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Communication

Rationally designed/constructed MnO_x/WO_3 anode for photoelectrochemical water oxidation

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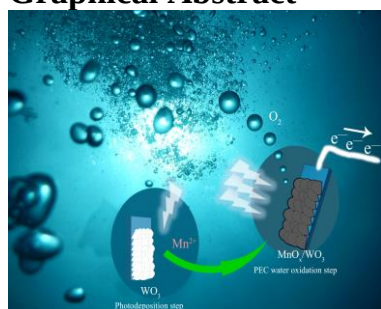
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Graphical Abstract



The activity of WO_3 photoanode could be improved efficiently after loading MnO_x by photodeposition. The maximum photocurrent density of composite photoanode is achieved with a deposition time of 3 min, which is higher than that of pristine WO_3 photoanode around 40%.

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ABSTRACT

Photoelectrocatalytic water splitting is an effective way to utilize the solar energy to solve the energy shortage. The valence band edge of WO_3 located at ~ 3 V vs. normal hydrogen electrode (NHE), which can offer enough potential to kinetically oxidize water for oxygen evolution reaction. However, water oxidation reaction kinetics is sluggish when only WO_3 is used as the photoanode. It is highly desirable to use cocatalyst to promote the kinetics. MnO_x loaded on the WO_3 photoanode through photodeposition methods improves the photoelectrochemical water oxidation performance. A maximum photocurrent density of composite photoanode is achieved with a deposition time of 3 min, which is higher than that of pristine WO_3 photoanode around 40%. MnO_2 is not only a cocatalyst for water splitting but also for improving oxidation selectivity. We tried to use two means to load MnO_x on WO_3 photoanode material. It is observed that loading a moderate amount of MnO_x on the WO_3 by photodeposition can promote the performance of the WO_3 photoanode.

Keywords: Photoelectrochemical water oxidation Tungsten oxide Manganese oxide Photodeposition Hydrothermal method

Energy is the basic element for the sustainability of human society and it is crucial for social and economic development. Nowadays, owing to the severe environmental pollution, global warming and energy shortage, it is urgent to optimize our existing energy structures, integrate available and potential energy resources to find a way for the future of mankind. Solar energy is a clean and well-stocked energy source, which is the ultimate energy in the existing energy resources that can satisfy our demand of energy [1].

Splitting water to produce hydrogen and oxygen is one convenient way for energy conversion [2]. The water splitting comprises of two half reactions, that is, one is the evolution of O_2 ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) and the other is evolution of H_2 ($4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$) [3]. The oxygen evolution reaction involves a process of four-electron transfer, which is more challenging than hydrogen evolution reaction [4].

Since Fujishima *et al.* [5] discovered that TiO_2 can split water under ultraviolet irradiation, many semiconductor materials have been researched for photoelectrochemical water splitting, such as BiVO_4 [6-8], Fe_2O_3 [9-11] and WO_3 [12,13]. WO_3 has a bandgap of 2.6 eV to 2.7 eV for visible light absorbability, and its valence band position is about 3 V (vs. normal hydrogen electrode (NHE)) to efficiently oxidize water [14]. Therefore, WO_3 semiconductor photoanode is chosen by us for researching the water oxidation reaction. However,

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