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Supporting Information (SI)

Ag-Functionalized $CuWO_4/WO_3$ Nanocomposite for Solar Water Splitting

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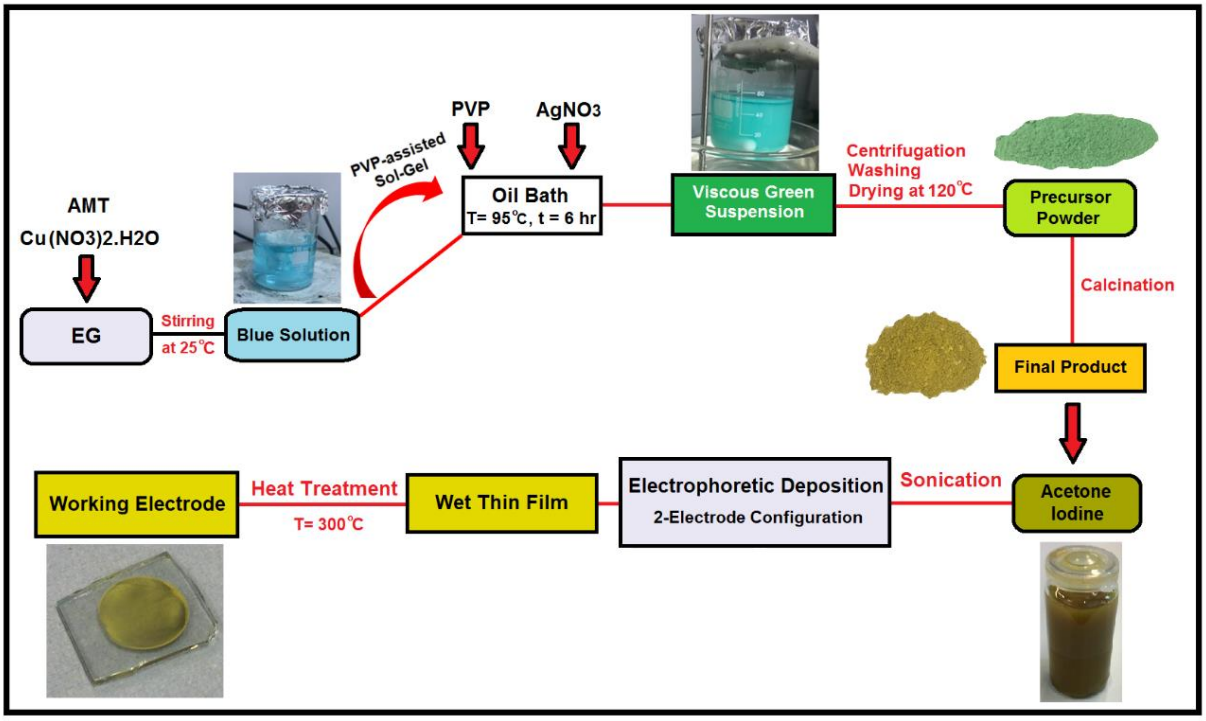

Scheme S1. Schematic diagram of the synthesis route and electrophoretic deposition of powders

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_{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_{front}/J_{back} ratio vs. electrodeposition time (Fig. S1). Electrodeposition time (e.g. film thicknesses) was changed for all samples to achieve highest current density during front-side illumination (J_{front}) and an optimal value of J_{front}/J_{back} ratio (due to higher electron transfer resistance in so high thicknesses causing smaller J_{front} compared to J_{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_{front}/J_{back} ratio of samples due to a sharp increase of charge transfer resistance and charge carrier recombination).

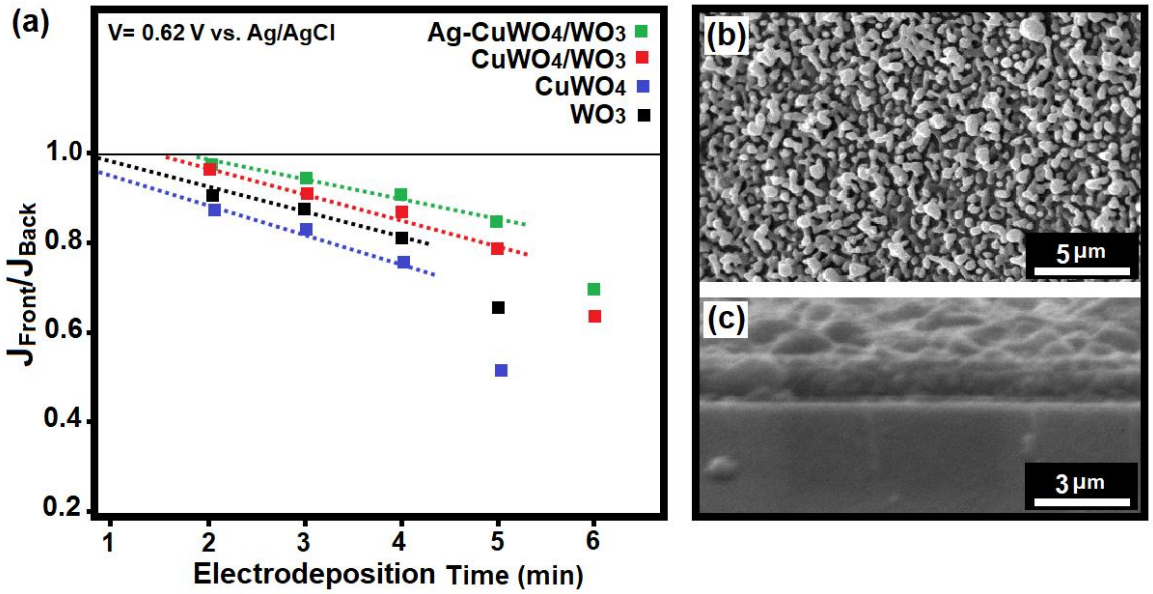

Fig. S1. (a) Different value of J_{front}/J_{back} ratio vs. electrodeposition time. (b) Top and (c) cross-sectional SEM images of optimal electrodeposited Film on FTO

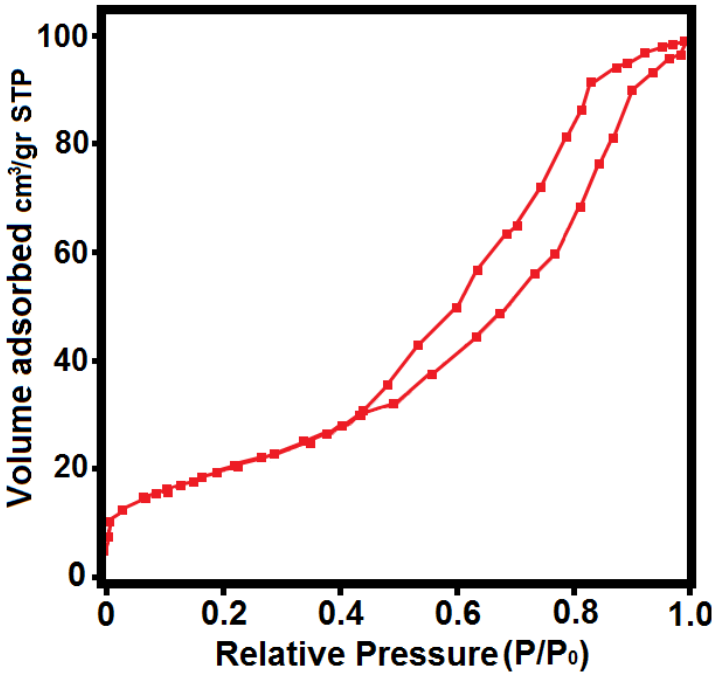

Fig. S2. Nitrogen adsorption-desorption isotherm of the PSG-obtained $CuWO_4/WO_3$ hetero-structure

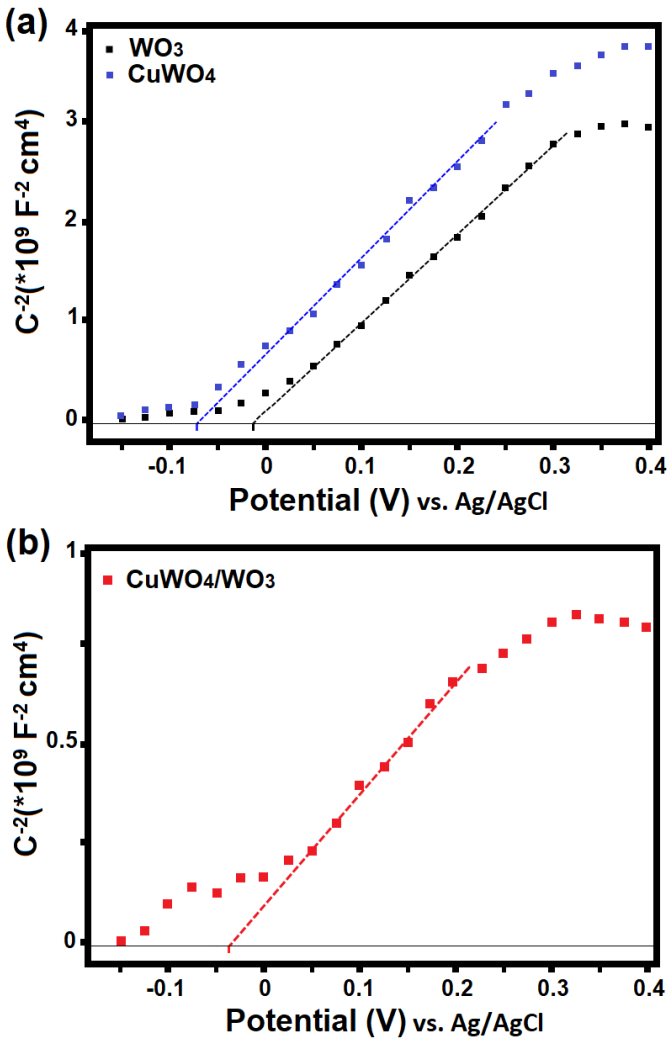

Fig. S3. Mott-Schottky plots (at the AC frequency of 2 kHz) of the as-prepared thin films in 0.1 M Na_2SO_4 electrolyte

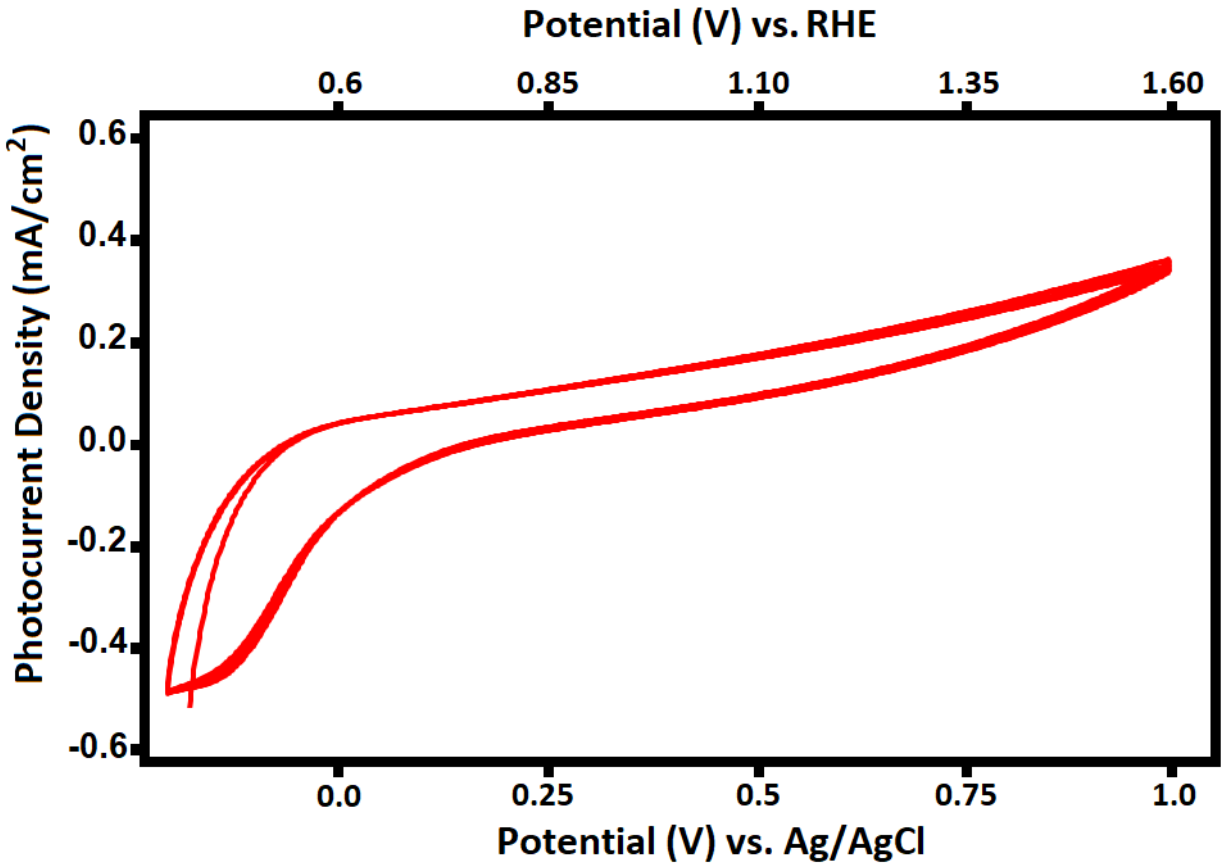

Fig. S4. Cyclic Voltammetry (CV) of the Ag functionalized composite electrode

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:

$$E_V = \chi - E_e + 0.5E_g \quad (1)$$

$$E_C = E_V - E_g \quad (2)$$

$$\chi \approx \left(\Pi_{k=1}^{P}\chi_k\right)^{\frac{1}{P}} \quad (3)$$

Where $E_e \approx 4.50$ 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, χ, 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 χ are about 6.32 and 6.59 for $CuWO_4$ and WO_3, respectively. According to their estimated band gaps and above equations, valence and conduction potentials are estimated about Ev=-7.43 eV, Ec= -5.21 eV for $CuWO_4$ and Ev= -7.9, Ec= -5.29 for WO_3 vs. vacuum (at pH=0) [S1] which were converted to pH=7 condition by Nernst equation (presented in Fig. 7a) [S2].

References

[S1] R. Salimi, A.A. Sabbagh Alvani, N. Naseri, S.F. Du, D. Poelman, New J. Chem. 2018, **42**, 11109-11116
[S2] R. V. De Krol, M. Gratzel, Photoelectrochemical Hydrogen Production, Springer, New York, NY, 2012.