

## SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF FE-DOPED TiO<sub>2</sub> PARTICLES VIA HYDROTHERMAL TREATMENT OF MICROEMULSION

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### ABSTRACT

*Un-doped titanium dioxide (TiO<sub>2</sub>) and iron (Fe)-doped TiO<sub>2</sub> particles were prepared using hydrothermal treatment of microemulsion method. The samples were characterized by scanning electron microscope (SEM) coupled with energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), and UV-vis spectrophotometer. Both the un-doped TiO<sub>2</sub> and Fe-doped TiO<sub>2</sub> particles produced using this method were in anatase crystal structure. The photocatalytic activity of the samples was investigated via degradation of methylene blue under UV light. 1% Fe-doped TiO<sub>2</sub> shows the best photocatalytic activity compared to other samples because of high charge separation efficiency and high lifetime of charge carriers.*

**Keywords:** titanium dioxide, Fe-doped, photocatalysts, methylene blue

### INTRODUCTION

The most popular choice of photocatalyst is titanium dioxide (TiO<sub>2</sub>), and much of the published work on photocatalysis uses this material. Since Fujishima and Honda [1] discovered the photocatalytic splitting of water on TiO<sub>2</sub> electrodes, research efforts have been attempted to enhance the photocatalytic properties efficiency of TiO<sub>2</sub>. The crystal structure of TiO<sub>2</sub> particles are known to exist in different forms such as anatase and rutile forms, with the former indicating a higher level of photoactivity [2]. Although many important fundamental results concerning photocatalytic reaction of bulk TiO<sub>2</sub> layers and coatings have been clarified by previous work, the photocatalytic properties of TiO<sub>2</sub> particles have not been studied extensively.

Recent applications of TiO<sub>2</sub> have involved self-cleaning [3], anti-bacterial [4], air purification [5], and water treatment [6]. When TiO<sub>2</sub> is exposed to UV light source (<385nm wavelength) such as sunlight, it absorbs UV waves which excites the electrons from the valence band to the conduction band leaving positive holes behind. The electrons and holes can react with water and oxygen in air to produce highly reactive hydroxyl radical and super-oxide ion. These radicals are able to oxidize and decompose various organic compounds into carbon dioxide and water. However, to date the applications of TiO<sub>2</sub> as photocatalyst have been limited to outdoor use due to the requirement of UV light.

Photocatalytic activity depends on the ability of the photocatalyst to create electron hole pairs which generate free radicals to undergo secondary reactions. One of the factors that effect photocatalytic activity is the electronhole recombination rate. If the recombination rate is very fast, then there is no time for any reactions to occur. Modifying the TiO<sub>2</sub> crystalline structure by doping the particles with small amounts of transition metal such as iron could improve photocatalytic activity by reducing the recombination rate of electron hole pairs and decreasing the band gap energy [7]. It can act as electron hole traps thus reducing the recombination rate of electron hole pairs and therefore increasing the lifetime of charge carriers [8]. Furthermore, transition metals could encourage the particles to absorb light at higher wavelengths, in the visible spectrum (>400 nm wavelength) [9]. This implies that the use of TiO<sub>2</sub> can be extended indoors where UV light is limited.

In this work, hydrothermal treatment of microemulsion method was used to produce Fe-doped TiO<sub>2</sub> particle in anatase form. This method was chosen because it could be carried out at milder reaction condition (reaction temperature < 250oC) without post-calcination to produce uniform particles with pure phase. The photocatalytic activity of the samples produced was studied via the degradation of methylene blue under UV light.

## MATERIALS AND METHODS

### *Preparation of samples*

The synthesis procedure was carried out according to Wu et al (1999) [10]. For the preparation of the reverse (water dispersed in oil) microemulsion system, 10 mL TritonX-100 was used as the surfactant, 6 mL hexanol as the cosurfactant, and 16 mL cyclohexane as the oil phase. 3.4 mL tetrabutyltitanate was dissolved in 8mL 5M nitric acid and was used as the aqueous phase.

The Fe-doped TiO<sub>2</sub> synthesis was carried out according to the same procedure described by Wu et al. [10] but was modified by the addition of different amounts of iron (III) nitrate nonahydrate (0.1 M) in aqueous phase.

Then the aqueous phase was added dropwise under stirring, making up the clear microemulsion. All the above steps were carried out at room temperature. The mixture was charged into a 100 mL Teflon lined stainless steel autoclave. The autoclave was then heated to 120°C and kept there for 13 h. After the hydrothermal treatment the precipitate found at the bottom of the autoclave was washed in a procedure that was repeated five times and involved redispersion in ethanol and centrifuging (6000 rpm) to remove the oil, surfactant, and cosurfactant. The product was then kept in a desiccator to dry. No further heat treatment was done.

### *Characterization method*

The morphology of the TiO<sub>2</sub> particles was studied by scanning electron microscope (SEM) coupled with energy dispersive X-ray analysis (EDX) using Leo 1455 VP SEM. The concentration of Fe dopant in the particles was determined using EDX in atomic percentage. The product was characterized using X-ray diffraction (XRD) in the range 20-60° (2θ) using Philips X'pert Pro PW3040 diffractometer (Cu Kα radiation λ= 0.154 nm) operated at 40kV and 30mA.

### *Photocatalytic study*

A schematic diagram of a simple photocatalytic reactor used in this study is shown in Figure 1. 400 mL of 6 ppm methylene blue was poured into a 500 mL cylinder which was placed on a magnetic stir plate. A 254nm UV lamp was immersed in the methylene blue. Then, 0.02 g of the particles was introduced inside the cylinder. An aquarium air pump (to distribute air evenly when the magnetic stir plate is switched on), UV light, and magnetic stir plate were switched on simultaneously and the timing was started. 6 mL of solution sample were taken out every minute for the first 10 minutes and every 5 minutes for the following 50 minutes. The samples were then placed in UV-vis spectrophotometer (Helios Alpha, Thermo Electron) to determine the absorbance value.

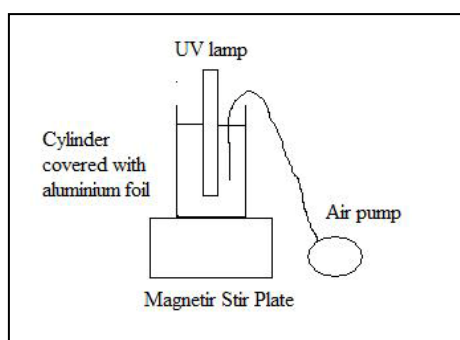


Figure 1: Schemcatic diagram of photocatalytic reactor used in this study

## RESULTS AND DISCUSSIONS

Figure 2 depicts the SEM micrographs of Fe-doped TiO<sub>2</sub> particles. It can be seen that the particles were inhomogeneous in size. The range of the particle size for different concentration of Fe dopant is between 1.25 μm to 8.75 μm with 5.15 μm as the average particle size.

According to Carneiro et al. (2007), if the iron concentrations are far more than its solubility in  $\text{TiO}_2$ , then an iron oxide surface enrichment is expected, leading to the formation of bigger particles [3]. In this work, we found that the size of the particles for different concentration of Fe dopant is about the same. This indicate that the concentration of Fe-dopant did not affect the sizes of the particles produced provided that iron concentrations did not exceed its solubility in  $\text{TiO}_2$ . From the effective radius of ions for a coordination number of 6,  $\text{Fe}^{3+}$  has ionic radius (0.645 Å) comparable to  $\text{Ti}^{4+}$  (0.605 Å) [12]. Thus,  $\text{Fe}^{3+}$  ion can be easily substitutes  $\text{Ti}^{4+}$  in the  $\text{TiO}_2$  lattice. Since iron has been incorporated into the lattice of  $\text{TiO}_2$ , the concentration of Fe dopant did not affect the sizes.

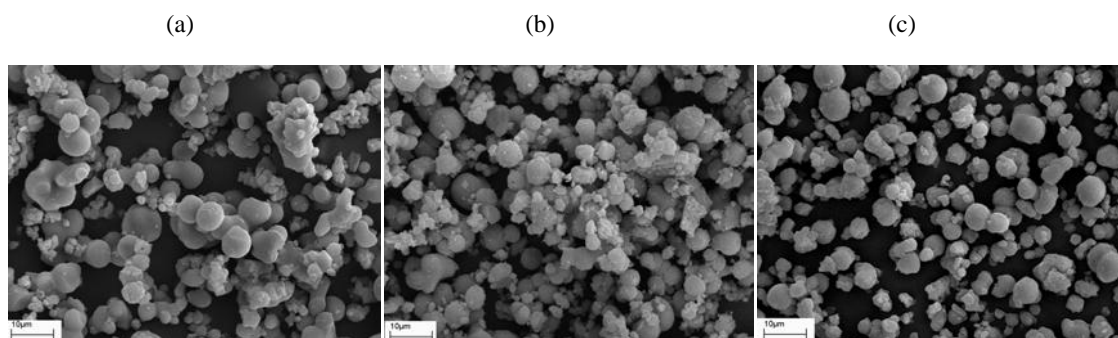


Figure 2: SEM micrographs of Fe-doped  $\text{TiO}_2$  at different Fe dopant concentration - (a)1%Fe dopant (b)2%Fe dopant (c)5%Fe dopant

The crystal structure of  $\text{TiO}_2$  samples were examined by XRD as shown in Figure 3. The peaks at 25.3, 37.8, 48.0, and 53.8 corresponds to the diffractions of the (1 0 1), (0 0 4), (2 0 0), and (1 0 5) planes of anatase respectively [13, 14]. These peaks confirmed that the  $\text{TiO}_2$  produced were in the anatase form. From the XRD data, there were no other detectable peaks to suggest the presence of rutile crystal structure. This result agreed with the findings of Wu et al. (1999) [10] and Andersson et al. (2002) [11] which showed only the peaks characteristic of the anatase phase in their XRD spectras.

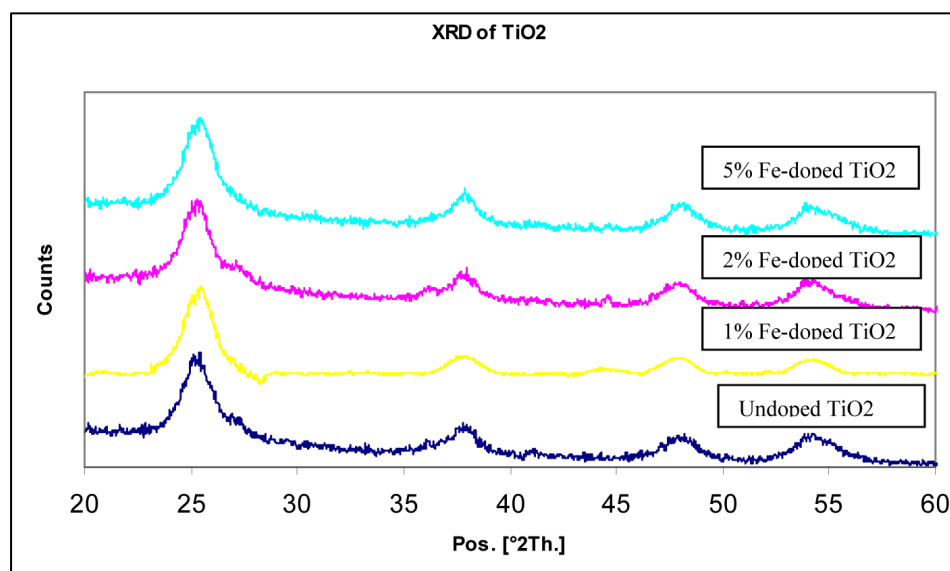


Figure 3: XRD spectra of un-doped  $\text{TiO}_2$  and Fe-doped  $\text{TiO}_2$

From Figure 3, it can also be seen that XRD spectra for particle samples still indicate the peaks characteristic of anatase phase no matter how much the concentration of dopant was. This proved that the addition of Fe dopant did not affect the crystal structure of the  $\text{TiO}_2$  particles obtained.

Figure 4 shows the results for the photocatalytic activity of  $\text{TiO}_2$  for different Fe dopant concentration. It can be seen that all of the  $\text{TiO}_2$  samples were able to decompose methylene blue indicated by the decrease in the methylene blue solution concentration throughout the 60 minutes of photocatalytic study. 1% Fe-doped  $\text{TiO}_2$  exhibited the highest photocatalytic activity compared to others. It even exhibited a photocatalytic activity higher than un-doped  $\text{TiO}_2$  due to the fact that small amount of  $\text{Fe}^{3+}$  ions can act as a photo-generated hole

trap and electron trap to inhibit the hole-electron recombination [15]. This would lead to higher charge separation efficiency and therefore high lifetime of charge carriers.

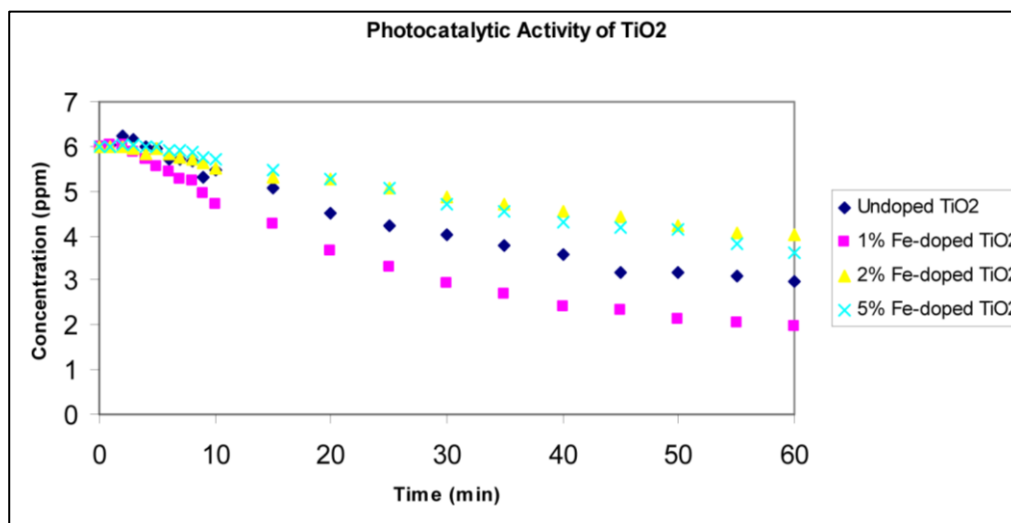


Figure 4: Photocatalytic activity of un-doped TiO<sub>2</sub> and Fe-doped TiO<sub>2</sub>

However 2%Fe-doped TiO<sub>2</sub> and 5%Fe-doped exhibited lower photocatalytic activity compared to un-doped TiO<sub>2</sub> and 1%Fe-doped TiO<sub>2</sub>. It is thought that this was due to excessive Fe deposits on TiO<sub>2</sub>, which would prevent the illumination of the TiO<sub>2</sub> particles caused by light blocking [16]. Less illumination of light could reduce the number of photogenerated electron-hole pairs and therefore decrease the photocatalytic activity of TiO<sub>2</sub>. Many researches have revealed that the photocatalytic activity of Fe-doped TiO<sub>2</sub> is strongly dependent on the Fe dopant concentration [15, 16]. For this particular study, the optimal Fe dopant concentration was found to be 1 atomic %. Different studies have revealed different optimal Fe dopant concentration due to different preparation methods, different characteristics of particles produced, and different type of photocatalytic studies.

## CONCLUSIONS

In this study, un-doped and Fe-doped photocatalysts were successfully synthesized via hydrothermal treatment of microemulsion method. The particles produced using this method were a few microns in size. Addition of Fe dopant did not influence the size and anatase crystal structure of TiO<sub>2</sub> produced. However, the photocatalytic activity of Fe-doped TiO<sub>2</sub> is greatly influenced by the Fe dopant concentration. The larger the concentration of Fe dopant, the worse the photocatalytic activity of TiO<sub>2</sub>. At 1 atomic % of Fe dopant concentration, photocatalytic activity of Fe-doped TiO<sub>2</sub> is higher than that of un-doped TiO<sub>2</sub>.

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