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Full paper

Cactus-like hierarchical nanorod-nanosheet mixed dimensional photoanode for efficient and stable water splitting

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ABSTRACT

A novel hierarchical ZnO nanorod-nanosheet mixed dimensional nanoarchitecture modified with CdS quantum dots and $Ni(OH)_2$ catalyst was designed as photoanode for photoelectrochemical water splitting. The FDTD simulation results demonstrated the better light utilization efficiency for the proposed novel mixed 2D/1D hierarchical structure and subsequently resulted in larger effective heterostructure interface area of photoanode which means the increased heterostructure interface area while maintaining evenly distributed light absorption especially at the bottom zone of 3D nanostructure. The applied bias photo-to-current efficiency of H-ZnO/CdS/$Ni(OH)_2$ reached 4.12%, 20.6 times that of ZnO nanosheets photoanode. More importantly, the efficient hole consumption characteristic of $Ni(OH)_2$ catalyst introduced the significantly improved photoelectrochemical stability. In such mixed dimensional hierarchical nanoarchitecture, each component contributed synergistically to the enhanced PEC performance, and this novel design may give impetus to promote the efficient and stable hydrogen generation via PEC water splitting.

1. Introduction

Photoelectrochemical (PEC) water splitting for hydrogen production by the direct utilization of sunlight is an ideal and renewable method [1]. The efficiency and stability of photoanodes are key factors in PEC cells, and some semiconductor materials (e.g., zinc oxide (ZnO) [2–4], titanium oxide (TiO_2) [5,6], and hematite (α-Fe_2O_3) [7,8], etc.) have been widely studied as photoanodes. Among these different materials, ZnO shows great potential as photoanode for water splitting, due to its various morphologies, non-toxicity and appropriate conduction/valence band edge [9]. Although one dimensional (1D) arrays offer direct pathways for charge carriers compared to zero dimensional nanoparticles, the photo-to-hydrogen efficiency of 1D arrays is still low because of the insufficient internal surface area. Fortunately, hierarchical ZnO nanostructures are extensively explored in order to simultaneously enlarge internal surface area and keep high electron transport efficiency. Bai et al. synthesized 3D-branched ZnO/CdS NWAs (1D nanorods synthesized on 1D nanorods)for solar water splitting and the optimal solar-to hydrogen efficiency reached 3.1% [10]. Zhang et al. constructed 3D ordered Au/branched ZnO NWs photoanode, which exhibited excellent PEC activities in both UV and visible region [11]. Recently, the hierarchical ZnO nanorod-nanosheet mixed dimensional architectures(1D nanorods directly synthesized on vertically aligned 2D nanosheets) have shown great potential for DSSCs. Such 1D/2D mixed-dimension hierarchical structure possess certain superiorities compared with former reported examples (1D nanorods synthesized on 1D nanorods) [12,13]. Here, the adopted hierarchical ZnO nanorod-nanosheet mixed dimensional architectures is the first time to be applied in the PEC water splitting system to best of our knowledge.

The poor absorption of visible light of the wide bandgap is the main reason that hinders PEC water-splitting performance. To increase the light-harvesting efficiency, many strategies have been taken to utilize visible light region of solar spectrum, including element doping [14–16], surface-plasmon-resonance of noble metal [11,17,18] and quantum dot [19,20]. Recently, quantum dots including CdS [21–23], CdSe [24–26] and CdTe [27,28] have been used to sensitize ZnO to

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expand absorption spectrum to visible region for photoelectrochemical application. Chen et al. demonstrated loading-tunable CdTe quantum dots sensitized ZnO nanowires exhibited an optimal photoconversion efficiency of 1.83%, which is more than 200% higher than that of pristine ZnO nanowires [28]. Furthermore, Li et al. designed novel double-sided CdS and CdSe quantum dots cosensitized ZnO nanowires for photoelectrochemical hydrogen generation [25]. Albeit the high photocurrent could be obtained by the sensitized QDs, the hole-induced anodic corrosion of cadmium chalcogenides still hindered the use of cadmium chalcogenide quantum dots, even in a sacrificial electrolyte containing Na_2S and Na_2SO_3 for a long time [29]. Recently, introducing catalysts to the surface of photoanode has been found effective as the water oxidation or hole consumption [30,31]. Seol et al. employed $IrO_x{\cdot}nH_2O$ on a CdSe/CdS cosensitized ZnO nanowire photoanode, resulting in improved stability and increased photocurrent [31]. Among various water oxidation catalyst, Ni-based materials (such as nickel-dihydrolipoic acid [32], nickel hydroxides [33] and nickel oxides [34]) have received good attention, due to their high catalystic activity, chemical stability, low toxicity and earth abundant. For example, Li et al. reported a high and stable photocurrent obtained by combining the Ti-doped hematite nanorods with $Ni(OH)_2$ [35]. Liu et al. synthesized ultrathin amorphous $Ni(OH)_2$ nanosheets onα-Fe_2O_3 films for Improved photoelectrochemical water oxidation [36]. It also has been reported by Mao et al. that $Ni(OH)_2$ coated ZnO photoanode exhibited an enhanced PEC performance compared to the pristine ZnO photoanode [37].

Herein we synthesized a well-known oxygen-evolution catalyst ($Ni(OH)_2$), on CdS coating layer sensitized hierarchical ZnO nanorod-nanosheet (H-ZnO) mixed dimensional nanoarchitecture photoanode in a PEC hydrogen generation system. The proposed novel mixed 2D/1D hierarchical structure showed better light utilization efficiency compared to 1D/1D hierarchical structure, resulting in larger effective heterostructure interface area of photoanode. This composite photoanode endowed a supreme applied bias photo-to-current efficiency (4.12%), 20.6 times compared to ZnO NSAs (0.2%) photoanode. More importantly, the photoanode exhibited significantly improved photoelectrochemical stability compared to H-ZnO/CdS photoanode in the neutral solution, with 49.2% of the initial photocurrent under illumination after 1 h, ascribed to efficient hole consumption capability of $Ni(OH)_2$.

2. Experimental section

2.1. Synthesis of hierarchical ZnO nanorod-nanosheet/CdS/Ni(OH)$_2$

Electrochemical deposition process was employed to synthesis ZnO nanosheets arrays (ZnO NSAs) on FTO substrate using an electrochemical workstation. The electrodeposition was performed at −1.0 V for 30 min at 70 °C in an aqueous electrolyte containing 0.05 M $Zn(NO_3)_2{\cdot}6H_2O$ and 0.1 M KCl. After the electrodeposition, the as-synthesized $ZnO/Zn_5(OH)_8Cl_2H_2O$ were washed with deionized water and then annealed at 450 °C for 30 min in air atmosphere to obtain ZnO nanosheets by decomposition of $Zn_5(OH)_8Cl_2H_2O$. 30 ALD cycles of ZnO seed layer were deposited on the surface of the ZnO NSAs at 85 °C. Diethylzinc (DEZ, 99.99%) and H_2O were used as the Zn and O precursors, respectively. Subsequently, the hierarchical ZnO nanorod-nanosheet arrays (H-ZnO) were obtained by hydrothermal growth in an equimolar concentration (5 mM) aqueous solution of zinc hydrate and hexamethylenetetramine aqueous solution for 4 h at 95 °C. Finally, the substrate with product was repeatedly rinsed with deionized water for several times and annealed in air at 450 °C for 3 h to remove residual surface salts.

The sensitization of CdS coating layer is a process by putting the H-ZnO into an aqueous solution of 20 mM $Cd(NO_3)_2$ and 20 mM thioacetamide at 40 °C in water bath for 10 min. Samples were then rinsed thoroughly with deionized water and air-dried. Then the H-ZnO/CdS were immersed in the 0.2 M $Ni(NO_3)_2{\cdot}6H_2O$ solution at 85 °C for 5 h, followed by washing with distilled water and drying for subsequent usage.

2.2. Structural and optical characterizations

The structure and morphology of the electrodes were characterized by X-ray diffraction (XRD) (Rigaku DMAX-RB, CuKα), field emission scanning electron microscopy (FE-SEM) (FEI QUANTA 3D). The formation of CdS and $Ni(OH)_2$ on the ZnO nanorods and the bonding characteristics were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The light absorption was recorded by UV–vis spectrophotometer (UV-2500, Shimadzu, Japan).

2.3. FDTD simulations

The electromagnetic simulations were accomplished by employing the FDTD method (Lumerical FDTD solutions). The unit cell of the structure was set as the simulation region using perfectly matched layer (PML) boundary conditions in the x-axis and y-axis. A plane-wave light source irradiated normally to the device was set to be transverse magnetic (TM) polarized, while one monitor was placed between the source plane and device surface in order to detect the device absorption. Complex refractive indices of ZnO and CdS are adopted from Palik's handbook of Optical Constants [38].

2.4. PEC measurement

The photoanode was fabricated by securing a copper wire on the exposed electric conductive parts of the FTO with a silver conducting paint. The substrate was subsequently sealed on all edge with epoxy resin except the active working area (0.5 cm^2). All electrochemical measurements were performed in a three electrode mode with a photoanode as the working electrode, a coiled Pt wire as counter electrode and a Ag/AgCl reference electrode, and 0.5 M Na_2SO_4 aqueous solution (with pH buffered to ~7) as the electrolyte. Electrochemical measurements were performed on an electrochemical workstation (Solartron SI 1287/SI 1260). All photoanodes were illuminated from the front side under AM 1.5 G illumination provided by a solar simulator (Oriel, 91159A). The white light intensity was 60 mW/cm^2 measured by a Si diode (Newport).

The applied bias photo-to-current efficiency(η_{ABPE}) was calculated from J_{ph}-V curves, assuming 100% Faradaic efficiency through the following Equation:$\eta_{ABPE}=\frac{I(1.23-V_{app})}{P_{light}}$, V_{app} is the applied external potential versus reversible hydrogen electrode (RHE). I is the externally measured current density at V_{app}. P_{light} is the power density of the incident light. The potentials were measured versus the Ag/AgCl reference electrode and converted to the reversible hydrogen electrode (RHE) scale using the Nernst function: $E_{RHE}=E_{Ag/AgCl}+E^{\circ}_{Ag/AgCl}+0.059pH$. E_{RHE} is the converted potential versus RHE. $E_{Ag/AgCl}$ is the external potential measured against the Ag/AgCl reference electrode. $E^{\circ}_{Ag/AgCl}$ is the standard electrode potential of Ag/AgCl reference electrode (0.1976 V versus RHE at 25 °C).

3. Results and discussions

The SEM images in Fig. 1(a, c and e) recorded the morphology evolutionary during the H-ZnO synthesis process. As shown in Fig. 1a, the prepared $ZnO/Zn_5(OH)_8Cl_2{\cdot}H_2O$ nanosheets with edge length of 2–4 μm and thickness of 100–200 nm was vertical to the FTO substrates, and there was a mass of gaps existing among the vertically aligned sheetlike crystals. After annealed in the air, the smooth surface (in the inset of Fig. 1a) turned into macroporous structure (in the inset of Fig. 1c) due to the pyrolysis of $Zn_5(OH)_8Cl_2{\cdot}H2O$:

$$Zn_5(OH)_8Cl_2{\cdot}H_2O \rightarrow 5ZnO+4H_2O\uparrow+2HCl\uparrow$$