Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supplemental Information:

1. Experimental Section

1.1 Synthesis of n-type $ZnFe_2O_4$ and p-type Co-$ZnFe_2O_4$

The n-type $ZnFe_2O_4$ film was prepared by the hydrothermal method. The FTO was ultrasonically cleaned through acetone, isopropanol, ethyl alcohol absolute and deionized water, respectively. The cleaned FTO was kept in a Teflon lined stainless steel autoclave. 0.15 M $FeCl_3 \cdot 6H_2O$, 0.10 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.15 M $NaNO_3$ were dissolved in 20 mL deionized water, stirring for 15 min to obtain precursor solution, which was poured into the Teflon lined stainless steel autoclave for 6 h at 100 °C. Then, the FTO was cleaned in deionized water and dried in air. Subsequently, the FTO was sintered at 550 °C for 2 h. After sintering, the FTO was immersed in 1 M NaOH solution for 12 h to remove unwanted ZnO thin layer. Eventually, the n-type $ZnFe_2O_4$ film was prepared. Most of the preparation progress of p-type Co-$ZnFe_2O_4$ was similar to that of n-type $ZnFe_2O_4$. The only difference was that 0.04 M $Co(NO_3)_2 \cdot 6H_2O$ was added to the precursor solution. Other conditions were remained unchanged.

1.2 Characterizations

The morphology and microstructure of samples were carried out on JEOL JSM-7800F scanning electron microscope (SEM) and JEOL JEM-2100 transmission electron microscopy (TEM). The crystal structures of samples were determined from data using an X-ray diffractometer (XRD, Rigaku-D/max-2500; Cu Kα radiation, λ=0.154059 nm, 40 kV, 150 mA). The elements of samples were identified via energy dispersive X-ray spectroscopy (EDS, AZtec from Oxford). The surface chemical states of samples were recorded by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi). The Fourier transform infrared (FTIR) spectrometry of samples were measured by RXI FTIR Spectrometer. The optical absorption performance of samples was examined by DU-8B UV-vis double-beam spectrophotometer. The PEC performance was probed in 0.5 M Na_2SO_4 electrolyte without sacrificial agent (pH=7), a standard three-electrode configuration that prepared films as working electrode, a platinum foil as counter electrode and an Ag/AgCl (in saturated KCl) electrode as reference electrode via an electrochemical workstation and irradiated with a Xenon lamp (AM 1.5 G, 100 $mW \cdot cm^{-2}$). The electrochemical impedance spectra (EIS) was collected on a three-electrode configuration, recorded under illumination at a potential of 0 V vs RHE and a frequency range of 10-100 kHz. The gas amounts of H_2 and O_2

were measured by a gas chromatograph.

The average grain size of samples was calculated by the Debye-Scherrer formula as follows [S1]:

$$D=0.94\lambda/\beta\cos\theta \quad (1)$$

Where D was the grain size, λ was the wavelength of radiation (λ=0.154059 nm), θ was the Bragg diffraction angle, β was the full width at half maximum on a 2θ scale.

The optical band gap was calculated as follows [S2]:

$$(\alpha h\upsilon)^n=A(h\upsilon-E_g) \quad (2)$$

Where α was the absorption coefficient, h was the Planck's constant, υ was the photon frequency, the n was 2 or 1/2 according to a direct or indirect band gap semiconductor, A was a constant and E_g was the optical band gap.

The Mott-Schottky plot was carried out in 0.5 M Na_2SO_4 solution to estimate the flat band potential of samples, the calculation was according to the following equations [S3, S4]:

$$\text{n-type semiconductor：}\ 1/C^2=(2/e_0\varepsilon\varepsilon_0N_d)[(V_a-V_{fd})-kT/e_0] \quad (3)$$

$$\text{p-type semiconductor：}\ 1/C^2=(2/e_0\varepsilon\varepsilon_0N_A)[(-V_a+V_{fd})-kT/e_0] \quad (4)$$

Where C was the specific capacitance, e_0 was fundamental electric charge, ε was the dielectric constant, ε_0 was the permittivity of vacuum, N_d was the donor density (n-type semiconductor), N_A was the acceptor density (p-type semiconductor), V_a was the applied potential, V_{fd} was the flat band potential, k was the Boltzmann constant and T was the temperature.

The collected Ag/AgCl potential was converted to the reversible hydrogen electrode (RHE) potential as follows [S5]:

$$E_{RHE}=E_{Ag/AgCl}+0.059pH+0.1976\ V \quad (5)$$

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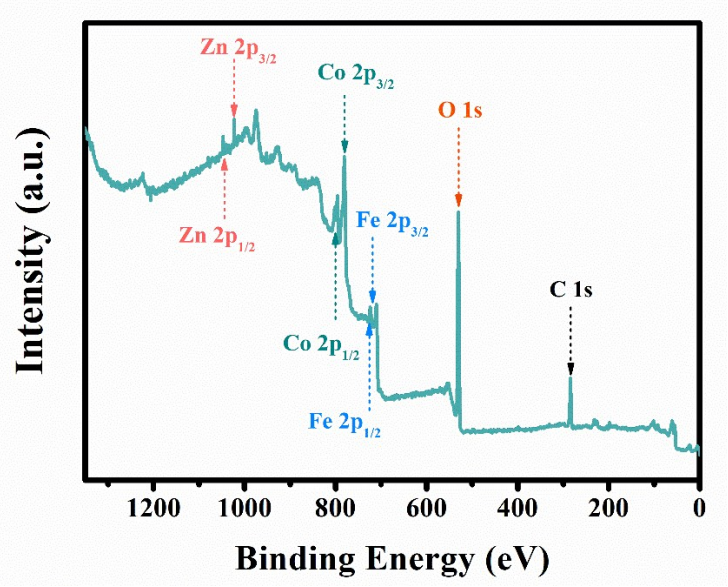
Tab.S1 Summary of XPS data about Zn 2p, Fe 2p, O 1s, Co 2p and C 1s of Co-$ZnFe_2O_4$



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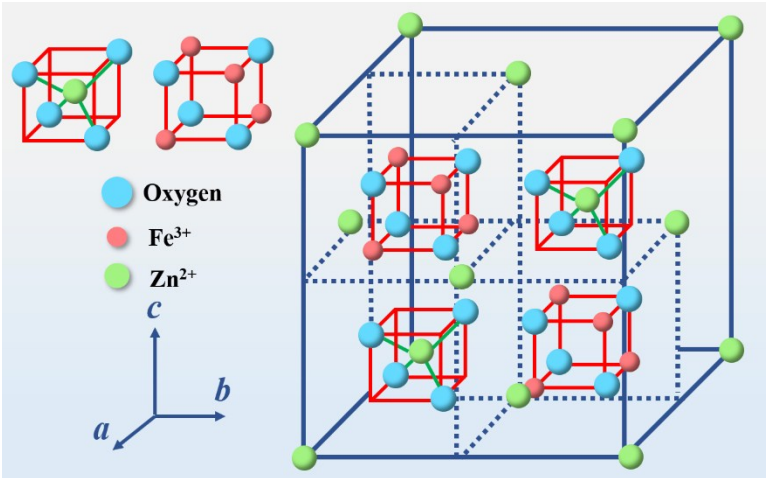
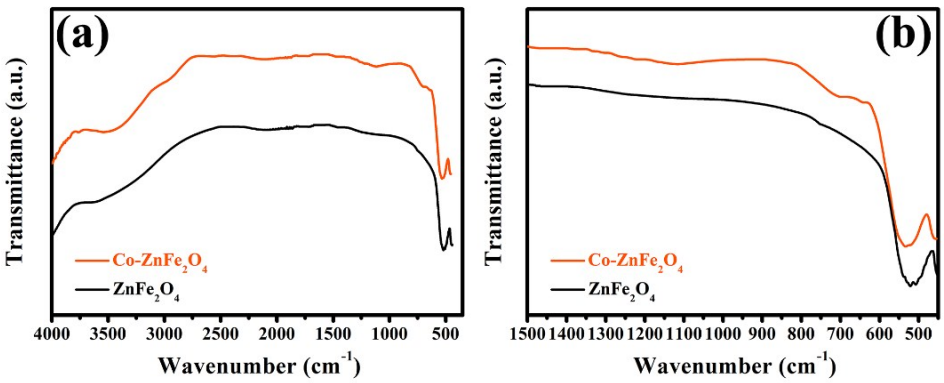


Fig.S2 Cell structure of spinel structure $ZnFe_2O_4$



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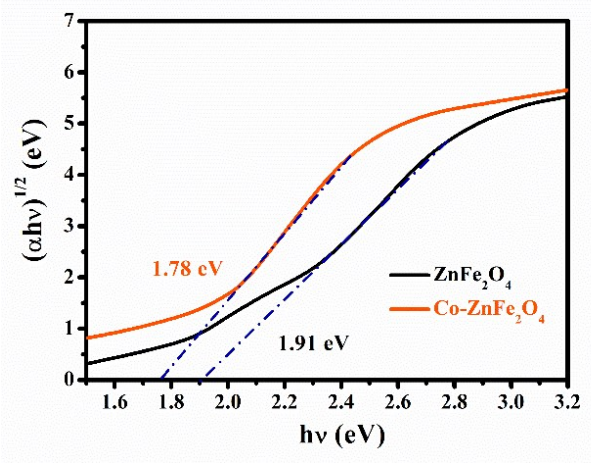


Fig.S4 Optical indirect band gap energy (E_g) of samples

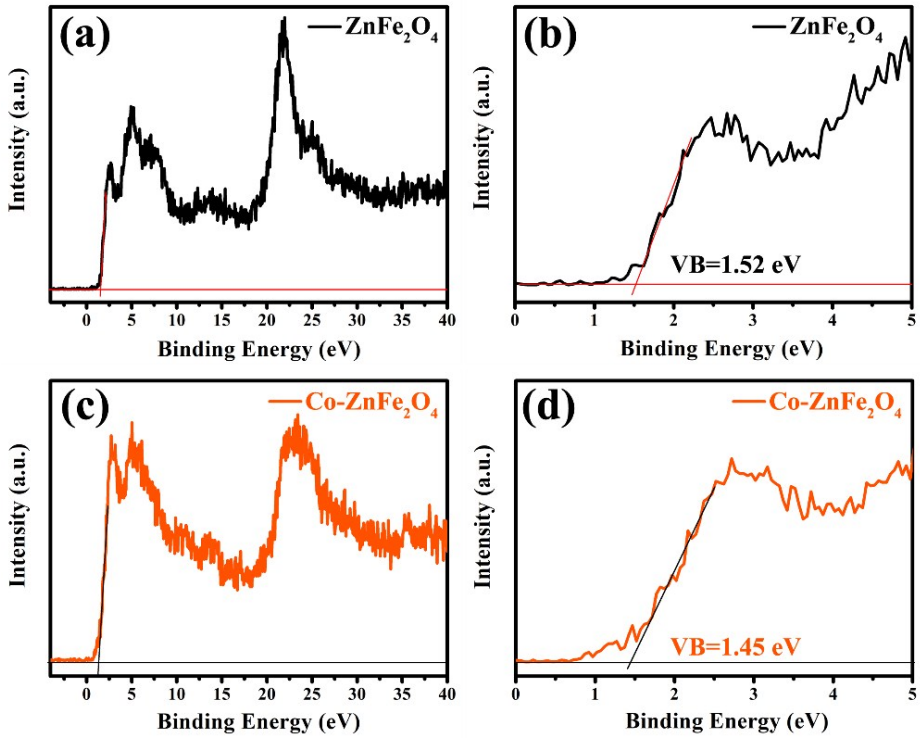
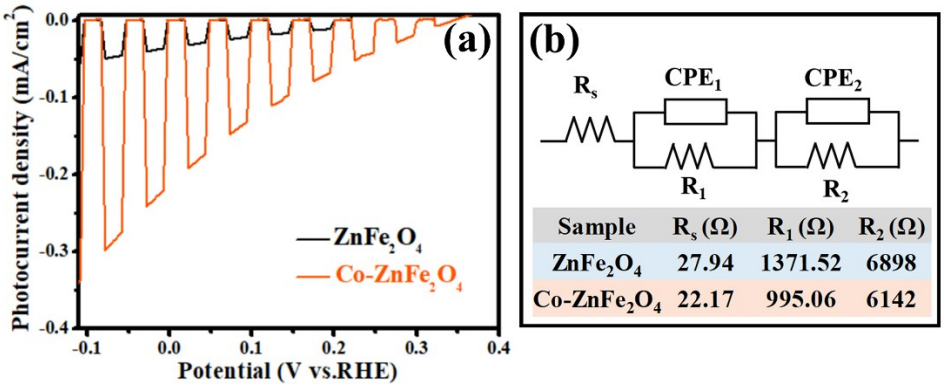
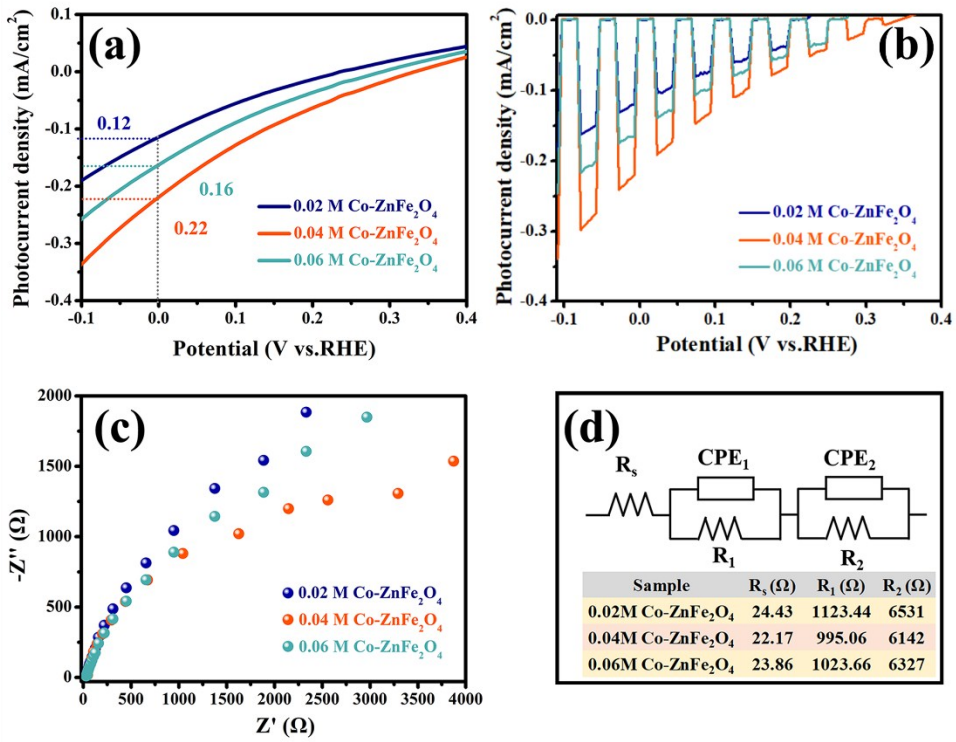


Fig.S5 XPS valence band spectrum (a) and enlarged spectrum (b) of $ZnFe_2O_4$, XPS valence band spectrum (c) and enlarged spectrum (d) of Co-$ZnFe_2O_4$



Sample	R_s (Ω)	R_1 (Ω)	R_2 (Ω)
$ZnFe_2O_4$	27.94	1371.52	6898
Co-$ZnFe_2O_4$	22.17	995.06	6142

Fig.S6 Chopped J-V curves (a), equivalent circuit model and related parameters of electrochemical impedance spectra (b) of $ZnFe_2O_4$ and Co-$ZnFe_2O_4$



Sample	R_s (Ω)	R_1 (Ω)	R_2 (Ω)
0.02M Co-$ZnFe_2O_4$	24.43	1123.44	6531
0.04M Co-$ZnFe_2O_4$	22.17	995.06	6142
0.06M Co-$ZnFe_2O_4$	23.86	1023.66	6327

Fig.S7 J-V curves (a), chopped J-V curves (b), electrochemical impedance spectra (c), equivalent circuit model and related parameters of electrochemical impedance spectra (d) of different concentrations of cobalt doped $ZnFe_2O_4$

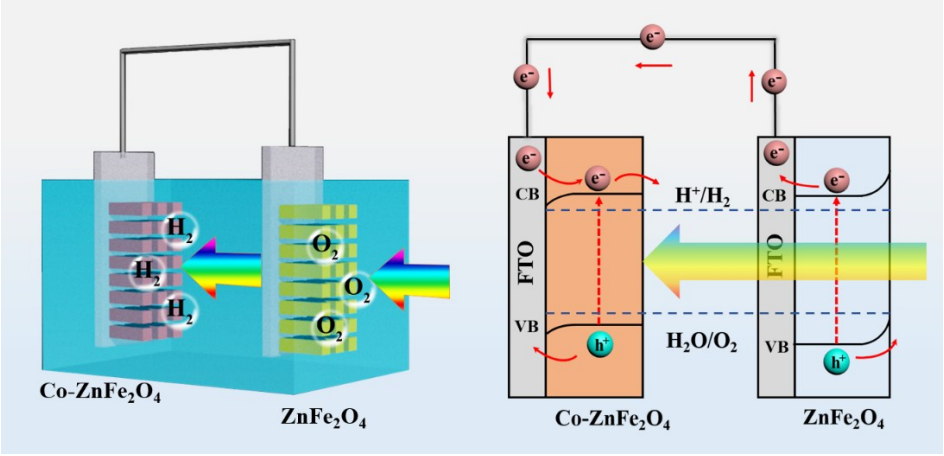
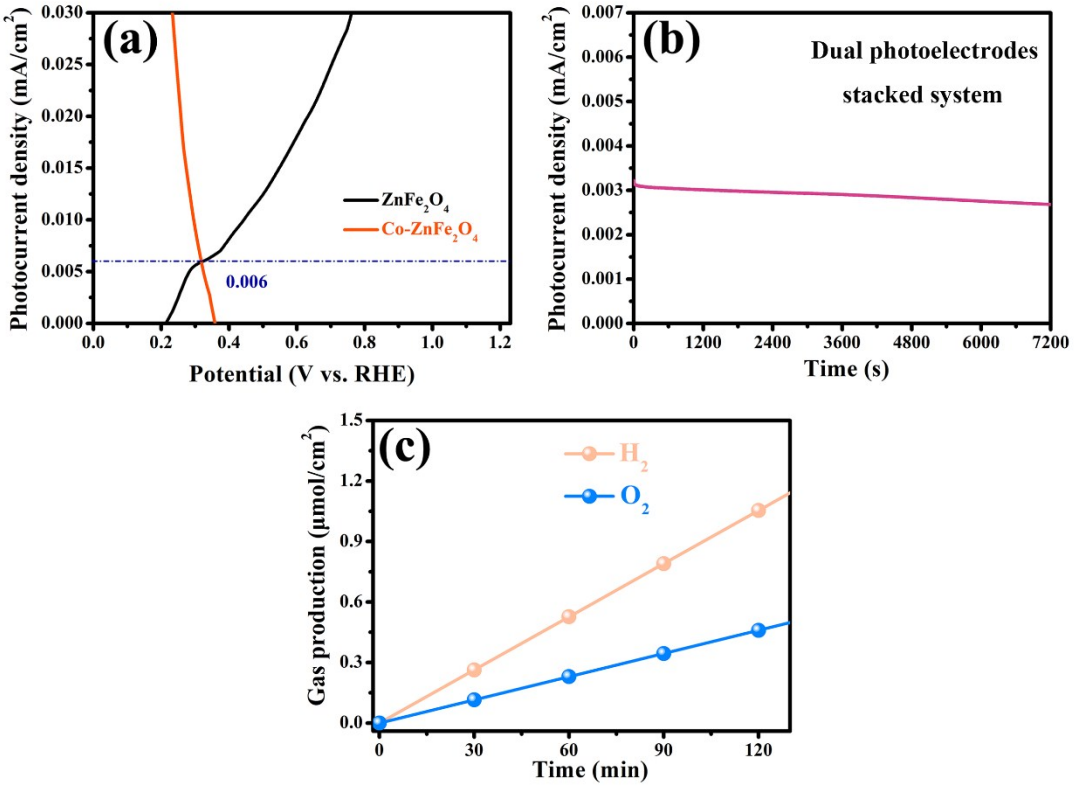


Fig.S8 Diagrammatic sketch about the charge transfer of the dual photoelectrodes stacked system



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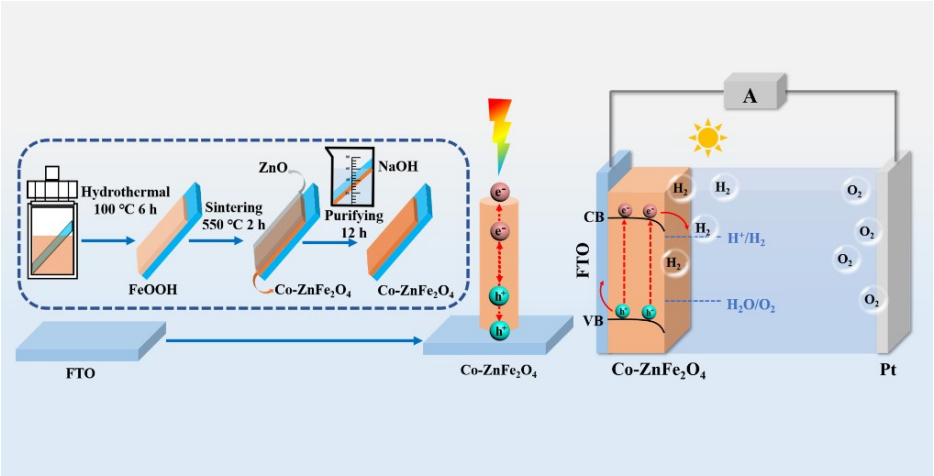

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Tab.S1 Summary of XPS data about Zn 2p, Fe 2p, O 1s, Co 2p and C 1s of Co-$ZnFe_2O_4$

Name	Atomic %	Start BE	End BE	Peak BE	Height CPS	Area (P) CPS.eV	Peak Type
Zn 2p	11.59	1058.67	1014.71	1022.81	12710.323	11996.41	Standard
Fe 2p	23.18	745.04	698.31	710.78	64893.762	67681.44	Standard
O 1s	46.37	539.15	524.44	529.73	134010.793	258564.19	Standard
Co 2p	2.24	815.69	768.82	780.93	28788.643	510661.82	Standard
C 1s	16.62	296.55	281.55	284.74	20864.942	29390.57	Standard

References:

[S1] Z. Zhang, M. F. Hossain and T. Takahashi, *Int. J. Hydrogen Energy*, 2010, 35, 8528-8535.

[S2] M. Chandrika, A. V. Ravindra, C. Rajesh, S. D. Ramarao and S. Ju, *Mater Chem Phys*, 2019, 230, 107-113.

[S3] W. Ma, X. Wu, K. Huang, M. Wang, R. Fu, H. Chen and S. Feng, *Sus. Energy. Fuels*, 2019, 3, 2135-2141.

[S4] Y. Xu, J. Jian, F. Li, W. Liu, L. Jia and H. Wang, *J. Mater. Chem. A*, 2019, 7, 21997-22004.

[S5] M. Li, L. Chen, C. Zhou, C. Jin, Y. Su and Y. Zhang, *Nanoscale*, 2019, 11, 18071-18080.