

Degradation of Phenol by Titanium Dioxide Powders

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ABSTRACT

Titanium dioxide (TiO₂) powders were synthesized by hydrothermal route using titanium isopropoxide (Ti[OCH(CH₃)₂]₄), ammonium hydroxide (NH₄OH) and nitric acid (HNO₃) as starting materials. The final pH of mixed solution was 1 and treated at 100 °C for 1 h in the hydrothermal vessel. The phase transition and morphology of TiO₂ powders were studied by X-ray diffractometer (XRD) and scanning electron microscope (SEM). Single-phase with anatase structure was obtained without calcination step. The average of particle size was 0.5 μm with agglomerate and irregular shape. The element chemical compositions of TiO₂ powders were determined by energy dispersive X-ray spectrometer (EDS). The element chemical compositions showed the characteristic X-ray energy levels of oxygen and titanium. The photocatalytic degradation of phenol with TiO₂ powders was investigated by UV/VIS Spectrophotometer.

Keywords: Titanium dioxide, phenol, hydrothermal route

INTRODUCTION

Organic toxicant such as phenol is caused by the extending of industrial manufactory. Phenol is a poisonous compound polluting water. Only small amount of phenol is harmful to health and it can cause cancer in human (Makgae *et al.*, 2008). In 2008 Busca *et al.* reviewed that “Phenol is rapidly absorbed through the skin and can cause skin and eye burns upon contact. Comas, convulsions, cyanosis and death can result from overexposure to it. Internally, phenol affects the liver, kidneys, lungs, and vascular system. The ingestion of 1 g of phenol is deadly for man.”

Titanium dioxide (TiO₂) powders are chemical stability, nontoxicity and inexpensive. So, it is widely used as a photocatalytic material (Tian *et al.*, 2009; Fujishima and Honda, 1972). Anatase, rutile and brookite are three crystalline structure of titanium dioxide. Rutile always is used as light scattering while anatase is used in photocatalysis and photon-electron transfer (Dhage *et al.*, 2003; 2004). There are many ways to synthesize TiO₂ such as co-precipitation methods (Carp *et*

al., 2004; Poznyak *et al.*, 1998), solvothermal method (Kolen'ko *et al.*, 2004; Jing *et al.*, 2004; Demazeau, 1999), sol-gel method (Jung *et al.*, 2008; Gotić *et al.*, 1996), combustion synthesis (Chinarro *et al.*, 2007) and microwave method (Addamo *et al.*, 2008). Nowadays, hydrothermal route is employed for preparing various kind of crystalline materials. Hydrothermal method is performed in a close system using water as solvent so this it is environmentally friendly.

In this research, TiO₂ powders were synthesized by a hydrothermal route. The phase, morphology, chemical element compositions were studied by X-ray diffractometer (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectrometer. The photocatalytic degradation of phenol with TiO₂ powders was investigated by UV/Vis Spectrophotometer.

METHODOLOGY

Synthesized of TiO₂ powders

Titanium dioxide (TiO₂) powders were synthesized by hydrothermal route. Titanium isopropoxide (Ti[OCH(CH₃)₂]₄, Aldrich, England), ammonium hydroxide (NH₄OH, BDH, England) and nitric acid (HNO₃, Merck, Germany) were used as starting materials. 6M NH₄OH solution was added to 0.05M Ti[OCH(CH₃)₂]₄ in an ice bath to form titanic acid (Ti(OH)₄) and then dissolved with 6M HNO₃ to form titanyl nitrate (TiO(NO₃)₂) (Pookmanee, 2008). 6M HNO₃ was added until the final pH value of mixed solution was 1. Mixed solution was transferred into the hydrothermal vessel (Ü TV18, Berghof, Germany) and treated at 100 °C for 1 h. Powders were dried in an oven (Gallenkamp, England) at 100 °C for 24 h and milled with agate mortar.

Characterization of TiO₂ powders

The phase of TiO₂ powders were studied by X-ray diffractometer (JDX-3530, JEOL, Japan) using the Ni-filtered monochromatic with CuK_α radiation. The detection range was 10-60° with the step size of 0.10° (20°/s/s). Confirmation structure of TiO₂ powders were obtained by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No.21-1272 and 21-1276.

The powders were dispersed with ethanol (C₂H₅OH, Merck, Germany) medium in an ultrasonic bath (136H, Ultrasonik, USA.) for 15 min and gold coated by fine coater (JSC1200, JEOL, Japan) for 1 min. The morphology and element chemical compositions were investigated by scanning electron microscope (JSM5410-LV, JEOL, Japan) and energy dispersive X-ray spectrometer (ISIS300, Oxford, England) with tungsten (W) filament K type, accelerate voltage of 20 kV, and working distance of 18 mm.

Degradation of phenol

0.1 g of catalyst TiO₂ powders were suspended in a 100 ml beaker containing 50 ml of phenol (C₆H₆O, Ajax, Australia). The concentration of phenol used for UV irradiation was 100 mg/l. The concentration of the catalyst TiO₂ powders in phenol aqueous solution was 2 g/l. After sonicated for 15 min, the pH value of the suspension was adjusted to 7.9±0.1 with 0.1M NH₄OH. Then, the above suspension was stirred in the dark overnight to adsorption-desorption equilibrium for

phenol and oxygen on the surface of TiO_2 . Subsequently, the obtained suspensions were illuminated with 6 watt UV lamp (Cole-Parmer, USA) under magnetic stirring. The lamp emitted ultra violet radiation with maximum intensity at 254 nm. After every given 30 min irradiation time, a sample of 5 ml suspension was withdrawn. Then, 4-aminoantipyrene ($\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}$, Aldrich, England) and potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$, Ajax, Australia), were added to the suspension (Torralba *et al.*, 2005), leaved for 30 min to form red color complex, centrifugated and filtered with $0.45\mu\text{m}$ cellulose acetate syringe filter (Filtrex, USA.). The residual concentration of phenol in the solution was measured with UV-VIS Spectrophotometer (U-2900, Hitachi, Japan) at 510 nm.

RESULTS AND DISCUSSION

XRD pattern analysis

Figure 1 shows the XRD patterns of TiO_2 powders synthesized by hydrothermal route treated at 100°C for 1 h. A single phase anatase structure of TiO_2 powders was obtained corresponding with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No.21-1272.

Intensity (a.u.)

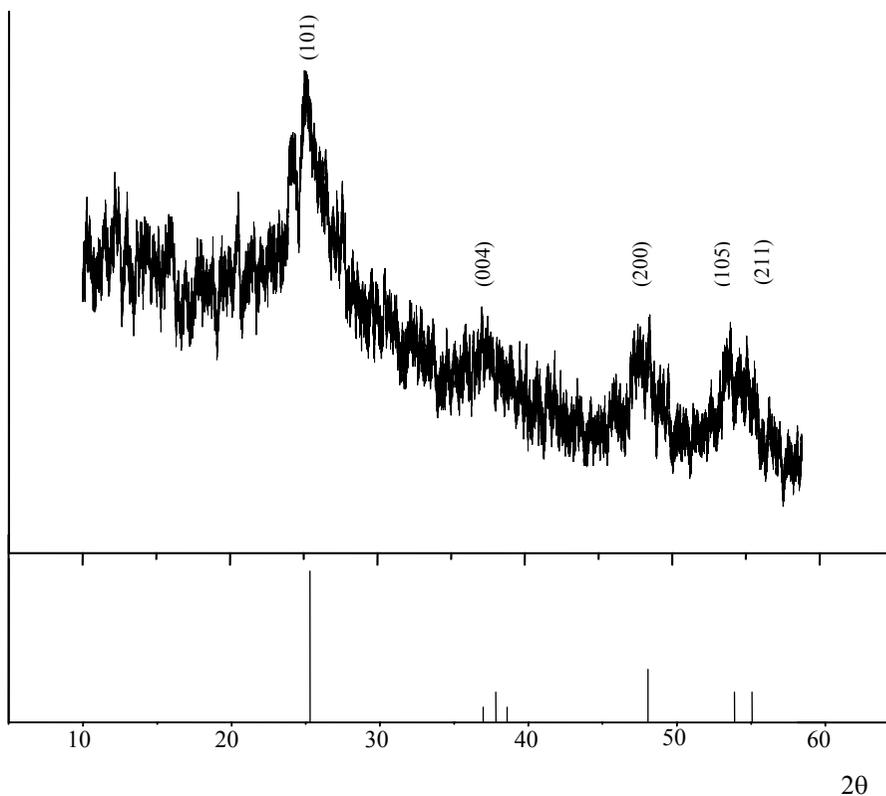


Figure 1 XRD pattern of TiO_2 powders synthesized by hydrothermal route

SEM micrograph and EDS spectra analysis

Figure 2 shows the SEM micrograph and EDS spectrum of TiO₂ powders synthesized by hydrothermal route treated at 100 °C for 1 h. The average particle size was 0.5 μm with irregular in shape and agglomerated together. The element chemical compositions show the characteristic X-ray energy level as follows: oxygen K_α = 0.523 keV and titanium K_α = 4.510 keV and K_β = 4.931 keV, respectively (Woldseth, 1973).

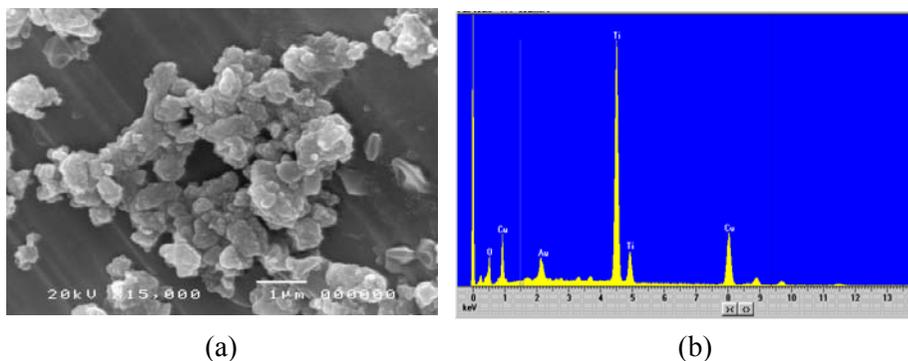


Figure 2 (a) SEM micrograph and (b) EDS spectrum of TiO₂ powders synthesized by hydrothermal route

Photocatalytic activity

The photocatalytic activities of TiO₂ powders were measured on the degradation of phenol in a liquid medium under UV irradiation. The UV–Vis absorption spectral change of the phenol solution with TiO₂ powders is shown in Figure 3. When the time for photodegradation increased, the absorbance and concentration of phenol solution decreased.

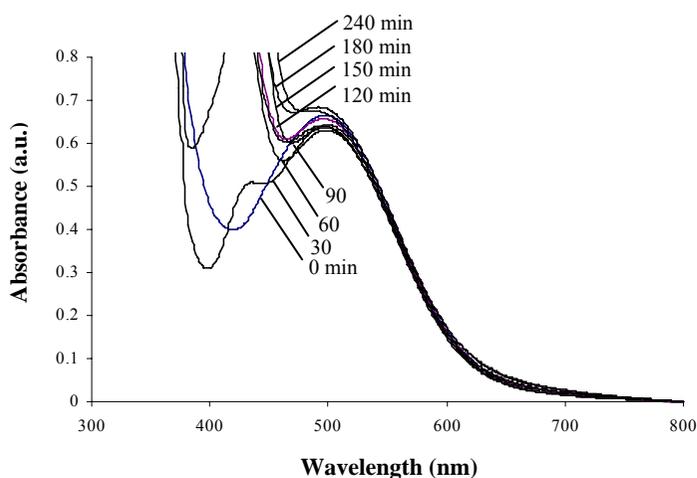


Figure 3 UV–VIS spectrum of photocatalytic degradation phenol over TiO₂ powders under UV irradiation at different time.

Figure 4 represents the variation of phenol concentration (C_t/C_0) with different irradiation time. The photodegradation of phenol over TiO_2 powders under UV irradiation is about 74% for 240 min.

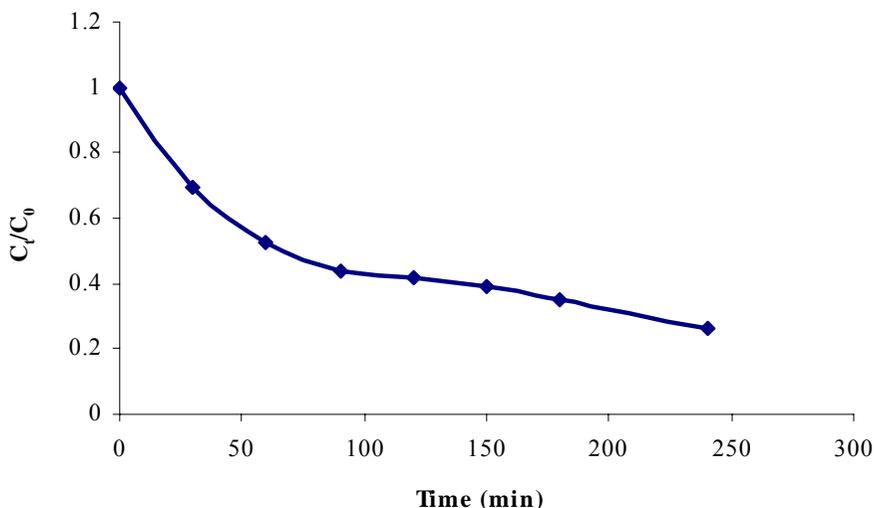


Figure 4 Photodegradation of phenol over TiO_2 powders under UV irradiation.

CONCLUSIONS

Titanium dioxide (TiO_2) powders photocatalysts with UV irradiation activities were successfully synthesized by hydrothermal route with titanium isopropoxide, ammonium hydroxide and nitric acid as starting materials. A single anatase structure of TiO_2 powders were obtained after hydrothermal reaction at 100 °C for 1 h without calcination step. The powders were agglomerated, irregular in shape with the average particle size in the range of 0.5 μm . The elemental constituents of the TiO_2 powders were identified by the energy dispersive value. The photocatalytic experiments can effectively enhance the photoactivities of TiO_2 powders in decomposition of phenol under UV irradiation.

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