Nanostructured Semiconductor Composites: Design, Preparation and Application for Solar-to-Chemical Energy Conversion and Storage

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The direct conversion of solar energy to chemical fuels provides an attractive long-term solution to the problem of ever-rising global energy demand. Solar powered water-splitting is an artificial photosynthesis that involves two half-cell reactions, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), and the solar energy is stored in the chemical bonds of the two products H_2 and O_2. Herein, we report the fabrication and application of composite photoanodes and photocathodes for efficient OER and HER, respectively.

The first composite photoanode we report here was prepared by modifying WO_3 nanoneedles (NNs) with nickel-borate (Ni-B_i). The high-aspect-ratio WO_3 NNs were employed as light-absorbing material and the Ni-B_i as oxygen evolving catalyst. We demonstrate that the WO_3 nanoneedles exhibit a high activity toward OER under illumination due to their unique nanostructure. The combination of Ni-B_i catalyst with WO_3 nanoneedles significantly enhances the photoactivity for OER by further negatively shifting the onset potential of the photocurrent and improving the photocurrent within the entire oxygen-evolving potential region. Moreover, the WO_3 NNs/Ni-B_i composite photoanodes exhibit superior stability to the WO_3 NNs photoanodes at all oxygen-evolving potentials.

The second composite photoanode we report is WO_3 NNs/Fe_2O_3, which were successfully prepared on FTO substrates, with WO_3 NNs as framework cores and small nanocrystals of α-Fe_2O_3 as porous shells. The α-Fe_2O_3 was used as co-ligher-harvesting materials because its absorption band covers the majority of the UV and visible portion of the solar spectrum. We demonstrate that modification of the WO_3 NNs with α-Fe_2O_3 greatly extends the light absorption band by red-shifting the onset absorption wavelength from 450 nm to 650 nm. The photocurrent of the composite photoanodes is 1.6 time higher than that obtained on pure WO_3 NNs photoanode. Cobalt phosphate (Co-Pi) was used as OER catalyst to modify the WO_3 NNs/Fe_2O_3 composite. The deposition of Co-Pi on the surface of WO_3 NNs/Fe_2O_3 composite significantly improve the photostability of the photoanodes by facilitating hole transfer from semiconductor oxides to water.

The last photoelectrode we report here is the CuO/Pd composite photocathode for HER. In this part of work, CuO films were prepared by a facile and cost-effective method that involves solution synthesis, spin-coating, and thermal treatment process. The resulting CuO films have a monoclinic crystal structure with bandgap energy of 1.56 eV and a conduction band position of 3.73 eV below the vacuum level in borate buffer solution. A photo-assisted electrodeposition method that ensures the deposition of Pd on the photoactive sites of CuO surface was developed to prepare CuO/Pd composite photocathodes. We demonstrate that the deposition of Pd on CuO not only enhances the photocurrent for HER but also significantly improves the photocatalytic stability of the CuO film.

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