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Short note

Si/Mo_4O_{11} nanowire arrays with enhanced photoelectrochemical performance

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ABSTRACT

To utilize Si nanostructures as photocathode for high-efficiency solar water splitting, a catalyst with low cost and high activity is inevitable to modify Si. In this study, employing the electrochemical deposition method, the surfaces of Si nanowire arrays were decorated with a novel non-noble metal electrocatalyst, Mo_4O_{11}. The morphology, chemical composition and structure of the as-synthesized Si/Mo_4O_{11} nanowire arrays were characterized in details. As photocathodes for photoelectrochemical water splitting, the Si/Mo_4O_{11} nanowire arrays exhibited more positive turn-on potential and larger photocurrent compared to Si nanowire arrays. The results demonstrate that the Si/Mo_4O_{11} nanowire arrays could be a promising candidate for solar water splitting.

1. Introduction

Si is a promising semiconductor for solar water splitting due to its appropriate band gap, excellent electronic properties and low cost [1–8]. However, the dynamics of hydrogen evolution reaction (HER) on the surface of bare Si is quite sluggish [9], thus a high over potential is generally needed to achieve a satisfied hydrogen evolution rate. To overcome this shortcoming, many HER catalysts were developed and modified on Si to improve the photoelectrochemical water splitting performance of Si. The best catalyst for HER is the noble metals including Pt [10–13], Pd [14] and Au [15,16]. Although excellent performance can be obtained from these noble metal catalysts, the low natural abundance and high cost of the catalysts inhibit their large-scale application in this field. For this reason, many efforts have been made to develop low-cost, high activity catalysts for HER of Si. Metal phosphides[17–19], such as NiP [20,21], CoP [22], MoP [23,24], FeP [25,26], CuP [27] were intensively investigated in recent years and found to exhibit high catalytic activity. Transition metal sulfide is another significant category of HER catalysts with high activity and low cost [28–32]. In addition, some metal oxides have been reported to exhibit excellent catalytic activity for HER. Especially, the molybdenum oxide have attracted attentions in recent years. It has been reported that the none-noble metal composite cathodes, such as the hydrothermal synthesized MoO_2/Ni foam, electrodeposited Ni-MoO_x films, exhibited excellent catalytic performance (high stability and activity) for HER [33–35]. Considering the good catalytic activity and low cost of molybdenum oxide, we fabricated a molybdenum oxide (Mo_4O_{11}) modified Si nanowire array photocathode. The Mo_4O_{11} nanoparticles were electrodeposited onto the surfaces of Si nanowires. Photoelectrochemical water splitting performance of Si nanowire arrays was significantly enhanced by the modification of Mo_4O_{11} nanoparticles.

2. Experimental

2.1. Preparation of Si/Mo_4O_{11} nanowire arrays

The Si/Mo_4O_{11} nanowire arrays were prepared by a two-step process. First, the p-Si nanowire arrays were synthesized via a typical metal-assisted chemical etching method, more details can be found in Ref. [36]. Second, Mo_4O_{11} was electrodeposited onto the surfaces of the p-Si nanowires. The Si wafer with p-Si nanowire arrays, SCE and Pt electrode were used as the working electrode, reference electrode and counter electrode, respectively. Aqueous solution containing 5 mM $(NH_4)_6Mo_7O_{24}$, 0.2 M NH_4Cl, and 0.04 M KCl was used as the electrolyte. Before and during the

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electrodeposition process, the electrolyte was deoxygenated by continuous bubbling Ar. A stationary potential of −1.2 V vs. SCE was applied to the working electrode for 20 min, and the Si/Mo_4O_{11} nanowire arrays were obtained.

2.2. Photoeletrochemical measurement

Photoelectrochemical measurements were performed in a three-electrode system. The Si/Mo_4O_{11} nanowire arrays were used as working electrode, a Pt foil and SCE were used as counter electrode and reference electrode. The electrolyte was deoxygenated aqueous solution containing 0.5 M Na_2SO_4. A 500 W Xe lamp passing through AM 1.5 filter with intensity of 100 mW/cm^2 was used as light source.

3. Results and discussion

The morphologies of the as-prepared samples were characterized by SEM, as shown in Fig. 1a and b. It can be observed from the SEM images that the morphology of as-prepared sample is almost the same with that of the Si nanowires [36,37]. The nanowires with length of about 30 μm are free-standing on the Si substrate. The EDS spectrum shown in Fig. 1c demonstrates the existence of Si, Mo and O elements in the nanowire arrays. To confirm the

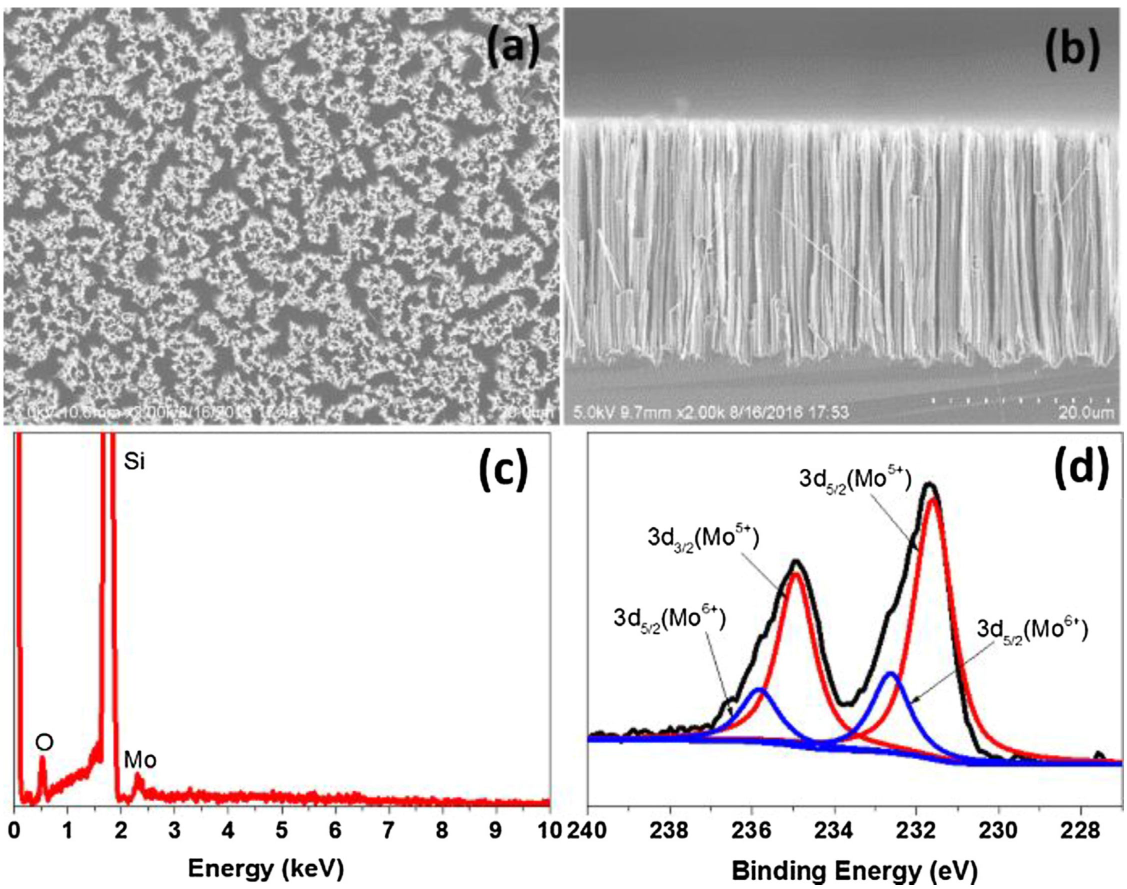

Fig. 1. (a) Top view SEM image, (b) side view SEM image and (c) EDS spectrum of the Si/Mo_4O_{11} nanowire arrays, (d) XPS spectrum of Mo 3d.

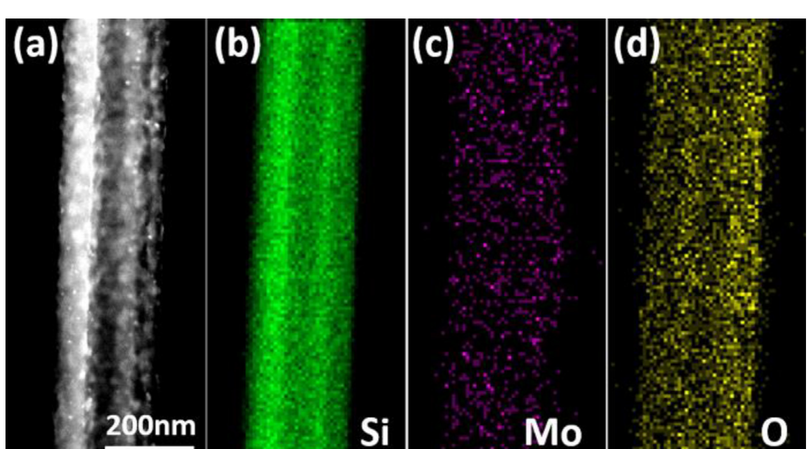

Fig. 2. (a) STEM image of an individual Si/Mo_4O_{11} nanowire, EDS mapping of (b) Si, (c) Mo and (d) O.

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