Anodic WO_3-Based Heterojunctions: Boosting Photoelectrochemical Water Splitting Efficiency

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Harnessing solar energy and converting it into chemical energy through photoelectrochemical (PEC) reactions offers a green and sustainable approach to energy conversion. However, PEC water-splitting devices that utilize wide band gap semiconductors often suffer from low efficiency, poor long-term stability, and a dependence on ultraviolet light absorption. Semiconducting metal oxides produced via anodization offer advantageous architectures and high surface area, making them attractive candidates for enhancing PEC performance. Among these, anodic tungsten oxide (WO_3), which absorbs part of the solar spectrum, serves as a promising platform for surface modification aimed at improving PEC activity. Various strategies have been developed to modify WO_3, including doping and coupling with other semiconductors, to enhance its photocatalytic and photoelectrochemical properties.

Here, we presents a comprehensive study on the development of anodically synthesized nanostructured WO_3-based heterojunction photoanodes for enhanced photoelectrochemical PEC water splitting. A range of surface engineering and doping strategies were employed to improve charge separation, light absorption, and photocatalytic activity.

The first strategy involved hydrothermal post-treatment, with enabled Fe doping of monoclinic WO_3 and the in-situ formation of $FeWO_4$ and Fe_3O_4 phases. These resulting heterojunctions significantly enhanced the photocurrent response — doubling that of pure WO_3 — and demonstrated long-term operational stability. The performance improvement was attributed to the creation of oxygen vacancies and favourable band alignment between n-type WO_3 and p-type $FeWO_4$, which enhanced charge carrier lifetime and transfer efficiency.

A second, complementary approach utilized one-step anodization of tungsten in cobalt fluoride-containing electrolytes, resulting in in-situ Co-F doping. This process produced nanoporous Co-F-WO_3 layers with up to a fivefold increase in PEC activity. Shifts in the photocurrent onset were associated with the synergistic effects of cobalt and fluorine dopants, as confirmed by optical and electrochemical analyses.

Finally, a third strategy focused on selenization of WO_3-$W_{18}O_{49}$ structures followed by copper deposition, forming complex WO_3–SeO_2–CuO heterostructures. These composite electrodes exhibited up to seven times higher PEC activity compared to pristine WO_3.

All materials were extensively characterized using SEM, EDS, XRD, Raman, XPS, UV-Vis DRS, and PEC techniques including linear voltammetry, electrochemical impedance spectroscopy, and Mott-Schottky analysis. The study underscores the potential of tailored WO_3-based nanostructures and heterojunctions as efficient and reusable photoanodes for solar-driven water splitting.

References

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