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Enhanced photocatalytic degradation of methyl red and thymol blue using titania–alumina–zinc ferrite nanocomposite

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ABSTRACT

Nanocomposite of magnetically separable, TiO_2–$ZnFe_2O_4$ with an intermediate layer of alumina has been synthesized by a multistep wet chemical process. UV–vis absorption spectra show a red shift of the absorption edges for the composite systems compared to single phase TiO_2. Magnetic measurements indicate that the $ZnFe_2O_4$ is ferromagnetic at room temperature with low coercivity when the applied field is low, typical of soft magnetic materials. After TiO_2 and alumina coatings, the samples show similar magnetic behaviour. Photocatalytic activity studies for methyl red and thymol blue degradation indicate an enhanced activity for the composites when the alumina interlayer is present between TiO_2 and $ZnFe_2O_4$. When Pd is used as a co-catalyst in TiO_2–$ZnFe_2O_4$, an enhanced activity is observed, which is comparable to that of TiO_2–Al_2O_3–$ZnFe_2O_4$. The present study leads to a new result that an insulating interlayer like alumina can enhance the photocatalytic activity of TiO_2 coated ferrites as much as that of a noble metal co-catalyst like Pd. The enhanced photocatalytic activity of TiO_2–Al_2O_3–$ZnFe_2O_4$ is attributed to the decrease in the migration of photogenerated charge carriers to zinc ferrite layer and due to the increased adsorption of the reactants on the surface of TiO_2–Al_2O_3–$ZnFe_2O_4$.

1. Introduction

Magnetically separable semiconductor photocatalysts are of significant interest currently due to their potential application in environmental cleaning especially polluted water [1–3]. Titania coated on different ferrites/iron oxides are used for this purpose as ferrite alone is not a good photocatalyst due to its lower valence band potential [4]. Though TiO_2–Ferrite composites have been widely studied for their photodegradation properties, in most of the cases, its photocatalytic activity is found to be lower than that of single phase TiO_2 due to the heterojunction effects [5]. When TiO_2 is in direct contact with the ferrites, the photoexcited charge carriers can migrate to it and can get recombined or induce photodissolution of the iron oxide resulting in lower activity. In order to overcome this problem, an insulating intermediate layer is placed in between TiO_2 and the magnetic oxides, which prevents the unfavorable migration of charge carriers from TiO_2 to underlying ferrite core [6].

Effect of an intermediate layer of silica in between TiO_2 and magnetic oxides like Fe_3O_4 [7], $CoFe_2O_4$ [6] and $NiFe_2O_4$ [8] on the photocatalytic activity has been studied and found that the presence of the intermediate layer enhances the photocatalytic activity of the system compared to the one without the intermediate layer. Chung et al. [8] synthesized the magnetic composite of TiO_2–$NiFe_2O_4$ and TiO_2–SiO_2–$NiFe_2O_4$ by a multistep spray pyrolysis process and found that the titania–silica layered particles showed better photocatalytic activity for methylene blue degradation compared to titania alone on nickel ferrite. Barium ferrite–silica–titania composite photocatalyst synthesized by precipitation method showed photocatalytic activity for the degradation of Procion red MX-5B dye under UV illumination and the photocatalytic activity increased after heat treatment at 773 K due to the improved crystallinity of the heat treated sample [9]. A core–shell type cobalt ferrite coated with silica and titania exhibited photodegradation activity for methyl orange comparable to that of heated sample and P25 TiO_2 [6]. The observed photocatalytic activity of the composite was correlated with the proper microstructure of this composite and the isolation function of the silica intermediate layer.

Spinel zinc ferrite is a semiconductor that has a band gap of 1.9 eV. It has been reported that a coupled semiconductor of TiO_2–$ZnFe_2O_4$ exhibits visible light photocatalytic activity as $ZnFe_2O_4$ can absorb visible light and transfer the photogenerated electron to TiO_2, due to the comparable conduction band potentials of these two catalysts [10]. Though, this coupled photocatalyst shows visible light activity for the photodegradation of organic

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pollutants, it is seen that its visible light activity is poor [6]. When this system is irradiated with UV radiation, injection of photogenerated charge carriers can take place from TiO_2 to $ZnFe_2O_4$, which can decrease its photocatalytic activity. Hence, it is of interest to study whether a new intermediate layer like alumina can enhance the photocatalytic activity of TiO_2–$ZnFe_2O_4$. It is expected that the alumina interlayer can minimize the migration of charge carriers from TiO_2 to zinc ferrite, which can enhance the photocatalytic activity. Besides, different oxides like titania, silica, alumina, etc. possess surface acidic property [11,12], which can influence the adsorption of dye on the catalyst surface and can enhance the photodegradation activity. In the present study, photocatalytic activity for the degradation of methyl red (Mr) and thymol blue (Tb) is studied using TiO_2–Al_2O_3–$ZnFe_2O_4$ catalyst and compared the activity with that of TiO_2–$ZnFe_2O_4$. Effect of a co-catalyst like Pd on the photocatalytic activity of TiO_2–$ZnFe_2O_4$ and TiO_2–Al_2O_3–$ZnFe_2O_4$ is also studied. Whereas alumina can reduce the heterojunction effect occurring in the coupled TiO_2–$ZnFe_2O_4$ catalyst, Pd metal can effectively separate the photogenerated charges.

2. Experimental

Crystalline zinc ferrite (ZF) was synthesized by citrate gel autocombustion method. High purity (AR grade) ferric citrate, zinc nitrate, citric acid were used as raw materials. The stochiometric amounts of individual metal nitrates and metal citrate were dissolved in doubly distilled deionized water to get a clear, transparent solution. The solution of citric acid was added to separate metal nitrate solutions to form metal–citrate complex. The above solutions were mixed together with constant stirring to get a homogeneous mixture. The mixture was heated slowly upto 373 K to obtain a fluffy mass and combusted to get the dry powder. This sample was further annealed at 973 K for 4 h. Alumina coating (20% by weight) was done on this ferrite (Al–ZF) by a wet chemical process. Ferrite powder was dispersed in aluminum nitrate solution followed by the addition ammonia drop by drop under constant stirring. The suspension was evaporated to dryness and calcined at 873 K for 4 h.

TiO_2 coating was done by sol–gel hydrolysis of titanium isopropoxide (Ti $(OC_3H_7)_4$) on ferrite (T–ZF)/alumina coated ferrtie (T–Al–ZF) nanoparticles followed by calcination treatment. ZF/Al–ZF nanoparticles were dispersed in titanium isopropoxide–isopropanol mixture (1:1 molar ratio). Water was slowly added to the above suspension under constant stirring. The resulting material was dried and calcined at 873 K for 4 h in air. Different concentrations of TiO_2 were loaded on ZF (10–40% by weight) to find out the optimum concentration of TiO_2 required to obtain the best photocatalytic activity. Palladium was loaded on this sample (Pd–T–Al–ZF) by a wet impregnation process using $PdCl_2$ solution followed by heating at 673 K for 2 h.

X-ray diffractometer (Philips model PW-1710) was used to identify the phases and the crystalline nature of the samples using Cr Kα radiation. Particle size was measured using a transmission electron microscope (TEM) (Philips, CM200, operating voltages 20–200 kV). Surface area was measured by Brunauer–Emmett–Teller (BET) technique using nitrogen as the adsorbing gas. Energy-dispersive spectroscopy technique (JSM-JEOL 6360) was used for the elemental analysis of the TiO_2 coated ferrites. The diffuse reflectance UV–vis (DR-UV–vis) spectra of the powders were recorded using a Jasco (model V-670) spectrophotometer equipped with an integrating sphere accessory. Barium sulphate was used as reference for the reflectance spectra. The high field vibrating sample magnetometer (VSM) (LAKESHORE-Model: 7404) at a maximum applied field of 15 kOe was used to measure the saturation magnetization, coercivity and remnant magnetization of all the samples. FTIR spectra were recorded in a Perkin–Elmer spectrometer using KBr pellets.

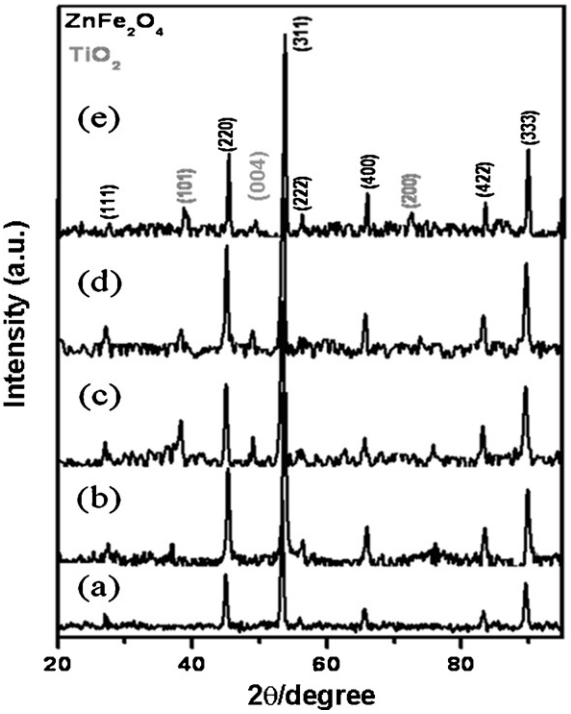

Fig. 1. Powder XRD patterns of (a) ZF, (b) T10–ZF, (c) T20–ZF (d) T30–ZF (e) T40–ZF.

For recording the spectra of Mr adsorbed on composite ferrites, samples were dispersed in aqueous Mr solution and kept in the dark with constant stirring for 10 h. The sample after separation was dried at 100 °C for 2 h before it was used for making pellets. Photoluminescence (PL) measurements were done with an Edinburgh Instruments FLSP 920 system with a 450 W Xe arc lamp as the excitation source and a red sensitive Peltier element cooled Hamamatsu R2658 PMT as the detector. The emission spectra were recorded with a resolution of 1.0 nm, by exciting the samples at 270 nm. All the emission patterns were corrected for the detector response and were measured at 1 nm resolution.

Photocatalytic reaction was conducted in a 100 cm^3 pyrex glass vessel containing 50 cm^3 of the aqueous dye solution (concentration: 50 ppm) having 100 mg of catalyst suspended in it. The solution was kept under constant stirring and irradiated with a UV lamp (8 W, wavelength 253 ± 50 nm), which was positioned over the glass beaker.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction (XRD) patterns of pure zinc ferrite and the composites having 10, 20, 30 and 40 percentage of TiO_2 on $ZnFe_2O_4$ nanoparticles. The diffraction pattern of ZF shows peaks corresponding to planes (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2) and (3 3 3) confirming the formation of spinel zinc ferrite (JCPDS Patterns No. 22-1086). Diffraction peaks corresponding to planes (1 0 1), (0 0 4) and (2 0 0) of anatase titanium oxide besides that of $ZnFe_2O_4$, are seen in the TiO_2 coated samples indicating the biphasic nature of the T–ZF samples. XRD pattern of T–Al–ZF (not shown) is almost similar to that of T–ZF and peaks corresponding to that of Al_2O_3 are not seen probably due to its poor crystallinity. The BET surface areas of ZF, T40–ZF and T40–Al–ZF are comparable and found to be $\sim 5\ m^2\ g^{-1}$.

Fig. 2(a–c) depict the transmission electron micrographs of ZF, TiO_2 (40%)/$ZnFe_2O_4$ (T40–ZF) and T40–Al–ZF samples. It is evident from Fig. 2(a) that the average particle size of ZF is around 80 nm. The superimposition of the bright spot with Debye ring pattern seen