On the Substantially Improved Photoelectrochemical Properties of Nanoporous WO3 Through Surface Decoration with RuO_2

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Abstract

Solar fuel generation, either through photochemical or photoelectrochemical (PEC) routes, is one of the most prominent pathways to harvest sunlight in order to contribute to a diversified and sustainable energy supply. Oxygen evolution reaction (OER) from aqueous solutions is the half reaction of different energy related reaction schemes, most importantly stoichiometric water splitting (H_2 generation) or CO_2 reduction. In this paper, we present PEC water oxidation (OER) on nanoporous WO_3 films, decorated with RuO_2 nanoparticles. The morphology and the composition of these nanostructured assemblies were characterized by high-resolution scanning electron microscopy, X-ray photoelectron spectroscopy, and cyclic voltammetry while their photo-electrochemical behavior was evaluated by photovoltammetry and incident photon-to-current conversion efficiency (IPCE) measurements. The O_2 evolution capability was directly assessed by determining the amount of evolved O_2 gas during PEC oxidation of water. The RuO_2 electrocatalyst substantially increased photoanodic current flow through facile transfer of photogenerated holes from WO_3 to the solution, thereby improving interfacial charge transfer kinetics. Both absolute and relative enhancement of photocurrents was analyzed as a function of the applied external bias potential giving important insight into the mechanistic details. Furthermore, the decisive roles of the amount of RuO_2 co-catalyst and thermal pretreatment were established by synthesizing hybrid assemblies with different RuO_2 coverage, and applying subsequent thermal treatment, respectively. Through careful optimization of the composition of the hybrid material, the IPCE value doubled at lower bias potentials and was increased close to the theoretical 100 % limit at higher positive potential values. These results demonstrate the synergy gained by combining the excellent photoanodic properties of nanoporous WO_3 with the robust O_2 evolution capabilities of RuO_2.

Keywords: Water splitting, Co-catalyst, Semiconductor, Solar energy, Synergy