

# NANO CORE-SHELL PHOTOCATALYSTS FOR TREATMENT OF WATER POLLUTANTS

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## Abstract

Nano-materials are considered as a part of nanotechnology which is expected to provide many applications in the future. However, separation and reuse of the nano materials are challenging for catalysis application in liquid phase reactions. In this research, nano core-shell containing TiO<sub>2</sub> which possess magnetic property have been synthesized using two methods: sol-gel method and modified sol-gel method. The materials have been characterized using different techniques such as X-ray Diffraction (XRD), Transmission electron microscopy (TEM). TiO<sub>2</sub> anatase structure of the catalysts have been verified from XRD patterns. The potential application for the treatment of water contaminated by organic pollutants has been investigated via the photocatalytic degradation of methyl orange (MO) and p-nitrophenol (NP) as models using the as-synthesized materials. The magnetic photocatalyst which was synthesized by the sol-gel method, exhibited comparable activity as the commercial TiO<sub>2</sub> (P25) after three hours reaction. However, the catalyst prepared by the modified sol-gel method performed high recyclability.

**Keywords:** Core-shell, Environment pollutant, Nano material, Photocatalytic degradation, TiO<sub>2</sub>

## Introduction

Vietnam is facing several environmental issues because of urbanization, planning, industrialization, and intensive farming. These factors have led to air pollution, water pollution, and noise pollution, particularly in urban and industrial centers like Ho Chi Minh City and Hanoi. Total flowrate of Vietnam's urban waste water was increased from 182 million m<sup>3</sup>/day in 2006 to 2.03 million m<sup>3</sup>/day in 2009. Especially, the water pollution has been in a level much higher than Vietnam standard [1]. In addition, amount of non-biodegradable organic compounds in urban waste water is significantly high. The COD values were almost two times higher than BOD values as reported from 2006 to 2009 which reported in the Vietnam national environmental report 2010 [1]. Therefore, advanced treatment processes are necessary for removal of organic pollutants in water.

Nano-materials have attracted much attention of researchers in all over the world and being considered as a part of nanotechnology which is expected to provide many applications in the future [2]. Small particles can give high surface area which is crucial in heterogeneous catalysis application since all chemical reactions are supposed to occur on the catalyst surface. In photocatalysis the energy supplies to the reaction is solar energy which is a sustainable, free energy and much available in Vietnam since it are located near the earth's equator. Photocatalysis method can be applied in treatment of contaminants in water and air. Among the materials interested, TiO<sub>2</sub> has been proved to be an excellent photocatalyst due to its high photocatalytic activity, non-toxicity and good stability [3]. For the treatment of water pollutants, it is important to recycle and reuse the catalyst after the photocatalysis process in the solution. However, nano materials which can give high

surface area are very difficult to separate after used because small particle sizes make them impossible to be filtered using ordinary filter.

The creation of magnetic nanoparticles has in recent years developed into an increasingly important research area at the frontier of advanced materials chemistry. Core-shell type nano-materials is a feasible solution for the drawback of applying nanomaterial in photocatalysis treatment of water contaminants [4-7]. When the core of the material has magnetic property, such as  $\text{Fe}_3\text{O}_4$ , the catalyst can be easily separated from the liquid solution by using a magnetic bar. In this study, magnetic core-shell  $\text{TiO}_2$  materials has been synthesized by sol gel method and modified sol-gel method. The materials were characterized and examined photocatalytic activity and recyclability.

## Experimental

### Synthesis and Characterization of Catalysts

Nano  $\text{Fe}_3\text{O}_4$  was synthesized using co-precipitation method using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  under nitrogen atmosphere. The nanoparticles were isolated by magnetic decantation and washed with ethanol several times to remove excess surface chemicals. The final product was dried in air at room temperature under vacuum and use as core material. The shell  $\text{TiO}_2$  was synthesized by sol-gel method using Titanium Tetra-isopropoxide (TTIP) (Merck) and Tetraethyl orthosilicate (TEOS) (Merck).

Two types of core-shell materials were synthesized.  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  which was made by directly coating  $\text{TiO}_2$  on  $\text{Fe}_3\text{O}_4$  particles by sol-gel method. The sample denoted as FeTi. Typically, a mixture of 3.0g TTIP and isopropanol was added to a solution of 50 ml isopropanol containing 1.0 g  $\text{Fe}_3\text{O}_4$ . A solution containing 11 ml isopropanol, 3.5 ml distilled water, and 0.15 ml  $\text{HNO}_3$  65% was added drop-wise to the above mixture for coating  $\text{TiO}_2$ . Reaction temperature was kept at  $75^\circ\text{C}$ . The final gel will be aged for 24 hours at room temperature, then be crushed, dried.  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$  which was made by coating  $\text{SiO}_2$  on  $\text{Fe}_3\text{O}_4$  by Stober sol-gel method [8] following by coating  $\text{TiO}_2$  on the two layer  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  by sol-gel method with similar procedure as FeTi except using  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  instead of  $\text{Fe}_3\text{O}_4$ . The sample denoted as FeSiTi-1. Another sample named FeSiTi-2 was prepared in different way (named "method 2"- a modified sol-gel method). A 7.5 ml mixture of distilled water and isopropanol (1:5 v/v) was added drop-wise to a solution containing 0.6 g TTIP in isopropanol and 0.1 g  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  which has been calcined at  $450^\circ\text{C}$  for 2 hours. The solution then mechanically stirred for 6 hours at  $45^\circ\text{C}$ . The solid was separated by a permanent magnet then washed three times by ethanol followed by drying at  $600^\circ\text{C}$  and calcined at  $500^\circ\text{C}$  for 2 hours.

The synthesized materials have been characterized by several techniques in order to understand the crystalline structure. Powder X-ray diffraction (XRD) has been conducted on a MultiFlex X-Ray Diffractometer (Rigaku Corp.) for verification of the crystal structure of the  $\text{TiO}_2$ ,  $\text{Fe}_3\text{O}_4$  which expectedly present in the materials. Transmission electron microscopy (TEM) was used to picture the particles for understanding the nano structure of the photocatalyst.

### Photocatalytic Activity Measurement

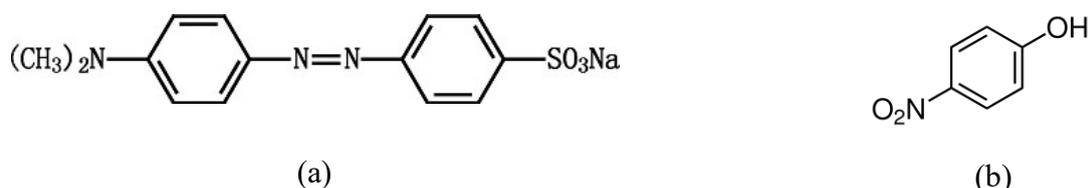


Figure 1. Chemical structure of MO (a) and NP (b)

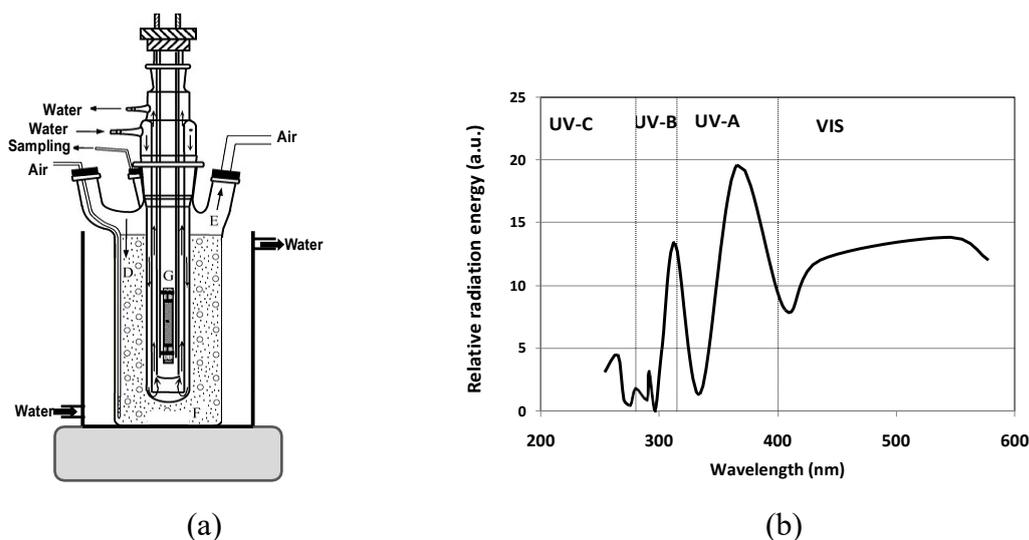


Figure 2. Experimental reactor for photocatalytic measurement (a) and radiation spectrum of the light source (b)

Methyl Orange (MO) and para-nitrophenol (NP) are used as pollutant models (Figure 1) since MO is a typical azo dye and NP is a typical phenolic compound whose concentration is restricted in water quality regulation. The photocatalytic activity was measured by a batch reactor as illustrated in Figure 2a using UV-VIS light whose radiation wavelengths are shown in Figure 2b. The 100 W UV-VIS light, which purchased from Senlight Co. - Japan, was located in the middle of the glass reactor. The maximum liquid volume of the batch reactor was 1.5 liter. A quartz jacket was used to cover the light to ensure all UV-VIS energy is able to transmit to the solution. Reaction conditions are fixed: MO/NP concentration was 50 ppm, catalyst loading is 0.5 g/l, at room temperature. Before radiation, the mixture of pollutant solution and catalyst was stirred for 30 minutes in dark. The concentration of MO and NP were analyzed by an UV-VIS spectrometer (Spectronic Genesys 2PC) at 465 nm and 320 nm, respectively. The decrease of COD value of NP solution was also examined to understand the mineralization of the photocatalytic reaction. Commercial TiO<sub>2</sub> P25 (Degussa) was also tested by the same system for comparison.

## Results and discussion

### Photocatalytic Activity

Photocatalytic activity for methyl Orange (MO) degradation are reported in Table 1. It can be seen that in the case of without catalyst (blank) MO has been converted 24% after 03 hours radiation. Therefore, a part of MO has been photo-degraded in the condition of experiments in this study. The result of Fe<sub>3</sub>O<sub>4</sub> was almost similar with blank case which indicates that photocatalytic activity of Fe<sub>3</sub>O<sub>4</sub> sample can be neglected. After coating TiO<sub>2</sub> by sol-gel method (sample FeTi), the conversion of MO after 03 hours UV-VIS exposure was increased significantly upto 87.0%. Thus, the presence of TiO<sub>2</sub> played crucial role in the photocatalytic reaction.

As reflected from Table 1, the catalytic performance of the three-layer materials (FeSiTi-1 and FeSiTi-2) was observed. Sol-gel coating TiO<sub>2</sub> directly on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles (FeSiTi-1) exhibited very high MO conversion (97.0%). On the other hand, photocatalytic activity of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> catalyst which synthesized by “method

2” (FeSiTi-2) was lower than that of FeSiTi-1. Conversion of MO using FeSiTi-2 was 67.3% after 03 hours reaction under UV-VIS light. The washing step in the “method 2” led to a decrease of TiO<sub>2</sub> amount in the FeSiTi-2 sample comparing with the FeSiTi-1 sample. Therefore, the catalytic performance of the FeSiTi-1 was higher than the FeSiTi-2.

Comparing with commercial TiO<sub>2</sub> (P25) in the last column of Table 1, it can be seen that although sol-gel coating samples (FeTi, FeSiTi-1) are exhibited high MO conversion, the activity of P25 is relatively higher than that of the two. However, it is important to note that the catalyst loading was 0.5g/liter for all materials. Therefore, the interesting thing is that after 03 hours reaction, conversion of MO using FeSiTi-1 was comparable with P25 even though FeSiTi-1 contains less amount of TiO<sub>2</sub>, which is proved to be the active catalytic component for photocatalytic reaction.

**Table 1. Photocatalytic Activity for MO Degradation**

Radiation Time (h)	MO Conversion (%)					
	Blank	Fe <sub>3</sub> O <sub>4</sub>	FeTi	FeSiTi-1	FeSiTi-2	Commercial TiO <sub>2</sub> (P25)
1.0	11.7	12.1	66.8	66.9	27.1	80.3
2.0	17.1	15.0	77.0	86.7	52.7	97.5
3.0	24.0	22.3	87.0	97.0	67.3	100.0

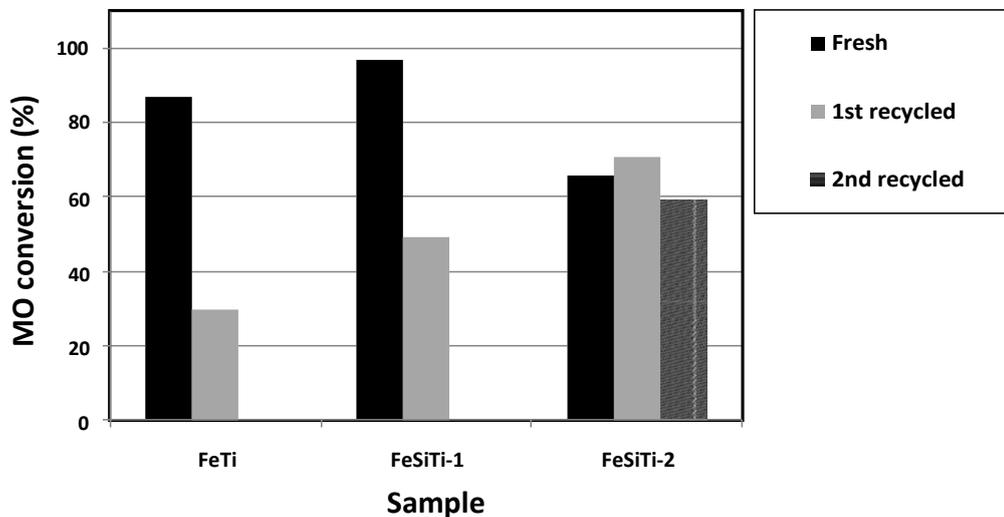


Figure 3. Recyclability of the photocatalysts

Figure 3 presents the results of the recyclability three photocatalysts (FeTi, FeSiTi-1, FeSiTi-2). After three hours photo-reaction, the catalyst was kept in the reactor by a permanent magnet, the solution was removed and new solution charged. A new photocatalytic activity measurement was then started in the similar procedure with the fresh catalyst. As seen from Figure 4 in the case of the two layer sol-gel catalyst (FeTi), catalytic activity of 1<sup>st</sup> recycled sample was shapely reduced. Catalytic performance of this sample was almost similar with Fe<sub>3</sub>O<sub>4</sub> sample (see Table 1). Thus, it is possible that

almost all TiO<sub>2</sub> layer has been released from the FeTi and only Fe<sub>3</sub>O<sub>4</sub> remained. Recycled FeSiTi-1 sample, which also synthesized using the same sol-gel method, exhibited better photocatalytic activity comparing to the recycled FeTi sample. The decrease of about half of MO conversion was observed in FeSiTi-1 sample.

On the other hand, FeSiTi-2 sample has shown good recyclability. After 2<sup>nd</sup> recycle, the photocatalytic activity of the material was almost unchanged. In the “method 2” the additional calcination step at 500<sup>o</sup>C may play important role in the structure stability of the FeSiTi-2 catalyst. Therefore, the “method 2” can result in stronger link between layers in the FeSiTi material leading to the high recyclability.

**Table 2. Photocatalytic Activity for NP Degradation**

Radiation Time (h)	NP Conversion (%)		
	Blank	Commercial TiO <sub>2</sub> (P25)	FeSiTi-2
1.0	4.7	61.9	21.9
2.0	18.4	94.4	40.2
3.0	26.8	100.0	64.5

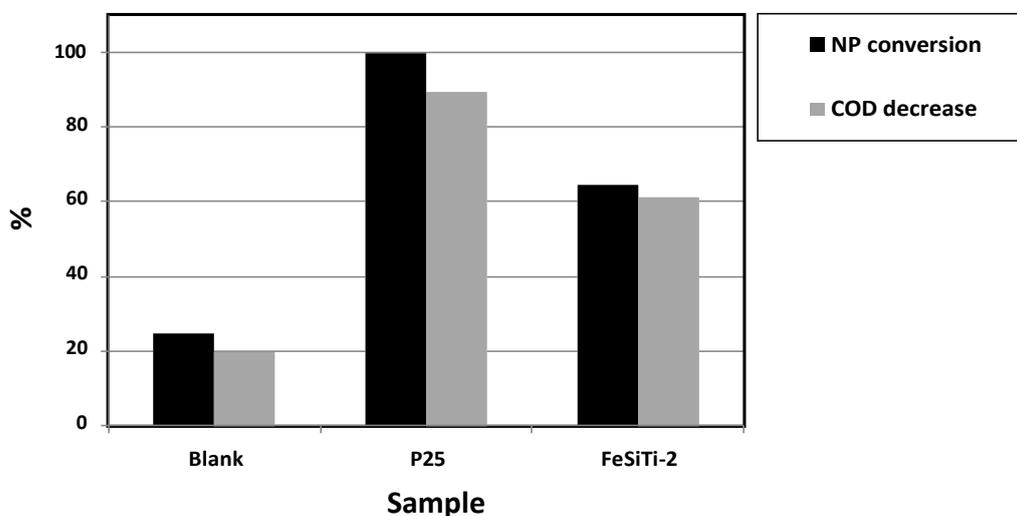


Figure 4. Comparison of NP conversion and COD decrease after 03 hours photoreaction

Results of photocatalytic degradation of p-nitrophenol (NP) are shown in Table 2. It can be seen that in the case of without catalyst (blank) NP has been converted 26.8% after 03 hours radiation. Therefore, similar with MO, a part of NP has been photo-degraded in the condition of experiments in this study. Commercial TiO<sub>2</sub> (P25) converted 100% of NP after 03 hours, while FeSiTi-2 converted 64.5% of NP.

In order to examine the ability of the photocatalysts for mineralization, chemical oxygen demand (COD) has been conducted and results are shown in Figure 4. Since the

difference of percentage of COD decrease and NP conversion are not really significant, it can be concluded that NP has been mineralized in the photocatalytic reaction.

## Characterization of the Catalysts

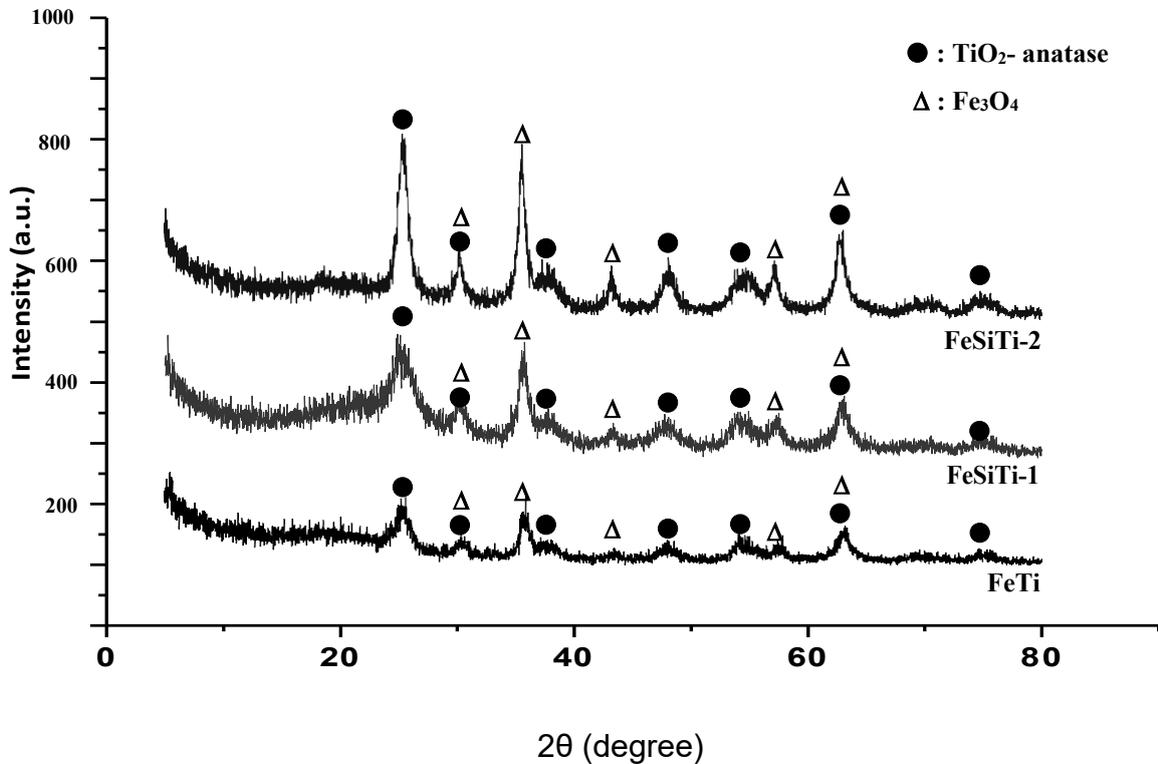


Figure 5. XRD patterns of photocatalysts

Crystalline structure of the photocatalysts was examined by XRD techniques as reported in Figure 5. The results confirm the presence of  $\text{Fe}_3\text{O}_4$  crystal in the materials. XRD characteristic peaks of anatase  $\text{TiO}_2$  were obtained in all tested samples. Intensity of the peaks is varied from sample to sample indicating that the crystallinities are different. Sample FeSiTi-2 is more crystalline than the other two because this sample has been calcined at high temperature. Combining with the recyclability test results in Figure 4, it can be found out that more crystalline the material, more  $\text{TiO}_2$  remain on the magnetic catalysts after using for photocatalytic reaction in water solution. This conclusion may be supported by TEM result of FeTi sample in Figure 6. Size of particles is about 100 – 150 nm. The image indicates that with sol-gel method, it is possible for coating  $\text{TiO}_2$  on  $\text{Fe}_3\text{O}_4$  particles but the link between the layers are not strong enough to keep  $\text{TiO}_2$  outer layer remain after reaction in water.

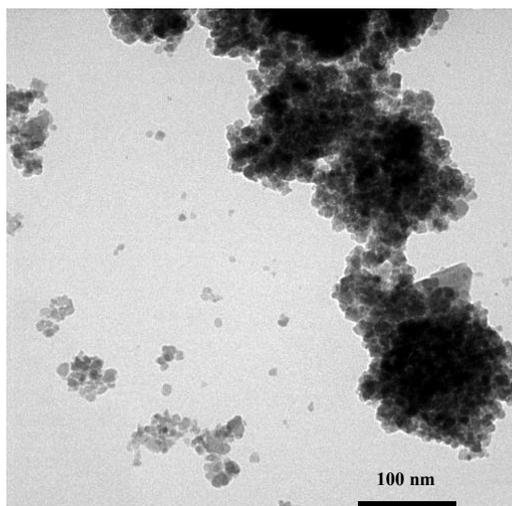


Figure 6. TEM images of sample FeTi

## Conclusions

The study investigates the synthesis and photocatalytic activity measurement of nano core-shell materials.  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$  materials have been synthesized by sol-gel method and modified sol-gel method. Presence of  $\text{Fe}_3\text{O}_4$  and anatase  $\text{TiO}_2$  are confirmed by XRD patterns. Crystallinity of FeSiTi-2 is much more than the other two tested materials. This is possibly one of reasons for the stable activity of the recycled FeSiTi-2 even though the fresh FeSiTi-2 showed less pollutant conversion than that of the others. In addition, photocatalytic reaction using FeSiTi-2 can mineralized the pollutant (NP) in the experimental conditions mentioned in this study. However, further data needed to be collected in order to deeply understand the stability of FeSiTi-2.

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