Electronic Supplementary Information

Formation of Internal P–N Junctions in Ta_3N_5 Photoanodes for Water Splitting

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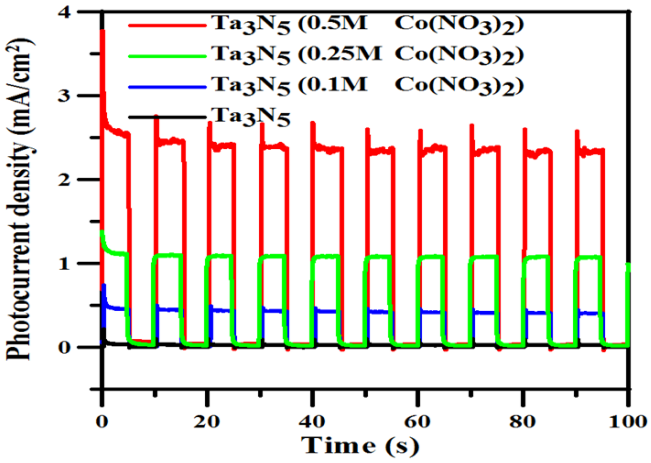
Electronic Supplementary Information for:

1. **The influence of the Co-doping degree on the photoelectrochemical performance of the Ta_3N_5-based photoanodes.**
2. **The Co $2p_{3/2}$ XPS spectra of the Ta_3N_5:Co film.**
3. **The photocurrents exhibited by the bare Ta and the Ta_3N_5:Co electrodes in a polysulfide redox couple (S^{2-}/S_x^{2-}) solution.**
4. **Calculation of solar energy conversion efficiency of the Ta_3N_5:Co photoanode.**
5. **A stability test of the Ta_3N_5:Co electrode by conducting a long-time photoelectrochemical reaction.**

1. The influence of the Co-doping degree on the photoelectrochemical performance of the Ta_3N_5-based photoanodes

(a)



(b)

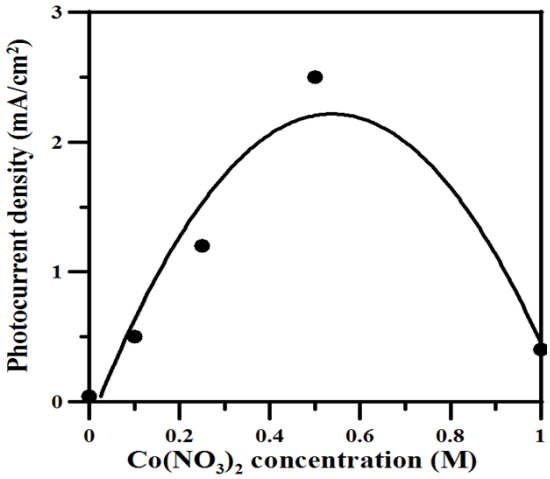


Figure S1. (a) Photoresponse of the Ta_3N_5:Co photoanodes obtained at an anodic bias of 0.5 V vs. Ag/AgCl and illuminated with chopped AM 1.5G simulated sunlight at 100 mW cm^{-2}. The photoanodes were obtained using $Co(NO_3)_2$ soaking solutions of varying concentrations (0–1 M). The electrolyte is a 0.5-M KOH aqueous solution (pH=13.6). (b) Variation of the photocurrent with the concentration of the $Co(NO_3)_2$ soaking solution.

2. The Co $2p_{3/2}$ XPS spectra of the Ta_3N_5:Co film

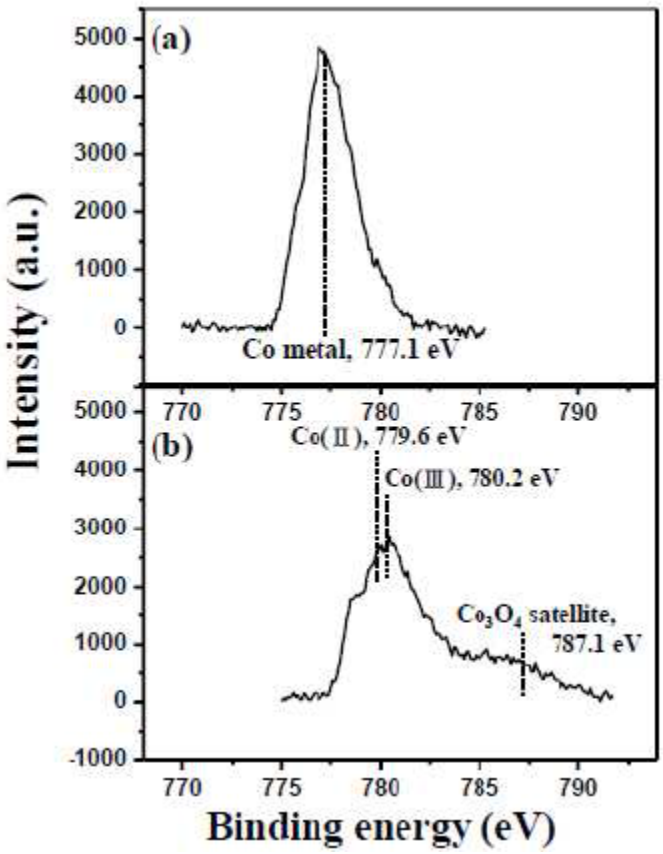


Figure S2. (a) The Co $2p_{3/2}$ XPS spectra of the as-received Ta_3N_5:Co film. The Co ions likely belong to $Co_{5.47}N$ because their binding energy is close to that of Co metal. (b) The Co $2p_{3/2}$ XPS spectra of the Ta_3N_5:Co film after the PEC reaction. The Co ions were oxidized to high-valence Co ions, likely belonging to Co_2O_3/Co_3O_4 (i.e., CoO_x).[1,2]

3. The photocurrents exhibited by the bare Ta and the Ta_3N_5:Co electrodes in a polysulfide redox couple (S^{2-}/S_x^{2-}) solution

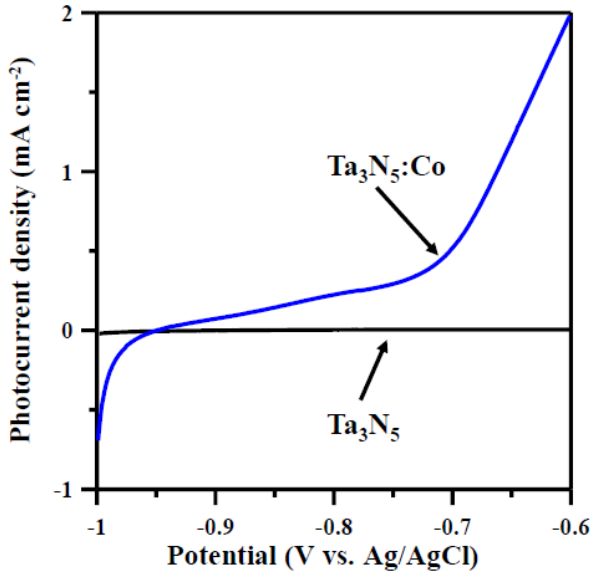


Figure S3. Current-potential characteristics of the Ta_3N_5 and Ta_3N_5:Co photoanodes with an anodic scan applied at 10 mV s^{-1} and illuminated with AM 1.5G simulated sunlight at 100 mW cm^{-2}. The electrolyte is a fast polysulfide redox couple (S^{2-}/S_x^{2-}) aqueous solution containing 0.24 M Na_2S and 0.35 M Na_2SO_3.

4. Calculation of solar energy conversion efficiency of the Ta_3N_5:Co photoanode

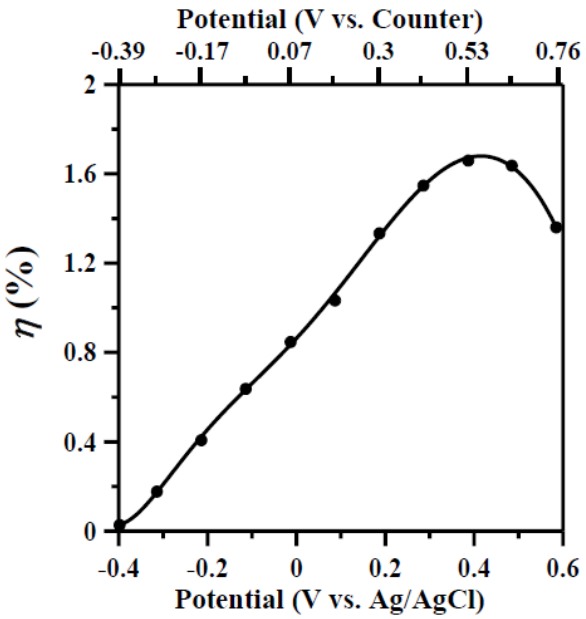


Figure S4. Applied bias photon-to-current conversion efficiency (η) of the Ta_3N_5:Co photoanode under varying bias potentials. The η values were calculated using the data of Fig. 7.[3,4]

5. A stability test of the Ta_3N_5:Co electrode by conducting a long-time photoelectrochemical reaction

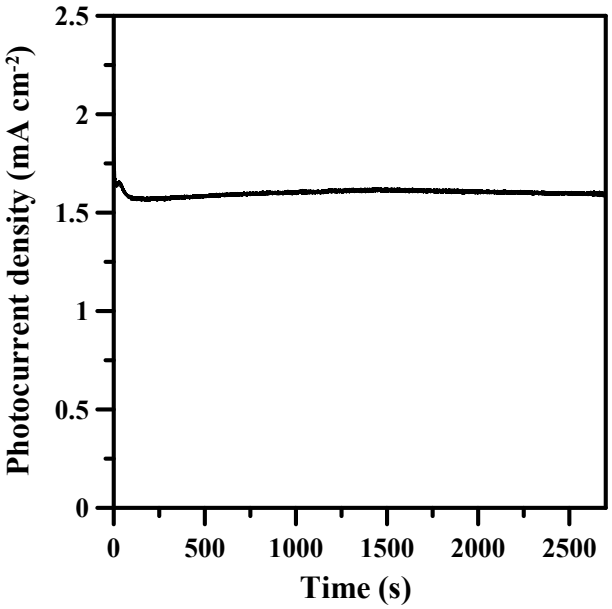


Figure S5. Photoresponse of the Ta_3N_5:Co photoanode obtained at an anodic bias of 0.53 V vs. counter (or 0.39 V vs. Ag/AgCl) and illuminated with AM 1.5G simulated sunlight at 100 mW cm^{-2}.

References

1. L. An, W. Huang, N. Zhang, X. Chen and D. Xia, *J. Mater. Chem. A*, 2014, **2**, 62-65.
2. B. J. Tan, K. J. Klabunde, and P. M. A. Sherwood, *J. Am. Chem. Soc.* 1991, **113**, 855-861.
3. A. J. Nozik and J. Miller, *Chem. Rev.* 2010, **110**, 6443–6445.
4. Z. Chen, T. F. Jaramillo, T. G. Deutsch, A. Kleiman-Shwarsctein, A. J. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E. W. McFarland, K. Domen, E. L. Miller, J. A. Turner and H. N. Dinh, *J. Mater. Res.* 2010, **25**, 3-16.