Nano Energy 26 (2016) 257–266

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Enhanced performance of photoelectrochemical water oxidation using a three-dimensional interconnected nanostructural photoanode via simultaneously harnessing charge transfer and coating with an oxygen evolution catalyst

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ARTICLE INFO

Article history:
Received 25 January 2016
Received in revised form
20 May 2016
Accepted 23 May 2016
Available online 24 May 2016

Keywords:
Water splitting
Photoelectrochemical reaction
Charge transfer
Three dimensional nanostructure
Bi_2MoO_6 nanosheet

ABSTRACT

The most important factors dominating photoelectrochemical (PEC) water splitting performance include light absorption, charge separation and transport, and surface chemical reactions. In order to meet these factors, a novel $Fe_xNi_{1-x}O/Bi_2MoO_6$/Si nanowire hierarchical nanostructure was produced using a metal-assisted chemical-etching and hydrothermal growth process, in which Si nanowires were used as backbones, Bi_2MoO_6 nanosheets as coating, and $Fe_xNi_{1-x}O$ nanoparticles (NPs) as surface catalysts. This integrated three-dimensional (3D) hierarchical nanostructure was applied as a photoanode in a PEC water reaction, and higher photostability and photocurrent density were gained. The excellent PEC performance was due to the 3D hierarchically structural effect, resulting in the enhancement of the surface-to-volume ratio, light harvest and high speed electron transport, and at the same time, terminal $Fe_xNi_{1-x}O$ NPs played the role of the surface catalyst effectively in order to accelerate the water splitting reaction and enhance photostability. Based on such an environmentally friendly hierarchical nanostructure, the study provided an efficient route to improve water-splitting performance and it could also be a model structure for similar electrode materials.

1. Introduction

Renewable and sustainable energy sources must be developed because of the current level of energy consumption and the disadvantages of the present energy sources, such as CO_2 emission and limited reserves of fossil fuels [1,2]. Solar-driven photoelectrochemical (PEC) water splitting into hydrogen and oxygen, a way to capture and convert solar energy by electrochemical catalysis into energy stored molecules, is being considered as a viable solution addressing the increased energy crisis [3,4]. The efficiency of PEC water electrolysis is largely determined by the properties of photoelectrodes, and considerable efforts have been devoted to exploring active photoelectrode materials, such as TiO_2 [5,6], WO_3 [7,8] and ZnO [9,10]. However, most of these materials possess relatively large bandgaps and absorb and utilize only a small portion of the solar spectrum. Among various transition metal oxide semiconductor materials, bismuth-based materials are more appropriate candidates since the Bi 6s in Bi(III) can hybridize with O 2p orbitals to form a new preferable hybridized valence band (VB). The band gap of Bi-based materials can be narrowed to harvest visible light. Particularly, one of the new classes of two-dimensional (2D) layered materials, Bi_2MoO_6, is especially attractive owing to its appropriate band gap (2.5–2.8 eV), as well as its excellent chemical stability, low cost, and corrosion resistance [11]. The energy bands of Bi_2MoO_6 straddle the water redox potentials, which is energetically suitable for water splitting. Some study results reveal that Bi_2MoO_6 can perform as an excellent photocatalyst and solar-energy-conversion material for water splitting and environmental decontamination under visible-light irradiation [12,13], suggesting that Bi_2MoO_6 is a promising candidate for both photocatalytic and PEC water splitting. However, the practical applications of Bi_2MoO_6 remain a challenge due to some inherent drawbacks, including inefficient charge separation and transportation, fewer activity sites, and poor selectivity of the desired reaction.

It is widely accepted that an excellent PEC water splitting performance needs to meet such requirements as high stability in

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http://dx.doi.org/10.1016/j.nanoen.2016.05.039
2211-2855/

aqueous solution, small band gap for wide spectrum response, a proper conduction/valence band (CB/VB) position satisfying water oxidization and reduction potentials, effective carrier separation and transportation, and fast surface chemical reactions [14]. Construction of a heterojunction between Bi_2MoO_6 and other semiconductors with a suitable band gap is an effective method to present promoted or new physicochemical properties, thus enhancing the photoconversion efficiency [15]. Up to now, many different materials have been applied to couple with Bi_2MoO_6, so as to improve its photocatalytic performance [16,17], but photoanodes based on Bi_2MoO_6 hetero-structurization materials are rarely reported. Although the construction of nanostructured Bi_2MoO_6 coupled with ZnO photoanode is reported [15], there is still rare report concerning a Bi_2MoO_6-based photoanode for PEC water splitting.

On the other hand, silicon, one of the most abundant elements in the earth crust, can be used as a photoelectrode because of its high visible-light-absorption property with a bandgap of ~1.12 eV. However, directly using Si as a PEC photoelectrode is difficult because of its improper band positions and its unstable surface in aqueous solutions. The VB position of Si is higher than the oxygen evolution reaction (OER) potential and is not suitable for water oxidation [18]. Therefore, an electrode composed of a semiconductor heterojunction has been proposed to overcome these shortcomings. In PEC systems, n/n heterojunction photoanodes composed of two n-type semiconductors, such as n-Si/n-TiO_2 [19] or n-Si/n-Fe_2O_3 [20], have been demonstrated to increase the photocurrent density and to shift the onset potential of the photocurrent as a type of dual-absorber system. Compared to the CB edge of TiO_2 or Fe_2O_3, the more negative potential of Si can give higher energetics for the reduction of electrons on the counter electrode, and the charge separation efficiency is enhanced in the metal oxide semiconductor [19]. In these cases, the photoanode composed of a small band gap semiconductor is protected by a stable semiconductor.

Meanwhile, with a high surface-to-volume ratio, one-dimensional (1D) Si nanostructures (Si nanowires, SiNWs) improve the light absorption capability, photocurrent collection and therefore power conversion efficiency, in comparison with a flat surface [21–23]. SiNWs also have the properties of more rapid electron transport along the long direction, shorter distance of carrier separation, and a lower amount of grain boundaries. These advantages make it suitable as a viable light-harvesting material and a well-established semiconductor for constructing solar-to-fuel conversion devices [24,25]. Even so, 1D NWs have a relatively smaller surface area compared to nanoparticles (NPs) and nanosheets, which would limit the light absorption and the electrochemical active sites. To maximize the PEC performance, it is necessary to design a structure combining both the fast electron path of 1D nanostructures and the large surface area of 2D nanosheets. The use of the 3D nanostructure with vertical semiconductor NWs and 2D nanosheets is an effective way to reduce the given overpotential for a required catalytic activity, because of their outstanding light absorption and large solid/electrolyte interfacial areas [22]. Therefore, it is highly desirable to tailor the Bi_2MoO_6/SiNW heterojunction arrays for improving the efficiency of energy conversion.

Additionally, the semiconductor material properties can be further improved by doping with appropriate impurities. Modification of the photoanode with a suitable oxygen evolution cocatalyst is equally important since it improves the efficiency by lowering the overpotential and preventing photocorrosion. Since the surfaces of semiconductor electrodes are not particularly catalytic for water oxidation, integrating a surface modifying water oxidation catalyst (WOC) with appropriate morphology onto photoanode structures is a feasible way to increase the PEC efficiency via creating electrode/electrolyte interfaces to reduce the charge recombination rate, change the water oxidation reaction mechanism and reduce reaction water oxidation kinetics [26–28]. For instance, Ni-based electrocatalysts have been widely used in electro-water splitting owing to their high catalytic activity, chemical stability, and low toxicity. A robust solar water splitting system is reported which uses a nickel oxide coated n-type Si photoanode and exhibits an enhanced PEC performance compared to a non-coated Si photoanode under neutral pH conditions [29]. Specifically, Fe-doped NiO nanocrystals ($Fe_xNi_{1-x}O$) are an efficient OER catalyst, whose electrocatalytic activity increases by almost an order of magnitude by introducing the Fe atoms into the structure, which makes it by far the highest among all reported FeNi oxide materials [30,31].

Driven by the above-mentioned successful developments, and in consideration of energy conversion efficiency, chemical stability and scalable construction, we here attempted to design and produce unique Si based hierarchical 3D nanostructures to achieve efficient PEC water splitting. In other words, ordered 1D SiNW arrays interconnected with 2D Bi_2MoO_6 nanosheets served as the photoanode, and were used to rectify in situ carrier transfer and separation. Then, an efficient co-catalyst of $Fe_xNi_{1-x}O$ NPs was modified onto the surface of the aligned 3D nanostructures, thus forming a junction cascade of $Fe_xNi_{1-x}O/Bi_2MoO_6$/SiNWs, on which $Fe_xNi_{1-x}O$ NPs acted as a hole acceptor and catalytic site to accelerate the surface water oxidation reactions. The band potentials of both Si and Bi_2MoO_6 suggested that electron transfer from Bi_2MoO_6 to Si and transfer of the holes to $Fe_xNi_{1-x}O$ NPs was possible, thus resulting in in situ separated electrons and holes by the heterojunction. By combining the fast transport path of electrons and almost full solar spectrum harvesting capability in SiNWs, the larger surface area of Bi_2MoO_6 nanosheets, and the dramatic water oxidation catalytic activity of $Fe_xNi_{1-x}O$ NPs, the water-splitting performance of the 3D $Fe_xNi_{1-x}O/Bi_2MoO_6$/SiNW photoanode was significantly improved compared to that of pristine SiNWs and Bi_2MoO_6/SiNWs. This efficient design strategy, consisting of two junctions, represented a successful example of a Bi_2MoO_6-based photoelectrode for water splitting, and was fully investigated in our work.

2. Experimental section

2.1. Production of the $Fe_xNi_{1-x}O/Bi_2MoO_6$/SiNW photoanode nanostructures

Vertically aligned SiNW arrays were grown from phosphorus-doped n-type Si (100) wafers using a metal-assisted chemical etching process similar to that used in previous work [32]. Briefly, Si wafer chips (cut into 1×2 cm^2) were cleansed by successive sonication in ethanol and acetone for 15 min and treated with a "piranha" solution (H_2SO_4:30% H_2O_2=3:1, v/v) to purify the surface. Subsequently, the chips were immersed in an HF solution (5%) for 5 min to obtain a hydrogen-terminated surface. Then, the chips were dipped into a solution of $AgNO_3$/HF (4.8 M/0.005 M) for 1 min After being rinsed with deionized water to remove Ag^+ ions, the chips were immediately transferred to an etchant solution containing 4.8 M H_2O_2.

Bi_2MoO_6 nanosheet/SiNW heterostructures were obtained using a solvothermal method [33]. 10 mL of ethylene glycol containing $Bi(NO_3)_3 \cdot 5H_2O$ (2 mmol) and $Na_2MoO_4 \cdot 2H_2O$ (1 mmol) were stirred for 30 min to obtain a clear solution. The as-prepared Si NW array plate with the coating side facedown was immersed in the solution, and then heated to 160 °C and maintained for 24 h in a 30 mL Teflon-lined autoclave. The obtained Bi_2MoO_6/SiNW hierarchical heterostructures were washed with deionized water