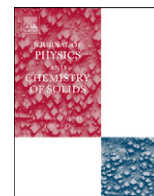




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# Preparation of Pt–TiO<sub>2</sub> composite particles by alcohol reduction method and their photocatalytic activities

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## ABSTRACT

Pt–TiO<sub>2</sub> composite particles were prepared by the alcohol reduction method in aqueous PVP solution and their photocatalytic performances for the degradation of methylene blue (MB) dye were investigated. The organosilane compound was used as a connecting agent between TiO<sub>2</sub> and Pt nanoparticles. X-ray photoelectron spectroscopy analysis revealed that the Pt–TiO<sub>2</sub> composite particles contained Ti, N, and Pt, and these results indicated that Pt nanoparticles were formed on the surface of TiO<sub>2</sub> particles. X-ray diffraction data showed that the Pt–TiO<sub>2</sub> composite particles had only the characteristic diffraction peaks of TiO<sub>2</sub> anatase structure. Pt–TiO<sub>2</sub> composite particles exhibited higher photocatalytic activity than bare TiO<sub>2</sub> particles for the degradation of MB.

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## 1. Introduction

Metal oxide nanoparticles have been researched intensively because of their prospective properties. Among them, TiO<sub>2</sub> has received a great deal of attention due to no harmful influence on environment, low cost, and high chemical stability. Moreover, TiO<sub>2</sub> nanoparticles have a unique optical property, so they are applied to many fields, such as UV-protection [1–3], photochromic devices [4–6], gas sensor [7], dye-sensitized solar cells (DSSCs) [8,9], and photocatalyst [10–12]. TiO<sub>2</sub> have three crystalline phases in general: anatase, rutile, and brookite. Generally, anatase phase TiO<sub>2</sub> shows the best photocatalytic performance compared to the other crystal phase because anatase phase increases the surface redox potentials and improve the lifetime of electron–hole pair compared with rutile phase [10].

Pt–TiO<sub>2</sub> composite particles have been widely studied for the improved photocatalytic performance on the degradation of various organic pollutants. By using Pt–TiO<sub>2</sub> composite particles as a photocatalyst, the charge carrier recombination rates can be reduced, so the photocatalytic performance is enhanced. The role of Pt nanoparticles coated onto the surface of TiO<sub>2</sub> is confirmed by measuring the Fe<sup>3+</sup>-mediated photocurrents generation under UV-illumination [13]. The reason why the Pt–TiO<sub>2</sub> composite particles show higher photocurrent is that Pt nanoparticles on the surface of TiO<sub>2</sub> enhance the rate of interfacial electron transfer on TiO<sub>2</sub> and retard the charge recombination process.

The alcohol reduction method was employed in this study to prepare Pt–TiO<sub>2</sub> composite particles. This method has been studied to produce metal colloids and has been applied to the preparation of metal-supported composite particles because this method has been known as a chemical reducing agent free method [14–16]. In this method, the reducing rate of metal ions is relatively slow, so the size of metal nanoparticles can be controlled and the metal nanoparticles are coated onto the surface of TiO<sub>2</sub> uniformly. When a chemical reducing agent is added to the system, it is hard to control the size of metal particles because the reducing rate is very fast [15].

In this study, the Pt–TiO<sub>2</sub> composite particles were prepared by alcohol reduction method with PVP. The spherical TiO<sub>2</sub> particles were selected in this study because they gave more reproducible results in the coating process compared to the particles of other shapes and they can be characterized relatively easily. The prepared composite particles were characterized by X-ray diffraction (XRD), field emission scanning electron spectroscopy (FE-SEM), energy dispersive spectrometer (EDS), high-resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS). In addition, the degradation of MB under UV irradiation was measured to evaluate the photocatalytic performances of Pt–TiO<sub>2</sub> composite particles.

## 2. Experimental procedure

### 2.1. Materials

The chemicals used in the synthesis were titanium (IV) isopropoxide (TIP, 97%, Sigma-Aldrich), 1-hexadecylamine (HDA,

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90%, Sigma-Aldrich), ethanol (EtOH, > 99.9%, Duksan), and potassium chloride (KCl, > 99.5%, Fluka). The 3-aminopropyl trimethoxysilane (APTMS, 97%, Sigma-Aldrich) was used to bind Pt nanoparticles onto the surface of TiO<sub>2</sub> particle and chloroplatinic acid hydrate (H<sub>2</sub>PtCl<sub>6</sub>, > 99.9%, Sigma-Aldrich) was used as a Pt ion source. Sodium hydroxide (NaOH, > 97%, Sigma-Aldrich) was used as a pH controlling solution for the reduction of platinum ions and polyvinyl pyrrolidone (PVP, K-15, M<sub>w</sub> 10,000, Junsei Chemical Co.) was employed as a nucleation-prompting agent and stabilizer for Pt nanoparticles onto TiO<sub>2</sub> surface. All chemicals were used as received without further purification. The water used in this study was deionized by Milli-Q Plus system (Millipore, France), having 18.2 MΩ electrical resistivity.

## 2.2. Synthesis of pure TiO<sub>2</sub> sphere particles

The pure TiO<sub>2</sub> spherical particles were synthesized by sol-gel method, as reported by Chen et al. [17]. The 1.324 g of HDA was dissolved in 157.8 g of ethanol, followed by the addition of 0.8 mL of KCl solution (0.1 M). To this solution, 4.224 g of TIP was added drop by drop under vigorous stirring at room temperature. After adding TIP, the resulting white TiO<sub>2</sub> suspension was kept static at room temperature for 12 h. Then, the TiO<sub>2</sub> spherical particles were collected by centrifuging, washed with ethanol three times and dried in air at room temperature. The resultant solid products were calcined at 450 °C for 2 h.

## 2.3. Preparation of Pt-TiO<sub>2</sub> composite particles

To prepare APTMS-functionalized TiO<sub>2</sub> particles, 1.0 g of synthesized TiO<sub>2</sub> particles was dispersed in 120 g of ethanol. The 0.036 mL of APTMS was added into the solution with stirring at room temperature for 3 h. The resulting precipitate was centrifuged and washed with ethanol, and the paste was dried at 70 °C for 24 h.

The alcohol reduction method was applied to the preparation of Pt-TiO<sub>2</sub> composite particles. The 0.3 g of APTMS-functionalized TiO<sub>2</sub> particles were dispersed into 77.15 g of ethanol and stirred for 1 h to mix together enough. And 0.1 g of PVP was completely dissolved in 20 g of ethanol. The H<sub>2</sub>PtCl<sub>6</sub> solution, prepared by adding 1 g of H<sub>2</sub>PtCl<sub>6</sub> into 2.73 g of ethanol, was added to the mixture solution and the loading rate of Pt nanoparticles is controlled by the amount of added H<sub>2</sub>PtCl<sub>6</sub> solution (0.05, 0.1, and 0.2 g). The solution was heated and refluxed at 83 °C with stirring. When the mixture solution boiled, 2.05 g of NaOH aqueous solution (0.25 M) was added drop by drop. After 3 h, the color of the solution was turned from white to black. The final products were collected by centrifuging and washed with ethanol and dried at 70 °C for 24 h.

## 2.4. Characterizations

The morphologies of bare TiO<sub>2</sub>, APTMS-functionalized TiO<sub>2</sub> and Pt-TiO<sub>2</sub> composite particles were investigated with FE-SEM (JEOL JSM-6701F). All samples were dried in vacuum oven at 70 °C and coated with carbon by sputtering at 15 mA for 3 min using a coating machine. HR-TEM images were taken through JEOL-2000EXII working at 2000 kV to study the surface morphology of the prepared particles. The samples of HR-TEM are obtained by dispersing a small dropping of the suspension with lower concentration onto a copper grid pre-coated with amorphous carbon. And then, the TEM grid was dried in drying oven at 40 °C for 1 day. The crystal forms of the prepared samples were measured by using X-ray diffraction (XRD) measurement. The XRD patterns were taken by a Rigaku-D/MAX RINT 2000 X-ray diffractometer using Cu Kα radiation ( $\lambda = 1.54 \text{ \AA}$ ) at a scanning

of  $10^\circ \text{ min}^{-1}$ . X-ray photoelectron spectroscopy (XPS) was used to investigate chemical bindings and the composition of the synthesized particles. The XPS data was taken by VG Multilab ESCA 2000 system. The surface area of P25, and bare TiO<sub>2</sub> particles which was synthesized in this study was measured by using BET (Belsorp-mini II).

## 2.5. Photocatalytic activities

MB degradation test under UV irradiation was conducted to evaluate the performance of Pt-TiO<sub>2</sub> composite particles as a photocatalyst. The 10 ppm MB solution was prepared and 0.1 g of prepared particles was added to the solution. The mixture was stirred for 1 h to obtain the equilibrium adsorption state. The reaction started as soon as the UV lamp (UVitec, dual wavelength,  $\lambda = 365 \text{ nm}, 254 \text{ nm}$ ) was turned on. The sampling time was 0, 40, 80, 120, and 160 min and the samples were centrifuged to remove the catalyst. The concentration of MB was measured by using a UV-vis spectrophotometer (Agilent 8453).

## 3. Results and discussion

### 3.1. Characterization of Pt-TiO<sub>2</sub> composite particles

APTMS was used as a chemical binder to immobilize Pt nanoparticles onto the surface of TiO<sub>2</sub> in this study. APTMS plays an important role in preparing Pt-TiO<sub>2</sub> composite particles. When APTMS is absent in this experiment, metal nanoparticles cannot be attached to the surface of TiO<sub>2</sub> homogeneously [16]. Moreover, APTMS treatment has some advantages, such as structural stability, uniform and complete coverage of the surface of TiO<sub>2</sub> particles with Pt nanoparticles [18]. The process of the formation for the Pt-TiO<sub>2</sub> composites is followed; the hydroxyl groups on the surface of TiO<sub>2</sub> react with the methoxy groups in APTMS, so the surface of TiO<sub>2</sub> can be functionalized with amine groups after the APTMS-functionalization process. And Pt nanoparticles are attached to the surface of TiO<sub>2</sub> by the electrostatic interaction between the amine groups of APTMS and Pt nanoparticles [16,19].

Fig. 1 shows the XRD patterns of bare TiO<sub>2</sub> particles, APTMS-functionalized TiO<sub>2</sub> and Pt-TiO<sub>2</sub> composite particles. Among the crystal structures of TiO<sub>2</sub>, anatase phase is preferred because it shows a better photocatalytic performance. Fig. 1a indicates that the structure of TiO<sub>2</sub> is amorphous structure before calcination.

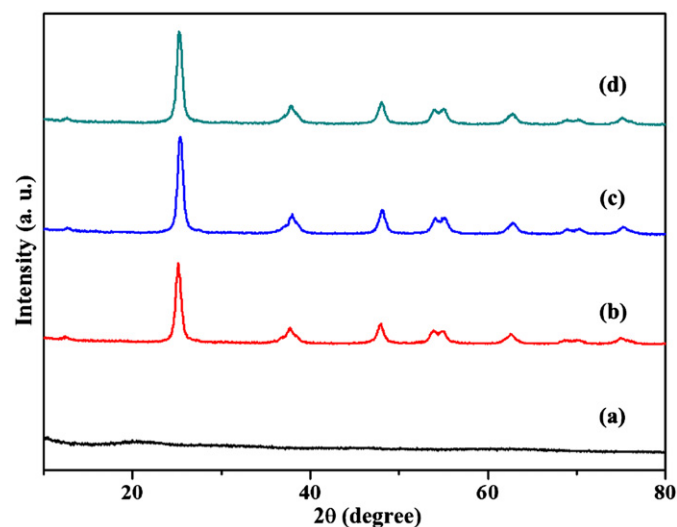


Fig. 1. XRD patterns of (a) not calcined TiO<sub>2</sub>, (b) calcined TiO<sub>2</sub> at 450 °C for 2 h, and (c) APTMS-functionalized TiO<sub>2</sub>, and (d) Pt-TiO<sub>2</sub> composite particles.

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