

Synthesis of Magnetically Separable Photocatalyst— TiO₂/SiO₂ coated Mn-Zn Ferrite—and Its Photocatalytic Study

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ABSTRACT

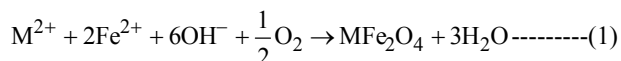
Magnetically separable photocatalysts are of much interest since they can be used for waste management application and with recyclable advantage. Several TiO₂ incorporated with magnetite have been synthesized but their preparation methods are not convenient. Our aim of this work is to minimize the complication of synthesis procedures and reduce the use of chemicals that were not actually converted to the composite, i.e., surfactant, emulsifier, and stabilizers. With our process, a manganese-zinc ferrite nanoparticle could be prepared by simple co-precipitation of three metal ions, Mn²⁺, Zn²⁺, and Fe²⁺ and the resulting nanoparticles were coated with silica and titania through sol-gel methods. The rate of base addition and reagent mixing were found to be crucial for the size of the forming magnetic particles. Transmission electron microscopy was used to reveal the morphology of magnetic core and silica as well as titania coatings. Vibrating sample magnetometer was used to measure the superparamagnetism of the composite, performing good saturating magnetization as high as 10-30 emu/g. In addition, the amorphous silica interlayer was found to be advantageous in cancelling the synergistic effect between the two metal oxides. This was observed by monitoring the improved photo-decomposition of methylene blue with UV-Vis spectrophotometer, indicating the possibility in environmental remediation.

Keywords: Titanium dioxide, photocatalyst, manganese-zinc ferrite, superparamagnetic, co-precipitation

1 INTRODUCTION

Titanium dioxide (TiO₂) is known to possess the decomposition ability on many organic and inorganic pollutants due to its generation of two strong oxidant species, ·OH and O₂^{·-} [1]. It is cheap, stable, non-toxic, and especially easy to be prepared via simple chemical process, so-called hydrolysis. However, its usual size in nanometer range leads itself to the difficulty in handling or storing although the suspending particles are in the most effective form. The immobilized TiO₂ on many substrates have been developed by many researchers, but loss of surface area

limits the photocatalytic activity [2-3]. TiO₂ coated on magnetic materials, such as magnetite or ferrite, in a form of core-shell particle, provides a better solution because it preserves high surface area and gains ability to be re-collected by external magnetic source. A suitable magnetic particle employed as a supporting core for titanium dioxide depositing can be prepared by several methods suggested in the literatures, such as co-precipitation, citrate precursor, hydrothermal, and microemulsion. The magnetic nanoparticle, which is mainly formed as soft ferrite, MFe₂O₄ where M = Fe, Mn, Zn, Ni, etc., can be synthesized based on Schikorr's reaction [4].



The crystalline structure of MFe₂O₄ is mostly formed as inverse spinel. It usually has large magnetic polarization and high electrical resistivity. However, the photocatalytic and magnetic properties of the composite can be less effective. This is due to the electron migration in the electronic states between the photocatalyst and magnetic ferrite. To solve this problem, it has been suggested to allow the presence of silica layer between the contact point of the two semiconductors [5].

Recent publications reported by other research groups describe the preparation method of these magnetically separable photocatalysts with their results [6-8]. We carried out the synthesis of TiO₂/SiO₂ coated Mn-Zn ferrite by using three preparation steps including co-precipitation of Mn-Zn ferrite, hydrolysis coating of silica, and hydrolysis coating of titanium dioxide. It was found that without a complex condition provided by stabilizer or emulsifier, the nanoparticles of Mn-Zn ferrite could be well-formed with narrow size distribution by co-precipitation methods. This was resulted from the homogeneous growth of nano-magnetic particles controlled by rate of reagent addition and reaction mixing. The photocatalytic reaction of the as-prepared catalyst was observed. The superparamagnetic property of the magnetic core enhanced the photocatalyst to be able for recovering and redispersing after use. The improvement of the photocatalysis is being investigated.

2 EXPERIMENTAL

2.1 Materials

All chemicals are of analytical grade and used without further purification. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and NH_4OH (30%) were purchased from Carlo Erba. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was purchased from Fischer. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was purchased from Rankem. Tetraethyl orthosilicate (TEOS) and titanium (IV) tert-butoxide (TBOT) were purchased from Fluka. Methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{ClS} \cdot 2\text{H}_2\text{O}$) was purchased from Unilab. Absolute ethanol and acetone were purchased from Merck.

2.2 Characterization methods

Scanning electron microscopic (SEM) and energy dispersive X-ray spectroscopic (EDS) measurement of the samples were obtained from HITACHI S-3400 microscope and EMAX Horiba, respectively. The transmission electron microscopy (TEM) was recorded by JEOL JEM 2010. X-ray diffraction patterns were obtained from X-ray diffractometer JEOL JDX 3530. Saturated magnetization (M_s) and hysteresis curve were recorded by Lakeshore 7404 Vibrating sample magnetometer.

2.3 Preparation of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (MZF)

A 1:1:1 mixture (30 mL) of 0.057 M Mn^{2+} , 0.057 M Zn^{2+} , and 0.23 M Fe^{2+} was added with 1.78 M NH_4OH solution (15 mL) while vigorously stirring. The resulting green solution was then heated in an oil bath up to 90-100 °C for 1 h. The mixture with dark brown precipitate was added with DI water (20 mL). The precipitate was washed with DI water and acetone then separated by centrifugation.

2.4 Preparation of SiO_2 -coated $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (S-MZF)

Typical method for the coating of silica on MZF was done by mixing MZF (180 mg) with 1:5 mixed solution of DI water and ethanol (30 mL). After dispersion by ultrasonicator, TEOS (30 μL) and 30 % aqueous ammonia (40 μL) were added and the hydrolysis was allowed to proceed for further 10 min. The other equal portions of these two reagents were added and this adding step was repeated until 450 μL total volume of TEOS was used. The resulting mixture was placed in a sonicator bath for 45 min. The resulting mixture was washed with water and ethanol using centrifugation. The collected precipitate was dried at room temperature.

2.5 Preparation of $\text{TiO}_2/\text{SiO}_2$ -coated $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (TS-MZF)

Typical method for the coating of titania on S-MZF (or MZF) was done by mixing S-MZF (150 mg) with 1:14

mixed solution of DI water and ethanol (75 mL) in a sonicator bath. This mixture was added with TBOT (0.5 mL) in absolute ethanol (10 mL). The resulting mixture was stirred in an oil bath at room temperature, subsequently heated up to 90 °C, and further maintained at this temperature for 2 h. A condenser was also used in order to prevent the vaporization of the solvent. The product was washed with DI water and ethanol, and then separated by centrifugation. The composite was received after drying at 60 °C for 24 h and calcined at 500 °C for 2 h.

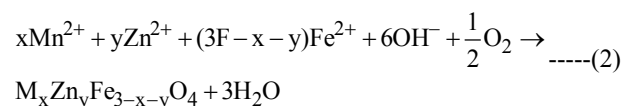
2.6 Photocatalytic reaction

An amount of catalyst (12 mg; MZF, TS-MZF, and T-MZF) was dispersed in a 60 mL of 5 ppm MB aqueous solution. The adsorption/desorption of MB molecules on photocatalyst surface was allowed until reaching equilibrium at 18 h in the dark. To conduct the experiment, each 3 mL of the catalyst suspensions was irradiated by 20 W of 366 nm low pressure UV lamp. At 10 min. interval, the catalyst was separated by centrifugation, and the MB removal was analyzed by monitoring the decrease of UV absorbance at 664 nm.

3 RESULTS AND DISCUSSION

3.1 Formation of magnetic nanoparticles by co-precipitation method

The chemical co-precipitation of MZF has been known to involve two sequencing steps of hydrolysis and oxidation of alkaline $\text{Fe}(\text{OH})_2$ in the presence of Mn^{2+} and Zn^{2+} at elevated temperature based on Schikorr's reaction to form inversed spinel structure. In this case,



Because of its simplicity, co-precipitation is one of the most preferable methods for the preparation of magnetic particles. However, the large polydispersity of the formed particles is always a critical problem. Four MZF particles shown in Table 1 were prepared by co-precipitation method

Table 1: Reaction conditions and particle sizes of MZFs

Sample code	Addition type	Dispersion type	Particle size (nm)
MZF1	One shot	Stirred	8.7±2
MZF2	Dropwise	Stirred	67.5±12
MZF3	Dropwise	Homogenized	10.8±2
MZF4	One shot	Stirred	49.4±14

using different mixing rate as well as the rate of reagent (base) addition. Suggested by Auzan [9], the growth of

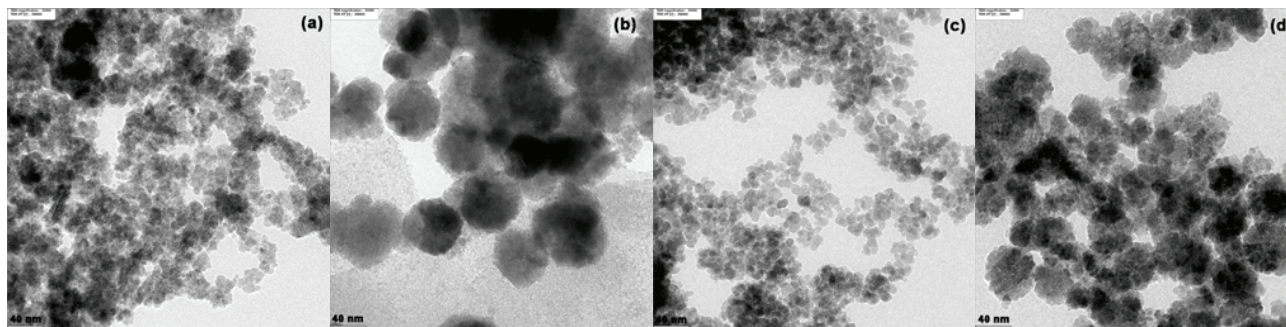


Figure 1: TEM images of (a) MZF1, (b) MZF2, (c) MZF3, (d) MZF4

magnetic nanoparticles by co-precipitation method can be controlled by two main practices. The addition of base reagent, which leads to the formation of nanoparticles, should be as fast as possible. Also, the mixing of the reaction solution should be at a very high rate. These will lead the reaction condition to approach the homogeneity that is essential for the uniform size nanoparticles with less aggregation. In our experiment, the two addition techniques, one shot and dropwise, of base solution were comparatively carried out. Figure 1a-d shows the TEM images of MZF samples prepared by the conditions in Table 1. It was obviously seen that the fast addition of NH_4OH resulted in small particles (MZF1) while the slow addition resulted in greater particle size (MZF2). However, the influence of homogeneity due to the mixing speed was more important than the initially formed particles as found that the homogenized reaction provided narrow-distributed particles with non-aggregated character in MZF3. Furthermore, MZF4 confirmed that when the volume of reaction increased, resembling the loss of homogeneity, the magnetic particles were formed variously in size and shape.

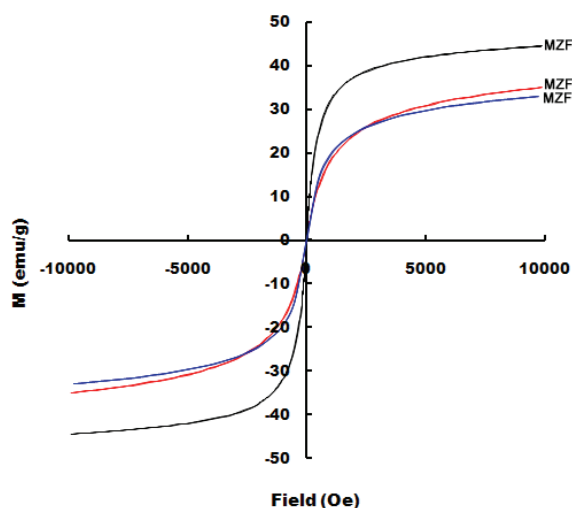


Figure 2: Magnetization measurement of MZFs at room Temperature

The superparamagnetic properties of the MZF samples were analyzed at room temperature by VSM. Figure 2 shows the hysteresis curves of MZF1, MZF3, and MZF4. The saturation magnetization of MZF3 ($M_s = 44.5 \text{ emu/g}$) was higher than the other two samples ($M_s = 35.0, 32.9 \text{ emu/g}$ for MZF1 and MZF4, respectively). This may be due to the uniformity of MZF3 particles formed in homogenized condition, contrarily to the stirred conditions that allowed the variation in size and thus crystallinity of MZF 1 and 4. Interestingly, the saturation magnetizations of these two were not different considerably, indicating of the complete formation of magnetic inducible materials by our synthetic design. In addition, the superparamagnetic property of MZF was confirmed as the hysteresis loop was not at all observed.

3.2 Coating of silica and titania on MZF

Silica coating on MZF was based on the intention to inhibit the electronic interaction between the core MZF and the TiO_2 layer. Figure 3 shows the TEM image of S-MZF that clearly demonstrate the coating layer of amorphous silica. The thickness of silica layer was approximately 10 nm on each S-MZF particle measured from the surface to its core size.

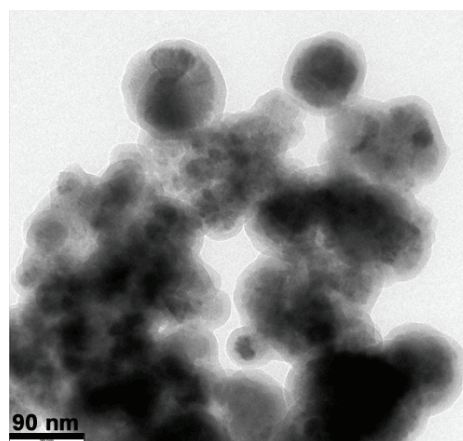


Figure 3: TEM images of S-MZF

Titania coating on S-MZF was confirmed by the TEM image shown in Figure 4. Due to a fast hydrolysis rate of TBOT, the TiO_2 crystals were formed as a rough layer of small granules covering entirely on the S-MZF particles. The X-ray diffraction patterns of the three samples are shown in Figure 4, confirming that each step of coating provides a new layer of the desired material.

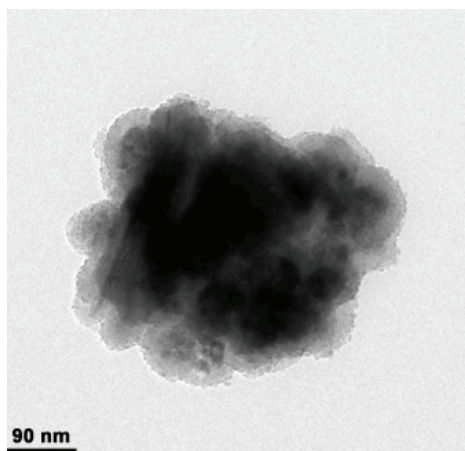


Figure 4: TEM image of TS-MZF

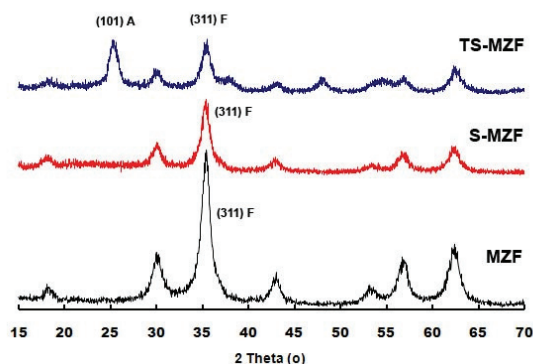


Figure 5: XRD pattern of the uncoated and coated MZFs

3.3 Photocatalytic activity

Figure 6 shows the photocatalytic activity of the prepared catalysts on methylene blue solution. After saturating small amount of samples with MB solution in dark place, the concentration decreased as the MB was adsorbed by the catalyst surface. When the composites were exposed to the UV radiation, the additional decrease of MB absorption was observed only in TS-MZF where as little or no change was found in the rest of the catalysts. This indicated that the photocatalysis was present in the three-layer composite, and thus the silica interlayers behave genuinely as an electron-transfer inhibitor of the two semiconductors. A similar photo-activity of T-MZF and MZF was attributed to the absence of silica interlayer.

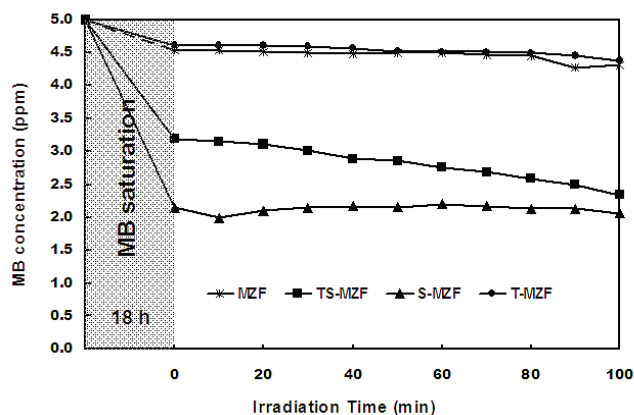


Figure 6: Decomposition of methylene blue by the prepared catalysts

4 CONCLUSION

A magnetically separable photocatalyst, $\text{TiO}_2/\text{SiO}_2$ coated Mn-Zn ferrite, was prepared and its properties were thoroughly analyzed. Via a simple co-precipitation method without involving preserved condition by stabilizer, monodisperse nanoparticles could be formed using proper mixing of reagents. The superparamagnetism of the particles was observed with rather high value reaching up to 40 emu/g. Activation of the titania/silica coated Mn-Zn ferrite by UV light was apparently observed which was certainly improved by silica interlayer between two semiconductors. These nanoparticles are promising in environmental remediation.

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