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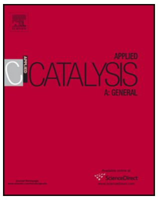

Simultaneous Pd^{2+} doping and Pd metal deposition on $(BiO)_2CO_3$ microspheres for enhanced and stable visible light photocatalysis

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ABSTRACT

The band structure and charge separation are two important factors that could largely determine the photocatalysis efficiency. In the present work, novel Pd/Pd^{2+} co-modified $(BiO)_2CO_3$ microspheres (Pd-BOC) were fabricated by a facile in situ one-pot hydrothermal process. The microstructure, interfical structure and electronic structure were investigated with a combined experimental and theoretical approach. The Pd-BOC was applied for photocatalytic removal of NO in air under visible light irradiation. The simultaneously Pd^{2+} doped and Pd metal deposited $(BiO)_2CO_3$ microspheres exhibited highly enhanced visible light photocatalytic activity and stability toward NO removal. DFT calculation indicated that the Pd^{2+} doping could narrow the band gap by taking part in the formation of valence band. The Pd deposition could improve the charge separation and transfer as revealed with surface photovoltage spectroscopy and transient photocurrent density measurement. These favorable two factors contributed to the enhanced visible light absorption and promoted charge separation, which led to dramatically enhanced visible light activity. The present work could provide new perspectives in co-modification of photocatalysts for high-performance applications.

1. Introduction

Nanomaterials for photocatalysis has attracted numerous interests in recent years because they can offer a feasible way to address energy or environment issues by directly harvesting energy from solar light and indoor illumination [1–5]. During the past decades, many semiconductor photocatalytic materials have been synthesized and the TiO_2 has been most widely investigated [6–9]. However, the high charge recombination rate and the necessity to use ultraviolet have limited the application of TiO_2 [10]. Therefore, the development of alternative visible light driven photocatalysts remains significance for practical applications. In general, the band structure and charge separation are two important factors that could largely determine the photocatalysis efficiency.

Recently, Bi-based photocatalysts have been investigated widely [11–18]. As an emerging Bi-based semiconductor, $(BiO)_2CO_3$ has received increased attention because of its unique morphology and multifunctional application in photocatalysis, supercapacitor, sensing and antibacterial [19–23]. However, as a photocatalyst, the visible light utilization efficiency is still low and the recombination rate of photo-generated electron-hole pairs of pure $(BiO)_2CO_3$ is high [7,11]. Many explorations have been carried out to enhance the visible-light photocatalytic activity of $(BiO)_2CO_3$, for instance, morphology control, element doping, metal deposition, and heterostructure formation in the aim of increasing the visible light utilization and charge separation efficiency [19,20,24–32]. Although much progress has been made on promoting the visible light photocatalysis of $(BiO)_2CO_3$, to the best of our knowledge, the modification of $(BiO)_2CO_3$ with Pd species has never been reported.

Here, we developed a facile in situ one-pot hydrothermal method for the synthesis of Pd/Pd^{2+} co-modified $(BiO)_2CO_3$ microspheres (Pd-BOC). The charge separation and transfer dynamics

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were investigated with surface photovoltage spectroscopy and transient photocurrent density measurement. The Pd-BOC exhibited highly enhanced photocatalytic activity for NO removal under visible light in comparison with pure $(BiO)_2CO_3$, N-doped $(BiO)_2CO_3$ and C_3N_4. The promotion effect of Pd/Pd^{2+} co-modification can be ascribed to the Pd^{2+} doping that reduced the band gap and the SPR effect of metallic Pd particles that improved the visible light absorption and separation of electron/hole pairs. This work could provide new insights into the design and modification of photocatalytic materials with simultaneous metal ion doping and metal deposition.

2. Experimental

2.1. Synthesis

All chemicals were reagent grade and used without further treatment. The Pd/Pd^{2+} co-modified $(BiO)_2CO_3$ (Pd-BOC) microspheres were synthesized as follows: sodium carbonate (0.46 g) was first dissolved in distilled water (70 mL) in a 100 mL autoclaved Teflon vessel and the mixture was then stirred for 10 min. Then, 5 mL of 0.04 mol/L palladium nitrate solution was added and stirred for further 10 min. Afterward, bismuth citrate (1.60 g) was added to the solution, and the mixture was stirred for 30 min to ensure all reagents were well-mixed. The resulting precursor suspension was hydrothermally treated at 160 °C for 24 h. After the mixture was cooled to room temperature, the resulting solid was filtered, washed with water and ethanol four times, and dried at 70 °C for 12 h to obtain the final sample. Pure $(BiO)_2CO_3$ (BOC) microspheres were prepared without adding palladium nitrate.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer equipped with intense Cu Kα radiation (Model D/max RA, Rigaku Co., Japan). The morphology, structure and chemical composition of the obtained products were analyzed using scanning electron microscope (SEM, JEOL model JSM-6490, Japan), transmission electron microscope (TEM, JEM-2010, Japan), and high-resolution transmission electron microscope (HRTEM). The Brunauer–Emmett–Teller (BET) specific surface area (SBET) of the samples were determined using a nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 100 °C for 12 h prior to measurements. X-ray photoelectron spectroscopy (XPS) measurement was carried out to investigate the surface chemical compositions and states with Al Kα X-ray ($h\nu = 1486.6$ eV) radiation source operated at 150 W (Thermo ESCALAB 250, USA). The UV–vis diffuse reflection spectra (UV–vis DRS) were obtained for the dry-pressed disk samples by using a Scan UV–vis spectrophotometer (UV-2450, Shimadzu, Japan) with 100% $BaSO_4$ as the standard sample. The surface photovoltage spectroscopy (SPS) measurements were conducted with a home-built apparatus, equipped with a lock-in amplifier (SR830) synchronized with a light chopper (SR540). Photoelectrochemical measurements were conducted with a three-electrode quartz cell on the CHI-660B electrochemical system. The saturated calomel electrode was the reference electrode, and platinum wire was used as counter electrode. The BOC and Pd-BOC were coated on the ITO glass to form stable films as working electrodes. The electrolyte was 0.1 M Na_2SO_4 solution. All the photoelectrochemical measurements are performed under visible light irradiation ($\lambda > 420$ nm).

2.3. Band structure calculation with density functional theory

Density functional theory (DFT) calculations were carried out using the Vienna ab initio simulation package (VASP). The generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) was used for the exchange correlation functional. The interaction between the core and the valence electrons was described with the projector augmented wave (PAW) method. The cutoff energy was set at 450 eV. Geometry relaxations were carried out until the residual forces on each ion converged to being smaller than 0.02 eV. A cell containing 64 atoms with 16 bismuth atoms, 8 carbon atoms and 40 oxygen atoms was used as the simulation $(BiO)_2CO_3$ model. We relaxed the $(BiO)_2CO_3$ to obtain an optimal structure. Then, based on the optimal structure of $(BiO)_2CO_3$, we construct Pd doped $(BiO)_2CO_3$ model by substituting a Pd atom with a Bi atom in ${(BiO)_2}^{2+}$ layer of $(BiO)_2CO_3$. The electronic structures were calculated based on the fully relaxed lattice parameters and ionic positions. For the calculation of the density of states (DOS), Monkhorst-Pack k-points were set to be 10 × 2 × 10.

2.4. Evaluation of photocatalytic activity

The visible light responsive photocatalytic activity of the as-synthesized samples was evaluated by removing NO at ppb-level in a continuous flow reactor (Figs. S1 and S2). The reactor had a capacity of 4.5 L (30 × 15 × 10 cm), made of polymeric glass and covered with Quartz-Glass. A commercial tungsten halogen lamp (100 W) was vertically placed outside and 20 cm above the reactor. A UV cut-off filter (420 nm) was used to remove UV light from the lamp. For the photocatalytic activity test, the as-prepared sample (0.20 g) was dispersed in distilled water (50 mL) in two beakers via ultrasonic treatment for 10 min and then spread on two glass dishes (12 cm in diameter). The coated dishes were dried at 60 °C and were placed at the center of the reactor after being cooled to room temperature. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to about 600 ppb by air streaming. The flow rates of the air stream and NO were controlled at 2.4 L min^{-1} and 15 mL min^{-1}, respectively. The gas streams were premixed completely by a gas blender. The relative humidity was controlled at 50% in the air stream. When the adsorption–desorption equilibrium was achieved, the lamp was turned on. The concentration of NO was measured every minute by a NO_x analyzer (Thermo Scientfic, 42i-TL), which also monitored the concentrations of NO, NO_2 and NO_x (NO_x represents NO + NO_2). The removal ratio (η) of NO was calculated using $\eta(\%) = (1 - C/C_0) \times 100\%$, where C and C_0 represents the outlet and inlet concentration of NO.

3. Results and discussion

3.1. Phase structure

The crystal structure of the as-prepared sample was analyzed by XRD, as shown in Fig. 1a. The typical diffraction peaks of the samples can be indexed to the tetragonal structure of $(BiO)_2CO_3$ (JCPDS-ICDD Card No. 41-1488) [19]. Compared with pure $(BiO)_2CO_3$, metallic palladium ($2\theta = 39.9$o) (JCPDS-ICDD Card No. 46-1043) can be identified on Pd-BOC sample [33]. The formation of Pd nanoparticles is originated from the in situ reduction of Pd^{2+} by the citrate ions. Note that no peaks related to palladium oxide can be observed. The enlarged view in Fig. 1b shows that the dominant peak of Pd-BOC shifts to lower angle, which indicates that the crystal structure of BOC is altered due to potential Pd doping. Because palladium nitrate is added in the precursor solution, the Pd^{2+} ions may be in situ doped into the crystal structure of BOC during hydrothermal treatment.