

Supporting Information

Rapid Activation of Co_3O_4 Cocatalyst with Oxygen Vacancies on TiO_2 Photoanodes for Efficient Water Splitting

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Materials and Instruments

All the reagents were analytical grade and used without further purification. Titanium butoxide ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$, 99.0 %) and dimethyl sulfoxide (DMSO) were purchased from Aladdin Industrial Corporation. Hydrochloric acid (HCl, 36-38 %) and ammonia solution (NH_3 , 25-28 %) were obtained from Shanghai Zhongqin Chemical Reagent Co., Ltd. Cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99.5 %) was supplied from Tianjin Kaixin Chemical Industry Co., Ltd. Potassium iodide (KI, 99.0 %), bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.0 %), nitric acid (HNO_3 , 65-68 %), vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$, 99.0 %), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99.0 %), sodium nitrate (NaNO_3 , 98.5 %) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7 %) was bought from Sinopharm Chemical Reagent Co., Ltd. F-doped Tin Oxide (FTO) was purchased from Kunshan SunLaiTe New Energy Co., Ltd. FTO glass was ultrasonically cleaned for 20 min each in acetone, isopropanol, ethanol and deionized water, and then soaked in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (3:1, volume ratio) solution for 1h to make the surface uniformly hydrophilic.

Scanning electron microscopy (SEM) images were taken using a field-emission scanning electron microscope (SU8020, Japan) with an accelerating voltage of 2 kV. Transmission electron microscope (TEM) measurements were performed on an FEI Tecnai TF20 microscope operated at 200 kV. The X-ray diffraction spectra (XRD) were characterized by Rigaku RINT-2000 instrument using Cu K α radiation (40 KV). X-ray photoelectron spectroscopy (XPS) was executed by an ESCALAB 250Xi photoelectron spectrometer utilizing X-ray monochromator as the excitation source. The photoluminescence spectra (PL) were measured by a fluorescence spectrophotometer (F-7000 FL, HITACHI) at room temperature with an excitation wavelength of 280 nm. H_2 and O_2 evolution were detected by a chromatography (GC) system (7890A, Agilent Technologies) every 20 min.

Method and model of first-principles calculation

Density Functional Theory (DFT) calculations were performed with the Vienna Ab-initio Simulation Package (VASP).^{3,4} The interaction between core ion and valence electron is described by the projector augmented wave method (PAW).⁵ The exchange correlation part is described with the spin-polarized generalized gradient approximations (GGA) in the scheme of Perdew, Burke, Ernzerhof (PBE).^{6,7} An energy cutoff of 500 eV was used in Monkhorst k-points sampling scheme⁸ (4×4×1 for geometry optimization, while a larger grid 8×8×1 was used for electronic structure computation). Conjugated gradient method was used to the geometry optimization and all the atomic coordinates were fully relaxed until the maximal force on each atom was less than 0.02 eV Å⁻¹, and the convergence condition for energy is 10⁻⁴ eV. Considering the strong correlation effect of transition metal, the Hubbard U correction (GGA+U) is used in this work. An effective Hubbard U of 3.52 eV is adopted for the d orbit of Co.⁹

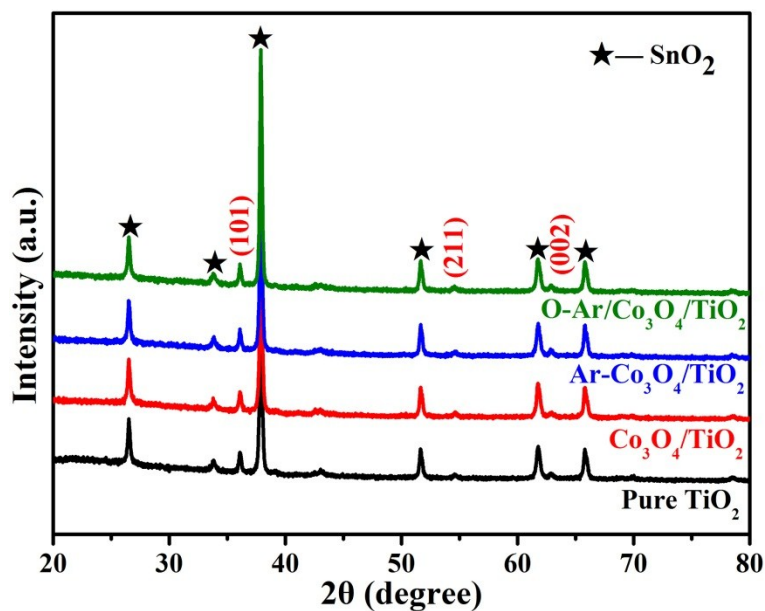


Fig. S1. XRD patterns of pristine TiO_2 (black line), $\text{Co}_3\text{O}_4/\text{TiO}_2$ (red line), $\text{Ar-Co}_3\text{O}_4/\text{TiO}_2$ (blue line), and $\text{O-Ar/Co}_3\text{O}_4/\text{TiO}_2$ (green line).

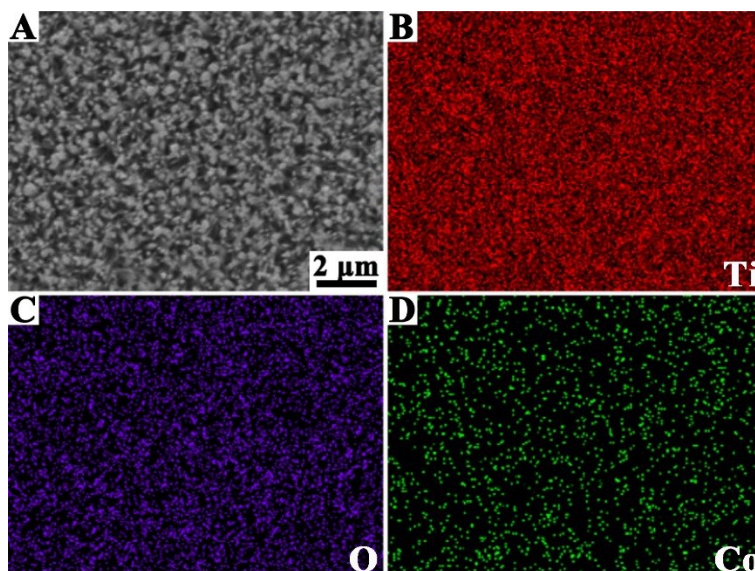


Fig. S2. (A) The corresponding SEM image of $\text{Co}_3\text{O}_4/\text{TiO}_2$ for EDS mapping; (B, C and D) EDS mapping of Ti (B), O (C), and Co (D) elements for $\text{Co}_3\text{O}_4/\text{TiO}_2$ photoanode.

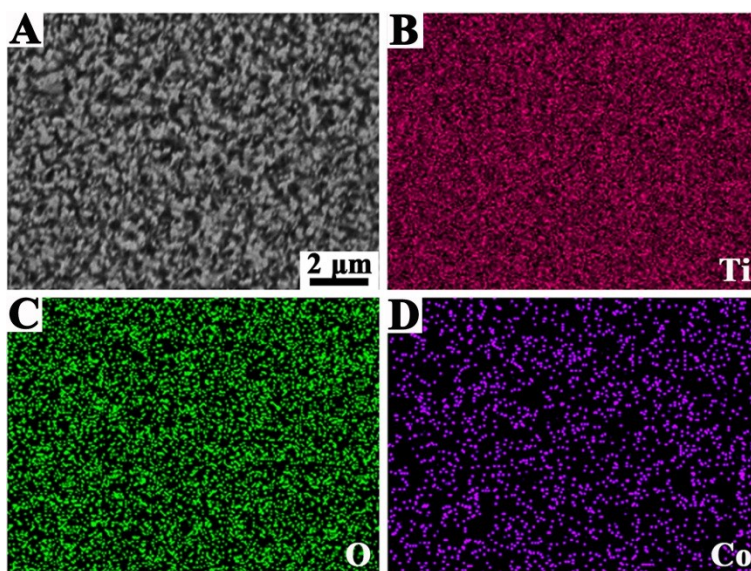


Fig. S3. (A) The corresponding SEM image of Ar-Co₃O₄/TiO₂ for EDS mapping; (B, C and D) EDS mapping of Ti (B), O (C), and Co (D) elements for Ar-Co₃O₄/TiO₂ photoanode.

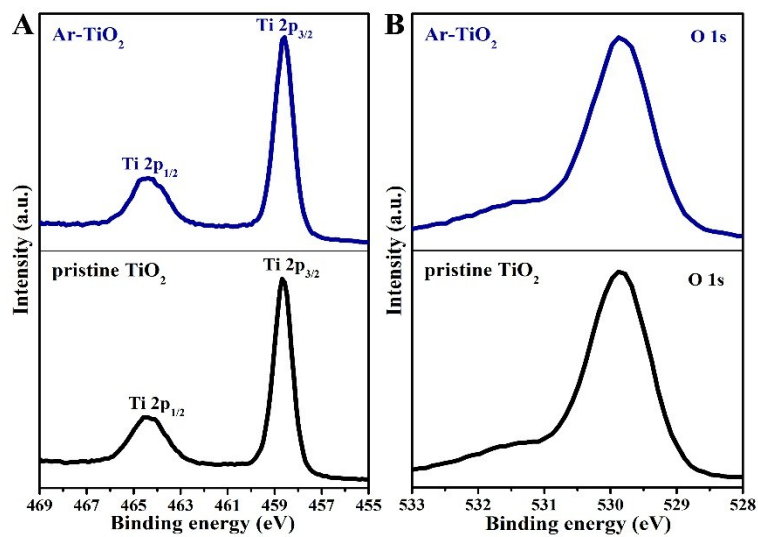


Fig. S4. (A) Ti 2p and (B) O 1s XPS high-resolution spectra of pristine TiO₂ and Ar-TiO₂ (pristine TiO₂ treated with Ar-plasma for 120s).

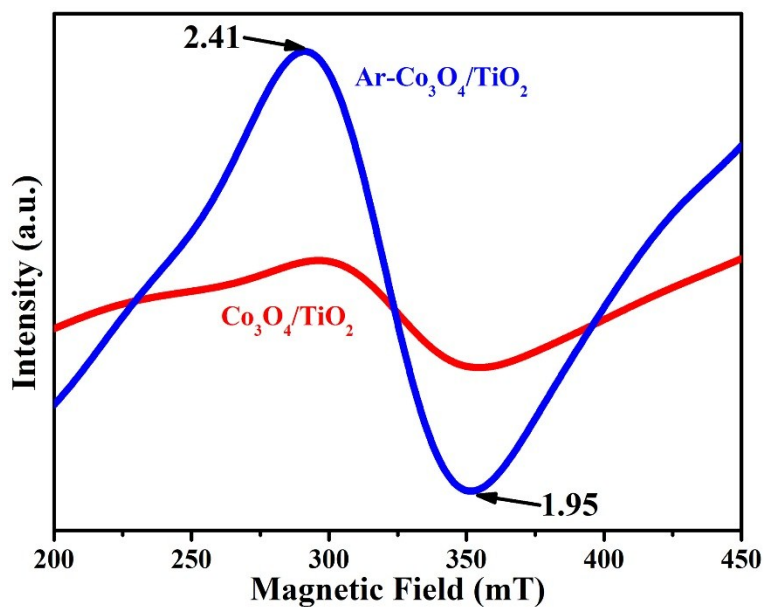


Fig. S5. Electron paramagnetic resonance (EPR) spectra of Co₃O₄/TiO₂ and Ar-Co₃O₄/TiO₂.

EPR results of Co₃O₄/TiO₂ and Ar-Co₃O₄/TiO₂ are shown in Fig. S5. It can be easily seen that the g-value of both spectra are the same whereas the peak intensities are enhanced for the sample of Ar-Co₃O₄/TiO₂. The peak intensity of EPR spectrum is correlated with the concentration of Co²⁺ ions, which implies that the more oxygen vacancies were produced during Ar-plasma treatment.

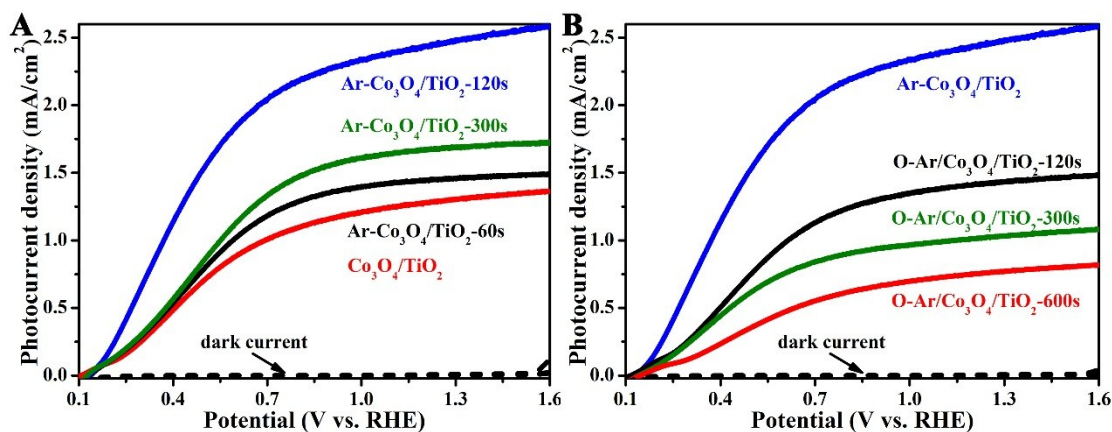


Fig. S6. (A) Linear sweep voltammetry (LSV) curves of the sample of Co₃O₄/TiO₂ treated by Ar-plasma for 60s (black), 120s (blue), and 300s (green). (B) Linear sweep voltammetry (LSV) curves of the sample of Ar-Co₃O₄/TiO₂ treated by O-plasma for 120s (black), 300s (green), and 600s (red).

From the Fig. S6A, The appropriate oxygen vacancy concentration on Co₃O₄ cocatalyst could provide more active sites for water oxidation. Initially, the photocurrent exhibits a trend of increase, and the best photocurrent of 2.5 mA cm⁻² was obtained for Ar-Co₃O₄/TiO₂-120s. However, the excessive oxygen vacancy would inevitably destroy the crystal structure of Co₃O₄ cocatalyst, which is adverse for hole transfer to participate in water oxidation reaction or even serve as the recombination center for photo-generated electron-hole pairs¹⁰. Therefore, the increasing the Ar-plasma treatment time up to 300s for producing more oxygen vacancies may result in a decreased photocurrent density Co₃O₄/TiO₂ photoanodes. It is worthwhile to note that the photocurrent is higher than theoretical value (integrating the absorption edge and AM 1.5G standard solar spectrum), which is because the TiO₂ nanorods show sub-band gap optical absorption after thermal annealing.¹¹ In addition, we experimentally prepared n-type TiO₂ nanorods remain contains localized defect states,¹² and these defect states also provide the visible light adsorption. For confirming the activation of oxygen vacancies, O-plasma was employed to bombard the Ar-Co₃O₄/TiO₂ for filling the oxygen vacancies of Co₃O₄. The

photocurrent density of Ar-Co₃O₄/TiO₂ has gradually decreased from 2.5 to 0.7 mA cm⁻² at 1.23 V_{RHE}, which could be ascribed to the reduction of oxygen vacancies. The above conclusions could be inferred by comparing the change of XPS results of Ar-Co₃O₄/TiO₂ (Fig. 2B and E) and O-Ar/Co₃O₄/TiO₂ (Fig. 2 C and F). All the analyses justify a believable view that the oxygen vacancies of cocatalyst (Co₃O₄) could significantly promote the PEC performances of TiO₂ photoanode

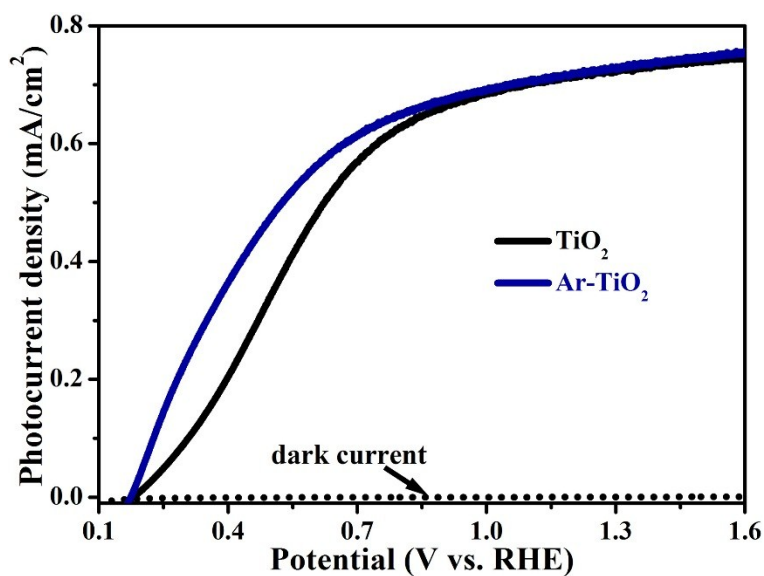


Fig. S7. Linear sweep voltammetry (LSV) curves of pristine TiO₂ and Ar-plasma treated TiO₂.

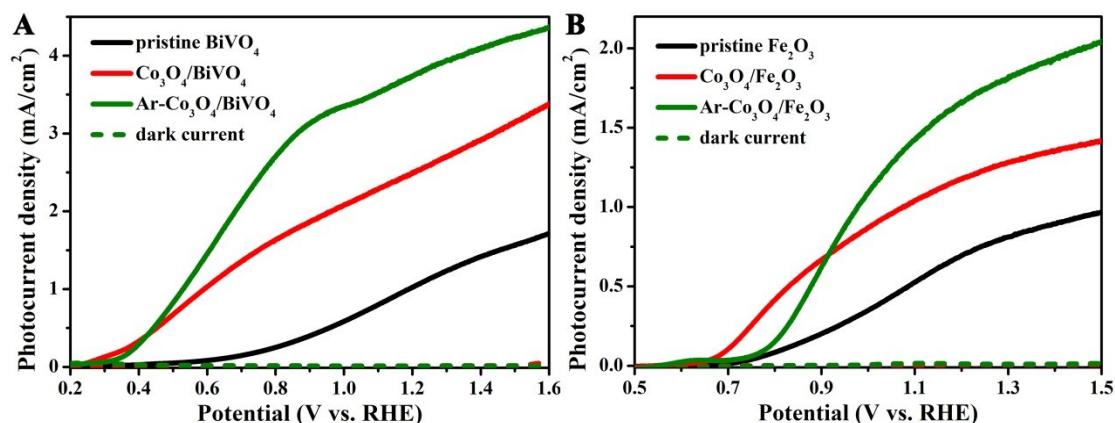


Fig. S8. Linear sweep voltammetry (LSV) curves for (A) BiVO₄ and (B) Fe₂O₃ electrodes.

The LSV curves of BiVO₄-based photoanodes were measured in 0.1 M PBS solution (pH=7) under AM 1.5G irradiation. As shown in Fig. S8A, the pristine BiVO₄ exhibits a photocurrent density of 1.0 mA cm⁻² at 1.23 V_{RHE}, the value could be improved to 2.5 mA cm⁻² after the modification of Co₃O₄. Further engraving by Ar-plasma, the photocurrent value of 3.8 mA cm⁻² was obtained. For Fe₂O₃-based photoanodes system, the similar enhancement of photocurrent density was observed by Co₃O₄ decoration and further Ar-plasma treatment (Fig. S8B). It should be note that the above two electrodes have not been optimized, and their photocurrent may be further improved by Co₃O₄ modification or Ar-plasma treatment. Overall, the Ar-plasma treatment has been demonstrated a rapid and highly efficient strategy to activate cocatalyst for achieving superior PEC properties.

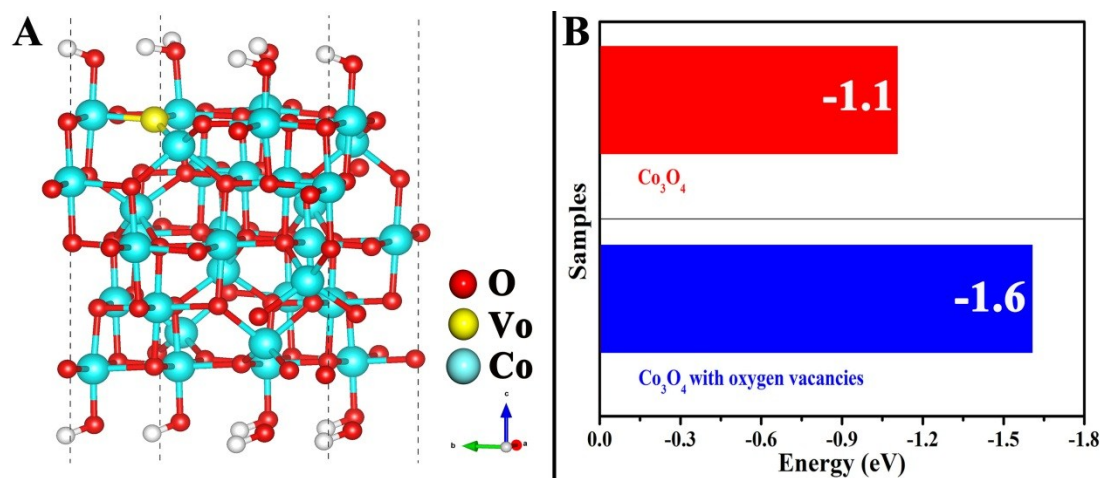


Fig. S9. (A) The optimized model for DFT calculations; (B) Calculated adsorption energies of water for pristine Co_3O_4 and Co_3O_4 with oxygen vacancies.

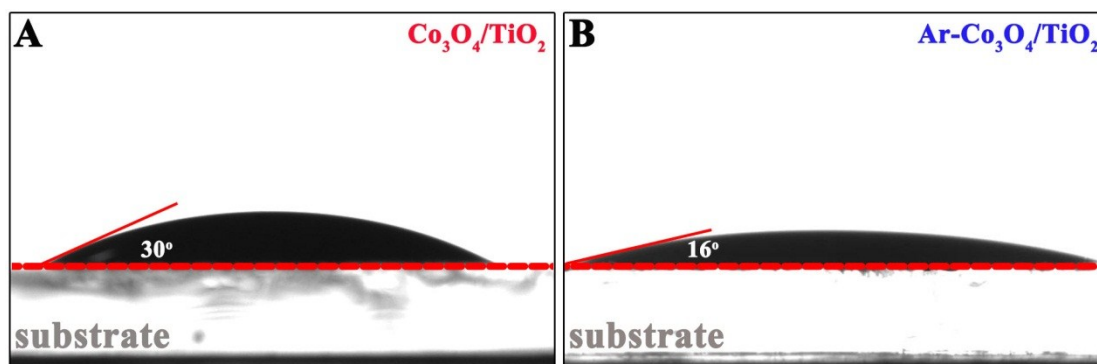


Fig. S10. Contact angle patterns of $\text{Co}_3\text{O}_4/\text{TiO}_2$ (A) and $\text{Ar-Co}_3\text{O}_4/\text{TiO}_2$ (B).

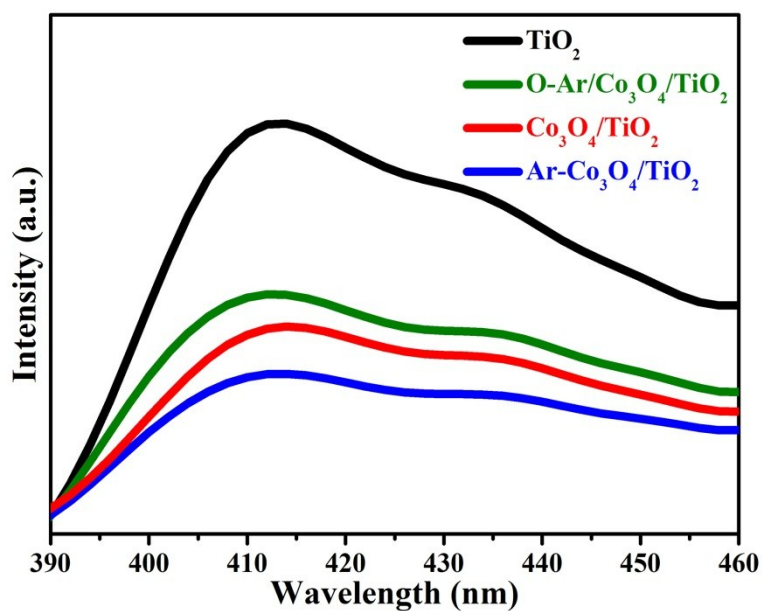


Fig. S11. Photoluminescence spectra (PL) of pristine TiO_2 (black), $\text{Co}_3\text{O}_4/\text{TiO}_2$ (red), $\text{Ar-Co}_3\text{O}_4/\text{TiO}_2$ (blue), and $\text{O-Ar/Co}_3\text{O}_4/\text{TiO}_2$ (green).

The PL spectra were employed to reveal the holes trapping capability of as-prepared samples. It is evident that $\text{Co}_3\text{O}_4/\text{TiO}_2$ exhibits a lower peak intensity than pristine TiO_2 , indicating that the very few electrons have fell back to valence band under the light excitation due to the high holes trapping capability of Co_3O_4 . That is the photogenerated holes transfer from TiO_2 to Co_3O_4 .

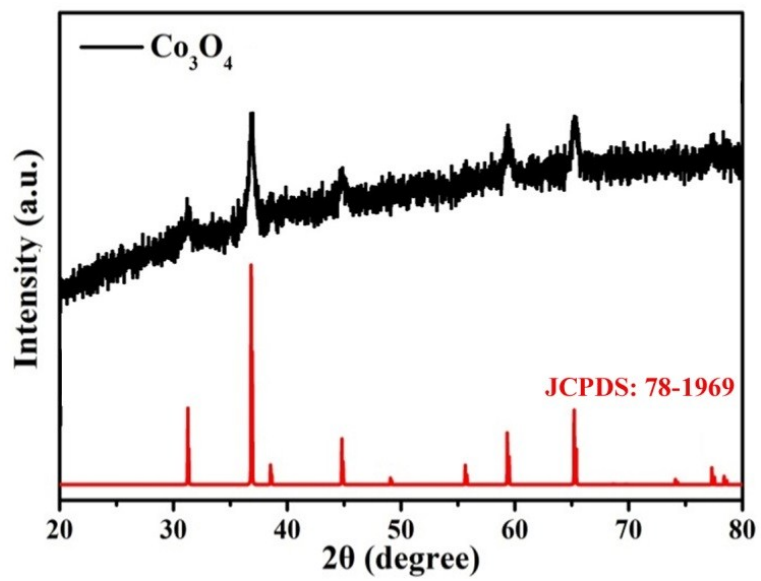


Fig. S12: The XRD patterns of Co_3O_4 .

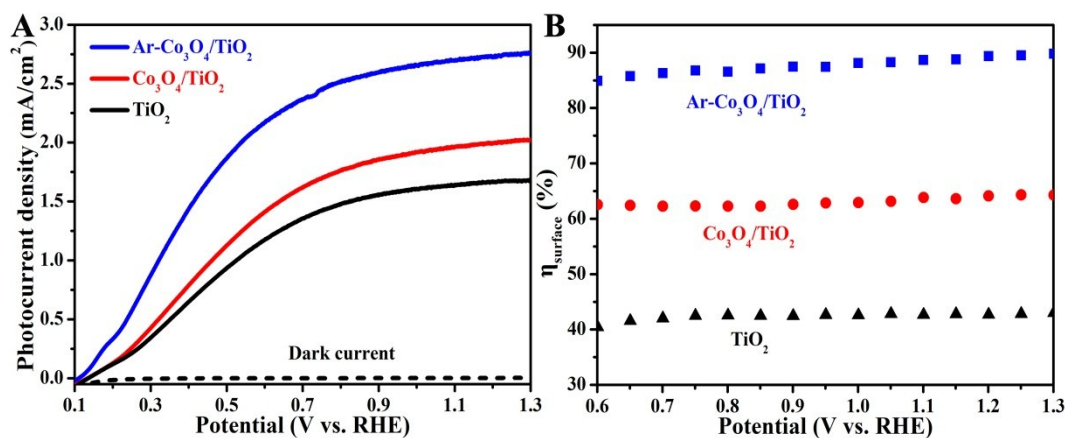


Fig. S13. (A) LSV curves for sulfite oxidation; (B) the calculated surface charge separation efficiency.

The surface charge separation efficiency could be estimated by the following equation:

$J_{PEC} = J_{abs} \times \eta_{bulk} \times \eta_{surface}$, where J_{abs} is the photocurrent density when completely converting the

absorbed photons into current. η_{bulk} is the charge separation in the electrode bulk. $\eta_{surface}$ is the

charge separation in the electrode surface. The surface recombination of charge carries can be

ignored when Na₂SO₃ (0.05 M) is added to the electrolyte ($\eta_{surface} = 100\%$). Therefore, the

$\eta_{surface} = J_{water} / J_{sulfite}$. The photocurrent densities for sulfite oxidation were shown in Fig. S13A, and

the corresponding $\eta_{surface}$ were shown in Figure S13B. It is clear that the value of pristine TiO₂ is

about 42 % at 1.23 V_{RHE}. After the decoration of Co₃O₄ cocatalyst, the $\eta_{surface}$ could be increased

to 64 % at the same potential. Further introducing the oxygen vacancies on cocatalyst, the

$\eta_{surface}$ of 90 % was obtained at 1.23 V_{RHE}. The calculated $\eta_{surface}$ is consistent with the EIS analysis,

illustrating that the interface charge separation efficiency could be accelerated by activating

Co₃O₄ with oxygen vacancies.

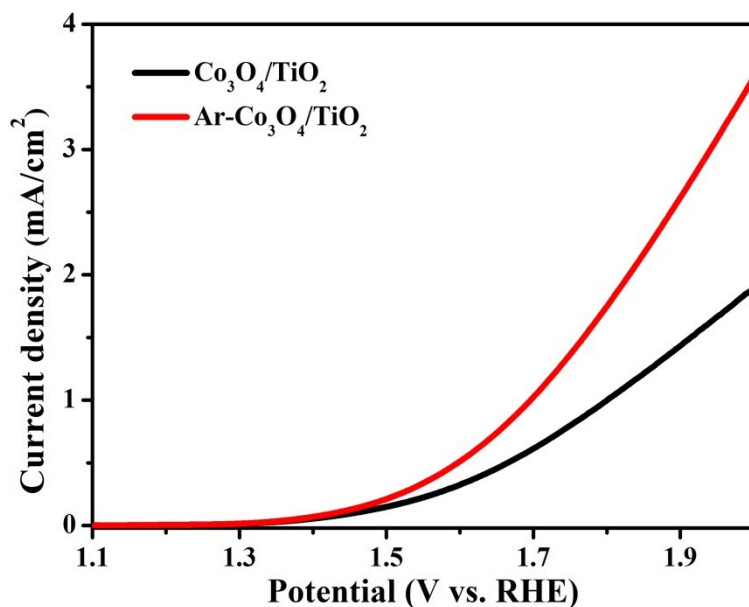


Fig. S14. The LSV curves of $\text{Co}_3\text{O}_4/\text{TiO}_2$ and $\text{Ar-Co}_3\text{O}_4/\text{TiO}_2$.

The electrochemical test was conducted in a standard three-electrode configuration. The Pt foil and saturated calomel electrode (SCE) were employed as counter electrode and reference electrode, respectively. The as-prepared samples ($\text{Co}_3\text{O}_4/\text{TiO}_2$ and $\text{Ar-Co}_3\text{O}_4/\text{TiO}_2$) were used as the working electrode. 0.1 M NaOH was used as electrolyte for the dark electrochemical activity analysis. As shown in Fig. S14, it can be clearly seen that $\text{Ar-Co}_3\text{O}_4/\text{TiO}_2$ exhibits higher electrocatalytic activity for water oxidation than the un-treated $\text{Co}_3\text{O}_4/\text{TiO}_2$ samples. These demonstrations may further confirm the important roles of oxygen vacancy in Co_3O_4 for promoting the PEC water oxidation activity.

Reference

- 1 T. W. Kim and K. S. Choi, *Science*, 2014, **343**, 990.
- 2 G. Dong, Y. Zhang and Y. Bi, *J. Mater. Chem. A*, 2017, **5**, 20594.
- 3 G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251.
- 4 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
- 5 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.
- 6 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 7 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, 1133.
- 8 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.
- 9 J. Wang, J. Liu, B. Zhang, H. Wan, Z. Li, X. Ji, K. Xu, C. Che, D. Zha, L. Miao and J. Jiang, *Nano Energy*, 2017, **42**, 98.
- 10 L. Xu, Q. Jiang, Z. Xiao, X. Li, J. Huo, S. Wang and L. Dai, *Angew.Chem. Int. Ed.*, 2016, **55**, 5277-5281.
- 11 M. Liu, N. D. L. Snapp and H. Park, *Chem. Sci.*, 2011, **2**, 80.
- 12 G. Wang, Y. Yang, D. Han and Y. Li, *Nano Today*, 2017, **13**, 23.