

Modulating Photoelectrochemical Water-Splitting Activity by Charge-Storage Capacity of Electrocatalysts

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Abstract : Photoelectrochemical (PEC) water splitting using semiconductors (SCs) provides a convenient way to convert sustainable but intermittent solar energy into clean hydrogen energy, and it has been regarded as one of most promising technology to solve the energy crisis and environmental pollution in modern society. However, the record energy conversion efficiency of a PEC cell (~3%) is still far lower than the commercialization requirement (~10%). The sluggish kinetics of oxygen evolution reaction (OER) half reaction on photoanodes is a significant limiting factor of the PEC device efficiency, and electrocatalysts (ECs) are always deposited on SCs to accelerate the hole injection for OER. However, an active EC cannot guarantee enhanced PEC performance, since the newly emerged SC-EC interface complicates the interfacial charge behavior. Herein, α -Fe₂O₃ photoanodes coated with Co₃O₄ and CoO ECs are taken as the model system to glean fundamental understanding on the EC-dependent interfacial charge behavior. Intensity modulated photocurrent spectroscopy and electrochemical impedance spectroscopy were used to investigate the competition between interfacial charge transfer and recombination, which was found to be dominated by the charge storage capacities of ECs. The combined results indicate that both ECs can store holes and increase the hole density on photoanode surface. It is like a double-edged sword that benefit the multi-hole participated OER, as well as aggravate the SC-EC interfacial charge recombination due to the Coulomb attraction, thus leading to a nonmonotonic PEC performance variation trend with the increasing surface hole density. Co₃O₄ has low hole storage capacity which brings limited interfacial charge recombination, and thus the increased surface holes can be efficiently utilized for OER to generate enhanced photocurrent. In contrast, CoO has overlarge hole storage capacity that causes severe interfacial charge recombination, which hinders hole transfer to electrolyte for OER. Therefore, the PEC performance of α -Fe₂O₃ is improved by Co₃O₄ but decreased by CoO despite the similar electrocatalytic activity of the two ECs. First-principle calculation was conducted to further reveal how the charge storage capacity depends on the EC's intrinsic property, demonstrating that the larger hole storage capacity of CoO than that of Co₃O₄ is determined by their Co valence states and original Fermi levels. This study raises up a new strategy to manipulate interfacial charge behavior and the resultant PEC performance by the charge storage capacity of ECs, providing insightful guidance for the interface design in PEC devices.

Keywords : charge storage capacity, electrocatalyst, interfacial charge behavior, photoelectrochemistry, water-splitting

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