Supplementary Information

A Tri-Functional Molecular Relay to Fabricate a Size-controlled CoO_x Nanoparticles & WO_3 Photoanode for Efficient Photoelectrochemical Water Oxidation

Gui-Lin Hu,[a] Rong Hu,[a] Zhi-Hong Liu,[a] Kai Wang,[b] Xiang-Yang Yan,[a] and Hong-Yan Wang[a]*

[a]Key Laboratory for macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710119, P. R. China.

[b]Scientific Research and Academic Office, Air Force Logistics College, Xuzhou, 221000, P. R. China.

Email: hongyan-wang@snnu.edu.cn;

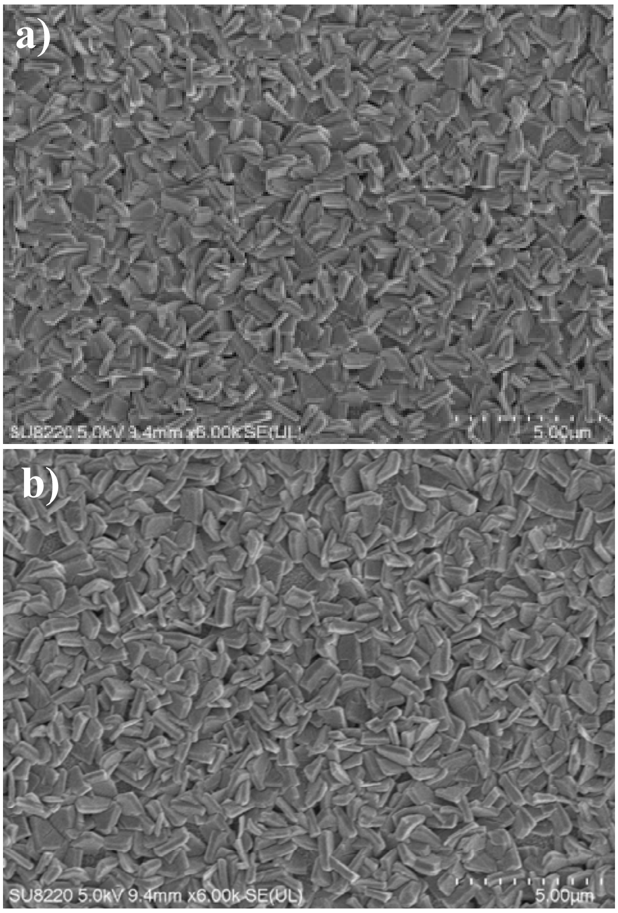


Figure S1. SEM of the bare WO_3 and C-M2P-CoO_x/WO_3 electrode.

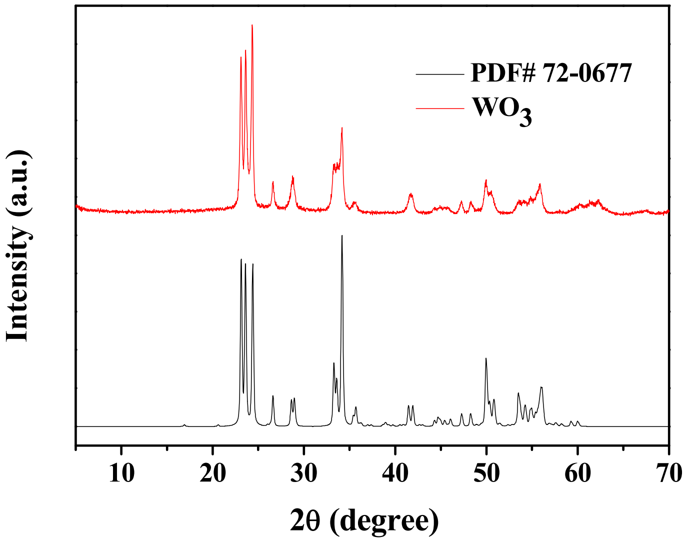
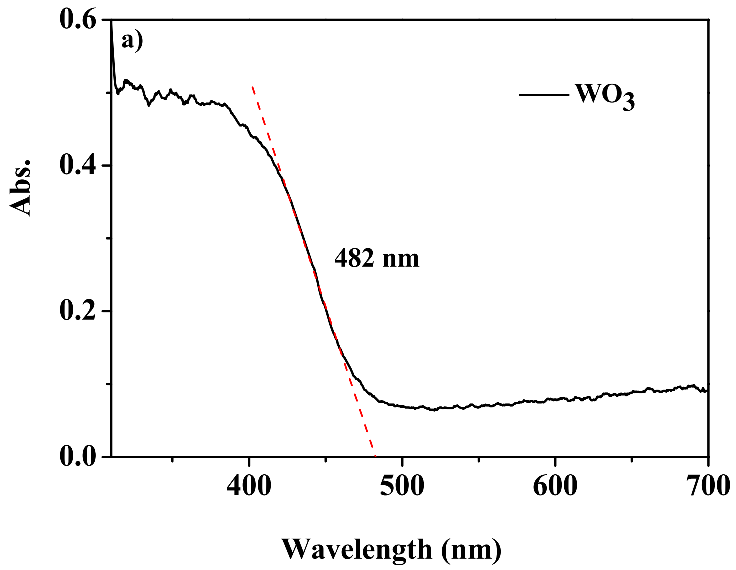


Figure S2. XRD of the bare WO_3.



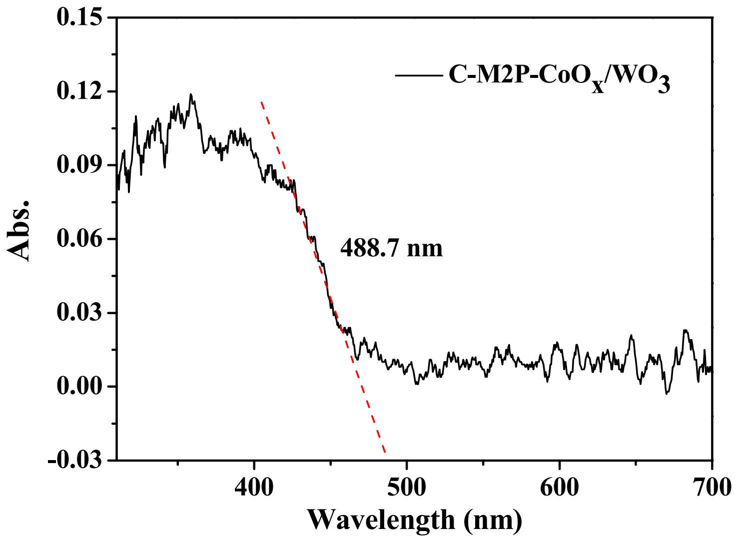


Figure S3. the UV-vis DRS of (a) WO_3 and (b) C-M2P-CoO_x/WO_3 films.

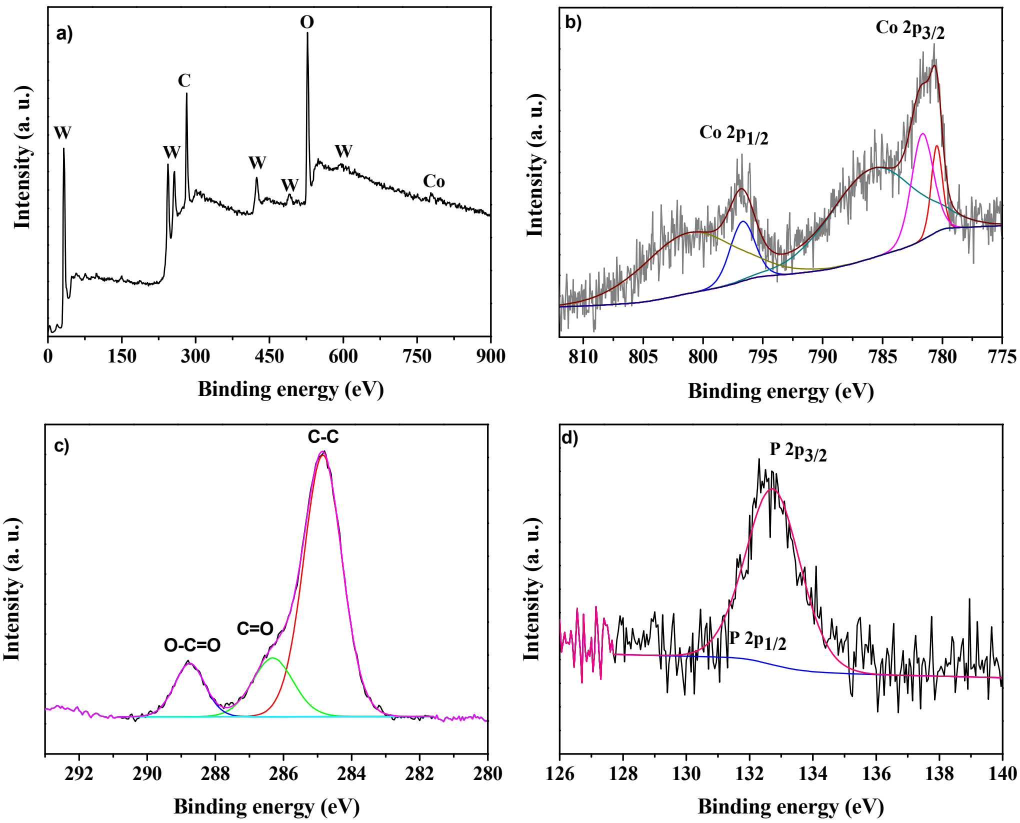
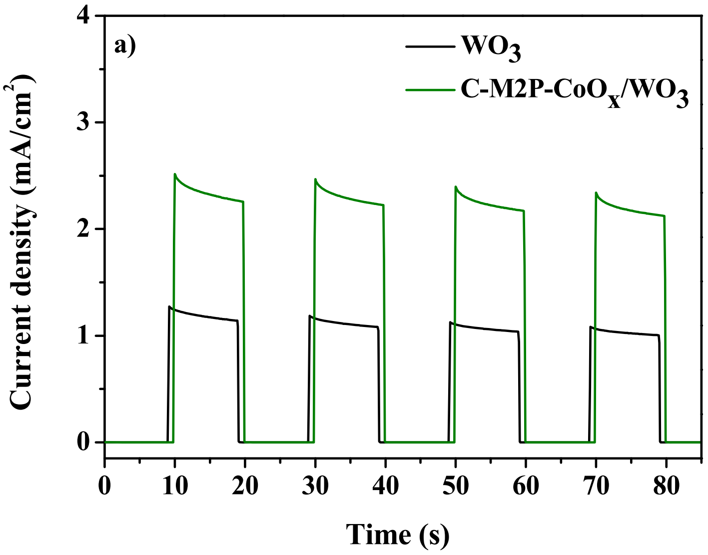


Figure S4. a) the XPS full scan and fine scan of b) Co, c) C and d) P on C-M2P-CoO_x/WO_3 films after 2 h photoelectrolysis.



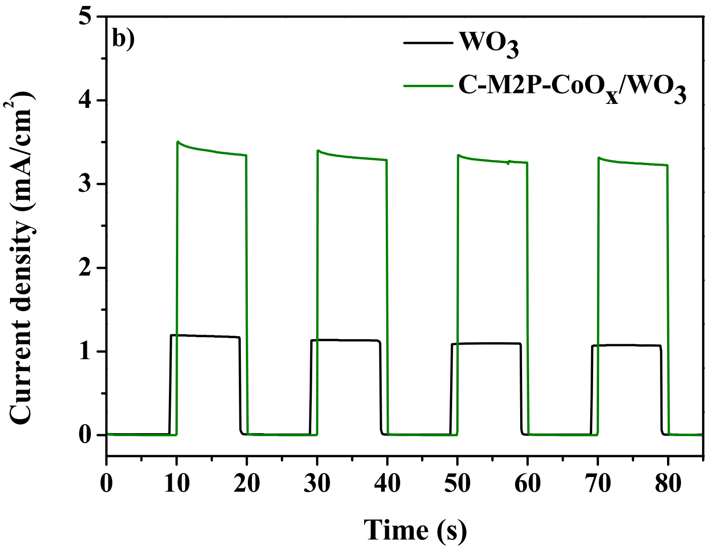
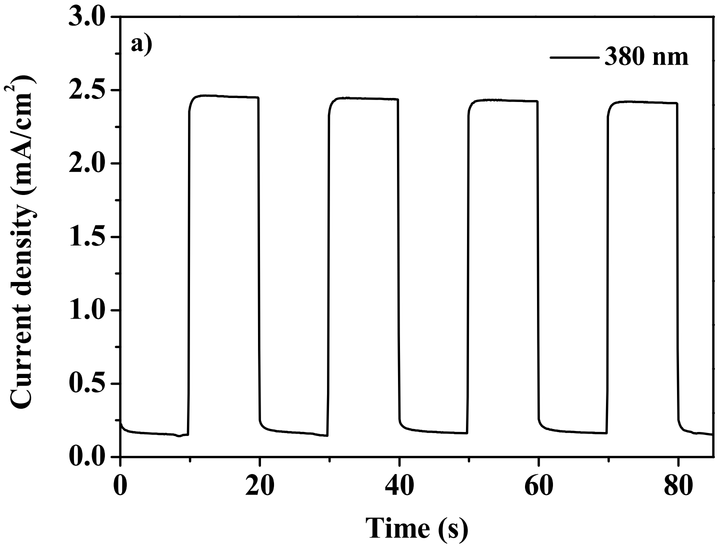
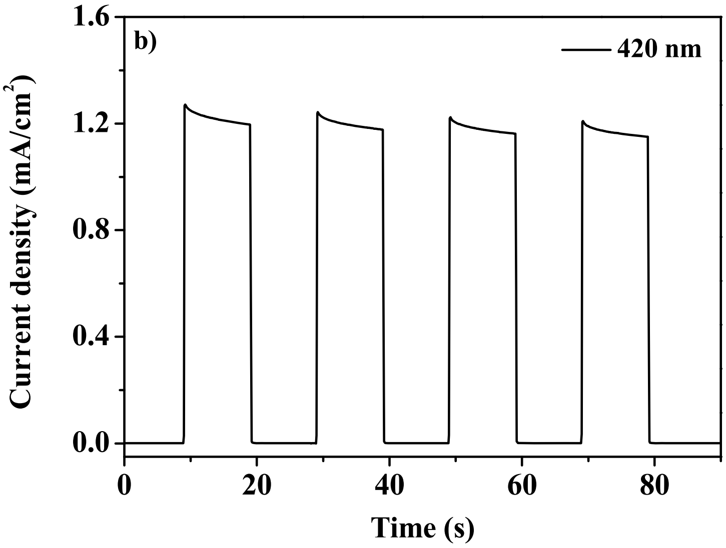
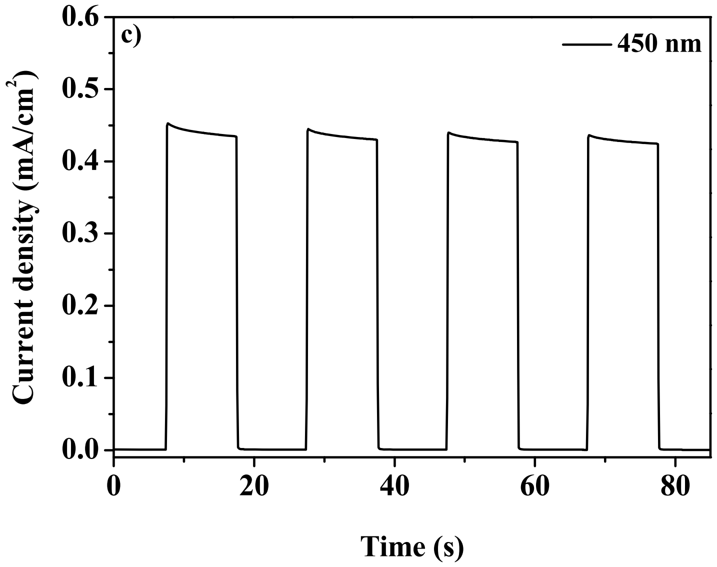


Figure S5. the photoelectrochemical behavior based on C-M2P-CoO_x/WO_3 electrode when applied different external bias at (a) 0.75 V and (b) 1.23 V under illumination by LEDs (λ =400 nm).


a)
380 nm
Current density (mA/cm^2)
Time (s)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80


b)
420 nm
Current density (mA/cm^2)
Time (s)
1.6
1.2
0.8
0.4
0.0
0
20
40
60
80



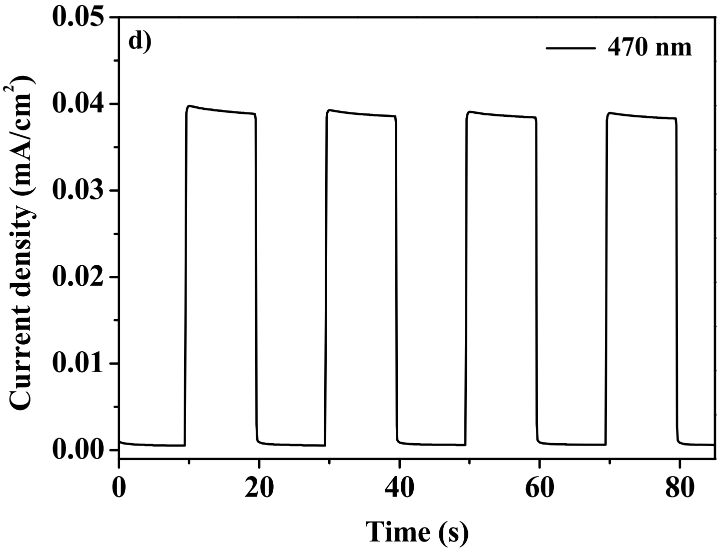


Figure S6. photocurrent densities based on C-M2P-CoO_x/WO_3 electrode under illumination by LEDs with λ (a) at 380 nm, (b) at 420 nm, (c) at 450 nm and (d) at 470 nm when applied 0.75 V external bias.

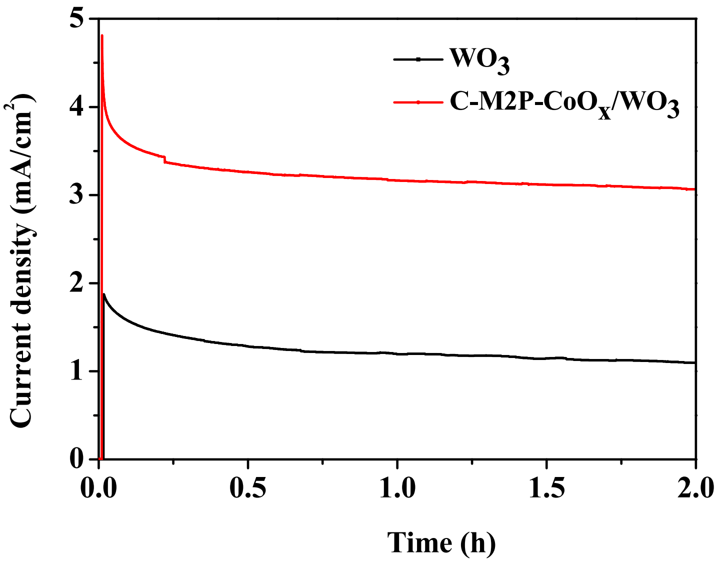


Figure S7. The controlled-potential electrolysis of water oxidation based on C-M2P-CoO_x/WO_3 electrode at 1.23 V under continued visible-light irradiation (λ = 400 nm).

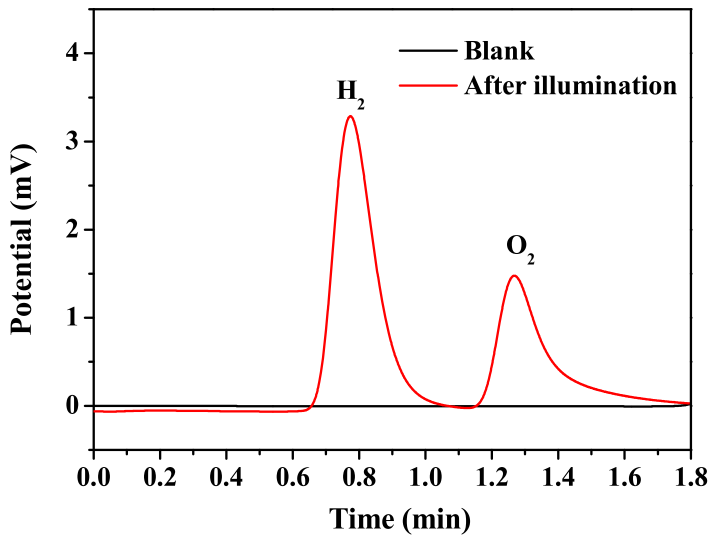


Figure S8. The detection of hydrogen and oxygen by GC based on C-M2P-CoO_x/WO_3 electrode after photoelectrolysis at 0.75 V under continued visible-light irradiation (λ = 400 nm). finite.

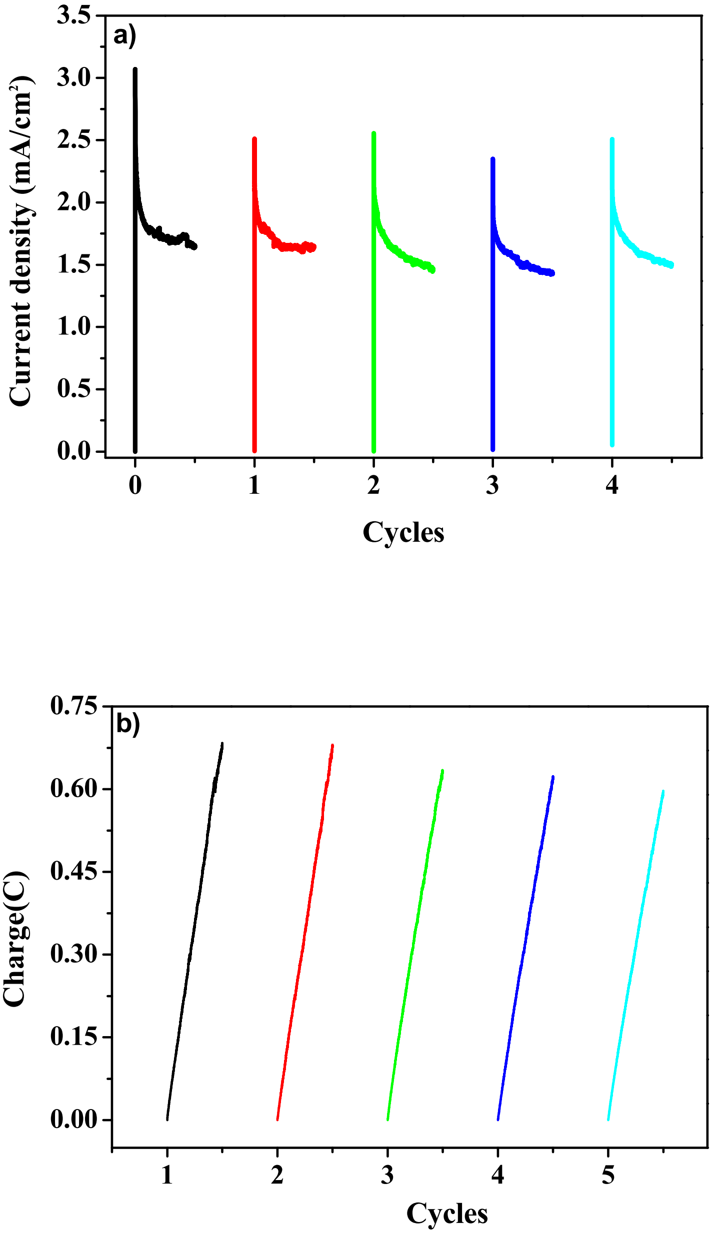


Figure S9. a) C-M2P-CoO_x/WO_3 electrode reused for bulk photoelectrolysis and performed for five cycles with 0.75V bias; b) the produced charge under continued visible-light irradiation (λ = 400 nm).

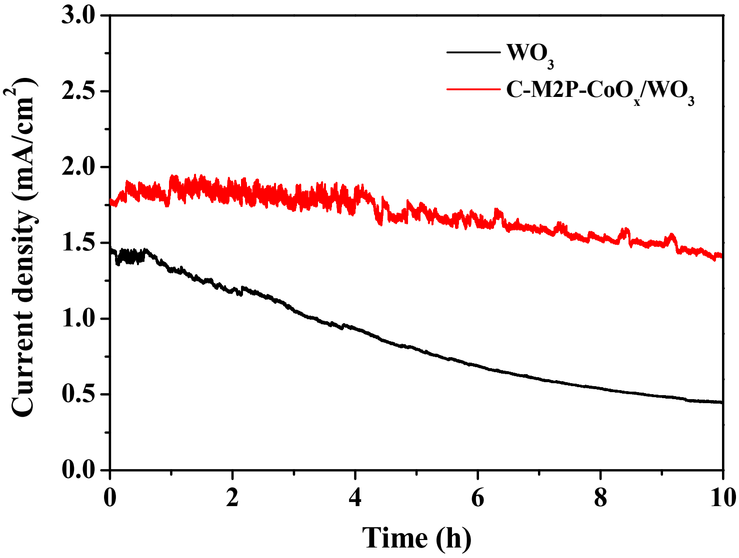


Figure S10. Controlled-potential electrolysis of water oxidation based on WO_3 and C-M2P-CoO_x/WO_3 for 10 h under continued visible-light irradiation (λ = 400 nm) with the bias at 0. 75 V.

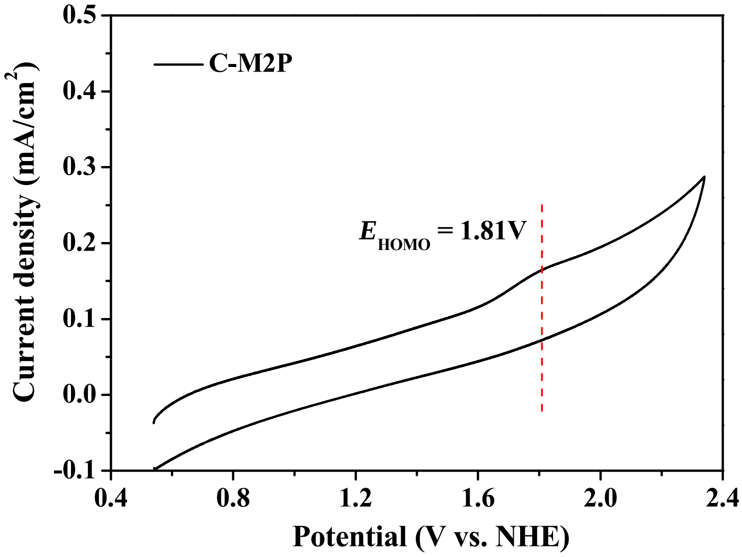
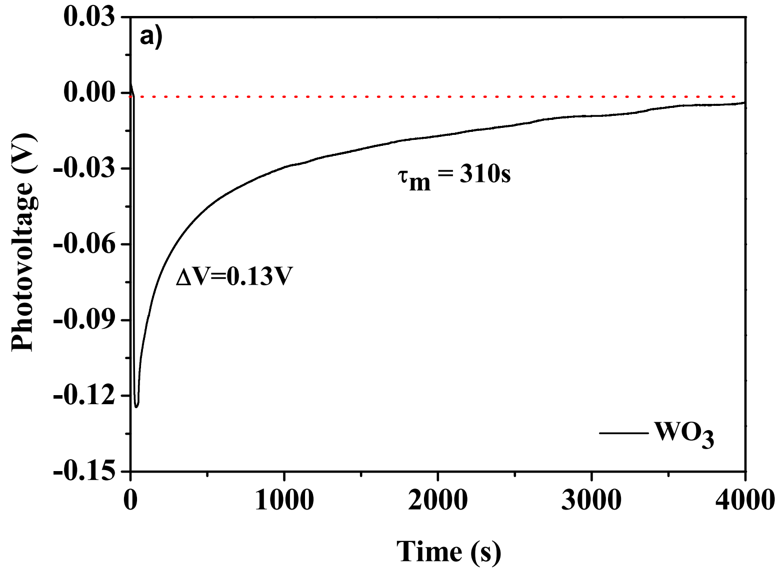


Figure S11. HOMO level measured based on CV of C-M2P vs. NHE. [1]



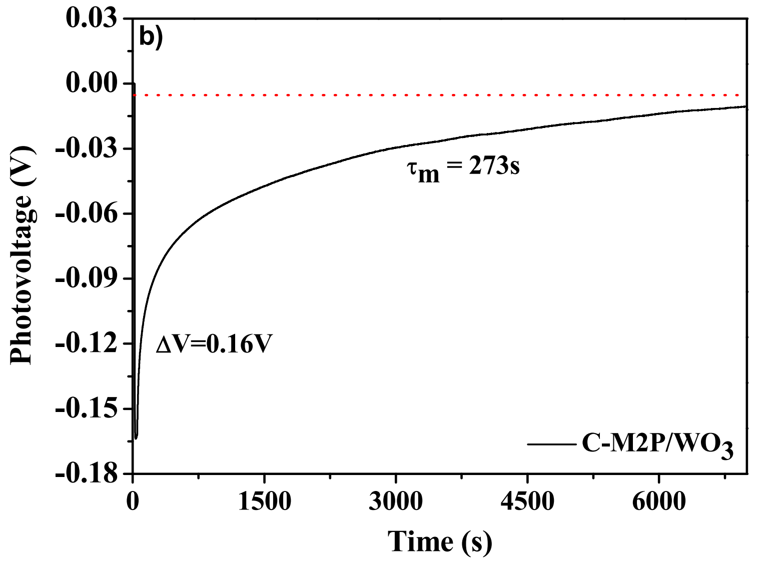


Figure S12. OCVD plots of (a) WO_3, (b) C-M2P/WO_3 photoanode with 400 nm LED lamp illumination from the electrolyte-electrode side (ΔV is the difference in voltage between dark and illumination conditions, τ_m is the decay lifetime).

It is noted that the measurement here operated for the complete charge decay of the WO_3, and C-M2P/WO_3 phooelectrode. The differences in ΔV compared with Fig. 7 might be originated from the experimental error. However, the decay trend among WO_3, C-M2P/WO_3 and C-M2P-CoO_x/WO_3 is clearly sustained.

The calculation for E_{CB} and E_{VB} for WO_3 film.

In general, a simple method can be applied to determine the band edge positions of CB and VB of a semiconductor respectively. The CB edge of a semiconductor at zero charge (pH_{zpc}) can be figured up using the following equation S1-2. [2]

$$E_{CB} = \chi - E^{e} - 1/2\ E_g \quad (1)$$

$$E_{VB} = E_g + E_{CB} \quad (2)$$

where E_{CB} is the CB edge potential, E_{VB} is the VB edge potential, and χ is the electronegativity of the semiconductor, expressed as the geometric mean of the absolute electronegativity of the constituent atoms, which is defined as the arithmetic mean of the atomic electron affinity and the first ionization energy. E^{e} is the energy of free electrons on the hydrogen scale, about equal to 4.5 eV.

The calculation for carrier densities N_d of C-M2P-CoO_x/WO_3 electrode.

The carrier densities of the prepared C-M2P-CoO_x/WO_3 electrode could be estimated using the Mott–Schottky equation. [3]

$$1/C^2 = (2/e_0\varepsilon\varepsilon_0 N_d)[(V - V_{FB}) - kT/e_0] \quad (3)$$

Where C is the specific capacitance (F cm^{-2}), e_0 is the electron charge, ε is the dielectric constant of WO_3 (ε = 20), ε_0 represents the permittivity of vacuum, N_d is the carrier density, V is the electrode applied potential, V_{FB} is the flatband potential and kT/e_0 is a temperature-dependent correction term.

ABPE measurement [4]

The applied bias photon-to-current efficiency (ABPE) was calculated from the LSV using the equation:

$$ABPE(\%) = \frac{(J_{light} - J_{dark}) \times (1.23 - V_{RHE})}{P_{light}} \times 100\% \quad (4)$$

Where V_{RHE} is the applied potential versus RHE, J_{light} and J_{dark} are the measured photocurrent and dark current respectively, and P_{light} (mW cm^{-2}) represnts the power density.

IPCE measurement [5]

IPCE measurement was carried out in a three-electrode setup with the assembled- electrode as the working electrode, platinum disk as counter electrode, and Ag/AgCl (3.0 M KCl) as reference electrode. IPCE was calculated according to equation:

$$\text{IPCE}(\%) = \frac{1240 \times J}{\lambda \times I} \times 100\% \tag{5}$$

Where, J represents the photocurrent density (mA cm^{-2}), λ is the wavelength of incident light (nm), and I is the intensity of the incident light (mW cm^{-2}).

The calculation for the lifetime τ_m based on Open circuit voltage decay (OCVD) plots.[6]

The calculated decay lifetime of each V−t profiles by fitting to a biexponential function with two time constants:

$$y(t) = A_0 + A_1 e^{-1/\tau_1} + A_2 e^{-1/\tau_2} \quad (6)$$

$$\tau_m = (\tau_1 \tau_2)/(\tau_1 + \tau_2) \quad (7)$$

where τ_m is the harmonic mean of the lifetime and the total half life is log(2 × τ_m).

Supporting References

[1] J. Volker, X. Zhou, X. Ma, S. Flessau, H. Lin, M. Schmittel, A. Mews, Semiconductor Nanocrystals with Adjustable Hole Acceptors: Tuning the Fluorescence Intensity by Metal-Ion Binding, Angew. Chem. Int. Ed. 49 (2010) 6865-6868.

[2] a) J. Huang, Y. Zhang, Y. Ding, Rationally Designed/Constructed CoO_x/WO_3 Anode for Efficient Photoelectrochemical Water Oxidation, ACS Catal. 7 (2017) 1841-1845; b) Y. Xu, M. A. Schoonen, The absolute energy positions of conduction and valence bands of selected semiconducting minerals, Am. Mineral. 85 (2000) 543-556.

[3] T. Zhang, Z. Zhu, H. Chen, Y. Bai, S. Xiao, X. Zheng, Q. Xue, S. Yang, Iron-doping-enhanced photoelectrochemical water splitting performance of nanostructured WO_3: a combined experimental and theoretical study, Nanoscale 7 (2015) 2933-2940.

[4] S. Berardi, G. L. Ganga, M. Natali, I. Bazzan, F. Puntoriero, A. Sartorel, F. Scandola, S. Campagna, M. Bonchio, Photocatalytic Water Oxidation: Tuning Light-Induced Electron Transfer by Molecular Co_4O_4 Cores, J. Am. Chem. Soc. 134 (2012) 11104-11107.

[5] A. Nattestad, A. J. Mozer, A. M. K. Fischer, C. A. Mishra, P. Bauerle, U. Bach, Highly efficient photocathodes for dye-sensitized tandem solar cells, Nat. Mater. 9 (2010) 31-35.

[6] a) Q. Ruan, M. K. Bayzit, V. Kiran, J. Xie, Y. Wang, J. Tang, Key factors affecting photoelectrochemical performance of g-C_3N_4 polymer films, Chem. Commun. 55 (2019) 7191-7194; b) Y. C. Pu, G. Wang, K .D. Chang, Y. Ling, Y. K. Lin, B. C. Fitzmorris, C. M. Liu, X. Lu, Y. Tong, J. Z. Zhang, Y. J. Hsu, Y. Li, Au Nanostructure-Decorated TiO_2 Nanowires Exhibiting Photoactivity Across Entire UV-visible Region for Photoelectrochemical Water Splitting, Nano Lett. 13 (2013) 3817-3823; c) W. Liu, L. Cao, W. Cheng, Y. Cao, X. Liu, W. Zhang, X. Mou, L. Jin, X. Zheng, W. Che, Q. Liu, T. Yao, S. Wei, Single-Site Active Cobalt-Based Photocatalyst with a Long Carrier Lifetime for Spontaneous Overall Water Splitting, Angew. Chem. Int. Ed. 56 (2017) 9312-9317.

End of Supporting Information