESULTS AND DISCUSSION

XRD and EDS: X-Ray powder diffraction (XRD) was carried out on a XRD-6000 X-ray diffractometer (Shimadzu, Japan) with CuK_α radiation (λ = 0.15406 nm, U = 40 kV, I = 30 mA) at a scanning rate of 0.02º s^{-1} in the 2θ range from 10-80º. Fig. 1(a) showed an X-ray diffraction spectrum of the Fe(III) doped MWCNTs/ZnO nanocompositesThe peak at 2θ = 26.05º was the characteristic peak of MWCNTs. Strong diffraction peaks appearing at 31.75, 34.41, 36.25, 47.54 and 56.62º were indexed to be the (100), (002), (101), (102) and (110) planes of ZnO with hexagonal wurtzite structure (JCPDS89-0510), respectively.

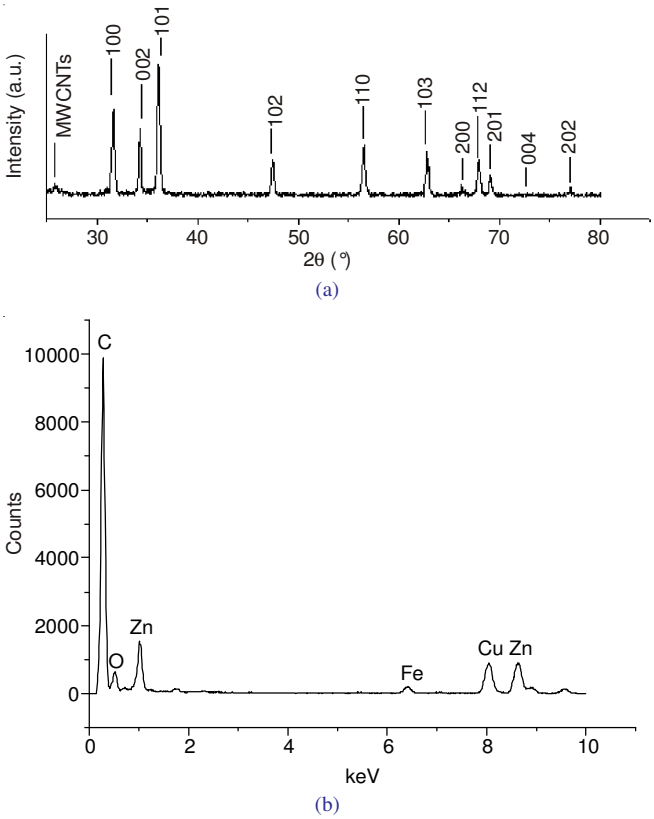


Fig. 1. XRD (a) and EDS (b) patterns of MWCNTs/Fe(III)/ZnO

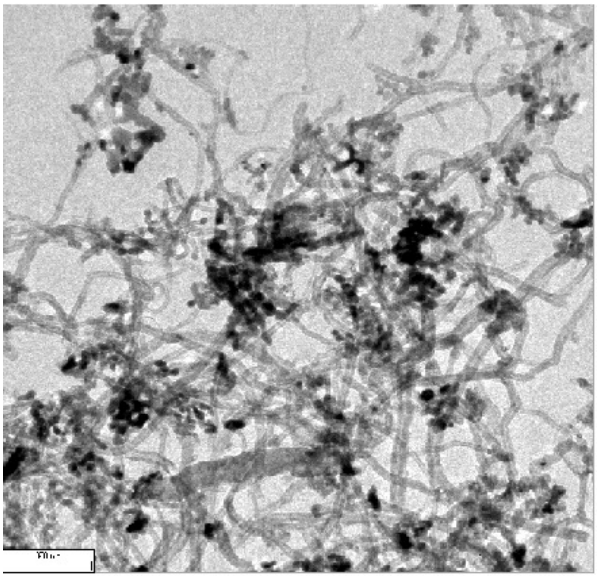
EDS of the MWCNTs/Fe(III)/ZnO (Fig. 1b) showed the presence of Fe, Zn, O and C elements in products, which demonstrated Fe(III) doped ZnO nanoparticles were introduced on the surface of MWCNTs.

TEM: The surface mophology of samples was observed on an H-800 transmission electron microscope (TEM, Hitachi).

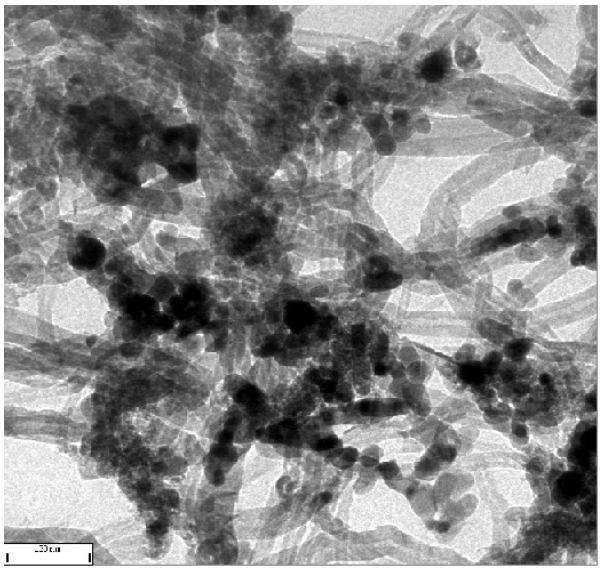
The TEM images of MWCNTs/Fe(III)/ZnO were shown in Fig. 2. The surface of MWCNTs was covered with a layer of nanoparticles. The size of nanoparticles was almost uniform and the average value estimated from Fig. 2 was 30-40 nm.

Photocatalytic activity: The photocatalytic results of pure ZnO nanoparticles, MWCNTs/ZnO nanocomposites and MWCNTs/Fe(III)/ZnO were showed in Fig. 3. As shown in Fig. 3, the photocatalytic activity of pure ZnO nanoparticles (curve a) was much lower than MWCNTs/ZnO nanocomposites (curve b), which showed that MWCNTs greatly enhance the photocatalytic activity of ZnO. At the same time, the photocatalytic activity of MWCNTs/Fe(III)/ZnO was superior to MWCNTs/ZnO nanocomposites.

The possible mechanism could be described as followed: under UV light irradiation, the valence band electrons of ZnO were excited and moved toward conduction bands, giving rise to the formation of electron and hole pairs. Due to the strong



(a)



(b)

Fig. 2. TEM images of MWCNTs/Fe(III)/ZnO

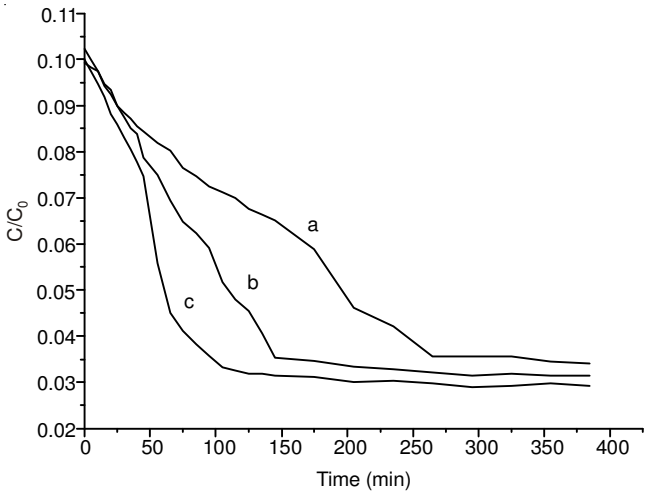


Fig. 3. Degradation results of methyl orange solution by pure ZnO nanoparticles (a), MWCNTs/ZnO nanocomposites (b) and MWCNTs/Fe(III)/ZnO (c) under exposure to UV light

interfacial connection between ZnO nanoparticles and MWCNTs, the excited e^- of the conduction band of ZnO nanoparticles could migrate to MWCNTs, which were relatively good electron acceptors[13,14]. So the recombination of the e^-/h^+ pairs was retarded, which resulted in the promotion of photocatalytic activity in ZnO nanoparticles. Another possible reason was the improvement of the dispersion of ZnO nanoparticles (from Fig. 2b) and thus the enhancement of the photo absorption efficiency of ZnO nanoparticles.

Fig. 4 showed the photocatalytic activity of MWCNTs/Fe(III)/ZnO with different dosage of Fe(III) ranging from 0.5 to 3.5 %, it was clear that as the dosage of Fe(III) reduced, the peaks decreased.

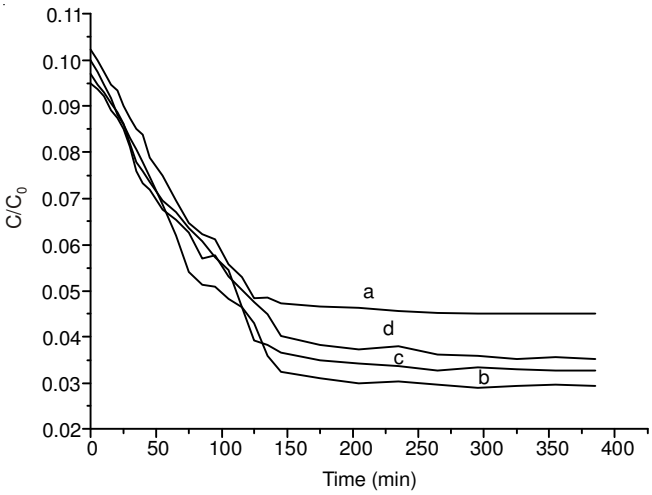


Fig. 4. Degradation results of methyl orange solution by MWCNTs/ZnO nanocomposites (a), MWCNTs/Fe(III)/ZnO(with 0.5 % Fe(III)) (b), MWCNTs/Fe(III)/ZnO (with 1.5 % Fe(III)) (c) and MWCNTs/Fe(III)/ZnO (with 3.5 % Fe(III)) (d) under exposure to UV light

The removal ratio of dye by MWCNTs/ZnO nanocomposites was 42 % (curve a) and the ratio of dye removed by MWCNTs/Fe(III)/ZnO could increase obviously (curve d, c and b). Effect of Fe(III) loading in ZnO on methyl orange removal was also investigated by varying the Fe(III) contents from 0.5-3.5 %. The removal ratio of methyl orange increased to 68 % within 150 min by using 0.5 % Fe(III) doped MWCNTs/ZnO, which indicated the positive role of Fe(III) ions. The dye removal was ascribed to the combination of ultrasonic irradiation and ZnO particles that led to the enhancement in the production of ·OH radicals, the Equations were shown as below. In this case, the improvement in the removal of dye could be attributed to the presence of Fe(III) ions doped in ZnO. The presence of the Fe(III) ions would also introduce more oxygen vacancies in the crystal lattice or on the surface of ZnO. These oxygen vacancies favoured the adsorption of water and the formation of surface hydroxyl group to consequently promote catalytic activity[15].

$$ZnO \xrightarrow{h\nu} e^- + h^+$$
$$e^- + O_2 \rightarrow \cdot O_2^-$$
$$\cdot O_2^- + H_2O \rightarrow HOO\cdot + OH^-$$
$$2HOO\cdot \rightarrow H_2O_2 + O_2$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+$$
$$Fe(OOH)^{2+}+) \rightarrow Fe^{2+} + HO_2$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$$

Conclusion

MWCNTs/Fe(III)/ZnO were fabricated using *in situ* chemical precipitation method. Close contact between ZnO and carbon nanotubes could improve the interfacial electron transfer and restrain the e^-/h^+ pair recombination of ZnO, by which photocatalytic activity was enhanced. MWCNTs could promote effectively the photocatalytic activity of ZnO nanoparticles in the elimination of organic dye. MWCNTs/Fe(III)/ZnO enhanced photocatalytic activity and MWCNTs/Fe(III)/ZnO(with 0.5 mol % Fe(III)) gave superior photocatalytic activity in the removal of methyl orange from aqueous solution.

ACKNOWLEDGEMENTS

This work was supported by National Natural Science Foundation for Young Scholars (No. 21205026) and Anhui Province Natural Science Foundation (No. KJ2013B061).

REFERENCES

1. Z.L. Wang, *J. Phys. Condens. Matter*, **16**, R829 (2004).
2. Z.L. Wang, *Mater. Today*, **7**, 26 (2004).
3. Z.Y. Jiang, Z.X. Xie, X.H. Zhang, S.-C. Lin, T. Xu, S.-Y. Xie, R.-B. Huang and L.-S. Zheng, *Adv. Mater*., **16**, 904 (2004).
4. J. Joo, S.G. Kwon, J.H. Yu and T. Hyeon, *Adv. Mater*., **17**, 1873 (2005).
5. C. Pacholski, A. Kornowski and H. Weller, *Angew. Chem. Int. Ed*., **41**, 1188 (2002).
6. H. Kim and W. Sigmund, *Appl. Phys. Lett*., **81**, 2085 (2002).
7. S.Y. Bae, H.W. Seo, H.C. Choi, J. Park and J. Park, *J. Phys. Chem. B*, **108**, 12318 (2004).
8. J. Sun, L. Gao and M. Iwasa, *Chem. Commun.*, 832 (2004).
9. L. Jiang and L. Gao, *Mater. Chem. Phys*., **91**, 313 (2005).
10. J. Zhu, W. Zheng, B. He, J. Zhang and M. Anpo, *J. Mol. Catal. Chem*., **216**, 35 (2004).
11. J. Wang, W. Sun, Z. Zhang, Z. Jiang, X. Wang, R. Xu, R. Li and X. Zhang, *J. Colloid Interf. Sci*., **320**, 202 (2008).
12. F.J. Zhang, W.C. Oh and K. Zhang, *Mater. Res. Bull*., **47**, 619 (2012).
13. Y. Sun, S.R. Wilson and D.I. Schuster, *J. Am. Chem. Soc*., **123**, 5348 (2001).
14. P. Serp, M. Corrias and P. Kalck, *Appl. Catal. A*, **253**, 337 (2003).
15. A. Mehrdad and R. Hashemzadeh, *Ultrason. Sonochem*., **17**, 168 (2010).