Supporting Information (SI)

Ag-Functionalized CuWO₄/WO₃ Nanocomposite for Solar Water Splitting

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Scheme S1. Schematic diagram of the synthesis route and electrophoretic deposition of powders
Electrophoretic Deposition

The working electrodes were prepared by electrophoretic deposition of the as-prepared powders on the fluorine-doped tin oxide (FTO) substrates. Briefly, after sonication of FTO in acetone, ethanol and DI water and drying with nitrogen, electrophoretic deposition was done in a two electrode configuration in sonicated acetone solution (10 mL) with iodine and the powders (30 mg) dissolved in the solution. By applying a bias of 40 V for different time between the FTO substrate and a Pt electrode, the powders were deposited. To achieve the highest current density during front-side illumination ($J_{\text{front}}$), 5 min for CuWO$_4$/WO$_3$ and Ag-CuWO$_4$/WO$_3$ and 4 min for WO$_3$ and CuWO$_4$ were used for thin film preparation according to the value of $J_{\text{front}}/J_{\text{back}}$ ratio vs. electrodeposition time (Fig. S1). Electrodeposition time (e.g. film thickness) was changed for all samples to achieve highest current density during front-side illumination ($J_{\text{front}}$) and an optimal value of $J_{\text{front}}/J_{\text{back}}$ ratio (due to higher electron transfer resistance in so high thicknesses causing smaller $J_{\text{front}}$ compared to $J_{\text{back}}$). Accordingly, 5 min for CuWO$_4$/WO$_3$ and Ag-CuWO$_4$/WO$_3$ and 4 min for WO$_3$ and CuWO$_4$ were used for electrodeposition thin film preparation to achieve more effective absorbance but not very large charge transfer resistance (longer time caused a significant drop in $J_{\text{front}}/J_{\text{back}}$ ratio of samples due to a sharp increase of charge transfer resistance and charge carrier recombination).

![Fig. S1.](image)

Fig. S1. (a) Different value of $J_{\text{front}}/J_{\text{back}}$ ratio vs. electrodeposition time. (b) Top and (c) cross-sectional SEM images of optimal electrodeposited Film on FTO.
Fig. S2. Nitrogen adsorption-desorption isotherm of the PSG-obtained CuWO₄/WO₃ hetero-structure
Fig. S3. Mott-Schottky plots (at the AC frequency of 2 kHz) of the as-prepared thin films in 0.1 M Na₂SO₄ electrolyte
Fig. S4. Cyclic Voltammetry (CV) of the Ag functionalized composite electrode
Estimation of the energy band:

In addition, the band edge positions were calculated according to the method proposed by Butler and Ginley, in which the band edge positions of a semiconductor at the point of zero charge can be estimated from the following formulas:

\[ E_V = \chi - E_e + 0.5E_g \]
\[ E_C = E_V - E_g \]
\[ \chi \approx \left( \prod_{k=1}^{P} \chi_k \right)^{\frac{1}{P}} \]

Where \( E_e = 4.50 \text{ eV} \) is the scale factor relating the reference electrode redox level to the vacuum level and \( E_g \) is the band gap. The absolute electronegativity of a semiconductor, \( \chi \), defined as the geometric mean of the electronegativity of the constituent atoms and \( P \) is the number of atoms in the crystal. Therefore, the relative band edge potentials of the semiconductors with respect to vacuum scale were estimated. Accordingly, calculated \( \chi \) are about 6.32 and 6.59 for CuWO₄ and WO₃, respectively. According to their estimated band gaps and above equations, valence and conduction potentials are estimated about \( E_v = -7.43 \text{ eV}, E_c = -5.21 \text{ eV} \) for CuWO₄ and \( E_v = -7.9, E_c = -5.29 \) for WO₃ vs. vacuum (at pH=0) [S1] which were converted to pH=7 condition by Nernst equation (presented in Fig. 7a) [S2].

References