

Characterization of Porous SiO₂-TiO₂ Photocatalyst and the Effect of PEG1000 Concentration

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A porous SiO₂-TiO₂ photocatalyst was prepared through co-sol-gel method for photocatalytic degradation of methyl orange. PEG1000 was used as a template to induce porous structure in the material. Photocatalytic degradation was conducted after adsorption equilibrium to identify the contribution of both adsorption and photocatalytic degradation. The prepared material was composed of anatase TiO₂ and amorphous SiO₂. Many small particles formed during grinding also scattered on the surface. The average pore diameter is 16.89 nm and the total pore volume is 0.3644 cm³ g⁻¹ along with specific surface area of 86.27 m² g⁻¹, as calculated by using BJH and BET methods. The SiO₂-TiO₂ composite may have the maximum photocatalytic activity and adsorption capacity using 0.04 mol/L of PEG1000 in the precursor.

Keywords: TiO₂, SiO₂, Photocatalysis, Composite.

INTRODUCTION

Photocatalytic oxidation of organic pollutants becomes one of the most studied new methods^{1,2}. Titanium dioxide is believed to be the most satisfactory photocatalytic material in dealing with environmental pollutant treatment³⁻⁵. People have also paid much effort on preparing porous TiO₂ in order to enhance photocatalytic activity⁶. Another method was to prepare composite materials that were composed of TiO₂ and other oxides, such as SiO₂⁷, ZrO₂⁸, WO₃⁹, Cu₂O¹⁰ and Ta₂O₅¹¹. There was no literature reporting the preparation and properties of porous TiO₂-Al₂O₃ composite photocatalyst that is prepared by one-step sol-gel method until we published a paper recently¹². In this paper, a porous SiO₂-TiO₂ photocatalyst was prepared through co-sol-gel method for photocatalytic degradation of methyl orange. PEG1000 was used as a template and the effect of PEG1000 concentration was also investigated. The materials were characterized by X-ray diffraction, scanning electron microscope, frontier transform infrared spectrophotometer and N₂-adsorption and desorption techniques.

EXPERIMENTAL

Sol-gel preparation: Porous SiO₂-TiO₂ catalyst was prepared according to a co-sol-gel process by the following method. Tetrabutyl titanate [Ti(OBu)₄, 2 mL] and ethyl silicate (0.0075 mL) were slowly added to ethanol under continuous magnetic stirring to obtain a mixed slurry and then PEG1000 template was added to the slurry. Another ethanol-water

solution was added to the mixed slurry to hydrolyze tetrabutyl titanate and ethyl silicate after the mixture was stirred for 1 h. The resulting slurry was still under continuous magnetic stirring until it became a gel. The gel was dried at 90 °C for 12 h and calcined at 500 °C for 3 h. Finally, the catalysts were grinded into fine powders and stored in the dark.

Scanning electron microscope images were taken on a HTACHI S-3400N scanning electron microanalyzer. The samples for SEM imaging were coated with a thin layer of gold film to avoid charging. The crystalline phases of the photocatalysts were measured by X-ray diffraction (XRD) with D/max-rB diffractometer using a CuK_α radiation. FT-IR spectra of the samples were recorded using a FT-IR spectrometer in the wavenumber range of 4000-400 cm⁻¹. The N₂-adsorption and desorption of the sample was measured by F-Sorb 3400 specific surface area and pore size distribution analytical instrument. Specific surface areas and pore size distribution were calculated from the N₂ desorption isotherms, according to Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method, respectively.

Photocatalytic activity: Photocatalytic activity of the photocatalyst was evaluated by measuring degradation rate of aqueous methyl orange under UV irradiation. In each experiment, 0.03 g of the photocatalyst was put into 50 mL of 10 mg/L aqueous solution of methyl orange in a 200 mL beaker. A 20 W UV lamp was suspended 11 cm above the solution. The lamp can irradiate UV light at wavelength of 253.7 nm with the intensity of 1100 mW/cm². In prior to turn on the

lamp, the solution was magnetically stirred for 0.5 h to ensure adsorption equilibrium. Methyl orange concentration was measured by a spectrophotometer (Shanghai Spectrum Instruments 721E) at its maximum adsorption wavelength of 466 nm. The suspensions were filtered through a Millipore filter (pore size 0.45 μm) before measuring. Irradiation time in the subsequent experiments was 0.5 h except for the prolonged examination.

RESULTS AND DISCUSSION

Sol-gel is a widely applied method used for preparation of nano-sized TiO_2 photocatalyst. In order to improve the properties of the prepared photocatalyst, some kinds of techniques such as transition metal doping and composite photocatalyst have been used to enhance the activity of the prepared materials. Porous materials are regarded as one of the promising choice in improving performance on pollutant treatment. Mesoporous and macroporous materials accompanied with large specific surface area are considered to be effective in advanced photocatalytic oxidation efficiency. In order to prepare proper porous material for the above mentioned purpose, template is always needed in the preparation process as the function of providing pore formation director.

In this work, a porous $\text{SiO}_2\text{-TiO}_2$ photocatalyst was prepared through co-sol-gel method using PEG1000 as the template. The XRD pattern of porous $\text{SiO}_2\text{-TiO}_2$ composite calcined at 500 $^\circ\text{C}$ for 3 h is shown in Fig. 1. The diffraction pattern is in accordance to anatase TiO_2 , without apparent peaks like rutile or brookite TiO_2 crystallines. There are no diffraction peaks of any form of crystallines SiO_2 . It indicates that the prepared material is composed of anatase TiO_2 and amorphous SiO_2 . The TiO_2 crystallite size calculated using Scherrer formula from the peak of (101) plane of the sample is 13.92 nm.

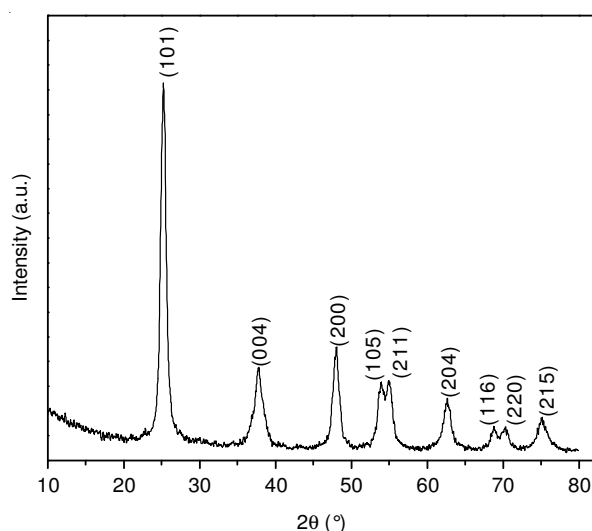


Fig. 1. XRD pattern of porous $\text{SiO}_2\text{-TiO}_2$ composite material calcined at 500 $^\circ\text{C}$ for 3 h

Fig. 2 shows the SEM image of porous $\text{SiO}_2\text{-TiO}_2$ composites calcined at 500 $^\circ\text{C}$ for 3 h. The surface of the sample was rough. Many small particles formed during grinding also scattered on the surface. Surface morphology is quite essential for photocatalytic activity of the materials. It is believed that

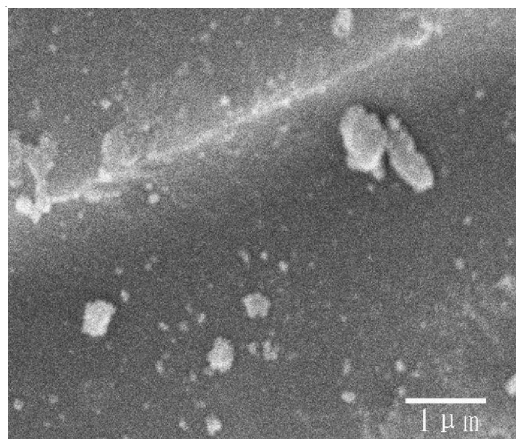


Fig. 2. SEM image of porous $\text{SiO}_2\text{-TiO}_2$ composite material calcined at 500 $^\circ\text{C}$ for 3 h

rough and porous structured surface with high surface area is capable of providing more active centers. The rough surface of porous $\text{SiO}_2\text{-TiO}_2$ composite clearly proves the function of PEG template.

FT-IR spectrum of porous $\text{SiO}_2\text{-TiO}_2$ composite material is shown in Fig. 3. The low-frequency absorption band at 489 cm^{-1} is attributed to the Ti-O-Ti vibration of the samples. The band at 1623 cm^{-1} corresponds to the bending vibration of O-H and the band around 3416 cm^{-1} is assigned to the surface adsorbed water and hydroxyl groups. No clear evidence of Si-O-Si or Si-O-Ti vibration is found in the FT-IR spectra, indicating that the samples were composed of TiO_2 and SiO_2 .

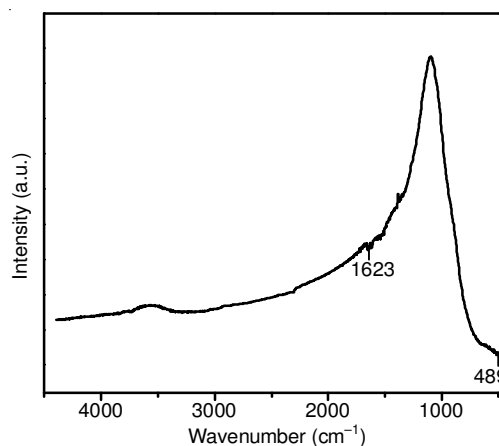


Fig. 3. FT-IR spectrum of porous $\text{SiO}_2\text{-TiO}_2$ composite material calcined at 500 $^\circ\text{C}$ for 3 h

Fig. 4 shows N_2 desorption isotherm (A) and pore size distribution (B) of $\text{SiO}_2\text{-TiO}_2$ composite. With the increase of relative pressure P/P_0 in Fig. 4A, the adsorption of N_2 on the material amplified apparently. When the relative pressure P/P_0 was between 0.7 and 0.9, the increment of adsorption was significant because of capillary condensation of nitrogen molecules in the pores of the material. Fig. 4B clarifies the mesoporous structures of the material. The pore size of the material is below 40 nm and the pore diameter mainly distributes in the range from 10 to 20 nm. The material has the maximum pore volume of 0.03434 $\text{cm}^3 \text{g}^{-1}$ when pore size is 13.87 nm. The average pore diameter is 16.89 nm and the total pore

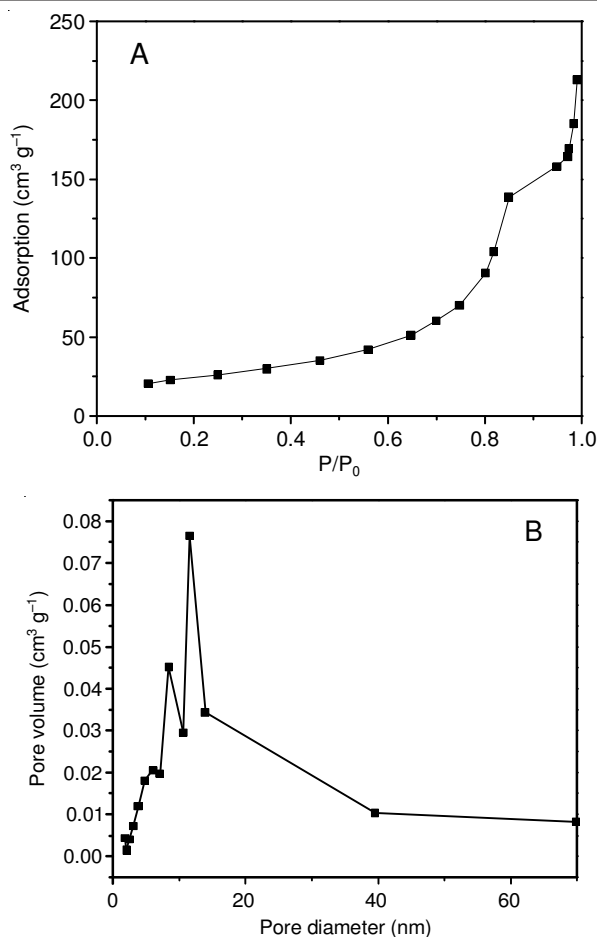


Fig. 4. N₂ desorption isotherm (A) and pore size distribution (B) of porous SiO₂-TiO₂ composite material calcined at 500 °C for 3 h

volume is 0.3644 cm³ g⁻¹ along with specific surface area of 86.27 m² g⁻¹, as calculated using BJH and BET methods.

The concentration of PEG1000 in the sol can influence morphology of porous structure in the material. Fig. 5 showed the photocatalytic efficiency and adsorption capacity of the material increased first with increasing PEG1000 concentration and then they declined at higher PEG1000 concentration. A reason is related to the remaining substances coming from insufficient burning of PEG1000 template during calcinations process. The SiO₂-TiO₂ composite may have the maximum photocatalytic activity and adsorption capacity using 0.04 mol/L of PEG1000 in the precursor.

Conclusion

A porous SiO₂-TiO₂ photocatalyst was prepared through co-sol-gel method using PEG1000 as the template. The diffraction pattern is in accordance to anatase TiO₂, without apparent peaks like rutile or brookite TiO₂ crystallines. The rough surface of porous SiO₂-TiO₂ composite clearly proves the function of PEG template. No clear evidence of Si-O-Si or Si-O-Ti

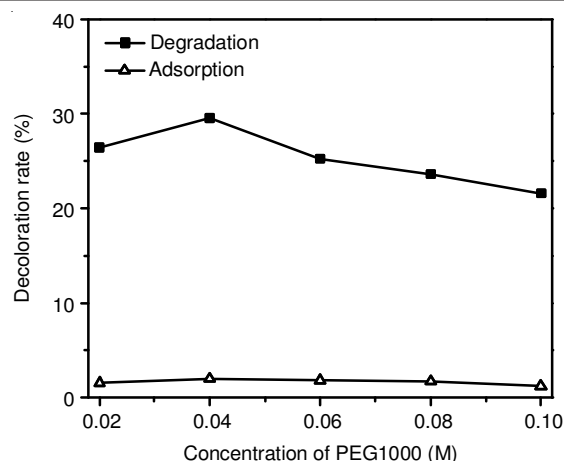


Fig. 5. Effect of concentration of (PEG1000) on the photocatalytic activity and adsorption capacity of porous SiO₂-TiO₂ composite materials

vibration is found in the FT-IR spectra, indicating that the samples were composed of TiO₂ and SiO₂. The pore size of the material is below 40 nm and the pore diameter mainly distributes in the range from 10-20 nm. The SiO₂-TiO₂ composite may have the maximum photocatalytic activity and adsorption capacity using 0.04 mol/L of PEG1000 in the precursor.

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