

# Fe<sub>3</sub>O<sub>4</sub>–ZnWO<sub>4</sub> hybrid microspheres: facile synthesis and magnetically recyclable photocatalytic performance

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Fe<sub>3</sub>O<sub>4</sub>–ZnWO<sub>4</sub> composite microspheres with magnetically recyclable photocatalytic performance have been firstly synthesised by a simple refluxing method under mild conditions. The as-prepared Fe<sub>3</sub>O<sub>4</sub>–ZnWO<sub>4</sub> composites show good photocatalytic efficiency in degradation of rhodamine B under UV light irradiation and can be recycled five times by magnetic separation without major loss of activity, the magnetic property of Fe<sub>3</sub>O<sub>4</sub>–ZnWO<sub>4</sub> sample has been studied also. Microspheres show potential use on dye degradation from the solution considering their magnetic recovery properties.

**1. Introduction:** Currently, photocatalysis has attracted increasing attention and tungstate has showed high photocatalytic performance, such as Bi<sub>2</sub>WO<sub>6</sub> [1], AgInW<sub>2</sub>O<sub>8</sub> [2] and so on. ZnWO<sub>4</sub> as a kind of tungstate was used widely in X-ray scintillators, photoluminescence [3–5] and ZnWO<sub>4</sub> has received considerable attention in the photocatalysis field [6, 7]. Nevertheless, recovery and reuse of suspended particulate catalysts in water were always complicated and expensive, therefore developing an effective method to construct easily recycled photocatalysts from the treated solution is highly desirable.

The composite materials of magnetite core and photocatalytic shell have been reported, which could combine the benefits of the activity of photocatalysts with the advantage of facile separation under an external magnet [8], as well as the low-cost and non-toxicity of magnetite (Fe<sub>3</sub>O<sub>4</sub>), for instance, polyaniline-modified Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> composite microspheres [9], Fe<sub>3</sub>O<sub>4</sub>/WO<sub>3</sub> hierarchical core-shell structures [10], hollow spherical Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> hybrid photocatalysts [11] and so on. However, fabrication of the above magnetic composite architecture usually requires multiple steps such as a linker shell (silica) [9] or relatively high temperature [10], which makes the synthetic route complicated and hinders the widespread industrial use of magnetic composite architectures.

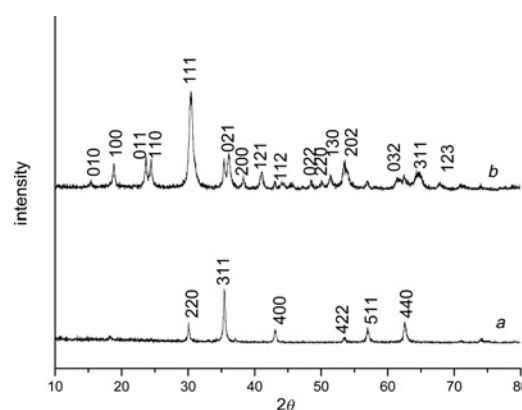
Here, we firstly report a facile way to construct Fe<sub>3</sub>O<sub>4</sub>–ZnWO<sub>4</sub> composite microspheres. Fe<sub>3</sub>O<sub>4</sub>–ZnWO<sub>4</sub> hybrid microspheres exhibited good photocatalytic property and easy recovery in an external magnetic field, and we have further studied their magnetic property.

## 2. Experimental

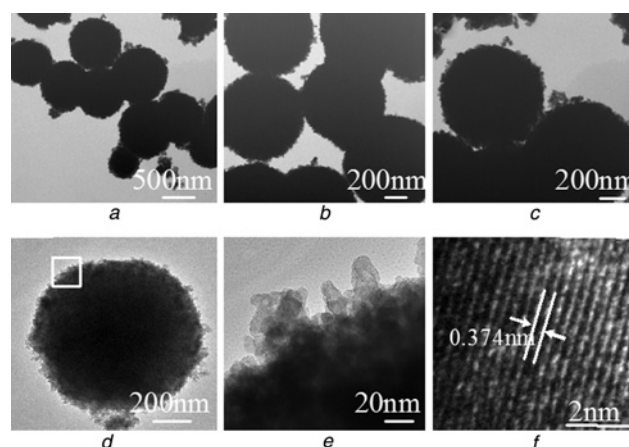
**2.1. Synthesis of Fe<sub>3</sub>O<sub>4</sub>–ZnWO<sub>4</sub> hybrid microspheres:** First, Fe<sub>3</sub>O<sub>4</sub> microspheres were synthesised by a solvothermal method in polyol medium according to the method published in the literature [12] with minor modification by reacting at 180°C for 12 h. Then, 100 mg Fe<sub>3</sub>O<sub>4</sub> microspheres were dispersed in a flask containing 60 ml of ethylene glycol and 1 mmol of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O dissolved in 10 ml of water was added into the flask. After the mixture was refluxed at 160°C for 3 h, 1 mmol Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O dissolved in 10 ml of water was added to the above solution and reacted for the next 9 h. The obtained products were filtered out and washed with absolute ethanol and distilled water several times to remove impurities and dried at 60°C for 4 h.

**2.2. Characterisation:** The obtained products were characterised by X-ray diffraction (XRD, Philips X'Pert Pro Super), a transmission electron microscope (TEM, Holland Philips Tecnai-12), high-resolution transmission electron microscopy (HRTEM,

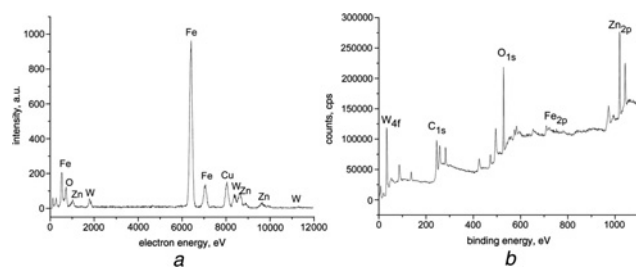
American FEI Tecnai G2 F30) and energy-dispersive X-ray analysis was obtained with an EDAX detector installed on the same HRTEM. X-ray photoelectron spectra (XPS) were collected on an ESCALab MKII X-ray photoelectron spectrometer, using



**Figure 1** XRD patterns  
a Fe<sub>3</sub>O<sub>4</sub> microspheres  
b Fe<sub>3</sub>O<sub>4</sub>–ZnWO<sub>4</sub> core-shell composite microspheres



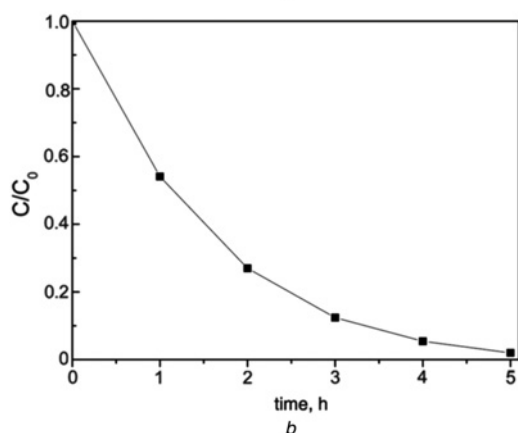
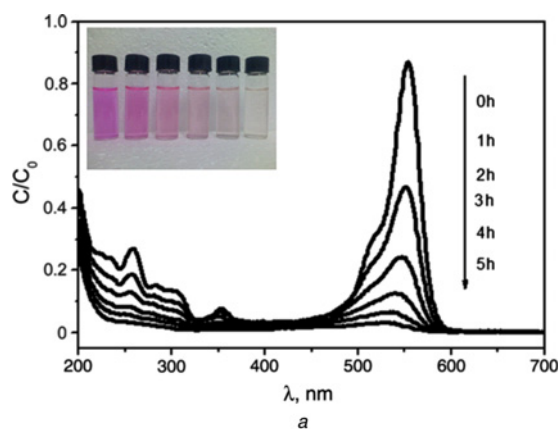
**Figure 2** TEM images and HRTEM images of Fe<sub>3</sub>O<sub>4</sub>–ZnWO<sub>4</sub> core-shell composite microspheres  
a–d TEM images  
e–f HRTEM images



**Figure 3** EDS and XPS of  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  core-shell composite microspheres  
a EDS  
b XPS

non-monochromatised Mg  $K\alpha$  X-ray as the excitation source. The magnetic measurement on a powder sample was performed on a vibrating sample magnetometer (VSM, EV7, ADE).

**2.3. Photocatalytic test:** The photocatalytic activities of the  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  hybrid microspheres were firstly evaluated by degradation of rhodamine B (RhB) in an aqueous solution under UV irradiation from a 250 W UV lamp ( $\lambda = 254$  nm). The photocatalyst (100 mg) was poured into 100 ml RhB aqueous solution ( $1 \times 10^{-5}$  M  $\text{l}^{-1}$ ) in a quartz reactor at room temperature under air. Before light was turned on, the solution was continuously stirred for 30 min in the dark to ensure the establishment of an adsorption-desorption equilibrium. The concentration of RhB during the degradation was monitored by colorimetry using a UV-vis spectrometer (Shimadzu UV-2101).



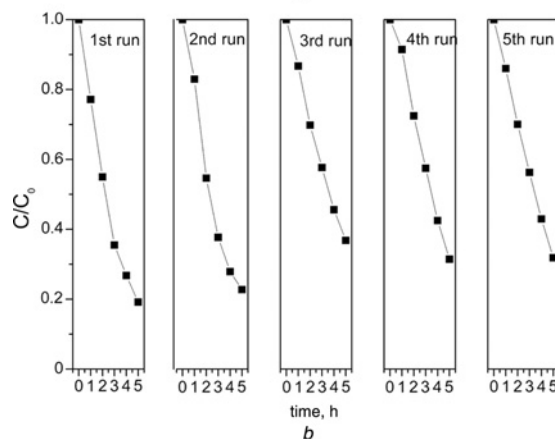
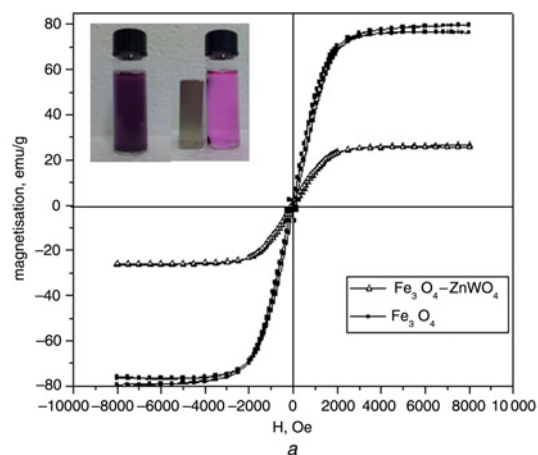
**Figure 4** UV-vis spectroscopic changes of aqueous RhB solution (Fig. 4a); degradation rate of RhB under UV light in presence of  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composite microspheres (Fig. 4b)

**3. Results and discussion:** Fig. 1 shows the XRD patterns of as-synthesised  $\text{Fe}_3\text{O}_4$  microspheres and  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  hybrid microspheres. In curve *a*, all the diffraction peaks can be indexed to a face-centred-cubic structure of magnetite (JCPDS Card No: 19-0629), in curve *b*, besides the corresponding peaks of magnetite, all the others can be indexed to a monoclinic phase of  $\text{ZnWO}_4$  (JCPDS Card No: 73-0554).

The morphology and structure of  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  core-shell microspheres was investigated by TEM and HRTEM observation as shown in Fig. 2. TEM images (Figs. 2a-d) indicated the composite structure of  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  with  $\text{Fe}_3\text{O}_4$  microspheres as the inner part and  $\text{ZnWO}_4$  nanocrystals coating on the surface of  $\text{Fe}_3\text{O}_4$  microspheres as the outer part; it can be found that the typical size of  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composite microsphere was about 750 nm. Fig. 2e shows an HRTEM image in the area marked by the square in Fig. 2d, which clearly shows the size of  $\text{ZnWO}_4$  nanocrystal was about 25 nm. Fig. 2f shows the enlarged lattice-resolved HRTEM image of certain  $\text{ZnWO}_4$  nanocrystal from Fig. 2e, the spacing of the observed lattice plane is  $\sim 0.37$  nm corresponding to the spacings of the (110) plane from  $\text{ZnWO}_4$ .

As shown in Fig. 3a, electron dispersive spectroscopy (EDS) of the core-shell structures shows the peaks of Zn, Fe, W and O elements, and the XPS spectrum in Fig. 3b indicates that the main peak values at 35.6, 284.8, 530.6, 710.51 and 1021.9 eV can be assigned readily to the binding energies of  $\text{W}_{4f}$ ,  $\text{C}_{1s}$ ,  $\text{O}_{1s}$ ,  $\text{Fe}_{2p}$  and  $\text{Zn}_{2p}$ , respectively. Therefore both the XPS and EDS results confirm that the products are  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composites.

The photocatalytic activity of  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composite microspheres was evaluated by degradation of RhB dye in water under UV light irradiation ( $\lambda = 254$  nm). Tetraethylated RhB is one of the most commonly used organic dyes for the textile industry. It



**Figure 5** Room-temperature magnetisation curves of  $\text{Fe}_3\text{O}_4$  microspheres and  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composites (Fig. 5a); five cycles of photocatalytic degradation of RhB from  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composite microspheres (Fig. 5b)

is always being widely studied as a representative water pollutant to evaluate the photocatalytic efficiency of the obtained photocatalysts [13]. The characteristic absorption of RhB at  $\lambda = 553$  nm was used to monitor the photocatalytic degradation process. Fig. 4a shows the temporal evolution of absorption spectra from aqueous RhB degraded with  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composite photocatalyst, as the intensity of main absorption peaks decreased or even disappeared because of degradation of RhB in water. As seen from Fig. 4b, RhB dye in water was fully degraded under UV radiation after 5 h, which is consistent with the colour change of the suspension from pink to colourless as the irradiation time increases gradually (inset in Fig. 4b).

The hysteresis loops of the  $\text{Fe}_3\text{O}_4$  microspheres and  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composites are shown in Fig. 5, which indicate the magnetic saturation ( $M_s$ ) values are about 78.7 and 25.7 emu/g, respectively. The decrease in magnetisation reveals the increased  $\text{ZnWO}_4$  nanocrystals on the surface of  $\text{Fe}_3\text{O}_4$  microspheres bringing down the magnetite fraction in each microsphere [14]. Strong magnetisation of the  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  hybrid photocatalysts indicates their rapid and convenient separation from aqueous solutions for recovery under an applied magnetic field, the inset in Fig. 5a shows black  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composites suspension in water immediately becoming clear under an external magnet. To investigate the recyclable photocatalytic performance of  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composites microspheres, five cycles of RhB dye degradation were examined under an external magnet for separation, as shown in Fig. 5b. One can see that the photocatalytic activity of  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  hybrid microspheres exhibits little loss activity for the photodegradation of RhB after five recycles. This fact indicates that the as-prepared  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composite microspheres own stable photocatalytic activity with easy separation under an external magnet for reuse in water treatment.

**4. Conclusion:** In summary, magnetically separable  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  hybrid photocatalyst with an  $\text{Fe}_3\text{O}_4$  microsphere as core and  $\text{ZnWO}_4$  nanocrystals as shell has been firstly fabricated through a simple refluxing method under mild condition.  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  hybrid microspheres exhibited good photocatalytic performance for degradation of RhB under UV light irradiation with easy recovery and little loss of activity for five times under an external magnetic field. The magnetic property study of the  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  composite sample shows ferromagnetism at room temperature. The results presented herein provide new insights into hierarchical  $\text{Fe}_3\text{O}_4\text{-ZnWO}_4$  core-shell microspheres as probable magnetic photocatalysts in water treatment and environmental protection.

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## 6 References

- [1] Ma D.K., Huang S.M., Chen W.X., Hu S.W., Shi F.F., Fan K.L.: 'Self-assembled three-dimensional hierarchical umbilicate  $\text{Bi}_2\text{WO}_6$  microspheres from nanoplates: controlled synthesis, photocatalytic activities, and wettability', *J. Phys. Chem. C*, 2009, **113**, pp. 4369–4374
- [2] Hu B., Wu L.H., Liu S.J., Yao H.B., Shi H.Y., Li G.P., *ET AL.*: 'Microwave-assisted synthesis of silver indium tungsten oxide mesocrystals and their selective photocatalytic properties', *Chem. Commun.*, 2010, **46**, pp. 2277–2279
- [3] Trots D.M., Senyshyn A., Vasylechko L., Niewa R., Vad T., Mikhailik V.B., *ET AL.*: 'Crystal structure of  $\text{ZnWO}_4$  scintillator material in the range of 3–1423 K', *J. Phys. Condens. Matter.*, 2009, **21**, pp. 325–402
- [4] Kalinko A., Kuzmin A.: 'A Raman and photoluminescence spectroscopy of zinc tungstate powders', *J. Lumin.*, 2009, **129**, pp. 1144–1147
- [5] Wang Z.L., Li J.H., Hao L.H.: 'Blue-green, red, and white light emission of  $\text{ZnWO}_4$ -based phosphors for low-voltage cathodoluminescence applications', *J. Electrochem. Soc.*, 2008, **155**, pp. J152–J156
- [6] Lin J., Zhu Y.F.: 'Controlled synthesis of the  $\text{ZnWO}_4$  nanostructure and effects on the photocatalytic performance', *Inorg. Chem.*, 2007, **46**, pp. 8372–8378
- [7] Zhao X., Zhu Y.F.: 'Synergetic degradation of rhodamine B at a porous  $\text{ZnWO}_4$  film electrode by combined electro-oxidation and photocatalysis', *Environ. Sci. Technol.*, 2006, **40**, pp. 3367–3372
- [8] Polshettiwar V.R., Luque R., Fihri A., Zhu H., Bouhrara M., Basset J. M.: 'Magnetically recoverable nanocatalysts', *Chem. Rev.*, 2011, **111**, pp. 3036–3075
- [9] Wang G., Yang M., Guo W.C., Gao H.Y.: 'Synthesis of polyaniline-modified  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  composite microspheres and their photocatalytic application', *Mater. Lett.*, 2011, **65**, pp. 2887–2890
- [10] Xi G.C., Yue B., Cao J.Y., Ye J.H.: ' $\text{Fe}_3\text{O}_4/\text{WO}_3$  hierarchical core-shell structure: high-performance and recyclable visible-light photocatalysis', *Chem. Eur. J.*, 2011, **17**, pp. 5145–5154
- [11] Xuan S.H., Jiang W.Q., Gong X.L., Hu Y., Chen Z.Y.: 'Magnetically separable  $\text{Fe}_3\text{O}_4/\text{TiO}_2$  hollow spheres: fabrication and photocatalytic activity', *J. Phys. Chem. C*, 2008, **113**, pp. 553–558
- [12] Deng H., Li X., Peng Q., Wang X., Chen J., Li Y.D.: 'Monodisperse magnetic single-crystal ferrite microspheres', *Angew. Chem. Int. Ed.*, 2005, **44**, pp. 2782–2785
- [13] Dai X.J., Luo Y.S., Zhang W.D., Fu S.Y.: 'Facile hydrothermal synthesis and photocatalytic activity of bismuth tungstate hierarchical hollow spheres with an ultrahigh surface area', *Dalton Trans.*, 2010, **39**, pp. 3426–3432
- [14] Xu H., Cui L., Tong N., Gu H.C.: 'Development of high magnetization  $\text{Fe}_3\text{O}_4$ /polystyrene/silica nanospheres via combined miniemulsion/emulsion polymerization', *J. Am. Chem. Soc.*, 2006, **128**, pp. 15582–15583