Supplemental Information for

Elucidating the Electronic Structure of $CuWO_4$ Thin Films for Enhanced Photoelectrochemical Water Splitting

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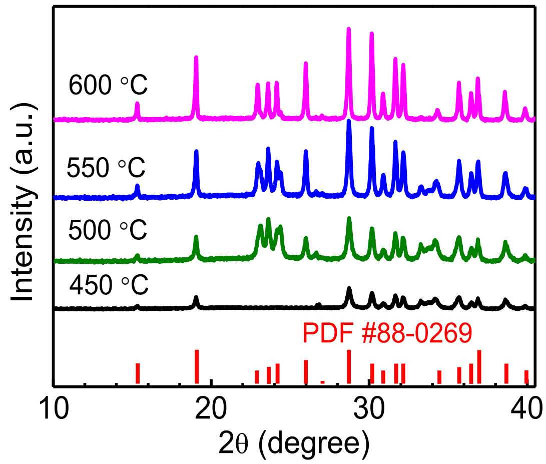

Figure S1. XRD patterns of the $CuWO_4$ thin films annealed at different temperatures, indicating that the crystalline phase of $CuWO_4$ starts to form at temperatures above 450 °C.

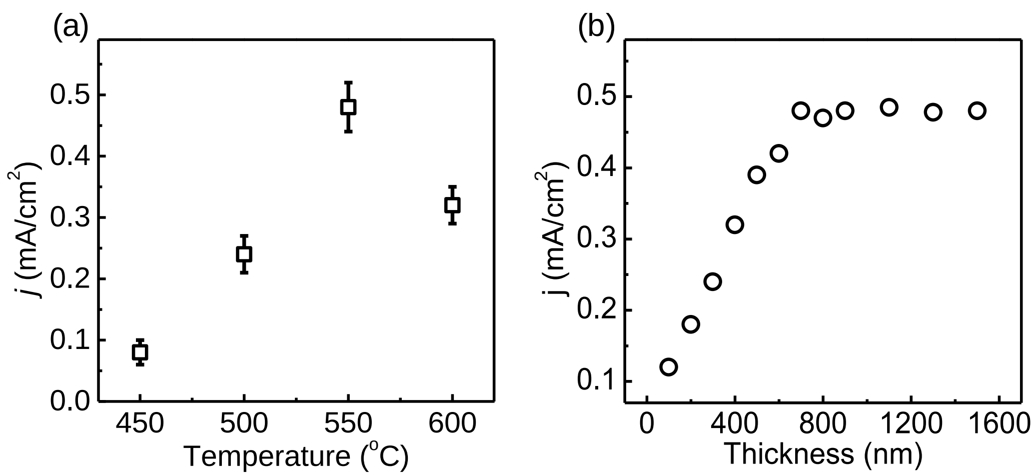

Figure S2. (a) Photocurrent densities of $CuWO_4$ photoelectrodes prepared by at different annealing temperatures, and (b) different film thickness; the photocurrent density obtained under simulated AM 1.5G at an applied bias of +1.23 V vs. RHE.

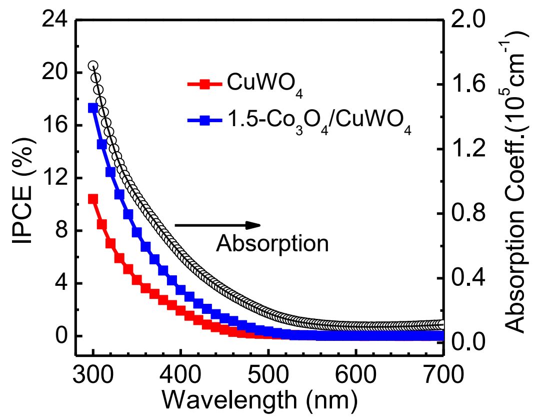

Figure S3: Incident photon-to-current conversion efficiencies (IPCE) spectra of $CuWO_4$ and 1.5 nm Co_3O_4 modified $CuWO_4$ at an applied bias of +1.23 V vs. RHE. The low IPCE in range of 400 nm - 500 nm is likely due to 1) low absorption coefficient of $CuWO_4$ because both of the valence band edge and conduction band edge are of Cu 3d character, i.e., optical excitation is partially forbidden; 2) hole state excited with low photon energy having a low mobility, similar to the case of Fe_2O_3.[1,2]

Table S1. The fitted R_{ct} values of Co_3O_4 /$CuWO_4$ heterojunctions with different Co_3O_4 thickness

	$CuWO_4$	1.5-Co_3O_4/$CuWO_4$	3-Co_3O_4/$CuWO_4$
R_{ct} (KΩ)	2.8	1.6	1.1

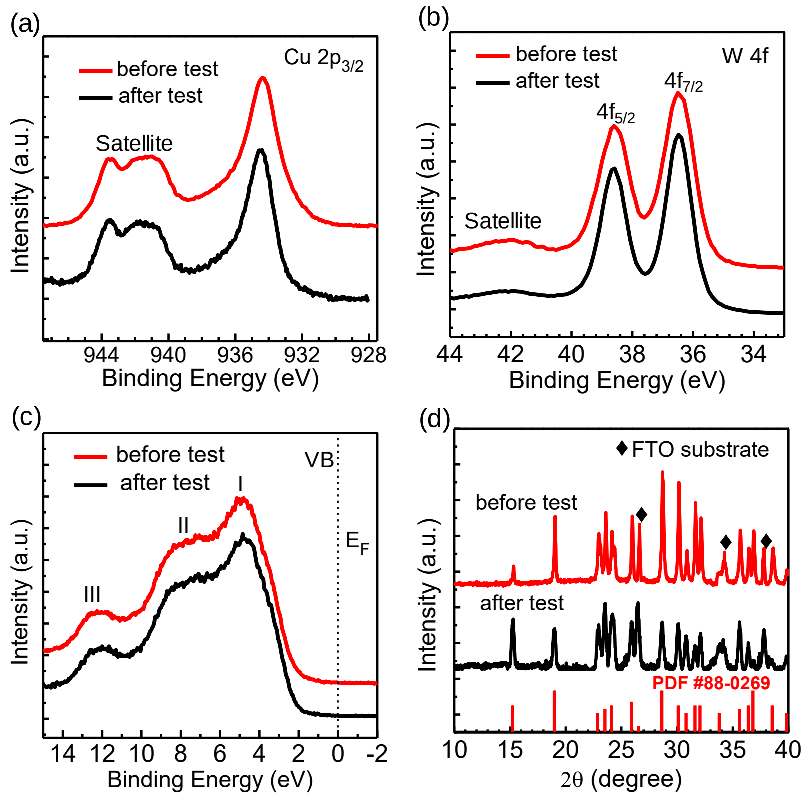

Figure S4. Comparisons of XPS spectra of the $CuWO_4$ photoanode before and after stability test (a) Cu $2p_{3/2}$, (b) W 4f and (c) valence band (VB); the Cu 2p, W 4f and VB spectra show very similar lineshapes before and after 10 hour stability test, indicating there is no much change of the electronic structures. (d) Comparison of XRD patterns for the $CuWO_4$ photoanode before and after stability test, showing pure phase of $CuWO_4$ before and after test.

Reference:

1. Lin, Y.; Zhou, S.; Sheehan, S. W.; Wang, D. Nanonet-Based Hematite Heteronanostructures for Efficient Solar Water Splitting. *J. Am. Chem. Soc.* **2011**, *133*, 2398–2401.

2. Kim, D. W.; Riha, S. C.; Demarco, E. J.; Martinson, A. B. F.; Farha, O. K.; Hupp, J. T. Greenlighting Photoelectrochemical Oxidation of Water by Iron Oxide. *ACS Nano* **2014,** *12*, 12199-12207.