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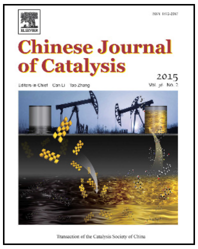

Article

Highly photostable palladium-loaded TiO_2 nanotubes and the active species in the photodegradation of methyl orange

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ABSTRACT

Highly photostable palladium-loaded TiO_2 nanotubes (Pd/TNTs) were prepared by a simple photo-decomposition method and characterized by inductively coupled plasma, X-ray diffraction, UV-visible light diffuse reflectance spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy, N_2 adsorption-desorption, and photocurrent measurement. TEM images showed that the samples had a tubular structure. XPS results revealed that most of the palladium was present as Pd^0. The photocatalytic performance was evaluated by monitoring the catalytic activity for the degradation of methyl orange solution under both UV and simulated sunlight irradiation. Pd/TNTs with 0.3 wt% Pd displayed higher activity than P25. The active species in the photocatalytic process were investigated by using different types of active species scavengers. h_{vb}^+ was the major reactive species in the photodegradation over the Pd/TNTs.

1. Introduction

Due to the non-toxicity and photostability, TiO_2-based nanomaterials are widely used as the semiconductor photocatalyst for water splitting and water and air purification [1–5]. However, the photocatalytic activity of TiO_2 is limited by its intrinsic defects. On the one hand, TiO_2 can be excited only by UV light, which is a small fraction of the solar spectrum. On the other hand, the high recombination rate of the photogenerated electron-hole pairs significantly reduces the photocatalytic efficiency. To overcome these drawbacks, many methods, such as the use of binary oxides, transition metal and nonmetal doping, dye sensitization, and supporting TiO_2 on activated carbon, carbon nanotubes, graphite, and polymeric graphitic carbon nitride, have been used to reduce the recombination rate of photogenerated electron-hole pairs or shift the optical response of TiO_2 to the visible light region [6–12].

In recent years, one dimensional TiO_2 nanostructure materials, including nanorods, nanowires, nanofibers, nanobelts, and nanotubes, have attracted great interest for their peculiar architecture, high mass transport rate, and remarkable light harvest property [13–15]. Among these materials, TiO_2 nanotubes (TNTs) have been widely seen as an optimal nanostructure for enhancing photocatalytic activity. In 1998, Kasuga et al.

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[16] developed a simple hydrothermal method to convert TiO_2 particles into nanotubes. Since then, the practical application of TNTs has been extensively investigated. It is well known that titanate nanotubes made via a hydrothermal treatment are formed by the scrolling of TiO_2 sheets and there are many coordinative unsaturated O atoms and OH groups on the inner and outer surfaces of the nanotubes. To keep the structure of the nanotube intact under irradiation, the amount of OH groups and unsaturated O atoms, which may induce the collapse of the nanotubes during calcination and irradiation, must be decreased [17,18]. In our previous work, we reported the photocatalytic degradation of methyl orange under UV irradiation over Pd-loaded TiO_2 nanofibers, which were prepared from $PdCl_2$ and hydrogen titanate nanotubes by a photodecomposition method [19]. The photocatalytic activity of TiO_2 was enhanced after palladium loading, but the nanotubular structure was destroyed in the process of irradiation, which was detrimental for the photocatalytic activity. Hence, it is essential to explore the preparation of TNTs with high photostability and photocatalytic activity.

In order to induce the response of the semiconductor to visible light, the deposition of noble metals on the semiconductor has been investigated. In particular, Pd loaded on semiconductors exhibits remarkable performance in photocatalytic reactions [20–23]. It is well known that Pd nanoparticles loaded on a semiconductor are used as an electron reservoir to prolong the lifetime of the electron-hole pairs photogenerated by the semiconductor, thereby enhancing the photocatalytic efficiency.

In this work, thermally stable TNTs were used as the support, and Pd nanoparticles were loaded on the TNTs by photodeposition to synthesis Pd/TNTs with high photostability and photocatalytic activity. The samples were characterized by X-ray diffraction (XRD), UV-Vis light diffuse reflection spectroscopy (DRS), transmission electron microscopy (TEM), X-ray photoelectron microscopy (XPS), and N_2 physisorption. In addition, the separation and transport efficiency of the photogenerated electron-hole pairs under UV irradiation were studied by photoluminescence (PL) spectroscopy measurements and photoelectrochemistry experiments. The photocatalytic activity was evaluated by the degradation of methyl orange (MO) under both UV and simulated sunlight irradiation conditions. The active species generated in the process of photodegradation were investigated by free radical and hole scavenging experiments.

2. Experimental

2.1. Synthesis of Pd/TNTs

All reagents were analytical grade and used without further purification.

TNTs were synthesized by the hydrothermal treatment reported in a previous report [16]. Pd/TNTs prepared according to the literature [19] were marked as Pd/TNTsA. TNTs and Pd/TNTs prepared according to the approaches reported previously [24] were marked as TNTsB and Pd/TNTsB, respectively.

Pd/TNTs were synthesized by a photodeposition method. In a typical synthesis, 0.5 g TNTs were dispersed in 20 mL aqueous $Pd(AC)_2$ solution (10 mL H_2O + 10 mL HAC), and the system was vigorously agitated for 12 h. After low energy sonication for 1 h, the mixture was centrifuged. In order to remove $Pd(AC)_2$ solution adsorbed on the surface of the TNTs, the TNTs were washed with distilled water. Then the TNTs were transferred into a quartz tube with 30 mL distilled water. The suspension was irradiated for 4 h by a 300 W high pressure mercury lamp under stirring at ambient temperature. The Pd/TNTsA-*X* and Pd/TNTsB-*X* (*X* refers to the Pd mass percentage) obtained were washed with distilled water and ethanol, and then dried at 40 °C in vacuum.

2.2. Characterization

The morphology and microstructure of the catalysts were analyzed by TEM (Philips T20ST). The chemical state of the elements in the catalysts was determined by XPS (Kratos Axis Ultra DLD multi-technique X-ray photoelectron spectrometer), and all binding energy (BE) was calibrated using C 1*s* (BE = 284.6 eV) as reference. The phase structure of the catalysts was characterized by XRD (Rigaku D/Max-2500 X-ray diffractometer with Cu K_α radiation). The bulk composition of the samples was measured by inductively coupled plasma (ICP-9000, USA Thermo Jarrell-Ash Corp). The optical response of the samples was characterized by UV-Vis DRS (UV3600 UV/Vis spectrometer). The specific surface area of the catalysts was measured at liquid N_2 temperature by the BET method (BET, JW-K). PL data were recorded on an Edinburgh FLS920P spectrophotometer, and the excitation wavelength was 380 nm.

2.3. Photocatalytic activity test

A photoreactor (XPA-7 series) was used to test the photocatalytic activity of the samples. In a typical photodegradation procedure, 0.05 g photocatalyst and 60 mL methyl orange solution (20 mg/L) were put in a quartz tube, which was irradiated with a 300 W high pressure mercury lamp or a 500 W Xe lamp under continuously stirring. At regular time intervals of irradiation, 5 mL of the liquid mixture was withdrawn and centrifuged, and the concentration of methyl orange in the clear solution was measured using a 752/752N UV-Vis spectrometer (Shanghai Sunny Hengping, China) at 463.8 nm, where methyl orange showed its maximum absorption. The results were corrected for the decomposition of methyl orange in the absence of catalyst and its adsorption on the catalyst.

2.4. Photocurrent (PC) measurement

The working electrode was prepared on a rectangle Ti foil (size 8 mm × 8 mm, thickness 0.127 mm, purity > 99.7%, Sigma-Aldrich), which was treated by sonication in acetone, alcohol, and water in sequence for 30 min before use. The cleaned Ti foil was chemically etched with a mixture of HF, HNO_3, and H_2O (V_{HF}:V_{HNO3}:V_{H2O} = 1:4:5) for 30 s followed by rinsing with