

Full paper

Design of continuous built-in band bending in self-supported CdS nanorod-based hierarchical architecture for efficient photoelectrochemical hydrogen production

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ABSTRACT

The ever-increasing desire for clean and renewable energy has triggered the development of novel materials for photoelectrochemical (PEC) water splitting. However, elaborate design of photoanode materials with high light-harvesting capability, high charge-separation efficiency and long-term stability for converting solar energy into hydrogen fuel is highly challenged. Herein, we fabricated the self-supported gradient oxygen-doped three-dimensional (3D) CdS branched nanorod array (Grad-O CdS), in which a continuous built-in band bending structure was constructed by gradually oxygen doping. The kinetically-confined anion exchange under non-equilibrium condition was confirmed to be critical to achieve the gradient doping. The obtained Grad-O CdS exhibited a large photocurrent density of $6.0 \pm 0.1 \text{ mA cm}^{-2}$ at 0.4 V vs. RHE, which could be maintained for over 42 h. Such excellent performance and stability can be attributed to the efficient separation of charge carriers, which benefits from its continuous built-in band bending caused by oxygen doping, and enhanced light-harvesting capability derived from the narrowing band gap and 3D hierarchical structure. This gradient doping strategy provides a valuable guideline for the design of efficient photoelectrode materials for the conversion of solar energy.

1. Introduction

Photoelectrochemical (PEC) conversion of solar energy to hydrogen (H_2) has been considered as a promising method to solve the global environmental issues and energy crisis [1–7]. However, the PEC efficiency is severely hindered by the sluggish separation process of photo-generated carriers [8–10]. Over the past decades, various well-designed strategies such as nanosizing [11], element doping [12–17], surface modification [18–21], hetero-junction [22–24], and their combinations [25–28] have been employed to increase the separation efficiency. Specially, the design of a built-in band bending through coupling different semiconductors with aligned band structure is highly attractive owing to the greatly enhanced separation ability of photogenerated carriers (PC) at the interface and their potential scalability [22,29]. Great progress has been made in construction of composite semiconductors, but the presence of defects at the sharp interface can trap the charges [4]. To eliminate these defects, tremendous efforts have also been made [30–32]. For example, the tactfully designed $\text{TiO}_2(\text{B})@$ anatase core@shell structure, in which the interface located between

two crystal phases with the same component, guarantees the expedite charge separation and transport [32]. Recently, the multi-step built-in band bending, which realized by a rational layer-by-layer spray pyrolysis strategy to synthesize BiVO_4 film with a 10-step gradient in the tungsten dopant concentration, has been found to remarkably enhance the separation efficiency of PC [31]. At present, it is difficult to obtain gradually adjustable composition. So, the fabrication of continuous and matching energy levels in photoelectrocatalysts, which lead to a continuous built-in band bending, is still highly challenged.

CdS, as a typical n-type semiconductor with a bandgap of 2.4 eV, is a good model photoanode for PEC conversion of solar energy to H_2 . The built-in band bending constructed in CdS by most conventional methods, including element doping or hetero-junction, induces the orientated transfer of photogenerated electrons from core to surface of CdS for photocatalytic H_2 evolution [33,34]. However, it is still a great challenge to obtain self-supported CdS nanorod as an efficient photoanode for PEC H_2 evolution, in which a continuous built-in band bending can induce the photo-generated electrons transferring *via* the surface-core-conductive substrate-counter electrode direction. In

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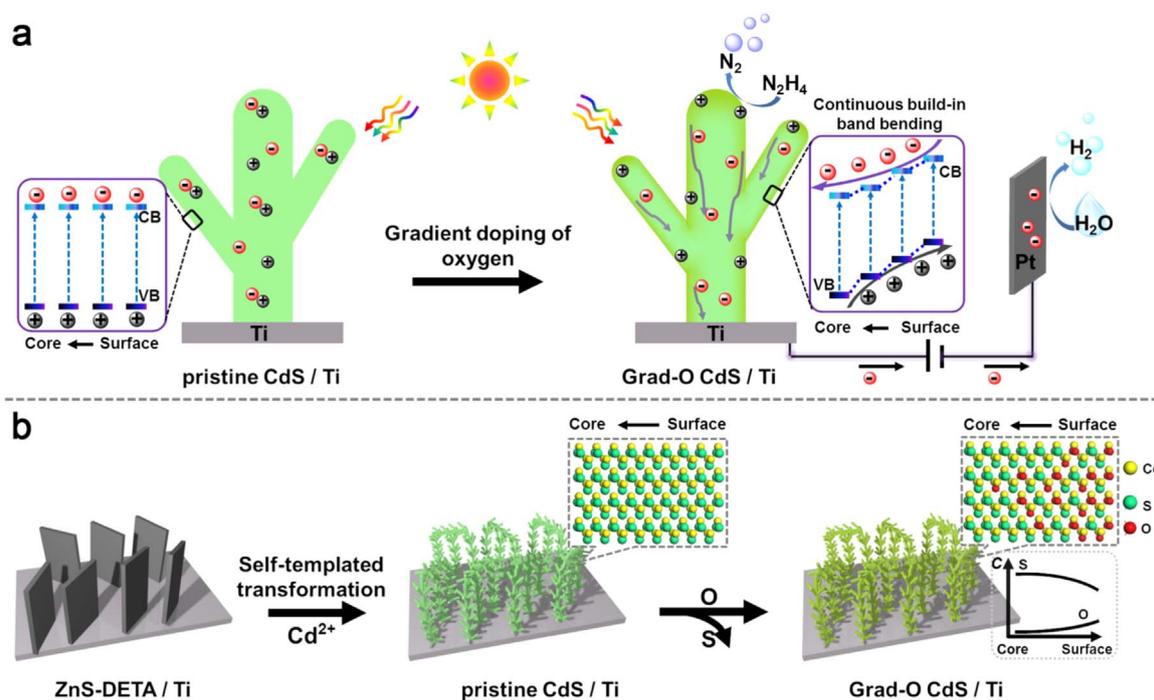


Fig. 1. Scheme illustration for (a) the electron transfer process of the Grad-O CdS in the two-electrode PEC cell, (b) the self-templated transformation from ZnS-DETA to Grad-O CdS.

addition, lowering the size of material is an important pathway to shorten the transfer distance of PC [11,35–37]. But the regular doping methods of nanomaterials with a size of below 20 nm usually make the products be uniformly alloying rather than gradient distribution [38,39]. Moreover, the hierarchical nanostructures grown on the current collectors as photoanodes can assure abundant solar capture, high surface area, and convenient charge transport from catalysts to electrode [8,40]. Therefore, it is highly desirable to explore a facile method to gradually adjust the doping concentration of self-supported 3D ultra-fine nanostructured CdS to obtain a continuous build-in band bending structure for high PEC performance.

Herein, we rationally designed a continuous built-in band bending through the gradient doping of oxygen in the self-supported hierarchically CdS branched nanorod, achieving highly efficient PEC performance of hydrazine oxidation reaction (HzOR) and hydrogen evolution reaction (HER), as shown in Fig. 1a. The kinetically-confined anion exchange under non-equilibrium condition was critical to achieve continuous gradient distribution by doping oxygen in radial direction of CdS nanorod. The experimental results and the first-principle density functional theory (DFT) revealed that the continuous built-in band bending, which was derived from gradient oxygen doping, induced the photo-generated electrons migrating along the direction of the surface-core-Ti substrate-counter electrode, while the photo-generated holes moved in the opposite direction at the same time. The directional transfer of PC can efficiently enhance the separation efficiency and further improve the catalytic activity.

2. Experimental section

2.1. Chemicals

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), thiourea ($\text{CH}_4\text{N}_2\text{S}$), chromic chloride ($\text{CdCl}_2 \cdot 5/2\text{H}_2\text{O}$), and sodium sulfate (Na_2SO_4) were purchased from Tianjin Guangfu Fine Chemical Research Institute, China. Diethylenetriamine (DETA) and hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd, China. Argon (containing 0.018 vol% O_2) was purchased from Tianjin Liufang High-tech Gas Co., Ltd, China. All chemicals were analytical

grade and used as received without further purification. Deionized water (DIW) was used throughout the experiments.

2.2. Synthesis of materials

2.2.1. Synthesis of 2D ZnS-DETA inorganic-organic hybrid nanosheets on Ti foil

In a typical procedure, $\text{Zn}(\text{NO}_3)_2$ (1.5 mmol) and $\text{CH}_4\text{N}_2\text{S}$ (1.5 mmol) were added into 7 mL DIW and then stirred for 5 min to form a clear solution. Subsequently, 28 mL DETA was slowly added into the above solution under constant slow stirring to form a homogenous solution (35 mL, $V_{\text{DETA}}: V_{\text{DIW}} = 4:1$). A piece of clean Ti foil ($1 \times 3 \text{ cm}^2$) was ultrasonicated with acetone, water, and ethanol aqueous solution for 10 min, respectively, and then immersed in the above-mentioned mixed solution. Then, the solution containing Ti foil was transferred into a 50 mL Teflon-lined autoclave, kept at 180 °C for 10 h and cooled down naturally to room temperature. The Ti foil with grayish precipitates on surface was collected and washed with deionized water and ethanol, and then dried under vacuum at room temperature for 6 h. The grayish samples growth on are $\text{ZnS}(\text{DETA})_{0.5}$, identified by our previous work [37]. In our manuscript, the hybrid sheets are named as ZnS-DETA.

2.2.2. Synthesis of pristine CdS on Ti foil

$\text{CdCl}_2 \cdot 5/2\text{H}_2\text{O}$ (0.6 mmol) was added into a 50 mL round-bottom flask with a mixed solvent of DETA (4.8 mL) and DIW (13.2 mL) under constant stirring. Then the as-prepared ZnS-DETA nanosheets on Ti foil were added into the above solution. The reaction system was kept at 100 °C for 10 h, and cooled down naturally to room temperature. The Ti foil with yellow CdS on surface was collected and washed with deionized water and ethanol, respectively, and then dried under vacuum at room temperature for 6 h.

2.2.3. Synthesis of Grad-O CdS on Ti foil

In a typical procedure, the Ti foil with pristine CdS on surface was put into a quartz boat and then placed in the center of the tube furnace connected with a vacuum pump. Before the calcination, the tube furnace was filled with O_2 (0.018 vol%)/Ar atmosphere. Then the pressure

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