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Short Communication

Fabrication of metallic platinum and indium oxide codoped titania nanotubes for the simulated sunlight photocatalytic degradation of diethyl phthalate

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ABSTRACT

Metallic platinum and indium oxide codoped titania nanotubes were fabricated by multicomponent assembly combined with solvothermal treatment. The prepared Pt/In_2O_3–TiO_2 nanotubes exhibited anatase phase with homogeneously dispersed metallic Pt nanoparticles. The material was used as a novel photocatalyst to degrade an aquous phthalate ester under the simulated sunlight irradiation, and the enhanced photocatalytic activity in comparison to In_2O_3–TiO_2 and TiO_2 nanotubes as well as Pt/In_2O_3–TiO_2 nanoparticles was obtained. The enhanced photocatalytic activity is explained in terms of efficient separation of the photogenerated electrons and holes due to the introduction of In_2O_3 and Pt as well as the nanotubular geometries.

1. Introduction

Semiconductor-mediated photocatalytic decomposition of organic pollutants has received considerable attentions. TiO_2 is one of the most investigated semiconductors due to its unique electronic structure and excellent photocatalytic performance. The practical applications of TiO_2 nanoparticles as the solar-irradiation-driven photocatalyst, however, are severely limited due to its large band gap and low quantum yield. For the purpose of the improvement of photocatalytic performance of TiO_2 nanoparticles, intense efforts such as doping through incorporation or decoration with metal ions, nonmetal ions, and semiconductors have been devoted to narrowing the band gap and/or to decreasing the photoexcited holes (h^+_{VB}) and electrons (e^-_{CB}) recombination rate [1]. Another strategy that is important to improve the photocatalytic performance of TiO_2 is to adjust its morphology and porosity. For example, TiO_2 nanotubes that combine the properties of conventional TiO_2 nanoparticles with the distinguishing features of nanotubes have been shown highly competitive and in many cases favorable to achieve the enhanced photocatalytic activity [2]. Compared with TiO_2 nanoparticles, the open mesoporous morphology of TiO_2 nanotubes can efficiently transfer the electrons along the 1D path, while its high specific surface area can lead to faster surface photocatlytic reaction rate [3,4].

Herein, metallic platinum and indium oxide codoped titania nanotube system (Pt/In_2O_3–TiO_2) was demonstrated for the purpose of further improve the photocatalytic activity of TiO_2-based materials. In_2O_3 is a low band gap (2.8 eV) semiconductor, and TiO_2 coupled with In_2O_3 is expected to promote the efficient separation of the h^+_{VB}–e^-_{CB} pairs [5]. Deposition of metallic platinum particles throughout TiO_2 nanotubes is based on their surface plasmon effect (SPR), which can lead to field enhancement in the vicinity of Pt particles and thus allowing more efficient charge transfer by capturing the e^-_{CB} [6]. Additionally, the nanotubular geometries of TiO_2 are expected to be beneficial for the enhanced photocatalytic activity of the prepared composite photocatalyst.

Conventionally, TiO_2 nanotubes are fabricated by anodization of Ti foil, however, the method is time-consuming and special conditions are needed. As for incorporation of the components within TiO_2 nanotubes, ion-exchange or impregnation method is generally applied [7]. The process suffers from problems such as leaching of the doped components, poor control over the loadings of the doped component, and aggregation of the doped component. In the case of noble metal doping, the generally used photodeposition and chemical reduction methods have the disadvantages of hard control of the size of the metal and severe aggregation of the metal clusters [6,8]. Herein, Pt/In_2O_3–TiO_2 nanotubes were fabricated by multicomponent assembly approach combined with solvothermal treatment using titanic acid nanotubes as the staring materials (Scheme 1a). Subsequently, their simulated sunlight photocatalytic activity was evaluated by the degradation of a kind of light insensitive compound, diethyl phthalate (DEP). DEP is a member of phthalate ester family that has wide

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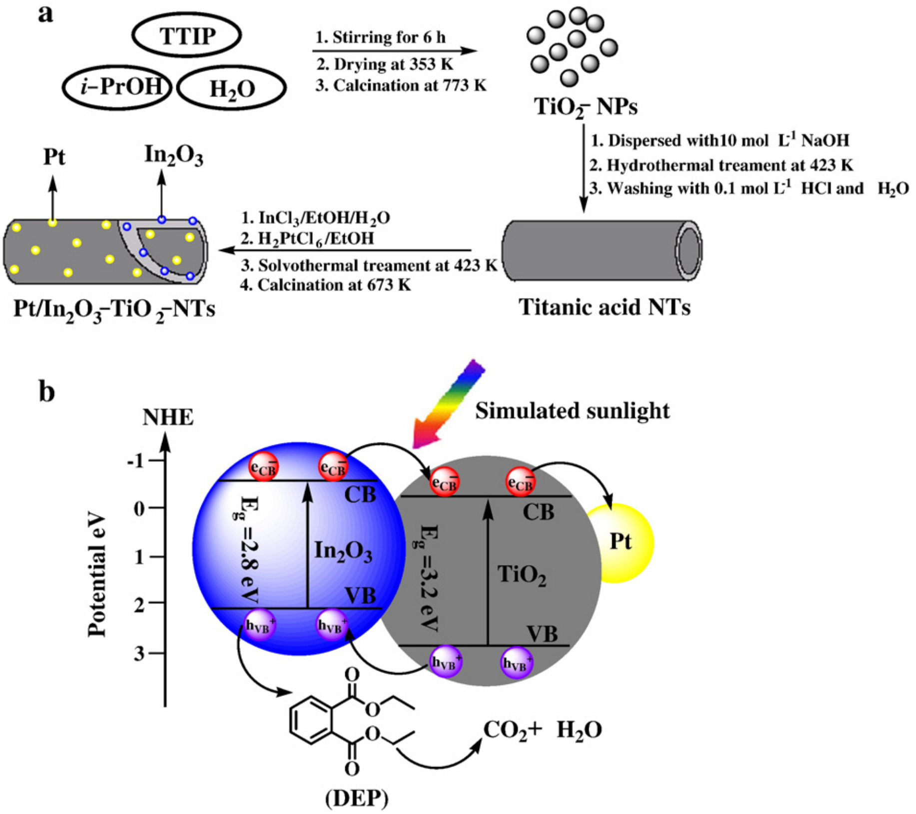

Scheme 1. (a) Process of fabrication of the Pt/In_2O_3–TiO_2–NTs; and (b) band gap structure and the simulated sunlight photocatalytic degradation of an aqueous DEP over the Pt/In_2O_3–TiO_2–NTs.

applications in the fields of industry and agriculture. The release of phthalates into the ecosystem or wastewater effluent has caused many human diseases and pollution due to their endocrine disrupting activity. The present work is expected to provide an efficient method to control the phthalate ester pollutions in water.

2. Experimental

2.1. Catalyst preparation

2.1.1. Titanic acid nanotubes

Titanium tetraisopropoxide (TTIP, 3.0 mL) was dissolved in isopropanol (*i*-PrOH, 18 mL) under vigorous stirring at room temperature for 0.5 h. Water (0.9 mL) was then added dropwise into the TTIP/*i*-PrOH solution under vigorously stirring for 6 h. The mixture was dried at 353 K for 12 h followed by calcination at 773 K for 3 h. The resulting TiO_2 powder (0.5 g) was dispersed into NaOH solution (10 mol L^{-1}, 25 mL), and the suspension was ultrasonicated for 30 min followed by hydrothermal treatment at 423 K for 48 h (heating rate of 2 K min^{-1}). The obtained precipitate was washed with HCl (0.1 mol L^{-1}) and water to pH 6–7, and then it was dried at 353 K overnight.

2.1.2. Pt/In_2O_3–TiO_2 nanotubes

The prepared titanic acid nanotubes (0.46 g) were dispersed into ethanol (EtOH, 16 mL) under vigorous stirring at room temperature. Subsequently, $InCl_3$•$4H_2O$ (0.14 g)/H_2O (0.66 mL)/EtOH (2 mL) and H_2PtCl_6•$6H_2O$ (0.03 g)/EtOH (2 mL) solutions were added dropwise into the above suspension successively under vigorously stirring. The resulting mixture was suffered from solvolthermal treatment at 423 K for 6 h, and the resulting precipitate was dried and washed with deionized water. The obtained powder was further dried at 353 K overnight prior to annealing in nitrogen gas flow at 673 K for 0.5 h. The final product was denoted as Pt/In_2O_3–TiO_2–NTs-(x, y), where x and y represent the doping of Pt and In_2O_3 (%), respectively.

2.1.3. Pt/In_2O_3–TiO_2 nanoparticles

TTIP (1.7 mL) was dissolved in *i*-PrOH (16 mL) under vigorous stirring at room temperature for 0.5 h, and then $InCl_3$•$4H_2O$ (0.14 g)/H_2O (0.66 mL)/EtOH (2 mL) and H_2PtCl_6•$6H_2O$ (0.03 g)/EtOH (2 mL) solutions were added dropwise into the above suspension successively under vigorously stirring. The subsequent steps are the same as those of the Pt/In_2O_3–TiO_2–NTs, and the product was denoted as Pt/In_2O_3–TiO_2–NPs-(x, y).

2.2. Catalyst characterization

Details are presented in Electronic Supplementary Information (ESI).

2.3. Photocatalytic tests

The simulated sunlight irradiation was supplied by a self-made solar simulator equipped with a 350 W xenon lamp and an IR cut filter. The equipment can provide uniform solar irradiance with the intensity from 0.1 W cm^{-2} (AM1.5 G artificial sunlight, ASTM E927-05 Class A standard) to 0.3 W cm^{-2}; meanwhile, its spectrum matches well with the natural solar light with main emission from 320 nm to 680 nm.

The photocatalytic reaction was carried out in a self-made quartz photoreactor with a diameter of 63 mm. The suspension containing the solid catalyst (100 mg) and an aqueous DEP (10 mg L^{-1}, 100 mL) solution was ultrasonicated for 10 min and then stirred for 60 min in the dark. The reaction temperature was maintained at 303 ± 2 K by circulation of water through an external cooling jacket. Changes of DEP concentrations were monitored by a Shimadzu LC-20A HPLC: C_{18}