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Grain boundary engineered metal nanowire cocatalysts for enhanced photocatalytic reduction of carbon dioxide

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ABSTRACT

The combination of metal cocatalysts with light-harvesting semiconductors is a promising route to improving the photocatalytic performance in CO_2 reduction reaction. However, owing to the high H_2O activation ability of metal surface, the H_2 evolution from water as a side reaction greatly decreases the activity and selectivity for CO_2 reduction. Herein, we demonstrate that the photocatalytic performance in CO_2 reduction can be promoted by grain boundaries (GBs) on metal cocatalysts. In this work, metal (Rh and Pd) nanowires with high density of GB were loaded on TiO_2 nanosheets, which acting as cocatalysts effectively reduce the H_2 evolution and greatly enhance the photocatalytic performance in CO_2 reduction as compared with the corresponding metal nanoparticle cocatalysts without GBs. Two effects are believed to contribute to this enhancement: (1) nanowire structure facilitates the interfacial electron transfer from TiO_2 to metal cocatalysts; (2) the GB terminations on the surface of metal cocatalysts are catalytically active sites for CO_2 reduction reaction. This work highlights the rational architectural design of cocatalyst for enhanced photocatalytic performance.

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1. Introduction

Photocatalytic reduction of carbon dioxide with water to value-added chemicals such as CO ($CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$) and CH_4 ($CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$) is an attractive and green route to address the depletion of fossil fuels and concomitant global warming problem [1–4]. Since the pioneering work by Inoue et al. [5], many semiconductors, such as TiO_2 [6,7], $ZnGe_2O_4$ [8], CeO_2 [9], and $W_{18}O_{49}$ [10] have been developed as photocatalysts in CO_2 reduction reaction. Among them, TiO_2 is the most widely used semiconductor due to a number of advantages including relatively high photocatalytic activity, low cost and toxicity, and good chemical and thermal stability [2,6,7]. However, the photocatalytic efficiency of bare semiconductors in CO_2 reduction reaction is greatly limited by the serious photo-generated electron-hole recombination in the bulk semiconductor as well as high activation energy of highly stable CO_2 molecules on the semiconductor surface [11,12].

Recently, noble metal, such as Pt [13], Pd [14], Ag [15], Au [16], and Cu [17] have been widely used as reduction cocatalysts to combine with the semiconductors in promoting the photocatalytic performance in CO_2 reduction reaction. On one hand, the metal cocatalysts extract the photo-induced electrons from the semiconductors in promoting the separation of electrons and holes [18]. On the other hand, the cocatalysts serve as reaction active sites in reducing the activation potential for CO_2 molecules, thus promoting the surface reaction in CO_2 reduction [19,20]. However, as reported by our groups and others, resulted from the high H_2O activation ability of metal cocatalyst surface, the photocatalytic reduction of H_2O to H_2 ($2H^+ + 2e^- \rightarrow H_2$) is a preferential or competitive reaction during the process of CO_2 reduction, which not only reduces the product yields owing to the loss of electrons in the side reaction, but also lowers the product selectivity [7,14]. Furthermore, the electron extraction ability of the metal cocatalysts remains to be improved in realizing the high yield of products for practical applications [21].

Surface and interface design of cocatalysts is a promising route to increase the photocatalytic activity and selectivity for CO_2

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reduction [22]. Adjusting the surface parameters of cocatalysts such as the composition, facet and phase not only realizes the high adsorption and activation ability for specific reactant molecules, but also prevents the side or back reactions [14,23,24]. While the interface parameters between the semiconductor and cocatalysts, such as interfacial area and facet, can be tailored to enhance the efficiency of electron transfer from semiconductor to the cocatalyst for surface reduction reaction [25,26]. Herein, we demonstrate that the photocatalytic performance in CO_2 reduction reaction can be promoted through increasing the density of grain boundary (GB) on the metal cocatalysts. In this work, metal (Rh and Pd) nanowires with high density of GBs were *in situ* grown on TiO_2 nanosheets to form semiconductor nanosheet supported nanowire cocatalyst hybrid structures. It was found that the nanowire structure facilitated the interfacial electron transfer from TiO_2 to metal cocatalysts, while the GB terminations on the surface of metal cocatalysts acted as highly active reaction sites for CO_2 reduction. As a result, both the photocatalytic CO_2 reduction activity and selectivity of the nanowire cocatalysts were superior to those of corresponding metal nanoparticle cocatalysts without GBs. As far as we known, it is the first report on the GB engineering on the surface of cocatalyst for enhanced photocatalytic performance.

2. Experimental

2.1. Chemicals

Sodium hexachlororhodate(III) (Na_3RhCl_6, Aldrich, 206288), poly(vinyl pyrrolidone) (PVP, M.W. ≈ 55000, Aldrich, 856568), sodium iodide (NaI, Aladdin, S104084) and sodium tetrachloropalladate(II) (K_2PdCl_4, Aladdin, P106044) were used in the synthesis. All other chemicals were of analytical grade and purchased from *Sinopharm Chemical Reagent* Co., Ltd. All the chemicals were used as received without further purification. The water used in all experiments was de-ionized (DI).

2.2. Preparation of photocatalysts

2.2.1. Synthesis of TiO_2 nanosheets
The TiO_2 nanosheets were synthesized by modifying a method in literature with hydrofluoric acid as a capping agent [27]. Caution! Hydrofluoric acid is extremely corrosive and toxic, and should be handled with extreme care.

2.2.2. Synthesis of TiO_2-Rh samples
In a typical synthesis, Na_3RhCl_6 (10 mg), NaI (75 mg), sodium ascorbate (NaAA, 40 mg) and PVP (160 mg) were dissolved in a mixture of 5 mL ethylene glycol (EG) and 1 mL H_2O suspension containing 100 mg TiO_2 nanosheets. The mixture was sonicated for around 5 min and heated at 170 °C for 5 min and 30 min to obtain TiO_2 nanosheets supported short and long Rh nanowires, respectively [28]. The as-obtained products were collected by centrifugating and washing several times with acetone, water and ethanol, and drying at 45 °C in vacuum. TiO_2 nanosheets supported Rh nanoparticles was prepared under the same experimental conditions as the TiO_2 supported Rh nanowires except without use of NaI, which was heated at 170 °C for 30 min. The TiO_2 nanosheets supported long Rh nanowires was further annealed at 280 °C under Ar protection for 3 h to obtain the annealed TiO_2-Rh nanowires.

2.2.3. Synthesis of TiO_2-Pd samples
In a typical synthesis of TiO_2 supported Pd nanowires, K_2PdCl_4 (7.6 mg) and PVP (800 mg) were dissolved in 10 mL of aqueous suspension containing 100 mg TiO_2 nanosheets. The resulting homogeneous suspension was transferred to a 20-mL Teflon-lined stainless-steel autoclave and then heated at 200 °C for 4 h before it was cooled to room temperature. The as-obtained products were collected by centrifugating and washing several times with acetone, water and ethanol, and drying at 45 °C in vacuum. As for the synthesis of TiO_2 supported Pd nanoparticles, PVP (120 mg) were dissolved in 8 mL EG suspension of TiO_2 nanosheets (100 mg), which was injected into a 50-ml flask, and pre-heated under magnetic stirring at 160 °C. Then 3 mL of EG solution containing K_2PdCl_4 (7.6 mg) was then added into the flask, and the reaction was allowed to proceed at 160 °C for 3 h. The product was collected and dried at 45 °C in vacuum. The TiO_2 nanosheets supported Pd nanowires was further annealed at 280 °C under Ar protection for 3 h to obtain the annealed TiO_2-Pd nanowires.

2.3. Sample characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. Powder X-ray powder diffraction (XRD) patterns were recorded by using a Philips X'Pert Pro Super X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectra (XPS) were collected on an ESCALab 250 X-ray photoelectron spectrometer, using nonmonochromatized Al-Kα X-ray as the excitation source. UV–vis-NIR diffuse reflectance data were recorded in the spectral region of 200–800 nm with a Shimadzu SolidSpec-3700 spectrophotometer. Photoluminescence (PL) spectra were recorded on a HITACHI F-7000 Spectrofluorometer. The molar ratios of metal to TiO_2 were measured as follows: the samples were dissolved with a mixture of HCl and HNO_3 (3:1, volume ratio), which was then diluted with 1% HNO_3. The concentrations of metal were then measured with a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS). The weight ratios of metal to TiO_2 were determined by sample weighing prior to the dissolution of metal for the ICP-MS measurements.

2.4. Photoelectrochemical measurements

3.0-mg as-synthesized products were dispersed in a mixture of 10-μL ethanol and 10-μL nafion, which were then uniformly spin dropped onto a 1 cm × 1 cm indium tin oxide (ITO)-coated glass by a spin coater (SC-1B, China). Subsequently, the ITO-coated glass was heated at 80 °C in a vacuum oven for 1 h. The photocurrents were measured on a CHI 660D electrochemical station (Shanghai Chenhua, China) in ambient conditions under irradiation of a 300-W Xe lamp (Solaredge 700, China). UV light was used as the illumination source, which was realized by using a 400-nm cutoff filter (short-wave-pass). The power density of UV light was measured to be 2.7 mW cm^{-2}. Standard three-electrode setup was used with the ITO coated glass as photoelectrode, a Pt foil as counter electrode, and a Ag/AgCl electrode as reference electrode. The three electrodes were inserted in a quartz cell filled with 0.5-M Na_2SO_4 electrolyte. The photoresponse of the prepared photoelectrodes (i.e., *I-t*) was operated by measuring the photocurrent densities under chopped light irradiation (light on/off cycles: 60 s) at a bias potential of 0.4 V *vs.* Ag/AgCl for 400 s. The electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 10^{-1}–10^5 Hz with an AC voltage amplitude of 10 mV at a bias potential of 0.4 V *vs.* Ag/AgCl.

2.5. Photocatalytic CO_2 reduction measurements

CO_2 photocatalytic reduction reaction was typically conducted in a 100 mL reactor (Perfect Light Company, Beijing). To remove possible trace organic contaminants, all the samples were treated at 160 °C for 3 h in air. The heat treatment at 160 °C can not influence the morphology of the samples with the reason that the