

Facile Synthesis of α -Fe₂O₃/ZnS Core/Shell Nanostructures for Photocatalysis

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ABSTRACT

Among various transition metal oxides, α -Fe₂O₃ is a widely studied material which is extensively used as photocatalysts, sensors, fine ceramics, data storage materials and pigments. ZnS is a II- VI group semiconductor which can be used for optical devices and catalysis. α -Fe₂O₃ and ZnS can be coupled together to improve their stability and efficiency as photocatalysts. In this paper, a simple, low temperature ultrasonication assisted precipitation method is employed to obtain α -Fe₂O₃/ZnS core/shell nanostructures. Their structural, compositional, morphological and optical properties are studied using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), high resolution transmission electron microscopy (HRTEM) and photoluminescence (PL) spectroscopy respectively. XRD proves the formation of rhombohedral phase of α -Fe₂O₃ and hexagonal phase of ZnS nanoparticles. EDS reveals the presence of Fe, Zn, O and S elements. α -Fe₂O₃/ZnS core/shell nanostructures exhibit spherical shape with core (α -Fe₂O₃) size of ~ 50 nm and ZnS shell of size ~ 30 nm as observed from the HRTEM image. The PL intensity of α -Fe₂O₃/ZnS core/shell nanostructures decrease rapidly when compared to pure α -Fe₂O₃ nanoparticles demonstrating the efficient charge separation of the composites. Therefore the electrons and holes could migrate more effectively to the surfaces of α -Fe₂O₃ and ZnS and hence α -Fe₂O₃/ZnS core/shell nanostructures can be used as good photocatalysts for the degradation of the contaminant dyes.

Keywords: α -Fe₂O₃/ZnS core/shell nanostructures, ultrasonication, co-precipitation, XRD, EDS, HRTEM, PL, photocatalyst

1. INTRODUCTION

In recent years, extensive research has been done to design and control fabrication of nanostructured materials with functional properties. The core/shell nanostructures with two or more functions have drawn much attention and they are fabricated with tailored optical, surface and structural properties [1]. Hematite (α -Fe₂O₃) is one of the most stable iron oxides with n-type semiconducting properties. Because of its low cost, simple production, environmental friendliness and excellent chemical stability, α -Fe₂O₃ has been intensively investigated in a variety of applications such as catalysts, pigments, water treatment, sensors and lithium ion batteries [2-9]. With a low

band-gap of 2.2 eV, α -Fe₂O₃ absorbs most of the visible light, becoming a promising visible-light-driven photocatalyst. However photo-induced electron-hole pairs in α -Fe₂O₃ are difficult to be separated which inhibits its further application as an efficient photocatalyst [10]. The synthesis of group II-VI semiconductor materials is gaining more interest due to their enormous uses in optical devices, catalysis and so on. ZnS is an important semiconductor compound of the II-VI group with excellent physical properties and wide band- gap of 3.7 eV at 300 K. It has been extensively investigated due to its potential for device applications such as window layers for solar cells, production of hydrogen, blue-light diodes, electro-luminescent

displays and antireflection coatings for infra-red devices [11]. One way to enhance the properties of both α -Fe₂O₃ and ZnS is to couple each other to improve their stability and efficiency as photocatalysts. A large portion of atoms are located on or near surfaces because of their high surface-to-volume ratio arising from the small particle size. This causes the surface states to act as luminescent quenching centers; to overcome these effects, accordingly core/shell structural nanomaterials have been developed. A great deal of effort has been devoted to the spherical core/shell nanostructures owing to their unique applications in fabrication of nanoscale devices [10, 12]. Hematite based core/shell nanostructures have been synthesized mainly by hydrothermal method [13-15]. An attempt has been made to synthesize α -Fe₂O₃/ZnS nanostructures by a low temperature simple co-precipitation method assisted with ultrasonication. In this article, the structural, compositional, morphological and optical properties of α -Fe₂O₃/ZnS nanostructures suitable for photocatalytic applications have been investigated.

2. EXPERIMENTAL

2.1. Synthesis of pure α -Fe₂O₃ nanopowder

The α -Fe₂O₃ nanoparticles were pre-synthesized by co-precipitation method. All chemicals used in this study were of analytical grade. In a typical process, Ferric nitrate nonahydrate [Fe(NO₃)₃·9H₂O] (0.025 M) was dissolved in double distilled water (500 ml). The solution was then mixed with 500 ml aqueous solution of urea [CO(NH₂)₂] (0.075 M) solution. The solution was then dispersed under vigorous magnetic stirring for 30 minutes. Appropriate amount of ammonia solution [NH₄OH] (0.16 M in 500 ml) was added to maintain a pH of 10. The resulting precipitate was dispersed further by ultrasonication (Powersonic 405) and then washed using double distilled water for 5 times and ethanol for 5 times. The final product of α -Fe₂O₃ was dried at 60°C in hot air oven for 7 hours and heat treated at 700°C for 2 hours.

2.2. Synthesis of pure α -Fe₂O₃/ZnS nanopowder

In order to make ZnS shells on the surface of α -Fe₂O₃ nanoparticles, the precipitation of zinc acetate [Zn(COOCH₃)₂·2H₂O] and sodium sulphide [Na₂S] was employed. 0.2 g of previously prepared α -Fe₂O₃ nanopowder was put into 200 ml double distilled water and ultrasonically (Powersonic 405) dispersed for 1 hour followed by slow

dropping of appropriate amount of 0.02 M of 100 ml Zn(COOCH₃)₂·2H₂O aqueous solution into the suspension under vigorous stirring. 10 minutes later, 0.02 M of 100 ml Na₂S aqueous solution was very slowly dropped into the above suspension to form ZnS shell. 0.75 M of 50 ml ammonia solution [NH₄OH] was added to promote the formation of ZnS shell over α -Fe₂O₃. The resulting product was then washed using double distilled water for 5 times and ethanol for 5 times and was dried at 60°C in hot air oven for 7 hours and heat treated at 400°C for 2 hours.

2.3. Characterization

The structural analysis of hematite (α -Fe₂O₃) and α -Fe₂O₃/ZnS core/shell nanostructures was performed by recording the X-ray diffraction (XRD) spectrum at 25°C using X-ray diffractometer (PANalytical X'Pert Pro) with Cu-K_α as the radiation source (wavelength: 1.54056 Å) at a step size of 0.05° over the 2θ range of 10° to 80°. The elemental analysis was carried out by energy dispersive X-ray spectroscopy (EDS) Bruker detector. The morphology of the samples was examined by high-resolution transmission electron microscopy (HRTEM) (JEOL 2100) operating at an accelerating voltage of 200 kV. Photoluminescence (PL) studies were carried out using a photoluminescence spectrophotometer (Varian Cary Eclipse) and the spectra were recorded at a scan rate of 600 nm/min in the range of 375 nm – 600 nm using an excitation wavelength of 355 nm.

3. RESULT AND DISCUSSION

3.1. XRD, EDS and HRTEM Analysis

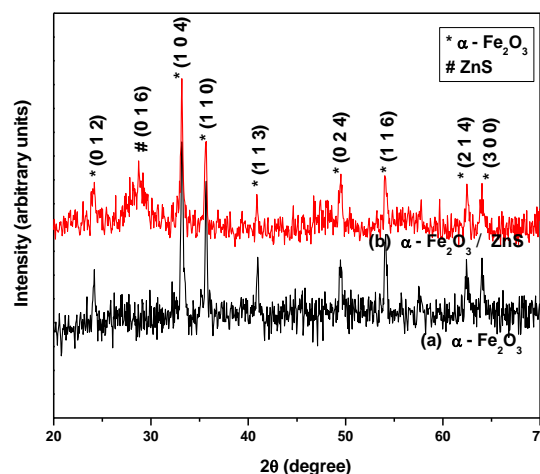


Fig.1: XRD pattern of pure α -Fe₂O₃ nanoparticles and α -Fe₂O₃/ZnS core/shell nanostructures

Fig.1 shows the XRD pattern of pre-synthesized α - Fe_2O_3 and final products of α - $\text{Fe}_2\text{O}_3/\text{ZnS}$ core/shell nanostructures. The XRD peaks of α - Fe_2O_3 can be indexed as the rhombohedral phase of iron (III) oxide matching well with the JCPDS card number 89-8104 corresponding to the powder diffraction pattern of standard hematite.

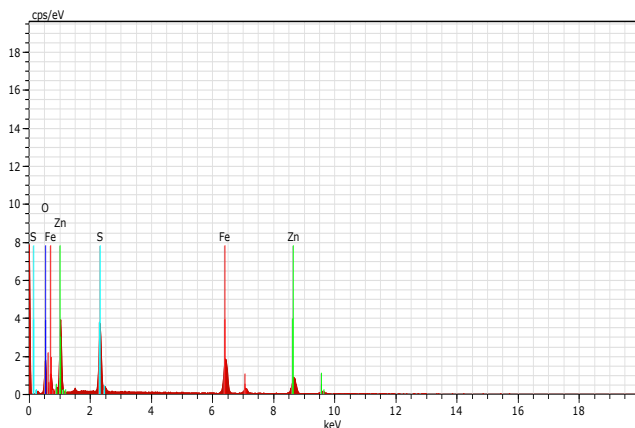


Fig.2: EDAX spectrum of α - $\text{Fe}_2\text{O}_3/\text{ZnS}$ core/shell nanostructures

No other impurity peaks are observed. The broadening of the XRD lines reflects the nanoparticle nature of the sample [16, 17]. In Fig.1(b), (016) plane is assigned to ZnS and is assigned to the hexagonal phase (JCPDS card number 83-2124). Thus XRD proves the formation of α - Fe_2O_3 and ZnS. The EDS spectrum confirms the presence of elemental Fe, Zn, S and O (Fig.2). The HRTEM image (Fig.3) at a magnification of 100 nm shows that the spherical core α - Fe_2O_3 nanoparticles (~ 50 nm) are surrounded by ZnS (~ 30 nm) shell.

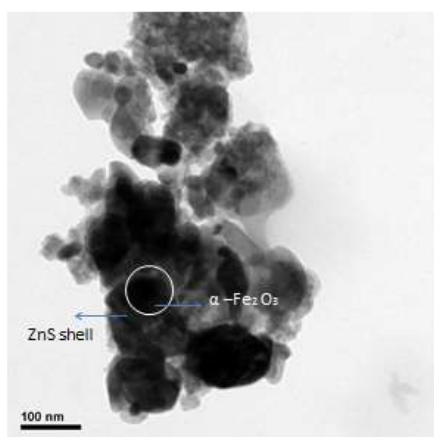


Fig.3: HRTEM image of α - $\text{Fe}_2\text{O}_3/\text{ZnS}$ core/shell nanostructures

3.2. PL Analysis

The photoluminescence emission peaks of α - Fe_2O_3 nanoparticles are observed at 410 nm, 434 nm, 460 nm, 485 nm, 520 nm and 563 nm as shown in Fig.4. The emission band around 410 nm was attributed to the ligand-to-metal charge-transfer (LMCT) transitions (direct transitions). There are some measurable emission peaks induced by the Fe^{3+} ligand field and exciton pair transitions (indirect transitions) in the visible region. The shift of emission wavelength to 525 nm – 560 nm as attributed to stronger 3d–4sp hybridization.

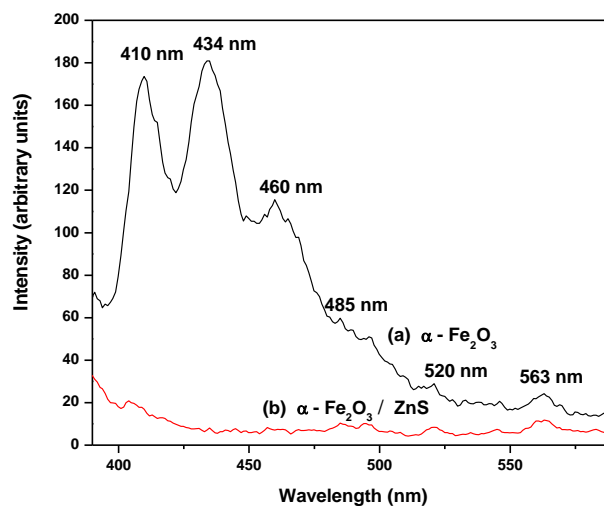


Fig.4: Room temperature PL emission spectra of pure α - Fe_2O_3 nanoparticles and α - $\text{Fe}_2\text{O}_3/\text{ZnS}$ core/shell nanostructures

The PL intensity of α - $\text{Fe}_2\text{O}_3/\text{ZnS}$ core/shell nanostructures decreased rapidly when compared to pure α - Fe_2O_3 nanoparticles demonstrating the efficient charge separation of the composites. Therefore the photogenerated electron-hole pairs could be separated more efficiently at the heterostructure and their recombination decreases. Subsequently the electrons and holes could migrate more effectively to the surfaces of α - Fe_2O_3 and ZnS and produce the hydroxyl radicals which could decompose the contaminant dyes as a powerful oxidant which supports enhanced photocatalytic activities [10, 18-23].

4. CONCLUSION

α - $\text{Fe}_2\text{O}_3/\text{ZnS}$ core/shell nanostructures are successfully synthesized by a simple, low temperature ultrasonication assisted precipitation method. These spherical shaped particles with core (α - Fe_2O_3) size of ~ 50 nm and ZnS shell of size ~ 30 nm exhibit PL peaks at 410 nm, 434 nm, 460 nm, 485 nm, 520

nm and 563 nm similar to the pure α -Fe₂O₃ nanoparticles but PL intensity is very smaller than that of the pre-synthesized α -Fe₂O₃ nanoparticles. This property suggests that α -Fe₂O₃/ZnS core/shell nanostructures can be used for the degradation of the harmful dyes in the environment and are promising to be used as high-performance visible light-driven photocatalyst.

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