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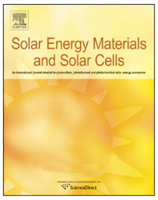

Enhanced photoelectrochemical activity and photocatalytic water oxidation of NiO nanoparticle-decorated $SrTiO_3$ nanocube heterostructures: Interaction, interfacial charge transfer and enhanced mechanism

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ABSTRACT

Here we demonstrate the enhanced photoelectrochemical (PEC) performance and photocatalytic activity towards water oxidation of n-type $SrTiO_3$ (STO) nanocubes coupled with p-type NiO nanoparticles (denoted as p-NiO@n-STO nanoparticle@nanocube), fabricated by calcining $Ni(NO_3)_2$-loaded STO nanocubes. High resolution transmission electron microscope studies show that intimate p–n junctions are formed between n-type STO and p-type NiO interfaces. As a p–n junction photoanode, the p-NiO@n-STO nanoparticle@nanocube nanostructures exhibit the enhanced PEC activity and photocatalytic water oxidation. The photocurrent density of the p-NiO@n-STO nanostructure electrode reaches 3.5 $\mu A\ cm^{-2}$, which is 7 times higher than that (0.5 $\mu A\ cm^{-2}$) for pure STO nanocube electrode at 0 V versus Ag/AgCl. The p-NiO@n-STO nanoparticle@nanocube nanostructures also exhibit pronounced photoresponse to generate O_2. The O_2 generation is about 100 μmol after irradiation 3 h with a 300-W Xenon lamp, which is about 1.7 times higher than that (60 μmol) of pure STO nanocubes. The intimate p–n junctions between p-NiO and n-STO interfaces accelerate holes migration from valence band of n-STO to that of p-NiO and reduction of the recombination of electron–hole pairs by the internal electrostatic field in the interface, which are believed to be the main reasons for enhanced PEC response and water-splitting performance of the as-prepared p-NiO@n-STO nanoparticle@nanocube nanostructures. The present work demonstrates that the p–n junction p-NiO@n-STO heterostructures have great potential applications in the field of photoelectrical devices and photocatalysis for water splitting.

1. Introduction

Splitting of water into hydrogen and oxygen gas by photocatalytic action has been considered as the most promising way to directly convert solar energy into chemical fuel with high energy density [1–8]. It has been demonstrated that photocatalytic nanostructure semiconductors are quite efficient in the applications of water splitting and oxidation [9–11]. However, the photoinduced electrons and holes of semiconductors are rapidly to decay through recombination, which significantly limits the practical applications of photocatalytic semiconductors in water splitting and oxidation. Therefore considerable efforts have been devoted to the fabrication and photoelectrochemical (PEC) activity and photocatalytic performance of photocatalytic nanostructure semiconductors with improved charge separation efficiency and enhanced water-splitting activity.

To improve the separation efficiency of the photogenerated electrons and holes, an effective strategy is to fabricate heterojunction nanostructures by coupling two or more semiconductors through appropriate band positions, because an internal electric field (IEF) established in a heterojunction region within the semiconductors can significantly promote the charge separation and facilitate the interfacial charge transfer efficiency to produce a high quantum yield [12–15]. Among heterogeneous nanostructures, p–n heterojunction nanostructures are expected to exhibit much higher PEC activity and photocatalytic performance for water splitting, because the unique structural feature within the p–n heterojunction nanostructures creates the space charge region at the junction, in which the photogenerated electrons are depleted, leading to an IEF from n-type semiconductor to p-type

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semiconductor. The established IEF drives electrons and holes to diffuse toward opposite directions. Consequently, the recombination of electron hole pairs is significantly reduced, thus improving the PEC activity and photocatalytic performance of p–n heterojunction nanostructures for water splitting [16–22]. So far only a few p–n heterojunction nanostructures with enhanced PEC activity and photocatalytic performance towards water splitting have been reported in recent literatures. The PEC properties of n-$BiVO_4$ modified by p-Co_3O_4 containing 0.8 wt% cobalt were reported, showing that the incident-photon-to-current efficiencies (IPCE) value of n-$BiVO_4$/p-Co_3O_4 was about 4 times higher than that of pure n-$BiVO_4$ at 420 nm [21]. It has been reported that ZnO/ZnS/CdS/$CuInS_2$ p–n junction heterostructures exhibit much higher visible light PEC activity toward water splitting than ZnO/ZnS/CdS and ZnO/ZnS films. At 480 nm, the ZnO/ZnS/CdS/$CuInS_2$ p–n junction heterostructure film shows the highest photocurrent of 10.5 mA/cm^2 and the highest IPCE of approximately 57.7% [22]. These studies encourage researchers to fabricate potential p–n heterojunction nanostructures to split water.

As reported in the previous literature, STO is a n-type semiconductor with an indirect band gap of 3.2–3.4 eV [23,24], and has a simple cubic perovskite structure with good flatband potential and photovoltage [25,26]. These unique structure features and properties lead STO to be able to photolyze the water and therefore to be considered as potential photoanode candidate in PEC water splitting [27–29]. As reviewed above, the heterogeneous nanostructures of STO coupled with other semiconductor through appropriate band positions are expected to exhibit the enhanced charge separation efficiency and PEC performance, which has been confirmed by recent achievements in PEC water-splitting performance of STO loaded with other semiconductors. For instance, it was reported that Cu_2O/STO p–n heterojunction photoelectrode exhibited the improved PEC water-splitting performance [30]. Especially, overall photocatalytic water-splitting activity and mechanism of NiOx–STO has been investigated systemically in the recent years. It has been believed that NiOx–STO is more likely a three component Ni–STO–NiO catalyst, in which Ni(0) serves as an electron trap (site for water reduction to generate hydrogen gas) and NiO serves as a hole trap (site for water oxidation to generate oxygen gas) [31,32]. However, there are a few studies on PEC and photocatalytic water-splitting performance of two component NiO–STO p–n heterojunction nanostructures. Here we present the fabrication of heterogeneous nanostructures of two component p-NiO@n-STO heterogeneous catalyst fabricated by coupling STO nanocubes with NiO nanoparticles, and its water-splitting performance by evaluating PEC and photocatalytic oxidation of water.

2. Experimental section

2.1. Materials

$SrCl_2 \cdot 6H_2O$ 99.9%, Na_2CO_3 99.9%, $Ni(NO_3)_2 \cdot 6H_2O$, NaCl 99.9%, P25 TiO_2, and nonyl phenyl ether (9) (NP-9) were purchased from Alfa Aesar. Water was purified to 18 MΩ/cm resistivity by using a pure water system (Mini-Qx-3000). Fluorine-doped tin oxide (FTO)-coated glass was purchased from Nippon Sheet Glass Company, Japan. FTO-coated glass was sliced to be 30 mm × 15 mm per piece.

2.2. Preparation of p-NiO@n-STO nanoparticle@nanocube heterostructures

p-NiO@n-STO nanoparticle@nanocube heterostructures were fabricated by the following two-step route. Firstly, STO nanocubes were synthesized by an environmentally friendly NaCl nonaqueous ionic liquid route. In a typical synthetic procedure, 2.0 g $SrCl_2 \cdot 6H_2O$ and 0.8 g Na_2CO_3 were ground for 10 min each before mixing together. The ground $SrCl_2 \cdot 6H_2O$ and Na_2CO_3 powders were mixed and ground for 15 min to form $SrCO_3$ powder. The as obtained $SrCO_3$ powders were then mixed with 0.6 g TiO_2 nanoparticles, 2.0 g NaCl and 3 mL NP-9 in an agate mortar, and were ground for 15 min. The mixed and ground powder was heated in a porcelain crucible with a horizontal tube electric furnace at 950 °C for 6 h, cooled gradually to room temperature in air, washed several times with distilled water to remove NaCl, and dried in an oven at 80 °C for 5 h. Secondly, p-NiO@n-STO nanoparticle@nanocube heterogeneity nanostructures were fabricated by calcining $Ni(NO_3)_2$-loaded STO nanocubes. Briefly, 200 mg STO nanocubes were added to a 10 mL aqueous $Ni(NO_3)_2 \cdot 6H_2O$ solution (78 mg, 10 wt% loading of NiO), and the components were thoroughly mixed by stirring for 60 min. This solution containing STO nanocubes was dried at 110 °C for 10 h and then annealed at 700 °C for 2 h to form p-NiO@n-STO nanoparticle@nanocube heterogeneity nanostructures.

2.3. Characterization

Powder X-ray powder diffraction (XRD) scans were conducted with a Rigaku (Japan) Dmax γA rotation anode X-ray diffractometer equipped with the graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å), employing a scanning rate of $0.02\,^{\circ}\,s^{-1}$ in the 2θ range from 10° to 80°. The size and morphology were evaluated by scanning electron microscope (SEM) (Hitachi S-4800). The microstructure features were investigated by transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM, JEOL-2100). The surface electronic states were determined by X-ray photoelectron spectroscopy (XPS, ESCSLAB 250Xi, UK). In the XPS spectra, all peaks of elements were calibrated according to the deviation between the C 1s peak and the standard binding energy of C 1s at 284.8 eV. UV–vis diffuse reflectance spectra (DRS) were recorded on a Lambda 950 UV/Vis/NIR spectrometer (Perkin-Elmer, USA) equipped with an integrating sphere.

2.4. PEC measurements

For PEC performance evaluations, the as-fabricated p-NiO@n-STO nanoparticle@nanocube heterogeneity nanostructure catalysts were needed to be fabricated into films. The detailed fabrication process of the films was described as follows: 1.0 mg of the prepared p-NiO@n-STO nanoparticle@nanocube powder was suspended in 1.0 ml water by sonication to make the dispersion with sample concentration of 1.0 mg mL^{-1}, and then 0.5 mL of the prepared dispersion was uniformly coated on a FTO glass electrode (1.0 × 1.0 cm^2) by drop coating and drying at 60 °C for 6 h. The measurements were conducted on a three-electrode configuration in a quartz cell. The prepared catalyst working electrode was placed into a cell with a Pt counterelectrode and Ag/AgCl reference electrode. Then 100 mL 0.1 M Na_2SO_4 buffer solution at pH 7 was added to cell and the solution was degassed with N_2 for 30 min. The light source employed in PEC activity was a 300-W Xenon lamp (wavelength of 200–2500 nm) with an AM 1.5 G filter. The linear sweep voltammograms were operated at 5 mV/s in a potential range from 0 to 1 V versus Ag/AgCl both in dark and under illumination.

2.5. Photocatalytic oxidation of water for O_2 evolution

The photocatalytic O_2 generation reactions were conducted in a closed gas circulation and evacuation system. Typically, under magnetic stirring, 50 mg of the prepared p-NiO@n-STO heterogeneity nanostructure catalyst was dispersed in 50 mL 0.05 M