



Synergistic effects in three-dimensional SnO₂/TiO₂/CdS multi-heterojunction structure for highly efficient photoelectrochemical hydrogen production

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ABSTRACT

Here, we present a kind of SnO₂ nanowires/TiO₂ nanoneedles/CdS quantum dots multi-heterojunction structure. In this rational heterojunction structure, three dimensional SnO₂ nanowires were directly grown on conductive fluorine doped tin oxide (FTO) glass by chemical vapor deposition method and served as the faster electron transport network for highly efficient photoelectrochemical system. Moreover, after artful design of branched TiO₂ nanoneedles on this network and then sensitized by CdS quantum dots, a multi-heterojunction structure of SnO₂/TiO₂/CdS was formed. This novel three dimensional multi-heterojunction structure exhibited remarkable performances on photoelectrochemical hydrogen production. The photocurrent density is as high as 8.75 mA cm⁻² at a potential of 0 V vs. saturated calomel electrode (SCE) by using the optimized conditions. More impressively, the photocurrent density is more than 4 times larger than that of single SnO₂-TiO₂ heterojunction (1.72 mA cm⁻²) at 0 V vs. SCE.

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1. Introduction

Hydrogen is one of the most expected fuels to solve the global energy crisis and environmental problems due to its high heat conversion efficiency and zero carbon emission. Currently, hydrogen is mostly obtained from nonrenewable resources, such as natural gas, petroleum, and coal. However, it is known that those nonrenewable resources have been depleted to a great extent. Thus, it is an urgent to find a new way for hydrogen production. Since Fujishima and Honda reported the successful photoelectrochemical (PEC) water splitting in 1972 [1], the extensive attention has been focused on semiconductor photocatalytic hydrogen production [2–6]. The most studied photocatalysts are metal oxide semiconductors, such as TiO₂ [7–11], ZnO [12,13], α-Fe₂O₃ [14–18] and WO₃ [19,20] due to their favorable band-edge position, excellent chemical stability, large photocorrosion resistance and low cost. However, the PEC performances of those catalysts are always suffer from two major problems: (1) the restriction of light utilization due to their large band gaps which

usually limit the light absorption just in the ultraviolet (UV) region; and (2) the fast recombination of photogenerated excitons because of the short diffusion paths of charge carries. As a result, these metal oxide semiconductors deliver poor PEC performances in hydrogen production. Therefore, it is quite necessary to design a high-efficiency PEC water splitting system, which can simultaneously combine the advantages of large light utilization (UV and visible regions), fast carrier transport and well matched energy levels with H⁺/H₂.

Material selection and structure design are two key issues for achieving those goals. To increase the light harvesting in visible range, doping with metal (Fe, [21] Sn [22] etc.)/nonmetal (C, [23,24] N [7,25] etc.) elements and sensitizing with narrow-bandgap semiconductor (CdSe, CdTe, CdS etc. [26–29]) in/on the surface of the metal oxide semiconductor have been applied. Yang et al. [13] reported N-doped branched ZnO nanotetrapods showing 0.99 mA cm⁻² at 0.31 V vs. Ag/AgCl (0.92 V vs. RHE) which is much higher than pure ZnO nanotetrapods (0.046 mA cm⁻²). The photocurrent enhancement was attributed not only to the novel nanostructure but also to the increased light absorption by narrowing ZnO band gap due to the N-doping. Another effective strategy is the design of different nanostructured photoelectrodes, which should possess high specific area and direct electron transport. Therefore, some heterojunction materials, such as ZnO/

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CuO [30], SnO₂/TiO₂ [31–33], TiO₂/Fe₂O₃ [34] and ZnO/TiO₂ [35,36] have been introduced into photocatalysts. Wang et al. [30] reported three dimensional (3D) ZnO/CuO heterojunction branched nanowires on copper foil/foam as the catalysts for PEC hydrogen production, which showed an enhanced photocurrent due to increased charge separation and enlarged reaction surface area/sites by the heterostructures. These structures explored the multiple-components semiconductor nanostructure to combine band gap and band alignment in the composite. Actually, applying these two approaches together is the most potential way to achieve combination of large light utilization, fast carrier transport and well matched energy levels simultaneously, therefore, further to improve the electrochemical performance of PEC water splitting.

In this work, we introduced branched TiO₂ nanoneedles on SnO₂ nanowire network (b-NW) as 3D high conductive backbone, and further decorated CdS quantum dots (QDs) onto their surface, forming a novel multi-heterojunction structure. Three main advantages were considered in this rational structure. Firstly, TiO₂ is the common used semiconductor material in photo-electrochemical system, such as dye-sensitized solar cell, photocatalysis and PEC water splitting. However, the dynamics of charge separation and transport are limited in TiO₂ due to its bad electron mobility. Here, the SnO₂ NWs were successfully developed on FTO glass to substitute TiO₂ as a high conductive network because SnO₂ has higher electron mobility ($\sim 100\text{--}200\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) than that in TiO₂ ($\sim 0.1\text{--}1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$). Secondly, we designed a TiO₂/SnO₂ heterojunction structure by epitaxial grow TiO₂ nanoneedles on SnO₂ NWs. On the one hand, these secondary structure can greatly increase the surface area and provide more sites for CdS loading. On another hand, a surface dipole layer from TiO₂ toward SnO₂ is formed and can reduce the recombination of electrons at the interfaces [37,38]. Thirdly, to further increase light absorption in this structure, CdS quantum dots were finally decorated on this heterojunction structure attributed to its narrow band gap of 2.4 eV. It was found that this designed b-NW-QD structure can serve as photoanodes for PEC water splitting and present excellent PEC performances. The electrochemical hydrogen production properties have been remarkably improved and superior to early efforts. The photocurrent density is as high as 8.75 mA cm^{-2} at a potential of 0 V vs. SCE which is over 4 times larger than that of SnO₂-TiO₂ heterojunction.

2. Experimental section

2.1. Synthesis of SnO₂ nanowires directly on FTO glass

The SnO₂ NWs were directly grown on FTO glass through chemical vapor deposition method. In the first step, a thin gold layer was sputtered on the FTO substrate. And then both the 50 mg Sn powder (center) and the FTO substrate ($\sim 1\text{ cm}$ away from the Sn powder) were placed in an alumina boat which was then located at the center of a quartz tube and keep at 620 °C for 4 h with the heating rate of 3.8 °C/min. During the process, a constant flow of Ar was fixed at 40 sccm, the corresponding pressure is 230 Pa. After the furnace was cooled to the room temperature, the substrates were taken out for the next procedure.

2.2. Preparation of SnO₂/TiO₂ b-NW heterojunction structure

For the heteroepitaxy growth of TiO₂ on SnO₂ NWs, we applied a solution growth method as reported in our previous work [39,40]. The as synthesized SnO₂ NW films were immersed in a brown glass bottle with an aqueous solution consisting of DI water (5 ml), HCl (0.05 ml) and TiCl₃ solution (0.1 ml 20 wt% of TiCl₃ in H₂O and HCl solution, Sinopharm Chemical Reagent Co., Ltd.,

Shanghai, China), and then keep at 75 °C for 90 min by oil bath. Followed by rinsing with DI water and subsequently annealed at 500 °C for 2 h in air.

2.3. Sensitized CdS quantum dots on b-NW heterojunction structure

The CdS quantum dots (QDs) were deposited onto the branched SnO₂/TiO₂ b-NW through a sequential chemical bath deposition method. Briefly, the FTO substrate coated with SnO₂/TiO₂ b-NWs was immersed into a 0.05 M Cd(NO₃)₂ aqueous solution for 4 min and rinsed in DI water for 30 s. Subsequently immersed into a 0.05 M Na₂S aqueous solution for another 4 min and rinsed in DI water for 30 s. The entire procedure was performed for one cycle, the desired deposition of CdS QDs was achieved after several cycles, which named as b-NW-QD-X (X is the cycle number). Finally, the film was annealed at 400 °C for 30 min in air.

2.4. Characterization

The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai F30). X-ray diffraction (XRD, Philips, X'pert pro, Cu K α , 0.154056 nm) was employed to characterize the structural properties of the samples. Raman scattering spectra were carried out on a Jobin-Yvon LabRam HR800 spectroscope (with a 532 nm line of Torus 50 mW diode-pumped solid-state laser) under the back-scattering geometry at room temperature. The absorption spectrum was studied by a UV-vis spectrophotometer (TU-1901). The sheet resistances were measured by four probe method (Guangzhou four-point probe technology Co., Ltd., China). Elemental analysis is performed on X-ray photoelectron spectroscope (XPS), which is carried out on a Kratos AXIS Ultra DLD XPS instrument equipped with an Al K α source at 10^{-9} Torr. Photovoltaic performance and electrochemical impedance spectroscopy (EIS) of the devices were obtained on an Electrochemical Work station (RST5200, Zhengzhou Shiruisi Instrument Technology Co., Ltd., China). EIS measurements were carried out in the frequency range from 0.01 Hz to 100 kHz at open-circuit voltage with a potential pulse of 10 mV in amplitude.

3. Results and discussion

The fabrication process of 3D b-NW-QD photoelectrochemical network is schematically illustrated in Fig. 1. In the first step, the SnO₂ NWs were directly grown on FTO substrate through CVD method (Fig. 1a and b). With the optimized growth temperature of 620 °C in our work, the FTO substrate keeps integrated and conductive after the growth of SnO₂ NWs. The effects of the annealing process to FTO during the SnO₂ growth step were characterized by SEM and four probe method as shown in Fig. S1. It is found that the grain shape and size changed a little bit, also the sheet resistances of the FTO increased from 19.5 to 1387 Ω /sq after annealing at 620 °C. As far as we known, there are a few reports on preparing SnO₂ NW directly on FTO glass due to the low endure temperature of the glass. Here we successfully synthesized SnO₂ NW on FTO conductive glass with small loss of sheet resistance. Then TiO₂ nanoneedles were branched out the SnO₂ NW trunk by a solution epitaxy growth process as reported in our previous work [41] (Fig. 1c). Finally, The CdS quantum dots (CdS QDs) were deposited onto the SnO₂/TiO₂ b-NWs through a sequential chemical bath deposition method forming b-NW-QD structure as illustrated in Fig. 1d. The schematic illustration of cross-section from b to d is shown in the top right of Fig. 1.

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