Enhanced photoelectrochemical water splitting with TiO_2@Ag_2O nanowire arrays via p-n heterojunction formation

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ABSTRACT

Nanostructured TiO_2@Ag_2O p-n heterojunction arrays were fabricated by combining the hydrothermal method with the chemical-bath method, and they were used as a photoelectrode in photoelectrochemical (PEC) cell for high-performance solar water splitting. To investigate the morphology, microstructure and composition, the pristine TiO_2 nanowire arrays (TiO_2 NWAs) and the TiO_2 nanowires decorated with Ag_2O nanoparticles (TiO_2@Ag_2O NWAs) were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectra (EIS). Nanostructured TiO_2 nanowire arrays were assembled with Ag_2O nanoparticles, producing a large number of nano p-n heterojunctions. The TiO_2@Ag_2O p-n heterojunction arrays showed a photocurrent density of 1.61 mA/cm^2 at 1.23 V vs. a reversible hydrogen electrode (RHE) in 0.5 M Na_2SO_4 electrolyte under simulated AM 1.5 illumination (100 mW/cm^2), two times higher than that of the pristine TiO_2 NWAs. The enhancement was attributed to the efficient electron-hole separation because of the p-n heterojunction interface between p-Ag_2O and n-TiO_2, which were revealed by the electrochemical impedance spectra including both Mott-Schottky and Nyquist plots with or without illumination. TiO_2@Ag_2O p-n heterojunction arrays were expected to have the considerably potential applications in solar water splitting.

1. Introduction

Photoelectrochemical (PEC) water splitting is a key step toward the realization of a sustainable carbon-neutral society, affording the efficient and economical conversion of abundant solar energy into chemical fuel [1,2]. Semiconductors such as classic semiconductors, multinary oxides, oxynitrides, chalcogenides and carbon-based semiconductors have been developed as PEC electrode materials for water splitting [1,3–6]. Since the first photoelectrochemical cell invented by Fujishima and Honda in 1972 [7], TiO_2 is always considered as a promising semiconductor material for solar water splitting, because of its high resistance to the photocorrosion, low-cost, nontoxicity and abundance [3,8–10]. One-dimensional nanostructured TiO_2 photoelectrode, such as nanotubes and nanowires, could provide excellent PCE performance resulted from the enhancement of light absorption and the efficient separation and transportation of charges [11]. Unfortunately, the unmodified TiO_2 photoelectrode suffers from the wide band-gap (anatase: 3.2 eV, rutile: 3.0 eV) and fast recombination of photogenerated electron-hole pairs, so applications of TiO_2 are limited

[3,12,13]. In recent years, various strategies such as doping with nitrogen [14], loading with cocatalysts [15,16], treating with hydrogen [9], and fabricating with heterojunctions [17] have been developed to solve the above issues.

Nowadays considerable efforts have been focused on the p-n heterojunction with two kinds of semiconductors, because heterogeneous nanostructures have advantages of enhancing the PEC performance. Two semiconductors are capable of expanding the absorption region of the light-harvesting materials to visible-light region. On the other hand, heterojunctions can effectively separate photogenerated electron-hole pairs by the built-in field (IEF). The p-n heterojunctions, such as p-Cu_2O/n-TaON [18], p-NiO/n-Ca_2BbO_3 [19], p-$CaFe_2O_4$/n-Fe_2O_3 [20] and p-$NiCo_2O_4$/n-InP [21], have been demonstrated to show enhanced PEC activity due to the efficient charge separation. Huang et al. fabricated a CuS/TiO_2 p-n composite electrode exhibiting a significantly excellent PEC activity [22]. Yuan et al. obtained a photocurrent density of 4.55 mA/cm^2 at 1.23 vs. RHE (Reversible hydrogen electrode) with TiO_2@Cu_2O p-n heterojunction photoelectrode, which was the highest among the reported values for TiO_2-based photoanode [17].

Ag_2O is a p-type semiconductor with a relatively narrow band-gap (E_g = 1.3 eV), which has the visible-light-driven photocatalytic ability for water pollution treatment [23,24]. Although TiO_2/Ag_2O composites had been synthesized for the PEC study [25–29], the photocurrent density of the reported structures was low and not sufficient for water splitting. In this paper, we loaded p-type Ag_2O nanoparticles on TiO_2 nanowire arrays to form the p-n heterojunction, and investigated their PEC water splitting performance. The formed p-n heterojunction could enhance the separation of electron-hole pairs between the interface of p-Ag_2O and n-TiO_2, and thus it improved the PEC water splitting activity. The TiO_2 photoelectrode was made up with well-separated and vertically oriented TiO_2 nanowires, synthesized by the hydrothermal method following an annealing procedure [30]. Then, Ag_2O nanoparticles with a p-type semiconducting nature were grown on the surface of n-type TiO_2 by a chemical-bath method. The formation of p-n heterojunction enhanced the charge separation by the built-in field. Furthermore, we investigated the interface property between TiO_2 and Ag_2O by the electrochemical impedance spectra (EIS), and proposed a PEC enhancement mechanism with the p-n heterojunction.

2. Experimental section

2.1. Synthesis of TiO2 nanowire arrays

TiO_2 nanowire arrays were grown on a fluorine-doped tin oxide (FTO) glass by a previously reported hydrothermal method [30]. The FTO glasses (FTO-P003, Kaivo) were cut into pieces of 1 cm × 3 cm × 1.6 mm substrate with surface resistivity of 15 Ω/sq. They were ultrasonically cleaned for 10 min in alcohol, acetone and deionized (DI) water, respectively. Then 10 ml of concentrated hydrochloric acid was diluted with 10 ml deionized water in a Teflon-liner (the volume is 40 ml), and 0.4 ml of titanium n-butoxide was added drop-by-drop to the above solution under magnetic stirring. Half hour later, two pieces of FTO glasses were placed at an angle against the wall with the conducting side facing down. The sealed Teflon-lined stainless steel autoclave was placed in an electric oven at 150 °C for 20 h and then cooled down to room temperature naturally. The glasses were thoroughly washed with DI water, scraped off some TiO_2-coated area to contact the conducting wire, and dried in an eclectic oven for 12 h. Finally, the samples were annealed in air at 500 °C for 5 h.

2.2. Synthesis of TiO2@Ag2O nanowire arrays

$TiO_2@Ag_2O$ NWAs were synthesized by a chemical-bath method. First of all, 80 mg sodium hydroxide was dissolved in 15 ml deionized water in a beaker. Then the pristine TiO_2 nanowire arrays on FTO glass were placed in the above beaker at an angle against the wall with the conducting side facing up. 700 μL of silver nitrate solution (10 mM) was added drop-by-drop in the above solution, and the breaker with TiO_2 NWAs was kept at 50 °C for 8 h. Finally, the FTO glass with $TiO_2@Ag_2O$ NWAs was washed with deionized water several times and dried in an electron oven at 60 °C. The procedures for the preparation of

$TiO_2@Ag_2O$ NWAs were illustrated in Scheme 1.

2.3. Characterization

An XD-3 diffractometer (Beijing PEPSEE, China) with Cu-Kα radiation was used to carry out the XRD experiment. Field emission scanning electron microscopy (SEM, Hitachi S-4800, Japan), transmission electron microscopy (TEM, JEOL-2100, Japan) and X-ray photoelectron spectroscopy (XPS, ThermoFisher, UK) were used to characterize the morphologies and compositions of nanowire arrays. Lambda 950 UV/Vis/NIR spectrophotometer (Perkin-Elmer, USA) was used to carry out the reflectance spectra.

2.4. Electrochemical measurement

The PEC characterizations of the photoelectrode were carried out in 0.5 M Na_2SO_4 solution by a potentiostat (PINE, USA), and a standard three-electrode method was used with a Pt counter electrode and Ag/AgCl reference electrode. The FTO photoelectrode were further cut into a piece of 1 cm × 1.5 cm with the conducting area, and the TiO_2-coated area was about 1 cm². The transient photocurrent (J-t) and the linear-sweep voltammetry (LSV) plots were recorded under chopped illuminations. During the experiment, the illumination was simulated AM 1.5 illumination (100 mW/cm²), unless otherwise specified. Hydrogen were generated during the PEC water splitting under illumination with a bias of 1.23 V vs. RHE, and gases were collected and measured by using the simple displacement method. The incident photon to current conversion efficiency (IPCE) was measured by using a QE/IPCE Measurement Kit (Newport, USA) with a bias of 1.23 V vs. RHE. The light from a monochromator was focused on the backside of the FTO glass to generate a photocurrent spectrum with an interval of 10 nm. The light intensity was measured by a 2936-R dual channel power/current meter, and the photocurrent was measured by the potentiostat (PINE, USA). Electrochemical impedance spectroscopy was also carried out in 0.5 M Na_2SO_4 solution by a potentiostat (CHI660D, Chenhua) with or without illumination. The Mott-Schottky plots were performed at a frequency of 1000 Hz, and the Nyquist plots were measured at the open circuit potential with the frequency from 0.1Hz to 1000 Hz.

3. Results and discussions

Fig. 1a-b represented typical SEM images of the pristine TiO_2 nanowire arrays grown on the FTO glass. Typical SEM images, XRD patterns and EDS plots of the $TiO_2@Ag_2O$ nanowire arrays were shown in Fig. 1c-f. The entire surface of the FTO glass was covered with TiO_2 nanowire arrays uniformly, as shown in the top view of the nanowire arrays (Fig. 1a). The TiO_2 nanowires were nearly vertical to the FTO substrate, and the length of the TiO_2 nanowire was 3.8 μm. The side facets of nanowires were smooth without any impurity such as particles. The surface morphologies of the $TiO_2@Ag_2O$ nanowire arrays revealed that a large number of Ag_2O nanoparticles were deposited on the surface of TiO_2 nanowires, and the diameter of the Ag_2O nanoparticle
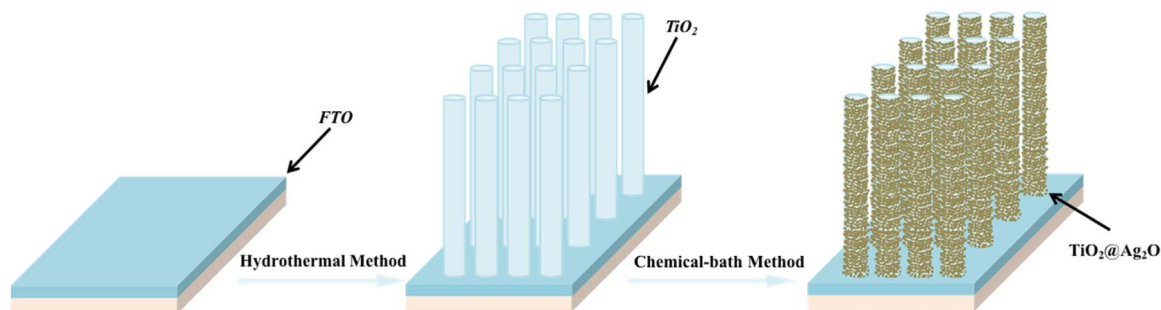
Scheme 1. Schematic illustration of the two-step fabrication process for the nanostructured $TiO_2@Ag_2O$ NWAs by combining the hydrothermal method and the chemical-bath method.