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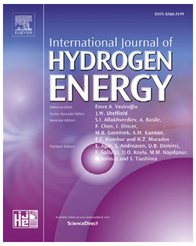

Enhancing photocatalytic H_2 evolution from water on CuO-Co_3O_4/TiO_2: The key roles of Co_3O_4 loading amounts

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ABSTRACT

Spatially controlled co-loading of both oxidation and reduction cocatalysts on semiconductor photocatalysts has been demonstrated to be favorable for photogenerated charge separation and thus enhanced photocatalytic activity. Herein, we presented a simple ball-milling method to improve photocatalytic H_2 production of TiO_2 by co-loading of oxidation cocatalyst Co_3O_4 with reduction cocatalyst CuO, wherein the Co_3O_4 loading amount was significant especially for TiO_2 loaded with sufficient or optimum CuO. In comparison with that on TiO_2 loaded with only CuO, the photocatalytic H_2 production from water over TiO_2 photocatalyst co-loaded with CuO and trace Co_3O_4 was enhanced by approximately 5.5 times, even though complex spatial control was not adopted. In contrast, remarkable improvement of photocatalytic activity after Co_3O_4 co-loading was only observed on TiO_2 photocatalysts loaded with less CuO in the presence of methanol. Better separation of photogenerated charges on the surface of dual-cocatalysts modified TiO_2 was further demonstrated by decreased luminescence as well as increased photogenerated electrons and hydroxyl radicals as compared to those loaded with only CuO.

Introduction

Photocatalytic water splitting into hydrogen has been considered as a promising strategy to solve the global energy and environmental issues [1–5]. The overall efficiency of photocatalytic water splitting is determined by the balance of thermodynamics and kinetics of the three major steps: absorption of light, charge separation and surface reduction or oxidation reactions [6,7]. The photogenerated electrons and holes may recombine if there are no suitable active sites available on the surface of semiconductors [8]. Therefore it is essential to load proper cocatalysts on the surface of photocatalysts to provide the active sites/reaction sites and facilitate oxidation or reduction reactions while suppressing the charge recombination and reverse reactions [9].

In general, the overall reaction rate is relevant to both oxidation and reduction reactions, so dealing well with both oxidation and reduction half reactions are equally important. Therefore great efforts have been made to co-load both reduction and oxidation cocatalysts on the surface of photocatalysts. In particular, greatly enhanced H_2 evolution was observed from water containing S^{2-} and SO_3^{2-} ions on dual cocatalysts modified sulfide [10] or oxysulfide photocatalysts [11]. The feasibility of modifying other semiconductor photocatalysts such as GaN: ZnO with both reduction and oxidation

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cocatalysts to improve overall water splitting activity was also demonstrated in 2010 although the loading amount of cocatalysts is relatively low and they are randomly distributed [12,13]. Li et al. [14] found that the coloading of Pd and IrO_x on TiO_2 could dramatically improve the photocatalytic H_2 production activity and reduce CO/H_2 ratio in the presence of methanol, especially when the two cocatalysts are in intimate contact. However, the activity improvement is usually observed in those with insufficient reduction cocatalyst loading and detrimental effect of co-loading oxidation cocatalyst was demonstrated in photocatalysts with sufficient reduction cocatalyst loading [15]. Recently, spatially separated loading of dual cocatalysts have attracted more and more attention accordingly to further improve the photocatalytic H_2 evolution of photocatalysts. For example, the spatial charge separation could be realized by selective deposition of suitable reduction and oxidation cocatalysts onto the different facets of photocatalysts since photogenerated charge could be separated between their different facets [16,17]. Domen et al. [15] presented a general method to realize the spatial separation of cocatalyst through a hollow structure. Pt and IrO_2 (or CoO_x) nanoparticles were loaded on the inner and the outer surface of Ta_3N_5, respectively, to facilitate the separation and migration of photoexcited electrons and holes toward the inner and outer surfaces, and thus the charge recombination and reverse reactions were suppressed. Although spatially separated co-loading of dual cocatalysts on semiconductors has been proved to be effective for improving the activity of photocatalytic water splitting, the decoration processes are usually complex and need to be carefully controlled [18–22]. It is still challenging to develop an easy alternative method for enhancing the photocatalytic activity through modification of both reduction and oxidation cocatalysts on photocatalysts.

In our previous work, we prepared highly efficient photocatalysts for H_2 production by simply grinding TiO_2 with Cu nanoparticles (NPs) and demonstrated good dispersion of Cu NPs on TiO_2 surface [23]. Here we extend this ball-milling method for modifying TiO_2 with CuO and Co_3O_4 respectively as reduction and oxidation cocatalysts by introduction of $Co(NO_3)_2$ into the grinding process. Thanks to such an easy method, loading amount of cocatalysts could be well controlled and the synergetic effects of CuO and Co_3O_4 on photocatalytic H_2 evolution from water with and without methanol were investigated in detail. Significant role of the Co_3O_4 loading amount was verified in improving the photocatalytic activity of CuO/TiO_2. The photocatalytic H_2 production activity in water was enhanced by approximately 5.5 times after co-loading trace Co_3O_4 on CuO/TiO_2, 4.2 times that observed on the optimum CuO/TiO_2 with sufficient CuO loading. The enhancement of the photocatalytic activity can be attributed to the effective separation and transfer of photoexcited electron-hole pairs as well as efficient surface reaction.

Experimental section

Preparation of photocatalysts

All the reagents were of analytical grade and used without further purification. Commercial Degussa TiO_2 powder (P25) was used as the photocatalyst. Copper nanoparticles with nominal size of 30 nm (aladdin) were used as the CuO source. $Co(NO_3)_2\cdot 6H_2O$ (Sinopharm Chemical Reagent Co., Ltd) was used for Co_3O_4 decoration. Resazurin was obtained from Aladdin. Sodium hydroxide, Terephthalic acid, ethanol (>99.7%) and methanol (>99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd.

$CuO-Co_3O_4/TiO_2$ photocatalysts were prepared by a simple ball-milling process. Typically, TiO_2 powder (1.0 g) and Cu NPs (0.1–2 wt % CuO *vs.* TiO_2) were put into a pot made of partial stabilized agate (80 mL), in which 25 agate balls of 10 mm diameter were placed. Then a certain amount (0.01–2 wt % Co_3O_4 *vs.* TiO_2) of 0.01 mol L^{-1} $Co(NO_3)_2$ ethanol solution (0.291 g $Co(NO_3)_2\cdot 6H_2O$ dissolved in 100 mL ethanol) was added into the pot, followed by milling at 300 rpm for 15 min. The slurry was then dried in an oven at 70 °C for 12 h and the obtained powder was ground and calcined at 350 °C for 2 h under an air atmosphere to acquire the $CuO-Co_3O_4/TiO_2$ photocatalyst. The CuO/TiO_2 photocatalyst was prepared in the same way except for that $Co(NO_3)_2$ ethanol solution was replaced by ethanol.

Characterization of photocatalysts

X-ray diffraction (XRD) patterns, acquired on an X-ray diffractometer (PAN alytical B.V. Empyrean) using Cu Kα irradiation ($\lambda = 1.5406$ Å) were used to confirm the phase structures of the obtained samples. Field emission transmission electron microscopy (FETEM) and high resolution transmission electron microscopy (HRTEM) were performed on a FEI Tecnai G2 F30 electron microscope with acceleration energy of 300 kV. The content of CuO and Co_3O_4 in the samples were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) with an optima 4300 DV spectrometer (Perkin Elmer). The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) of the samples was analyzed by nitrogen adsorption in ASiQ (Quantachrome, USA). X-ray photoelectron spectra (XPS) were conducted on an AXIS-ULTRA DLD XPS system (Kratos) equipped with an Al Kα monochromated X-ray source. Photoluminescence (PL) spectra were operated at room temperature on a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer with a He-Cd laser (325 nm) as light source. UV–vis absorption spectra of the samples were obtained by a UV–vis spectrophotometer (U3900H, Hitachi).

Photocatalytic H_2 evolution

The photocatalytic reaction was carried out in an online system (CEL-SPH2N, Au Light, Beijing). A 300 W Xe lamp with a total light intensity of 600 mW cm^{-2} was used as the light source. For a typical photocatalytic reaction, 20 mg photocatalyst was suspended in 100 mL of pure water or methanol aqueous solution (30 vol %). The system was then vacuumed to completely remove the dissolved oxygen using a vacuum pump before illumination. The gas sample was analyzed by an online gas chromatograph (GC) once an hour using a thermal conductivity detector (TCD) with Argon as a carrier gas.

The quantum efficiency (QE) was calculated with the following equation. The amount of H_2 was measured by a GC