Preparation of NiFe$_2$O$_4$ - TiO$_2$ nanoparticles and study of their photocatalytic activity

Do Quoc Hung*, Nguyen Kim Thanh

Le Quy Don Technical University, 100 Hoang Quoc Viet Street, Ha noi, Viet Nam.

Received 30 October 2011, received in revised form 24 November 2011

Abstract. In this article, the authors describe the method for preparation of NiFe$_2$O$_4$ – TiO$_2$ magnetic nanoparticles and present the results on study of their photocatalytic activity. NiFe$_2$O$_4$ nanoparticles have been prepared by coprecipitation using spraying technique with subsequent hydrothermal processing. NiFe$_2$O$_4$-TiO$_2$ composite nanoparticles were prepared by covering thin films of TiO$_2$ on the surface of NiFe$_2$O$_4$ particles using sol – gel technique. Different techniques such as XRD, TEM, SEM were used to characterize NiFe$_2$O$_4$ and NiFe$_2$O$_4$ – TiO$_2$ composite nanoparticles obtained from the mentioned procedure. It is shown that prepared NiFe$_2$O$_4$ – TiO$_2$ nanoparticles are particles of a composite material which consists of trevorite NiFe$_2$O$_4$ and anatase TiO$_2$ phases. TEM study has showed that the particles size is of about 20nm. The VSM measurement has demonstrated that nickel ferrite nanoparticles and NiFe$_2$O$_4$ – TiO$_2$ composite nanoparticles are superparamagnetic with saturation magnetization (Ms) of about 40 emu/g and 20 emu/g, respectively; remanences (Mr) and coercive forces (Hc) being near to zero for both the materials. The composite NiFe$_2$O$_4$ - TiO$_2$ nanoparticles are used to degrade methyl orange dye. After 14 hours, methyl orange with the initial concentration of $10^{-4}$M is degraded 98.2%. Thanks to magnetic properties, the nanocomposite photocatalyst NiFe$_2$O$_4$ - TiO$_2$ can be easily collected for reuse.

Keywords: Magnetic nanoparticles, superparamagnetism, NiFe$_2$O$_4$-TiO$_2$ nanocomposite, photocatalysis.

1. Introduction

Magnetic nanoparticles of ferrites MFe$_2$O$_4$ (M : Ni, Mn, Zn, Cu...) recently attracted attention of many authors because they can be used for wide applications, such as high density information storage materials, ferrofluids, high frequency devices, magnetic refrigerants, gas- and biosensors [1, 2, 3]. Their advantages are high saturation magnetization, superparamagnetism, stability of properties at high frequencies, mechanical and chemical durability. Being semiconductors, spinel ferrites are also promising materials for spintronics [4]. On the other hand, TiO$_2$ is a well known semiconductor photocatalyst because of its capabilities of removing toxic organic and inorganic matters from the air and water environments as well as disinfection activity [5, 6, 11]. During treatment of wastewater with...
TiO₂, TiO₂ nanpowders can not be recovered, causing additional expense and problems of solid wastes, because filtering nanostructured TiO₂ is also a problem in the long-term water treatment. Fixation of TiO₂ photocatalyst on different supports as fibers, or zeolites could be a solution for this problem, but in this case the mobility of the catalyst is not high. If TiO₂ nanoparticles were embedded in the magnetic nanpowders, the problem of recovering TiO₂ for recycling and preventing environmental negative impacts can be resolved. Such magnetic nancomposite materials containing TiO₂ will have high mobility, large contact area with wastewater, which will increase environment treatment efficiency, and they can be easily recolllected by using an external magnetic field. Magnetic particles, which play the role of a photocatalyst carrier, must be nontoxic and stable in the environment. For the mentioned reasons, in this research, we have chosen nancomposite powder NiFe₂O₄–TiO₂ as the object of our study.

2. Experiment

2.1 Process of synthesizing nanostructured NiFe₂O₄

Diagram of experimental procedure for synthesis of nickel ferrite nanpowders and schema of apparatus for co-precipitation reaction are shown in Fig. 1.a and Fig. 1.b, respectively. Liquid mixture of solutions NiCl₂ 0.1 M + FeCl₃ 0.2 M prepared from NiCl₂.4H₂O and FeCl₃.6H₂O is contained in the 10 liter pressure vessel (2). The 10 liter pressure vessel (3) contains the solution NaOH 0.8 M. A flow of compressed air is blown through the pipe (1) into the two vessels so that the liquids come out of two containers in the mist form at the nozzles (4) and (5). Spray speed at the two nozzles are similar at 0.5l/min. Co-precipitation reaction occurs in a 50 liter vessel (6) containing NaOH 10⁻⁴ M to keep the reaction environment at the constant pH = 10. A reddish-brown precipitate in the colloidal paste form is obtained from this reaction. The precipitate was washed carefully then mixed with water and put into special reactor of 6 liter capacity for hydrothermal processing. Hydrothermal process was conducted at temperatures of 120°C, 140°C, 160°C during 4 hours. Temperature was measured by a thermocouple which is mounted inside the reactor in direct contact with the slurry. After the reaction ends, the obtained brown magnetic powder has been collected by magnet and washed with distilled water before drying.
2.2. Process of synthesizing the composite \( \text{NiFe}_2\text{O}_4 \cdot \text{TiO}_2 \) nanoparticles.

Firstly, \( \text{TiO}_2 \cdot n\text{H}_2\text{O} \) gel is synthesized from the hydrolysis of \( \text{TiCl}_4 \cdot 5.5 \text{ ml TiCl}_4 \) equivalent to 5g \( \text{TiO}_2 \) and 4.8 ml Diethanolamin \( \text{NH} (\text{C}_2\text{H}_4\text{OH})_2 \) were mixed in 100 ml ethanol 99.7 %. This mixed solution is frozen down to \( 10^\circ \text{C} \) and added with 100 ml of distilled water. This solution is strongly stirred and heated until the clear milky white color appears. The reaction temperature is about \( 30^\circ \text{C} \) at \( \text{pH} < 1 \). Then the solution \( \text{NaOH} 1\text{M} \) is slowly dropped into the mixture until \( \text{pH} = 7 \) to obtain a milky white jelly solution of \( \text{TiO}_2 \). By this time, 5 g of synthesized \( \text{NiFe}_2\text{O}_4 \) is added under vigorous strong stirring within 1 hour for uniform distribution of powder in the \( \text{TiO}_2 \) gel. The precipitate is filtered, washed, dried at \( 100^\circ \text{C} \) and, finally, calcinated at \( 500^\circ \text{C} \) for 1 hour.

2.3. Characterization of synthesized materials

For characterization of obtained materials and nanoparticles, we have used standard techniques such as XRD (Siemens D5005 with CuKα radiation), TEM (EM 1010, JEOL ), VSM (DMS 800).

2.4. Experimenting on photocatalysis of the \( \text{NiFe}_2\text{O}_4 \cdot \text{TiO}_2 \) composite nanoparticles.

Photocatalytic features of the \( \text{NiFe}_2\text{O}_4 \cdot \text{TiO}_2 \) composite nanoparticles are studied through the process of methyl orange decomposition. Irradiation from 15W UV fluorescence lamp is used for illumination. Glass boxes containing 10ml of \( 10^{-3}\text{M} \) orange methyl and 100mg of nanocomposite material are illuminated with UV irradiation through the free surface during 2, 4, 6, 8, 10, 12, 14 hours, respectively. After illumination, nanocomposite powders are separated from the boxes by using external magnetic field. The remaining liquid shall be measured the absorption spectra on UV-VIS 2450 PC (Shimadzu, Japan) to determine the concentration of methyl orange.
3. Results and discussions

3.1. Crystallization of NiFe$_2$O$_4$ by hydrothermal processing

XRD pattern and TEM image of the material obtained immediately after the co-precipitation and hydrothermal processing are shown in Fig. 2 and Fig. 3, respectively. We can see that the co-precipitate is in the form of amorphous glue clusters without distinct particles, while powders obtained after hydrothermal process are single-phase crystalline NiFe$_2$O$_4$. TEM image in Fig. 3.b indicates shape particles with an average size of about 20 nm.

According to [7, 8], this amorphous form also contains much H$_2$O and only become dehydrated completely at temperature of above 600°C. We use the hydrothermal method to crystallize the amorphous material in the temperature range 120 – 160°C, which is much lower than the sintering method (600 - 1000°C).

![Fig. 2. XRD pattern (a) and TEM image (b) of the reddish-brown precipitate.](image)

![Fig. 3. XRD pattern (a) and TEM image (b) of NiFe$_2$O$_4$ nanoparticles prepared at hydrothermal temperature 160°C.](image)

Therefore, it can be said that in spite of the low temperature (120 - 160°C), during the hydrothermal process under high pressure (9.5 atm), in the reactor occurs dehydration of precipitate and crystallization of NiFe$_2$O$_4$. 
3.2. Effects of hydrothermal temperature on size and properties of NiFe$_2$O$_4$ nanoparticles

![TEM images of NiFe$_2$O$_4$ nanoparticles](image1)

**Fig. 4.** TEM images of NiFe$_2$O$_4$ nanoparticles hydrothermalized at a)120°C; b)140°C; c)160°C.

![Magnetic properties](image2)

**Fig. 5.** Superparamagnetism of NiFe$_2$O$_4$ nanopowders obtained at different hydrothermal

Fig. 4 shows TEM images of NiFe$_2$O$_4$ nanopowders, obtained at hydrothermal temperatures of 120, 140, and 160°C, respectively. One can see that, when the hydrothermal temperature is increased, particle size and shape did not change significantly. This is understandable, because at so low temperatures, the thermal energy is not sufficient to allow small particles to assemble together into large particles.

Contrary to particle size, the magnetic properties of powders are improved remarkably when the hydrothermal temperature increases, as shown in Fig. 5. Magnetic saturation is increased significantly with increasing of hydrothermal temperature. In the region with high magnetic field, when the temperature increases, the magnetic saturation also increases from 37 emu/g (corresponding to the temperature of 120°C) to 44 emu/g (corresponding to temperature 160°C). We can see also that the powders are typically superparamagnetic with remanences (Mr) and coercive forces (Hc) being near to zero. This is very important when we want to recollect the photocatalyst TiO$_2$ materials distributed in environment for reuse by using an external magnetic field.
3.3. Properties of anatase TiO$_2$ - NiFe$_2$O$_4$ composite nanophotocatalyst

Fig. 6 shows XRD pattern and TEM image of obtained TiO$_2$-NiFe$_2$O$_4$ composite nanoparticles. We can see typical peaks of anatase TiO$_2$ at diffraction angles 25°, 37°, 38°, 48°, 54°, 55°, 63° along with typical peaks of NiFe$_2$O$_4$. So the particles are composite of anatase TiO$_2$ and NiFe$_2$O$_4$. TEM image shows that TiO$_2$-NiFe$_2$O$_4$ nanoparticles have average particle size of 10 - 30 nm. Therefore, this material has high surface area, suitable for heterogeneous catalyst applications.

Fig. 6. XRD pattern (a) and TEM image of the nanocomposite material Anatase TiO$_2$ - NiFe$_2$O$_4$

In Fig. 7 are shown results of study on photocatalytic capability of the obtained TiO$_2$-NiFe$_2$O$_4$ composite nanoparticles. Methyl orange is mixed from the standard chemical which always exists in the form of anions with pH > 7, so it can has only one color carrying form and in UV-Vis absorption spectrum it has only one characteristic absorption peak at 461 nm in accordance with [9, 10]. Fig. 7.a shows how absorbance spectra of methyl orange solution change with UV illumination time and Fig. 7.b demonstrates the kinetics of degradation of methyl orange by composite photocatalyst under UV illumination.

We can see that the concentration of methyl orange after processing time of about 14 hours, is only 1.7 $\times$ 10$^{-6}$ M, i.e about 98.2 % of the original substance is decomposed after processing. Such the obtained composite powders show good photocatalytic properties, they can decompose effectively dye and can be used for removing other chemical in wastewater.
The detailed mechanism of TiO$_2$ catalyzed dye degradation was studied in some research [12,13]. When aqueous TiO$_2$ suspension is irradiated with light energy greater than its band gap energy ($E_g=3.2$ eV), conduction band electrons (e•) and valence band holes (h•) are generated

\[(e^-/h^+) \text{TiO}_2 \rightarrow e^- (\text{TiO}_2) + h^+ (\text{TiO}_2)\]

The photo-generated electrons can react with O$_2$ adsorbed on the TiO$_2$ surface or dissolved in water reducing it to superoxide radical anion O$_2$•

\[\text{TiO}_2(e^-) + O_2 \rightarrow \text{TiO}_2 + O_2^-\]

The photo-generated holes can react with H$_2$O oxidizing them into OH • radicals.

\[\text{TiO}_2(h^+) + H_2O \rightarrow OH^- + H^+ + \text{TiO}_2\]

So the role of nano TiO$_2$ anatase in the photocatalytic process is to transfer electrons from H$_2$O to O$_2$. The resulting O$_2$•, OH • radical, being very strong oxidizing agents (OH • standard redox potential is +2.8 V), can oxidize the methyl orange dye to CO$_2$ and H$_2$O.

The major advantage of this photocatalyst is that due to the magnetic properties of NiFe$_2$O$_4$, the NiFe$_2$O$_4$-TiO$_2$ nanoparticles can be collected for reuse, thus bringing significant economic benefits and eliminating the risk of additional pollution source (TiO$_2$ solid particles) in the wastewater treatment process.

4. Conclusions

We have successfully synthesized NiFe$_2$O$_4$ nanoparticles with average particle size of about 20 nm by using spraying - coprecipitation process with subsequent hydrothermal treatment. Advantages of this process are very low processing temperature, high productivity, good stability and excellent superparamagnetic performances of the nanoparticles. This technological process can be easily
expanded to industrial scale for large scale production of NiFe$_2$O$_4$ nanoparticles and can be applied for synthesizing nanoparticles of different ferrites MFe$_2$O$_4$, as well as oxides and other materials. At the same time, we also successfully synthesized composite NiFe$_2$O$_4$ - TiO$_2$ nanoparticles, which are simultaneously good superparamagnetic and photochemical catalyst. This will facilitate the solution of problems of collection expensive TiO$_2$ photochemical catalyst for reuse, and also reduce the risk of contamination of TiO$_2$ solid waste during the environment processing.

References