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Synthesis and Characterization of $CaFe(Si_2O_6)$@SiO_2@titania Core-Double Shell Magnetic

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ABSTRACT

The title core-double shell magnetic materials, $CaFe(Si_2O_6)$@SiO_2@titania, were successfully fabricated using $CaFe(Si_2O_6)$ beads. The magnetic $CaFe(Si_2O_6)$ core was covered by internal-shell silica thin films and external-shell titania nanoparticles. The coated silica shell on $CaFe(Si_2O_6)$ beads was prepared by the sol-gel method using tetraethyl orthosilicate (TEOS) precursor. The external titania shell covered on $CaFe(Si_2O_6)$@SiO_2 was prepared by hydrothermal processes at 180 °C for 48 hours using TiO_2 particles and NaOH solution as precursors. The outer titania shell on $CaFe(Si_2O_6)$@SiO_2 was made utilizing hydrothermal procedures at 180 °C for 48 hours, with TiO_2 particles and NaOH solution as precursors. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), powder x-ray diffraction spectroscopy (XRD), and nitrogen adsorption-desorption apparatus were used to analyze the produced materials. The effects of NaOH concentration and TiO_2 precursor quantity were studied. Titania nanorods were elongated as the NaOH concentration increased. When the dosage of TiO_2 precursor was increased, the nanorod shape changed to the nanowire.

INTRODUCTION

Industrial effluents containing hazardous metals, dyes, and other organic materials are harmful to the environment by restricting light penetration and are potent carcinogens to mammals causing severe health risks [1–3].

In the wastewater treatment field, photocatalysis is an alternative treatment that can be used for organic wastewater treatment by using light irradiation to generate radicals that can entirely oxidize and mineralize them into carbon dioxide, water, and other simple inorganic substances [4-6].

TiO_2 nanoparticles and other titania materials are effective photocatalysts that have been wildly studied due to their ability to treat organic pollutants, are less toxic, and are applicable to apply in large-scale applications [6-7]. However, the recovery of TiO_2 from the treated wastewater after wastewater treatment is difficult to practically process, especially when the catalyst size is in the nanoscale. Separation processes by centrifugation and filtration are typically used, however these methods are complicated and require long-time operations. A promising technique for producing photocatalyst for practical wastewater treatment is to use magnetically photocatalytic material, which can be easily separated and reused by applying a magnetic field. Using magnetically photocatalytic material, which can be easily separated and reused by applying a magnetic field, is a potential technology for manufacturing photocatalyst for practical wastewater treatment. The synthesis of separable magnetic-photocatalyst composite materials by modified core-shell preparation process is a potential material for overcoming the separation problems [8–10].

There are several methods for the titania-based coating process, such as the electrochemical process [11], the modified sol-gel method [12], and the chemical deposition technique [13]. However, those are complicated and not suitable for practical production. The hydrothermal process is an appropriate technique that has been commonly used to coat titania nanoparticles on the substrate due to its simplicity [14]. However, the coating of titania onto the surface of magnetic particles directly would decrease the photocatalytic efficiency due to the photo dissolution and the transfer of electrons–holes from titania to the magnetic particle. Thus, an intermediate SiO_2 layer between magnetic particles and titania film is required to prevent the photo dissolution by sol-gel method using tetraethyl orthosilicate (TEOS) as silica precursor [15].

Therefore, in this research, $CaFe(Si_2O_6)$@SiO_2@titania core-double shell magnetic materials will be fabricated using $CaFe(Si_2O_6)$ core. The magnetic $CaFe(Si_2O_6)$ beads will be coated by internal-shell silica thin films and external-shell titania nanoparticles, respectively. The sol-gel method will prepare the coated silica shell on $CaFe(Si_2O_6)$ beads. The external titania shell will be fabricated by hydrothermal processes. The as-synthesis materials will be characterized to confirm the presence of each phase and physical morphology.

METHODOLOGY

Synthesis of silica coating on magnetic particles by sol-gel method

The coating of SiO_2 onto the surface of magnetic particles ($CaFe(Si_2O_6)$; F1) was carried out by the sol-gel polycondensation process in an acidic medium. First, magnetic particles are impregnated in ammonia solution for 20 minutes and then dispersed in a mixing solution (1.8 mL methanol, 6 mL distilled water, 1 mL of 1 M HCl, and 5.6 mL of TEOS). After the gelation was complete, the resulting product $CaFe(Si_2O_6)@SiO_2$ was dried at 80 °C for 24 h to remove the excess water content (F1S1).

Titania nanoparticles coating by hydrothermal process

The obtained 0.2 g of $CaFe(Si_2O_6)@SiO_2$ were suspended in 10 mL of 3, 6, and 10 M NaOH in the hydrothermal processes. After that, 0.1 or 0.2 g TiO_2 particles were added to the solution. Note that F1S1HT*x*-*y*M refers to the core-double shell magnetic materials prepared by using dosage TiO_2 precursor of *x* (0.1 and 0.2 g) and NaOH concentration of *y* (3, 6, and 10 M). The solution was stirred for 30 min, and then the mixture was transferred to Teflon lined stainless steel autoclave with 70% filing and heated to 180 °C for 48 h. The name list of synthesized $CaFe(Si_2O_6)@SiO_2$@titania and their relative synthetic conditions are shown in Table 1.

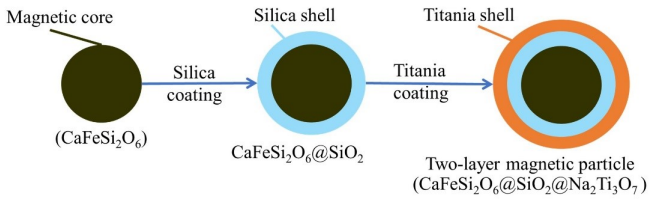

Figure 1. Schematic illusion of the preparation process for photocatalyst.

Table 1. List of sample name and their relevant synthetic conditions.

Sample code	TiO_2 [g]	NaOH [M]
F1	-	-
F1S1	-	-
F1S1HT0.1-3M	0.1	3
F1S1HT0.1-6M	0.1	6
F1S1HT0.1-10M	0.1	10
F1S1HT0.2-3M	0.2	3
F1S1HT0.2-6M	0.2	6
F1S1HT0.2-10M	0.2	10

Characterization

The elemental composition and morphology of $CaFe(Si_2O_6)@SiO_2$@titania were confirmed by using the field-emission scanning electron microscopy (FE-SEM, JSM 6335 F) with energy-dispersive X-ray spectroscopy (EDS). The phases of the samples were identified by using X-ray diffraction (XRD, Advance, Bruker). The specific surface area of the samples was carried out by nitrogen adsorption-desorption apparatus (Autosorb MP, Quantachrome) at -196 °C.

RESULTS AND DISCUSSION

This research presented the coating effect of SiO_2 and TiO_2 on magnetic particles ($CaFe(Si_2O_6)$). Following the changes in the crystal structure at each synthetic step were evaluated by powder-X-ray diffractometer. The XRD pattern of the samples is shown in Figure 2. For the control sample without any coating process (F1), only the diffraction peaks of $CaFe(Si_2O_6)$ were presented. After coating the SiO_2 layer onto the surface of magnetic particles ($CaFe(Si_2O_6)$), the diffractogram presented a broad pattern of an amorphous SiO_2 around 23° (F1S1). This confirmed the well-covered amorphous SiO_2 onto the $CaFe(Si_2O_6)$. The XRD pattern of both F1S1HT0.1 and F1S1HT0.2 can be assigned to $Na_2Ti_3O_7$ structures. These indicated that the titania nanoparticles were well covered onto the $CaFe(Si_2O_6)@SiO_2$ after hydrothermal process.

The morphology of magnetic particles was investigated by FE-SEM, as shown in Figure 3. This result demonstrated the bare surface of magnetic particles before coating SiO_2 as shown in Figure 3(a). Figure 3(b) illustrated the roughness surface with accumulated small particles on a spherical morphology of magnetic beads, which can assume that the silica layer preserved a spherical morphology and the well glazed on the magnetic beads. The Si composition (EDS results as shown in Table 2) of F1S1(14.5% atomic) was higher than F1 (3.1%)

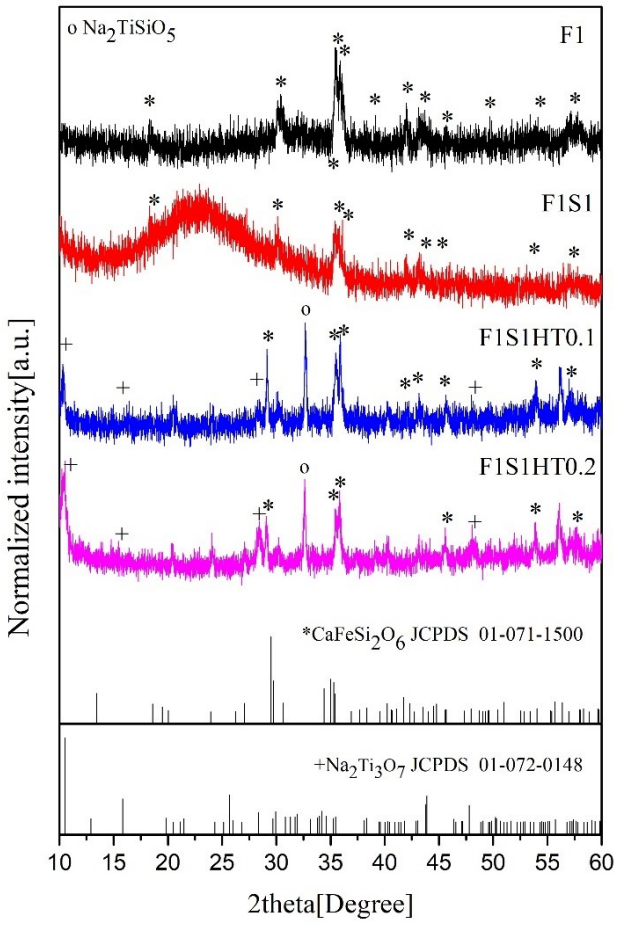

Figure 2. XRD pattern of the as-synthesis materials illustrated the crystal structure of $CaFe(Si_2O_6)$ core (F1), silica coated on $CaFe(Si_2O_6)$ (F1S1)and $CaFe(Si_2O_6)@SiO_2$@titania (F1S1HT0.1 and F1S1HT0.2).

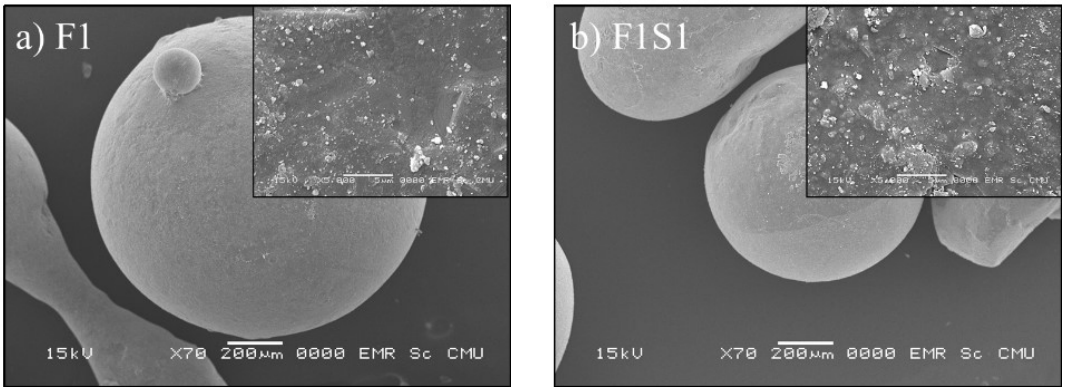

Figure 3. SEM images of (a) F1 and (b) F1S2.

according to the core materials were covered by SiO_2. However, the specific surface area of F1S1 (S_{BET} = 0.44 m^2/g) was smaller than F1 (S_{BET} = 0.93 m^2/g).

The FE-SEM images of magnetic particles core covered by internal silica thin films and external titania particles ($CaFe(Si_2O_6)$@SiO_2@titania) were shown in Figure 4. The F1S1 sample was coated with titania particles by hydrothermal processes at 180 °C for 48 hours with various TiO_2 dosages (0.1 and 0.2 g) and NaOH concentrations of 3, 6, and 10 M, as shown in Figure 4. The physical appearance from all samples shows the semi-spherical morphology with a rough surface. As listed in Table 2 and Table 3, the SEM-EDS results presented that when an increasing amount of TiO_2 dosage in the hydrothermal reaction, the %atomic of Ti increase correlated with the amount of deposited titania particles from TiO_2 dosage.

As a good mineralizer, NaOH was chosen to modify the SiO_2 surface for supporting the TiO_2 shell. The effect of NaOH concentration on the morphology of deposited titania particles was shown in Figure 5. The synthesized titania particles revealed a discreet polyhedron shape at low NaOH concentrations, such as at 3 M (Figure 5d). Whereas the higher NaOH concentrations promoted, the smaller titania nanoparticle size and the morphology change to be needle-like shape, as shown in Figure 5(d-f). The high concentration NaOH can dissolve and recrystallize TiO_2 to end up with rod-like morphology [16]titanium isopropoxide (TTIP. The length of the particle tends to be elongated by the increasing of base concentration.

CONCLUSIONS

The $CaFe(Si_2O_6)$@SiO_2@titania core-double shell magnetic materials was achieved via using sol-gel process and hydrothermal method. The synthesis of $CaFe(Si_2O_6)$@SiO_2 by sol-gel method used 5.6 mL of TEOS. The optimum condition of hydrothermal method was 10 M of NaOH concentration and 0.2 g of dosage TiO_2 precursor at 180 °C for 48 hours. The expected result showed that the amorphous silica

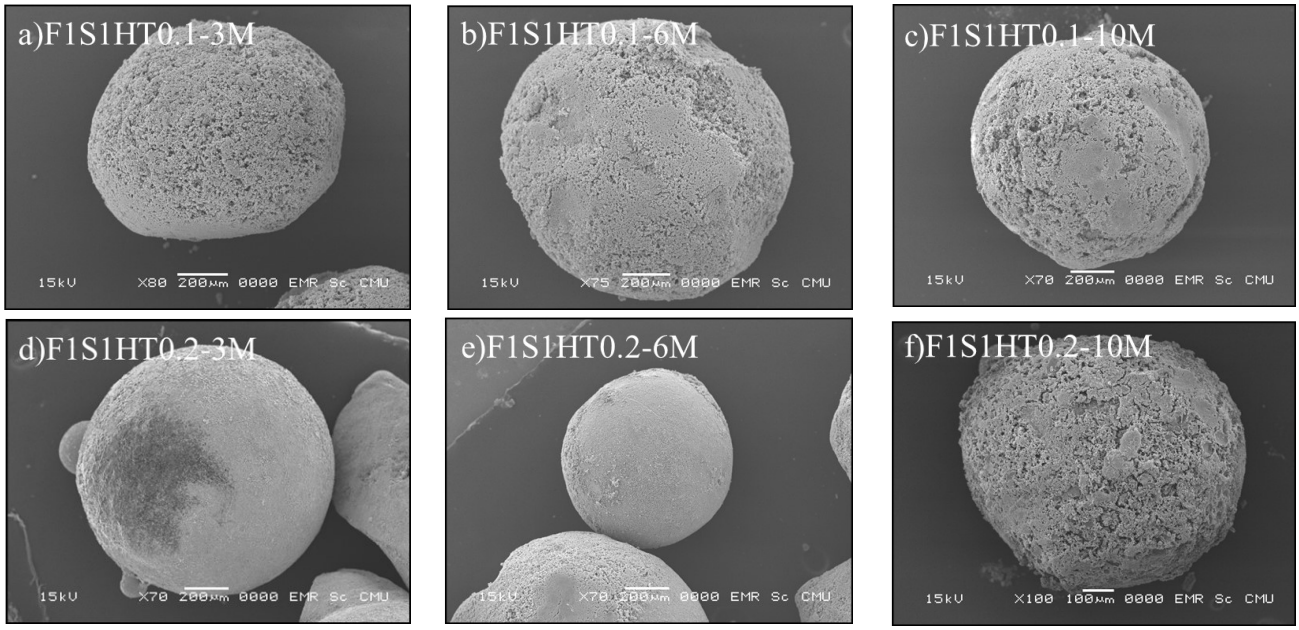

Figure 4. SEM images of $CaFe(Si_2O_6)$@SiO_2@titania showing the physical appreance of the catalyst particles.

Table 2. chemical composition of F1, F1S1 and F1S1HT0.2-10M.

Samples	Elements (atomic%)						S_{BET}(m^2/g)
	Fe	Si	O	Ca	Ti	Na	
F1	11.7	3.1	47.6	17.5	-	-	0.93
F1S1	15.8	14.5	42.1	9.6	-	-	0.44
F1S1HT0.2-10M	-	-	64.0	-	22.7	13.2	2.40

Table 3. The chemical composition of F1S1HT0.1 and F1S1HT0.2 in the difference of base NaOH concentrations (3, 6 and 10 M) and average particle size of samples with standard deviation (S.D.).

Samples	Elements (atomic%)			Average titania particles size (μm)	S.D.
	Ti	O	Na		
F1S1HT0.1-3M	19.6	69.8	6.8	1.28	1.06
F1S1HT0.1-6M	19.9	70.4	8.1	0.41	0.34
F1S1HT0.1-10M	14.8	68.0	6.1	0.90	0.55
F1S1HT0.2-3M	32.8	55.3	8.2	1.19	1.42
F1S1HT0.2-6M	23.3	63.5	6.9	1.50	1.57
F1S1HT0.2-10M	22.7	64.0	13.2	2.27	1.23

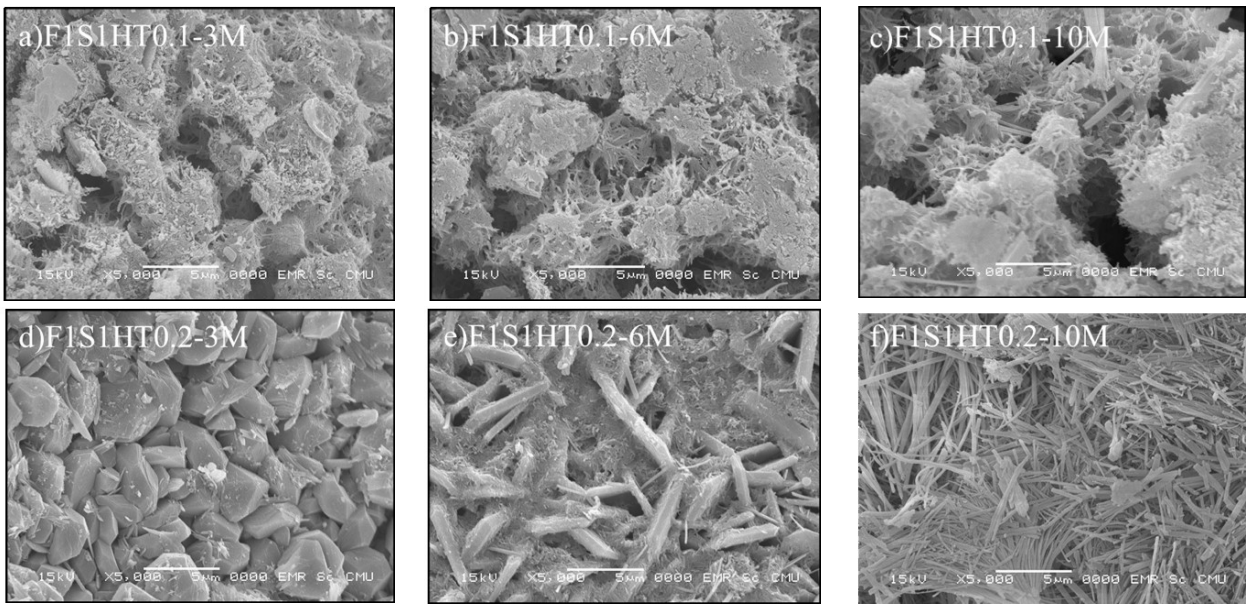

Figure 5. SEM image of $CaFe(Si_2O_6)$@SiO_2@titania illustrating the titania morphology varying by the NaOH concentrations and the amount of TiO_2 precursor.

was observed by XRD pattern after coating silica on the crystalline $CaFe(Si_2O_6)$ beads by sol-gel method. The pattern of $Na_2Ti_3O_7$ structure was presented after hydrothermal treatment with TiO_2 precursor. $Na_2Ti_3O_7$ morphology was elongated as a result of the greater NaOH concentration. When the dosage of TiO_2 precursor was increased, the titania nanorod became a nanowire. The EDS result on the surface of the double core-shell materials showed that the elemental composition was Ti, O, and Na. The highest surface area of the material was 2.40 m^2/g.

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