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Title: Design of photoanodes for photoelectrochemical water splitting

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Abstract:

Photoelectrochemical water splitting (PEC) is a promising sustainable and environment- friendly technique used for the conversion of solar energy to chemical energy. It comprises two half-cell reactions, hydrogen evolution reaction (HER) which takes place on photocathode, and oxygen evolution reaction (OER) which takes place on photoanode. The photoanode which brings about the oxidation of water is a key element of the PEC water splitting reaction since the OER in PEC water splitting is a slow step due to its multielectron requirements. Thus, the development of efficient photoanodes for water oxidation is an important requirement for the improvement of PEC water-splitting technology. In 1972, Fujishima and Honda reported the PEC water splitting using single-crystal TiO2 as photoanode and platinum as the cathode which ignited the interest of researchers in the development of other semiconductor-based materials which can play the role of efficient photoanodes. However, the high electron-hole recombination, poor charge transport properties, lower stability, limited absorption, and photocorrosion of the available photoanodes. Thus, various strategies have been adopted to modify these photoanodes to improve their PEC performance such as morphology and facet control, doping, co-catalysts, and hetero- and homo-junctions, etc. The main aim of this thesis is the design of modified photoanodes which leads to better photoelectrochemical performance. In the present thesis, modified CdS photoanodes have been prepared with the help of multi-walled carbon nanotubes (CNTs) and CoPi which has significantly improved the charge-carrier separation properties of CdS and monitored the kinetics of charge-transfer via transient absorption spectroscopic studies. BiVO4 photoanode has been modified with various loadings of Mn2+ where 1% Mn-BiVO4 has shown the highest photocurrent density. Cu2WS4 which is a less explored photoanodic material has been modified using two different techniques. In one case, a ternary system Cu2WS4-CNT-FeOOH has been synthesized whereby the photogenerated charge carriers have been extracted using CNT and FeOOH to lower the electron-hole recombination. In another case we have substituted W6+ with various loadings of isovalent Mo6+ in Cu2WS4 and monitored the photoelectrochemical properties. The design of these modified photoanodes has provided effective methods to deal with the limitations associated with already existing photoanodes.

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