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Full Length Article

Efficient tungsten oxide/bismuth oxyiodide core/shell photoanode for photoelectrochemical water splitting

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ABSTRACT

The novel WO_3 nanorods (NRs)/BiOI core/shell structure composite is used as an efficient photoanode applied in photoelectrochemical (PEC) water splitting for the first time. It is synthesized via facile hydrothermal method and, successive ionic layer adsorption and reaction (SILAR) process. This facile synthesis route can achieve uniform WO_3/BiOI core/shell composite nanostructures and obtain varied BiOI morphologies simultaneously. The WO_3 NRs/BiOI-20 composite exhibits enhanced PEC activity compared to pristine WO_3 with a photocurrent density of 0.79 mA cm^{-2} measured at 0.8 V vs. RHE under AM 1.5G. This excellent performance benefits from the broader absorption spectrum and suppressed electron-hole recombination. This novel core/shell composite may provide insight in developing more efficient solar driven photoelectrodes.

1. Introduction

Environmental contamination and energy crisis have been global concern that human beings are facing in recent years. Thus there is a growing attention that must be paid to environmental protection. The development of efficient clean energy is in demand [1–3]. Hydrogen converted from abundant and renewable sunlight has been regarded as one of the most promising clean energy in a sustainable society. Future generation of renewable hydrogen energy from solar energy will depend largely on the PEC water splitting and photocatalysis [4]. The improvement of PEC energy conversion efficiency relies on the semiconductors used as photoelectrode materials which should be stable, competent and abundant in storage. A number of oxide semiconductors including TiO_2, ZnO, Co_3O_4, Fe_2O_3 and WO_3 have been considered as the excellent photoelectrode materials since Fujishima and Honda reported the TiO_2 PEC water splitting phenomenon in 1972 [5–10]. Recently, WO_3 has been widely applied in PEC water splitting, due to its resilience to photocorrosion effect in aqueous solution, harvest of visible-light and the efficient electron transport properties. Cristino et al., for instance, have synthesized highly efficient WO_3 electrodes through potentiostatic anodization of metallic tungsten that has been successfully used for water electrolysis with a value of 70% to 90% in 1 M H_2SO_4 [11].

Although these semiconductors show remarkable photocatalytic properties and energy conversion efficiencies, they could not meet commercialization requirement of PEC water splitting technology due to the absorbance of the specific light spectrum, the poor durability under irradiation, and the insufficiently high catalytic capability. To overcome these drawbacks, a variety of ways have been proposed such as nanostructures morphology engineering (nanowires, nanoflakes, nanobowls, and nanoparticles) [12], mental and non-mental semiconductors doping [13], construction of binary or ternary composite [14,15]. The core/shell structures have been investigated in vertically aligned core/shell TiO_2/WO_3 nanorod arrays [16], WO_3/$BiVO_4$ core/shell nanowire [17] and Fe_3O_4/WO_3 hierarchical core-shell structure [18]. In these composite configurations, the coupled photoelectrodes are composed of oxide semiconductor materials, which can only absorb a small portion of the solar spectrum. Bismuth oxyhalides BiOX (X = F, Cl, Br and I) are regarded as new type of brilliant photocatalysts, which possess significant photocatalytic activity in visible light range. Due to their special anisotropic layered-structures and strong absorption in the visible light region, bismuth oxyhalide nanomaterials have received a great deal of attention in recent years [19,20]. Among these compounds, BiOI, with a band gap of 1.8 eV, has the strongest photo response to the visible light and exhibits the best visible-light photocatalytic activity [21]. Feng et al. reported that BiOI/$CdWO_4$

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heterojunction is able to effectively separate the photogenerated carriers [22].

So far, there are still few researches on the combination of both WO_3 and BiOI to form a core/shell structure for the application in PEC water splitting. In the present work, we report a facile two-step method to fabricate a novel and uniform core/shell electrode by mixing WO_3 nanorods with BiOI nanosheets-assembled nanospheres that serves as the photoanode. In addition, successive ionic layer adsorption and reaction (SILAR) for BiOI nanosheets synthesis is different from the conventional methods such as electrospun [23]. This method is facile, controllable, cost-effective and capable of forming uniform nanostructures [24]. Moreover, the investigation into optimal ratio of WO_3 and BiOI is carried out by using different cycles of BiOI nanosheets. It is worth to note that the excellent photocatalytic activity is achieved by virtue of the appropriate band gap as well as their unique core/shell structure. Therefore, this present work might broaden a promising concept in PEC water splitting by combining BiOI and WO_3, resulting in an efficient photoelectrode.

2. Experimental section

2.1. Preparation of WO_3 NRs

Initially, the WO_3 NRs were fabricated as the reported reference [25]. To be specific, the precursor solution was consisted of a certain amount of sodium tungstate dehydrate ($Na_2WO_4{\cdot}2H_2O$) and potassium oxalate monohydrate ($K_2C_2O_4{\cdot}H_2O$) which mixed in deionized water and the pH value was adjusted to 1.0 by hydrochloric acid (HCl). Secondly, the precursor solution was transferred to the Teflon-lined capacity autoclave with the fluorine-doped tin oxide (FTO) glass substrate placed in it. Finally, the WO_3 nanorods were achieved through a hydrothermal process and kept at 180 °C for 24 h. Moreover, the above samples were annealed at 550 °C for 2 h to crystallization.

2.2. Preparation of WO_3 NRs/BiOI core/shell structure

The WO_3 NRs/BiOI core/shell structure was prepared via SILAR method and BiOI was grown on the surface of WO_3 NRs. In a typical experimental, 0.01 M bismuth nitrate penthydrate ($Bi(NO_3)_3{\cdot}5H_2O$) was dissolved in ethylene glycol under stirring to form solution A. 0.01 M potassium iodide (KI) was dissolved in distilled water under stirring to form solution B simultaneously. The FTO glasses with WO_3 NRs were successively immersed in solution A and solution B for 20 s each. After each immersion process, the obtained samples were rinsed several cycles with de-ionized water and absolute ethanol to remove excess impurity ions. In order to achieve optimized WO_3 NRs/BiOI, the immersion cycle was repeated a couple of cycles. A series of WO_3 NRs/BiOI composites were prepared by adjusting the repeated cycles of SILAR cycles. Specifically, the obtained samples were defined as WO_3 NRs/BiOI-10, WO_3 NRs/BiOI-20 and WO_3 NRs/BiOI-30, represented for the samples with 10 cycles, 20 cycles and 30 cycles of SILAR process, respectively.

2.3. Characterization

The crystal structure and phase compositions are identified using X-ray diffraction (XRD, Rigaku-D/max-2500 with Cu Kα radiation) at 40 kV and 200 mA. The morphologies of as-obtained samples are observed by a scanning electron microscope (SEM, JEOL, and JSM-7800F) and a transmission electron microscopy (TEM and HRTEM, JEOL, JEM-2100). The optical properties are investigated by a DU–8 B UV–vis double-beam spectrophotometer at room temperature. PEC water splitting tests are conducted through

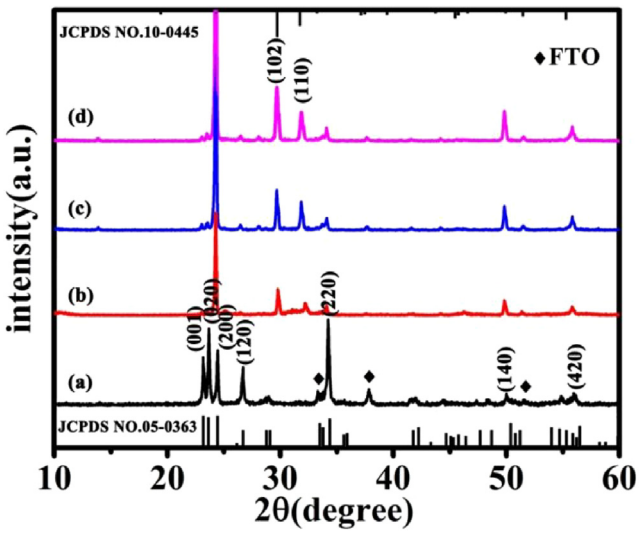

Fig. 1. XRD patterns of (a) WO_3 NRs, (b) WO_3 NRs/BiOI-10, (c) WO_3 NRs/BiOI-20 and (d) WO_3 NRs/BiOI-30.

an electrochemical workstation, a three-electrode configuration, with WO_3 NRs and WO_3 NRs/BiOI composites on FTO as the working electrode, a platinum foil as counter electrode, and saturated Ag/AgCl as reference electrode, respectively. The electrolyte is H_2SO_4 (1 M) and the potential of Ag/AgCl has been converted to the reversible hydrogen electrode (RHE) in the results. The working electrode is under AM 1.5G (100 mW cm^{-2}) illumination. Electrochemical impedance spectroscopy (EIS) measurement is performed on the workstation. The oxygen evolution is detected by voltammetric diagnostic with Pt sheet microelectrode (1 mm * 3 mm) in the three-electrode configuration solar cell under the controlled bipotentiostat condition (the scan rate controlled at 50 mV s^{-1}).

3. Results and discussion

SILAR cycles as a synthetic parameter has been optimized for the preparation of WO_3 NRs/BiOI composite. Various WO_3 NRs/BiOI composites with different SILAR cycle numbers (i.e. 10, 20 and 30) are denoted as WO_3 NRs/BiOI-10, WO_3 NRs/BiOI-20 and WO_3 NRs/BiOI-30, respectively. Fig. 1 displays the XRD patterns of WO_3 NRs and WO_3 NRs/BiOI composites with different SILAR cycles along with the standard XRD pattern generated from both WO_3 and BiOI. It is found that the as-prepared WO_3 NRs is pure phases as a monoclinic phase (Fig. 1(a)). The diffraction peaks are consistent with a space group of P21/a14 (JCPDS Card No. 05-0363). Moreover, the other diffraction peaks are attributed to the FTO substrate marked with "♦". All curves shown in Fig. 1(b)–(d) are well indexed to XRD peaks of tetragonal BiOI (JCPDS No.10-0445) and monoclinic WO_3. On the one hand, the diffraction peaks of BiOI become stronger upon more SILAR cycles, as proved in Fig. 1(b)–(d). On the other hand, the intensities of diffraction peaks reflected from WO_3 NRs become weaker in the WO_3 NRs/BiOI composites, suggesting that the crystal growth of BiOI may affect that of WO_3 NRs.

To further identify the chemical composition and element contents of the WO_3 NRs/BiOI composite, the energy dispersive X-ray spectrum (EDS) measurement is conducted. Fig. 2 presents the SEM images of three sets of WO_3 NRs/BiOI as well as their corresponding EDS spectrum. The EDS survey spectrum in Fig. 2 (b), (d) and (f) indicate that WO_3 NRs/BiOI composite is composed of W, O, Bi and I elements. It is unambiguously seen that the contents of both Bi and I increase with long SILAR cycles whilst the intensity of W peak decreases, in agreement with the XRD patterns above. It is the different SILAR cycles that play an important role on the change