



New Insight into Enhanced Photocatalytic Activity of Magnetic MWNTs/TiO₂ Nanocomposites

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Using the carbon nanotubes as carrier and tetrabutyl titanate as precursor, MWNTs/TiO₂ nanocomposites are prepared by a sol-gel method, then MWNTs/TiO₂/Fe₃O₄ nanocomposites (magnetic MWNTs/TiO₂ nanocomposites) are prepared by a co-precipitation method. The sample is characterized by X-ray powder diffraction, scanning electron microscopy, energy dispersive spectroscopy and transmission electron microscopy. The photocatalytic experiments of MWNTs/TiO₂/Fe₃O₄ nanocomposites are carried out using methyl orange aqueous solution as model pollutant under ultraviolet light. The results indicate that the photocatalytic activity of MWNTs/TiO₂/Fe₃O₄ nanocomposites is the best as the content of MWNTs is about 23 % in MWNTs/TiO₂ nanocomposites. The degradation ratio of methyl orange can reach 95 % in 4 h at pH 3. With the help of Fe₃O₄, MWNTs/TiO₂/Fe₃O₄ nanocomposites can be quickly separated from solution under strong outer magnetic field and used repeatedly.

Keywords: Magnetism, MWNTs/TiO₂/Fe₃O₄, Nanocomposites, Photocatalysis, Methyl orange.

INTRODUCTION

Photocatalytic reactions on the surface of semiconductor solid have attracted much attention in view of their practical applications in environment-cleaning materials such as self-cleaning tiles, glasses and windows^{1,2}. Among many kinds of reported photocatalyst materials, nano TiO₂ has been widely studied for decades due to its excellent photocatalytic activity, chemical and biological inertness and low cost. In order to improve the photocatalytic activity of nano TiO₂, a number of materials are introduced to form nanocomposites with TiO₂. Multi-walled carbon nanotubes (MWNTs) are the famous one among these materials^{3,4}.

Due to unique structure-dependent electronic, mechanical and chemical properties, MWNTs have been the object of intensive studies over past decades⁵. As a good carrier, many inorganic nanoparticles^{6,7} such as TiO₂⁸, Fe₂O₃, CdS⁹ and ZnS¹⁰ are introduced onto the surface of MWNTs and the properties of inorganic nanoparticles are enhanced more or less.

In spite of the prominent photocatalytic activity of MWNTs/TiO₂ nanocomposites, its practical application seems to be limited for some reasons, among which separation of photocatalysts from solution is a difficult problem. The introduction of magnetic materials is an alternative to solve this problem in terms of easy preparation, low cost, flexibility and active surface

for adsorption of metals and ligands. With the support of magnetic materials, photocatalysts can be easily separated under outer magnetic field¹¹. During last few years, various forms of iron oxides such as FeO (wustite), Fe₂O₃ (iron III oxides), α -Fe₂O₃ (hematite), β -Fe₂O₃ (β -phase) and γ -Fe₂O₃ (maghemite) have been successfully deployed in catalysts¹²⁻¹⁵.

In this work, our aim is the enhancement of photocatalysts activity of TiO₂ nanoparticles with the support of MWNTs and easy separation of nanocomposites containing Fe₃O₄ nanoparticles. TiO₂ nanoparticles are introduced on surface of MWNTs by sol-gel method and Fe₃O₄ nanoparticles are introduced by co-precipitation method. In photocatalytic experiment, MWNTs/TiO₂/Fe₃O₄ nanocomposites are tested to degraded methyl orange solution under UV light and then separated from solution by an external magnet.

EXPERIMENTAL

MWNTs (≥ 90 % purity) were purchased from Shengzhen Nanotech Port Co., Ltd. The average outer diameter of MWNTs was between 20 and 50 nm, the length was up to a dozen micrometres. Tetrabutyl titanate [Ti(OC₄H₉)₄, AR], acetic acid (AR), nitric acid (AR), Ethanol (AR) and methylene blue (AR) and ammonia solution (28 wt %) were all purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used directly as received without further purification.

Synthesis of MWNTs/ TiO₂ composites: MWNTs/TiO₂ composites were prepared by sol-gel method. 35 mL ethanol, 10 mL Ti(OC₄H₉)₄, 3 mL CH₃COOH were added into a 100 mL flask in turn, the mixture was stirred for 30 min and called solution A. 15 mL ethanol, 3 mL deionized water and 1 mL HNO₃ (65 %) were mixed into another flask in turn, the mixture was called solution B. 1.5632g MWNTs and PEG-4000 were added in B solution.

Solution B was added into solution A drop by drop with vigorous stirring, the pH of mixed solution was adjusted to 3 with HNO₃ solution(1 mol/L) and the mixture was kept at 40 °C for 2 h. After 2 h, the product (MWNTs/TiO₂ composites) was collected, rinsed with deionised water repeatedly, dried at 80 °C and calcined at 550 °C for 2 h.

Synthesis of MWNTs/TiO₂/Fe₃O₄ nanocomposites: The *in situ* co-precipitation method employed here was as follows: 2.3505 g FeCl₃·6H₂O and 1.2040 g FeSO₄·7H₂O were dissolved into 20 mL deionized water in flask, then 1 g MWNTs/TiO₂ composites were added into flask with vigorous stirring under argon atmosphere. After 5 min, 1.5 mol/L ammonia solution was added into the suspension drop by drop until the value of pH reached 8. The mixture kept still at 60 °C for 2 h. The final product (MWNTs/TiO₂/Fe₃O₄ nanocomposites) was collected, rinsed with deionized water repeatedly and dried at 80 °C for 12 h.

Photocatalytic property of MWNTs/TiO₂/Fe₃O₄: Pure TiO₂ nanoparticles, MWNTs/TiO₂ composites and MWNTs/TiO₂/Fe₃O₄ nanocomposites were used as photocatalysts, respectively. The photocatalytic experiments were carried out at 25 °C. 50 mg photocatalyst and 50 mL methyl orange solution (initial concentration: 8 mg/L) were mixed into a beaker. The mixture was stirred in the dark for 3 h to reach adsorption saturation. After 3 h, the photocatalytic experiments were carried out under UV light (Philips UV lamp, maximum radiation at 365 nm, 80 W) with stirring. 1 mL solution was taken out at regular intervals, diluted to 10 mL and centrifuged at 16000 rpm for 5 min. The supernatant liquid was analyzed by UV-visible spectroscopy for the methyl orange concentration and the maximum absorbance of methyl orange was at 464 nm.

X-ray powder diffraction was carried out on a XRD-6000 X-ray diffractometer (XRD, Shimadzu, Japan) with CuK_α radiation ($\lambda = 0.15406$ nm, U = 40 kV, I = 30 mA) in the 2 θ range from 20 to 80°. The surface morphology of sample 0s was observed on an H-800 transmission electron microscope (TEM, Hitachi, Japan), EDS (Oxford X-Max 20 mm²) and SEM (JEOL JSM-7500F).

RESULTS AND DISCUSSION

The XRD pattern of MWNTs/TiO₂/Fe₃O₄ composites was shown in Fig. 1. The peak at 2 θ = 26.05° was the characteristic peak of MWNTs. Strong diffraction peaks appearing at 25.28°, 37.93°, 48.38° were indexed to the (101), (004), (200) planes of anatase structure phase of TiO₂ (JCPDS78-2486), respectively. Diffraction peaks appearing at 30.28°, 35.66°, 43.33°, 53.77° were indexed to the (220), (311), (400), (422), (511) and (440) planes of the face centered cubic (fcc) structure phase of Fe₃O₄ (JCPDS89-4924), respectively.

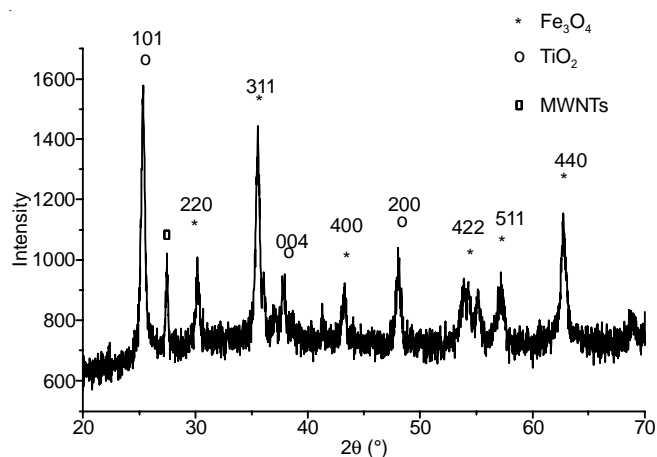


Fig. 1 XRD patterns of MWNTs/TiO₂/Fe₃O₄ nanocomposites XRD

TEM, SEM and EDS: The TEM and SEM images of MWNTs/TiO₂/Fe₃O₄ nanocomposites were shown in Fig. 2. The surface of MWNTs was covered with a layer of nanoparticles. The size of nanoparticles was almost uniform and the average size estimated from image was 20-30 nm. EDS of the MWNTs/TiO₂/Fe₃O₄ nanocomposites showed the presence of Fe, Ti, O and C elements in products, so the result was in agreement with the result from XRD.

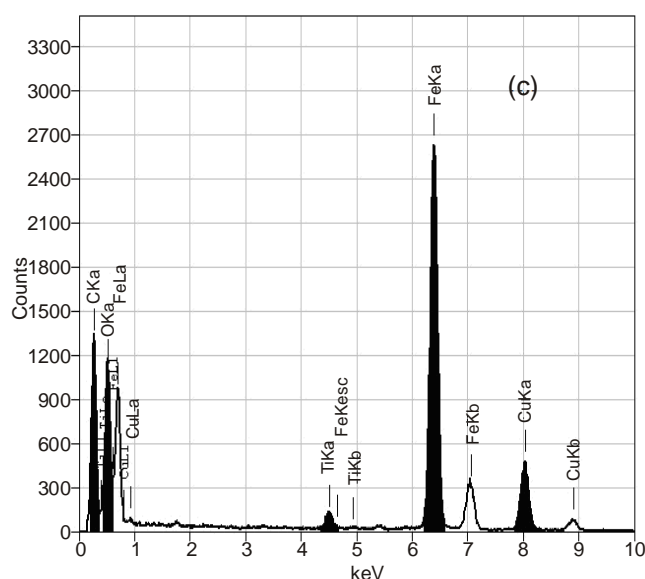
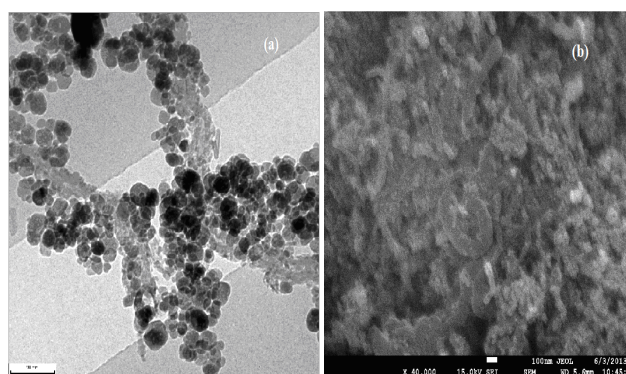


Fig. 2. (a) TEM, (b) SEM images and (c) EDS patterns of MWNTs/TiO₂/Fe₃O₄ nanocomposites

Photocatalytic activity: The photocatalytic activity of Fe_3O_4 nanoparticles, pure TiO_2 nanoparticles and MWNTs/ $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanocomposites were studied, the concentration of methyl orange used in experiments was 8 mg/L. The photocatalytic results were showed in Fig. 3. The concentration of methyl orange slightly change in the presence of Fe_3O_4 nanoparticles, this result indicate Fe_3O_4 did not have any photocatalytic capacity. Compared with Fe_3O_4 , the photocatalytic degradation of methyl orange solution was obvious in the presence of TiO_2 nanoparticles and MWNTs/ $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanocomposites. The photocatalytic activity of pure TiO_2 nanoparticles was lower than MWNTs/ $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanocomposites, which showed that MWNTs greatly enhance the photocatalytic activity of TiO_2 .

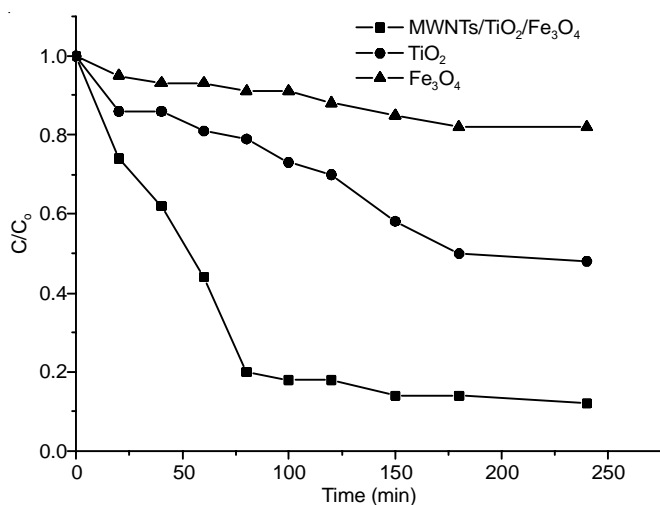


Fig. 3. Conversion of methyl orange (initial concentration: 8 mg/L, 50 mL) as a function of degradation time under exposure to UV light with different conditions (after adsorption 3 h)

The possible mechanism could be described in Fig. 4. The excellent electron accepting properties of MWNTs could aid in suppressing the recombination of photogenerated electron-hole pairs. The role of MWNTs was to act as an electron reservoir to trap electrons emitted from TiO_2 particles due to irradiation by UV light, thus hindering electron-hole pair recombination and improving the photocatalytic activity of TiO_2 .

Furthermore, MWNTs within nanocomposites increased the specific area available for adsorption of pollutants¹⁶. As a result of these effects, MWNTs/ TiO_2 nanocomposite structures were expected to enhance photocatalytic activity compared to single-component TiO_2 structures¹⁶.

Conclusion

In conclusion, we have demonstrated that photocatalytic MWNTs/ $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanocomposites were prepared by a simple co-precipitation method (TiO_2 nanoparticles were prepared by sol-gel method). The incorporation of MWNTs was to act as an electron reservoir, which helped to trap electrons emitted from TiO_2 particles due to irradiation by UV light. With the help of introduction of MWNTs, MWNTs/ $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanocomposites showed enhanced photocatalytic

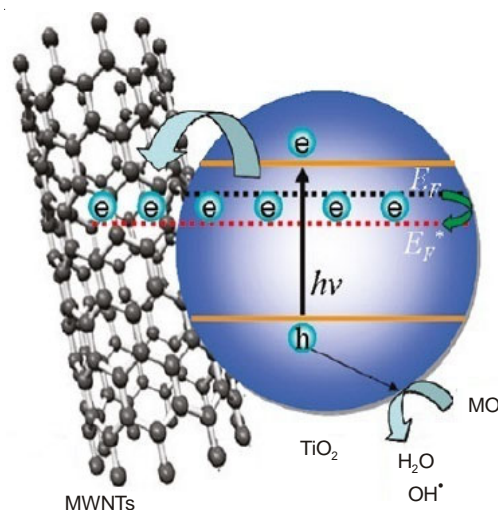


Fig. 4. Model picture demonstrating MWNTs as an electron reservoir to trap electrons emitted from TiO_2 nanoparticles due to UV irradiation

activity of degrading methyl orange, at the same time, it could be removed from solution with the help of Fe_3O_4 nanoparticles after photocatalytic activity, collected and used repeatedly.

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REFERENCES

1. M.A. Henderson, *Surf. Sci. Rep.*, **66**, 185 (2011).
2. M. Anpo and P.V. Kamat, *Environmentally Benign Photocatalysis-Application of Titanium Dioxide-Based Materials*, Springer: New York (2010).
3. H. Lin, X. Ji, Q. Chen, Y. Zhou, C.E. Banks and K. Wu, *Electrochem. Commun.*, **11**, 1990 (2009).
4. Z. Yigit and H. Inan, *Water Air Soil Pollut. Focus*, **9**, 237 (2009).
5. R.H. Baughman, A.A. Zakhidov and W.A. de Heer, *Science*, **297**, 787 (2002).
6. B. Ahmmad, Y. Kusumoto, S. Somekawa and M. Ikeda, *Catal. Commun.*, **9**, 1410 (2008).
7. A.P. Toor, A. Verma, C.K. Jotshi, P.K. Bajpai and V. Singh, *Dyes Pigments*, **68**, 53 (2006).
8. S. Qu, F. Huang, S.N. Yu, G. Chen and J.L. Kong, *J. Hazard. Mater.*, **160**, 643 (2008).
9. J.H. Shi, Y.J. Qin, W. Wu, X.L. Li, Z.X. Guo and D.B. Zhu, *Carbon*, **42**, 455 (2004).
10. S. Ravindran, S. Chaudhary, B. Colburn, M. Ozkan and C.S. Ozkan, *Nano Lett.*, **3**, 447 (2003).
11. (a) K.V.S. Ranganath and F. Glorius, *Catal. Sci. Technol.*, **1**, 13 (2011); (b) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara and J.-M. Basset, *Chem. Rev.*, **111**, 3036 (2011).
12. N. Anand, K.H.P. Reddy, T. Satyanarayana, K.S.R. Rao and D.R. Burri, *Catal. Sci. Technol.*, **2**, 570 (2012).
13. S. Rostamizadeh, N. Shadjou, M. Azad and N. Jalali, *Catal. Commun.*, **26**, 218 (2012).
14. D. Rosario-Amorin, M. Gaboyard, R. Clerac, L. Vellutini, S. Nlate and K. Heuze, *Chem. Eur. J.*, **18**, 3305 (2012).
15. C. Yang, J.J. Wu and Y.L. Hou, *Chem. Commun.*, **47**, 5130 (2011).
16. K. Woan, G. Pyrgiotakis and W. Sigmund, *Adv. Mater.*, **21**, 2233 (2009).