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Tungsten Sulfide Enhancing Solar-Driven Hydrogen Production from Silicon Nanowires

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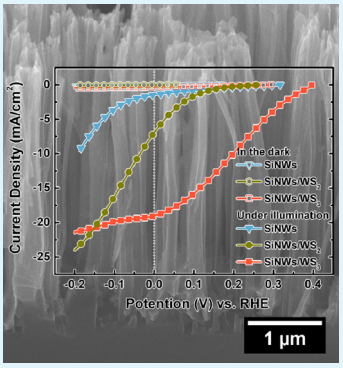
Supporting Information

ABSTRACT: Tungsten sulfides, including WS_2 (crystalline) and WS_3 (amorphous), were introduced to silicon nanowires, and both can promote the photoelectrochemical hydrogen production of silicon nanowires. In addition, more enhancement of energy conversion efficiency can be achieved by the loading of WS_3, in comparison with loading of WS_2. Polarization curves of WS_3 and WS_2 suggest that WS_3 has higher catalytic activity in the hydrogen evolution reaction than WS_2, affording higher energy conversion efficiency in silicon nanowires decorated with WS_3. The higher electrocatalytic activity of WS_3 correlates with the amorphous structure of WS_3 and larger surface area of WS_3, which result in more active sites in comparison with crystalline WS_2.



KEYWORDS: *silicon nanowires, tungsten sulfide, hydrogen evolution reaction, photoelectrochemical*

1. INTRODUCTION

Photoelectrochemically splitting water to hydrogen (H_2) and oxygen (O_2) accomplishes simultaneously the harvesting of solar energy and the storage of solar energy into a clean chemical fuel (H_2), and therefore is gaining extensive and increasing attention with respect to the global energy crisis and environmental issues.[1] In principle, a promising photocathode with efficient H_2 generation capability in a photoelectrochemical water splitting cell should be able to sufficiently utilize the solar spectrum, and should have fast hydrogen evolution reaction (HER) kinetics so that photogenerated electrons in the photocathode can effectively reduce species in electrolyte into H_2 instead of recombining with photogenerated holes.

Silicon (Si) can absorb photons with wavelengths ranging from UV to near IR, and has been widely applied in the field of solar energy conversion, including solar cell and photoelectrochemical water splitting.[2,3] It is further demonstrated that one-dimensional Si nanostructures (Si nanowires, SiNWs) can improve the absorption capability and therefore power conversion efficiency, in comparison with their bulk counterpart.[4−6] However, similar to other semiconductors, the intrinsic HER kinetics of Si is slow. This shortage results in the low energy conversion efficiency (η) of a photocathode constructed from native bulk Si or SiNWs.

Introducing a HER electrocatalyst to the Si surface can improve the HER kinetics of Si-based photocathodes, and this configuration has been investigated for several decades.[2] However, the widely used and high performance HER electrocatalysts are expensive and rare earth metals (e.g., Pt[2]). Consequently, the practical application of such catalysts in photocathodes is limited. Although various nonprecious HER electrocatalysts have been reported, only a limited amount of them have been applied to photocathodes, including Ni−Mo alloy,[7] NiO_x,[8] Mo_3S_4 cluster,[9] MoS_2 film,[10] and MoS_3 particles.[11]

On the other hand, although the application of tungsten sulfide in HER has been demonstrated, including in electrocatalysis[12,13] and photocatalysis,[14,15] the application of tungsten sulfide in photocathodes has not yet been reported. Furthermore, the research concerning HER catalytic activity of tungsten sulfide is focused on the development of various morphologies of tungsten sulfide.[16−18] The influence of structure and/or chemical composition of tungsten sulfide on its HER catalytic activity has not been explored.

In this article, the systematic investigation on the photoelectrochemical hydrogen production capabilities of SiNWs decorated with tungsten sulfides is introduced. Two kinds of tungsten sulfides, including WS_3 (amorphous) and WS_2

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