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## Special Section on Advanced (Non-Carbon) Materials

### Synthesis and photocatalytic application of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO fine particles prepared by two-step chemical method

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Composite iron oxide-Zinc oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO) was synthesized by two-step method: in the first one step uniform  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles were prepared through a hydrolysis process of ferric chloride at 80 °C. In the second step, the ZnO particles were included in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles by a zinc acetate [Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O] assisted hydrothermal method at low temperature (90°C±C). The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and ZnO phases were identified by XRD, energy dispersive X-ray analysis (EDX). The photoreactivities of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO nanoparticles under UV irradiation were quantified by the degradation of formaldehyde.

**Keywords :** Photocatalysis, oxide nanoparticles.

**1. Introduction :** The increasing concern on the safety in laboratory and industrial activities has generated great interests in fast reliable gas detection. In recent years, zero-dimensional nanoparticles and one-dimensional nanoscale materials, for example, ZnO, SnO<sub>2</sub>, WO<sub>3</sub> and MnO<sub>2</sub> nanoparticles and nanorods, have been investigated to fabricate new semiconductor gas sensors [1 – 4], due to their fine particle size and large surface area. The gas-sensing mechanism involves the chemisorption of oxygen on the surface of these oxides, followed by charge transfer during the reaction of oxygen with target gas molecules [5].

Zinc oxide is an important oxide semiconductor for sensing applications to toxic and combustible gases [6, 7]. Generally, ZnO sensors provide a wide variety of advantages, such as low cost, short response time, easy manufacturing, and small size, compared to the traditional analytical instruments.

However, its working temperature is rather high, normally at 400 – 500 °C, and the selective response ability is poor. In recent years, the study on ZnO gas-sensing materials has become one of the major research topics, and the research is focused on improving their preparation method and decreasing their working temperature [8, 9].

The synthesis of composite particles consisting of magnetic cores and luminescent cells such as  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO has gained acceptance in few years due to its magnetic, photoluminescence and catalytic properties [10]. Also, as active element in gas sensors [11]. This type of composite particles has biological and biomedical potential applications such as detection of cancer cells, bacteria and viruses, and magnetic separation [12]. Recently Ruipeng Fu *et al.* [13] prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO composite particles via a simple solution method, and investigated its morphology; indicating that the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO composite

particles are of typical sphere-like morphology with diameter in the range of 300 - 400 nm. Also, the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO composites exhibit magnetic response to an external magnetic field and efficient characteristic emissions of ZnO under UV excitation.

Dong Kee Yi *et al.* [14], by a two step synthesis obtained silica-coated nanocomposite particles preserved the magnetic properties of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and optical properties of CdSe QDs. Hongwei Gu [10] reported on a one-pot chemical synthesis method for generating heterodimers of nanoparticles by taking advantage of lattice mismatch and selective annealing at a relatively low temperature. They deposited amorphous CdS on the surface of FePt nanoparticles to form a metastable core-shell structure in which the CdS transformed into a crystalline state upon heating. Moreover, the core-shell structures which have sizes less than 10 nm, also exhibit both superparamagnetism and fluorescence. Ites of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> magnetic nanoparticles (MPs) and CdSe photoluminescent quantum dots (QDs), its analysis showed that the presence of CdSe increased the effective magnetic anisotropy of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> containing particles, indicating that the QDs were closely connected to MPs, concluding that the SiO<sub>2</sub>/MPs-QDs nanocomposite particles preserved the magnetic properties of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and optical properties of CdSe QDs. Hongwei Gu [10] reported on a one-pot chemical

In this work, we report on a two-step solution phase controlled hydrolysis method to synthesize  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO composite particles. In the first step,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were synthesized by a hydrolysis process of ferric chloride as a source material. In the second step, zinc acetate [(Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O)] was taken as starting materials. Compared to other sensor elements, these core/shell particles exhibit a high gas sensitivity, short response/recovery time and can work at relatively low temperatures.

#### Materials and Methods :

**Materials :** Ferric chloride, FeCl<sub>3</sub>, HCl, deionized water, Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O, Ammonia.

#### Methods :

##### 1. Preparation and Synthesis :

**1.1 Preparation of Fe<sub>2</sub>O<sub>3</sub>/ZnO core/shell particles :** Fe<sub>2</sub>O<sub>3</sub>/ZnO core/shell particles were prepared through a hydrolysis process of Zn<sup>2+</sup> in the presence of Fe<sub>2</sub>O<sub>3</sub> particles. Uniform Fe<sub>2</sub>O<sub>3</sub> particles were also prepared through a hydrolysis process of ferric chloride at 80 °C as literature described. Stock solution of 3M FeCl<sub>3</sub> and 0.2M HCl was mixed in 1:3 ratio, and deionized water was added until final concentration become of Fe<sup>3+</sup> 0.01M. This mixture was preserved in water bath at 96 °C for 24 h. Resultant solution was used for further reaction.

Twenty milliliters of Fe<sub>2</sub>O<sub>3</sub> nanoparticles were dispersed in 200 ml deionized water. Then 20 mg Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O was introduced to the solution, and the suspension was heated in an water bath at 40 °C under vigorous stirring. Twenty milliliters of 5 % ammonia was added into the suspension in 0.5 hr and the reaction was maintaining the temperature for 1 hour. Finally, the colloids were sintered at 400 °C for 2 hours, yielding the desired Fe<sub>2</sub>O<sub>3</sub>/ZnO nanoparticles in below furnace.

##### 1. Physical Characterization :

**2.1. XRD X-Ray diffraction :** XRD spectra studies of Fe<sub>2</sub>O<sub>3</sub>/ZnO nano particles the materials were performed in the Rigaku Miniflex-II Desktop XRD diffractometer coupled to a Cu X-ray tube, the Cu-K $\alpha$  wavelength of which was selected by means of the nickel filter. The crystallite size was calculated from the width of the XRD peaks by using Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where,  $D$  is the average crystalline size,  $\lambda$  is the X-ray wavelength used,  $\beta$  is full width at half-maximum intensity and  $\theta$  is the Bragg's angle in degrees.

**2.2. Energy-dispersive X-ray analysis :** EDAX of Fe<sub>2</sub>O<sub>3</sub>/ZnO core/shall nano particles were done by JEOL make Model JSM 5810 LU scanning electron microscope equipped with an X-ray energy dispersive spectroscopy (EDAX)

**2.3 Photocatalytic Degradation :** For studying photocatalytic degradation of formaldehyde, a series of tests were performed to evaluate the conversion of formaldehyde by adsorption, photolysis, and photocatalysis. The photocatalytic degradation of formaldehyde by  $\text{Fe}_2\text{O}_3/\text{ZnO}$  was carried out in a 100 ml Quartz glass reactor. Illumination with light of wavelength  $\lambda > 300$  nm was provided by a 125 W high pressure UV lamp. An initial concentration of formaldehyde was 0.2 ppm in 300 ml DI water. Experiments were performed at a fixed pH value with varying time. First sample were taken at interval of Ten minutes.  $\text{Fe}_2\text{O}_3/\text{ZnO}$  (0.01 mg) was introduced to the reaction mixture and samples were taken at a regular interval of ten minutes at room temperature.

### 3. Results and Discussion :

#### 3.1 X-Ray diffraction (XRD) Measurement :

Figure (1) shows the XRD patterns of ZnO and  $\text{Fe}_2\text{O}_3$ . All the diffraction peaks can be readily indexed to a wurtzite phase of ZnO (JCPDS 79-0205) and a hematite phase of  $\text{Fe}_2\text{O}_3$  (JCPDS 82-1503). The apparent broadening of these peaks indicates crystallite size of the as-obtained nanoparticles, which is estimated to be about 40 nm from its XRD data. The fact that no distinct peaks existed except the patterns of ZnO and  $\text{Fe}_2\text{O}_3$  [10, 11].

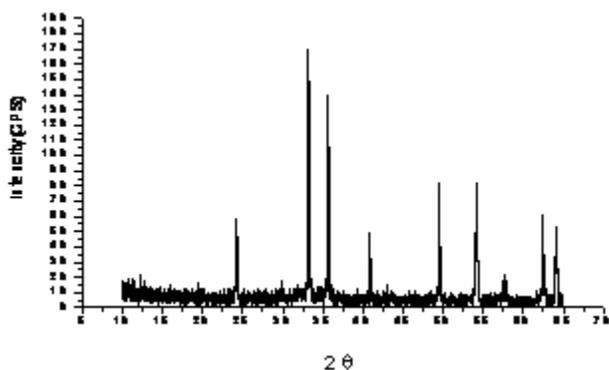


Figure (1) : XRD spectra of  $\text{Fe}_2\text{O}_3/\text{ZnO}$  nanoparticles.

$2\theta$ (deg)	Highest intensity peak (cps*deg)	Interplanar distance dÅ	Cell values a,b,c	Corresponding Plane (h, k, l)	Phase
33.153	100	d=2.740Å	5.0356, 13.7489	(1, 0, 4)	Wurtzite, (JCPDS 79-0205)
36.253	95	d=2.4759Å	3.2498, 5.2066	(1, 0, 1)	Hematite, (JCPDS 82-1503)

Table (1) : XRD Data for  $\text{Fe}_2\text{O}_3/\text{ZnO}$  core/shall nano particles. Average Crystalline Size is 40 nm.

#### 3.2 Energy-dispersive X-ray spectroscopy :

Energy-dispersive X-ray spectroscopy (EDAX) shows the presence of O, Fe, and Zn.

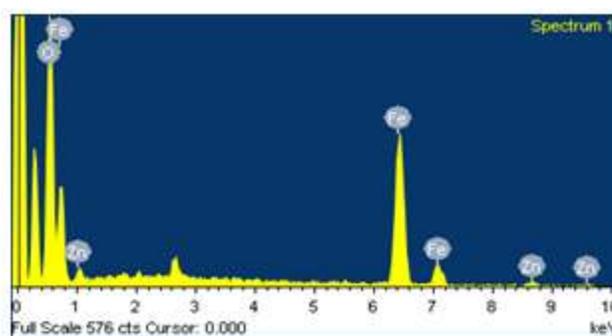


Figure (2) : EDAX spectra of  $\text{Fe}_2\text{O}_3/\text{ZnO}$  nanoparticles.

According to atomic weight stoichiometry corresponding amount of O, Fe, and Zn were observed to be 31.49 %, 64.49 %, and 1.93 % respectively.

Element	Weight %	Atomic %
O	31.49	61.80
Fe	64.49	36.26
Zn	4.03	1.93
Totals	100.00	

Table (2) : Proportion of elements

**3.3 Photocatalytic degradation :** The rate of the photodegradation obtained from experiments are depicted in Table (3). It is clear from Table (3) that for all the formaldehyde, the rate of the photodegradation increases with an increase in time.

Table (3) : COD data of Fe<sub>2</sub>O<sub>3</sub>/ZnO composite material.

Sample	Time (min)	Material	COD mg/L
A	10	Formaldehyde	439.59
B	20	Formaldehyde	416.34
C	30	Formaldehyde	408.78
D	10	Formaldehyde + Fe <sub>2</sub> O <sub>3</sub> /ZnO	339.34
E	20	Formaldehyde + Fe <sub>2</sub> O <sub>3</sub> /ZnO	316.05
F	30	Formaldehyde + Fe <sub>2</sub> O <sub>3</sub> /ZnO	263.16

**3. Conclusions :** We synthesized compact  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO composite particles by a two step hydrolysis process. Crystallite size estimated from XRD spectra is about 40 nm. The phases and purity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO composites were investigated by XRD, EDAX and PL analysis and revealed that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and the ZnO nanoparticles conserved their respective phases. From photoluminescence studies of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO composite particles can be conclude that the ZnO and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles preserved the unique optical property.

#### References :

- [1] Z. W. Pan, Z. R. Dai, Z. L. Wang, Nanobelts of semiconducting oxides, *Science* 291 (2001) 1947 – 1949.
- [2] P. D. Yang, H. Q. Yan, Controlled growth of ZnO nanowires and their optical properties, *Adv. Funct. Mater.* 12 (2002) 323 – 331.
- [3] X. Wang, Y. D. Li, Selected-control hydrothermal synthesis of  $\alpha$ - and  $\beta$ -MnO<sub>2</sub> single crystal nanowire, *J. Am. Chem. Soc.* 124 (2002) 2880 – 2888.
- [4] X. L. Li, J. F. Liu, Y. D. Li, Large scale synthesis of tungsten oxide nanowire with high aspect ratio, *Inorg. Chem.* 42 (2003) 921 – 924.
- [5] P. Esser, W. Gopel, Physical adsorption on single crystal zinc oxide, *Surf. Sci.* 97 (1980) 309 – 318.
- [6] A. Jones, T. A. Jones, B. Mann, The effect of the physical form of the oxide on the conductivity changes produced by CH<sub>4</sub>, CO, and H<sub>2</sub>O on ZnO, *Sens. Actuators.* 5 (1984) 75 – 88.
- [7] S. Saito, M. Miyayama, K. Koumoto, Gas-sensing characteristics of porous ZnO and Pt/ZnO ceramics, *J. Am. Ceram. Soc.* 68 (1985) 40 – 43.
- [8] S. Pizzini, N. Butta, D. Norducci, M. Palladino, Thick film ZnO resistive gas sensors analysis of their kinetic behavior, *J. Electrochem. Soc.* 136 (1989) 1945 – 1948.
- [9] H. Nanto, T. Minami, S. Takata, Zinc oxide thin film ammonia gas sensors with high sensitivity and excellent selectivity, *J. Appl. Phys.* 60 (1986) 482 – 484.
- [10] Hongwei Gu et al., Facile One-Pot Synthesis of Bifunctional Heterodimers of Nanoparticles : A Conjugate of Quantum Dot and Magnetic Nanoparticles, *J. Am. Chem. Soc.* 126 (2004) 5664.
- [11] Teixeira et al, Evaluation of a Fe<sub>2</sub>O<sub>3</sub>-based graphite-epoxy tubular electrode as pH sensor in flow injection potentiometry, *J. Bra. Chem. Soc.* 11 (2000) 27 - 31.
- [12] Deseng Wang et al., Superparamagnetic Fe<sub>2</sub>O<sub>3</sub> Beads–CdSe/ZnS Quantum Dots Core–Shell Nanocomposite Particles for Cell Separation, *Nano Lett.* 3(2004) 409.
- [13] Ruipeng Fu *et al.*, Preparation and characterization of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO composite particles, *Mater. Lett.* 62 (2008) 4066.
- [14] Dong Kee Yi, *et al.*, two step synthesis obtained silica-coated nanocomposites of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> magnetic nanoparticles (MPs) and CdSe photoluminescent quantum dots (QDs), *J. Am. Chem. Soc.* 127 (2005) 499.