Supporting Information

Enhanced photoelectrochemical water splitting performance of

hematite photoanodes via uniform Ti and gradient Ge co-doping

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1. Experimental section

Materials Fluorine-doped tin oxide (FTO) substrates (F: SnO₂, 7 Ω /cm²), Iron(III) chloride hexahydrate (FeCl₃·6H₂O, \geq 99.0%, Aladin), Titanous chloride (15.0~20.0wt% TiCl₃ basis in 30% HCl, Energy Chemical), Germanium(IV) oxide (GeO₂, 99.99%, Energy Chemical), Acetone (Greagent, GR), Ethanol (Greagent, \geq 99.7%, GR), Nickel(II) chloride hexahydrate (NiCl₂·6H₂O, \geq 98.0%, Chron Chemicals), Sodium fluoride (NaF, \geq 98.0%, Tianjin Guangfu technology development co. ltd), Hydrogen peroxide solution (H₂O₂, 30%, Xilong Scientific).

Preparation of bare Fe₂O₃ and Ti:Fe₂O₃ To grow Ti:FeOOH on fluorine-doped tin oxide conductive glass (FTO), the cleaned FTO glass was placed in 20 ml of 150 mM FeCl₃ and 10 ul 15.0~20.0wt% TiCl₃ mixed solution and heated in an oven at 100 °C for 3 h. Followed by, the Ti:FeOOH samples were washed with deionized water. Finally, the Ti:FeOOH were annealed and calcined to form Ti:Fe₂O₃. Specifically, the annealing calcination was done in two stages: first, using a tube furnace to heat the material to 550°C for two hours and then for 15 minutes at 730°C. Similar procedures are used to prepare bare Fe₂O₃, with the exception that TiCl₃ is not added during the hydrothermal process.

Preparation of Ti-Ge:Fe₂O₃ Ti-Ge:Fe₂O₃ was obtained by impregnating Ti:FeOOH in a certain amount of GeO₂ for a certain period of time, followed by a two-step annealing and calcination method.

Preparation of NiFeOOH/Ti-Ge:Fe₂O₃ To prepare NiFeOOH/Ti-Ge:Fe₂O₃ photoanode, cyclic voltammetric electrodeposition was performed. The deposition electrolyte solution contained 5 mM FeCl₃, 3 mM NiCl₂, 5 mM NaF, 0.1 mM NaCl, and 0.1 M H₂O₂, and was gently stirred during the synthesis. The potential was cycled between -0.49 and 0.41 V using a scan rate of 200 mV s⁻¹ for 3 cycles.

2. Photoelectrochemical Measurements

On a CHI 760E workstation (CH Instruments Co.) with a three-electrode configuration, all photoelectrochemical measurements of photoanodes were carried out.

The working photoanode (1*1 cm²), Pt plate (1*1 cm²), and saturated Ag/AgCl electrode served as the working electrode, counter electrode and reference electrode, respectively. The light source was simulated solar light irradiation with AM 1.5 G filter (100 mW/cm², Perfect Light, PLS-SXE-300). Light was illuminated from the front of the FTO substrate for all test. Linear scanning voltammogram (LSV) were performed at scan rate was 10 mV/s. Electrochemical impedance spectroscopy (EIS) plot of 1.23 V vs RHE was obtained with an alternating current amplitude of 10 mV and a frequency range of 0.01 to 10⁵ Hz. Mott-Schottky analysis was conducted in dark condition with potential range from -0.6 to -0.1 V vs Ag/AgCl with different frequencies. The electrolyte was 1.0 M NaOH solution (pH=13.6). All potentials were converted to the reversible hydrogen electrode (V vs RHE) using the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$. Argon gas was passed into the electrolyte solution for 30 min before performing the experiment.

3. Computational Formula

Applied bias photon-to-current efficiency (ABPE) was calculated according to the J-V plots. When assuming a Faraday efficiency of 100%, APBE can be expressed by the following equation:

$$ABPE = \frac{I \times (1.23 - V_{\text{bias}})}{P_{\text{light}}}$$

where I (mA/cm²) represents the photocurrent density, V_{bias} represents the applied potential versus RHE, P_{light} represents the incident illumination power density (100 mW/cm²).

The incident photon to current efficiency (IPCE) was determined using a SCS10-PEC system including Omni- λ 300 monochromator (Zolix Instruments Co., Ltd.) at 1.23 V_{RHE} in a 1.0 M KOH electrolyte. The IPCE result was calculated using the equation:

$$IPCE(\%) = \frac{1240 \times I(mA/cm^2)}{P_{mono}(mW/cm^2) \times \lambda(nm)}$$

where I (mA cm²) is the measured photocurrent density at a specific wavelength, λ (nm) is the wavelength of incident light, and P_{mono} (mW/cm²) is the monochromatic illumination power intensity at a specific wavelength.

The charge separation efficiency ($\eta_{separation}$) is the ratio of the photogenerated carriers that can actually reach the surface of the electrode material to the photogenerated carriers that can theoretically be produced by the photoelectrode. The charge injection efficiency ($\eta_{injection}$) can be defined as the ratio of the photogenerated carriers that actually participate in the surface catalytic reaction to the photogenerated carriers that can reach the surface of the electrode material. The $\eta_{separation}$ and $\eta_{injection}$ can be calculated from J-V plots. Then, the charge separation efficiency was expressed by using the following equation: ^[5, 6]

$$\eta_{separation} = rac{J_{sodium \, sulfite}}{J_{abs}} imes 100\%$$

The surface charge transfer efficiency was calculated by using the following the equation: ^[5, 6]

$$\eta_{\text{injection}} = \frac{J_{water}}{J_{abs}} \times 100\%$$

Where J_{abs} refers to the unity converted photocurrent density from the light absorption, while J_{sodium sulfite} represents photocurrent density with 0.2 M Na₂SO₃ in the 1.0 M KOH electrolyte, J_{water} refers to photocurrent density without 0.2 M Na₂SO₃ in the 1.0 M KOH electrolyte, respectively.

Mott-Schottky (M-S) plots were generated under dark with a voltage of 20 mV at a frequency of 1 kHz. In the M-S plot, the flat band potential and the carrier densities of the photoelectrode are measured according to following equation:

$$N_D = \frac{2}{e\varepsilon\varepsilon_o} \left[\frac{d(\frac{1}{c^2})}{dv} \right]^{-1}$$

Where, c is the space charge capacitance in the semiconductor (obtained from M-S curves), e is the electron charge, ε is the vacuum permittivity (8.85×10^{-12} F m⁻¹), ε^0 is the relative dielectric constant of hematite ($\varepsilon_0 = 80$), N_D is the charge donor density (cm⁻³), V is the electrode applied potential, V_{fb} is the flat band potential, κ is the

Boltzmann's constant (1.38×10^{-23} J K⁻¹) and T is the absolute temperature (K).

In order to evaluate the lifetime of charge carriers, fitted Bode plots based on the EIS spectra are shown in Fig. S7. The lifetime (τ) of the photogenerated charge can be calculated from the following equation:

$$\tau = 1/(2\pi F_{peak})$$

where F_{peak} is the maximum frequency peak.

According to Kanata-Kito model, the built-in electric field of materials can be calculated as follows:

$$E = \sqrt{\frac{-2V_s\rho}{\varepsilon\varepsilon_0}}$$

where E represents the intensity of the built-in electric field; V_s stands for the surface potential detected via KPFM; ρ is surface charge density, which will be obtained by the integral value of the current density (Fig.S16); ϵ_0 is the dielectric constant measured by the vector network analyzer; ϵ refers to the vacuum dielectric constant (8.854 × 10⁻²³ J K⁻¹).

4. Supplementary Figures.



Figure S1. Preparation process of hematite base photoanode



Figure S2. Localized magnification of XRD



Figure S3. EPR measurements of bare Fe₂O₃, Ge:Fe₂O₃, Ti:Fe₂O₃ and Ti-Ge:Fe₂O₃



Figure S4. Top-view SEM images of (a) bare Fe₂O₃; (b) Ti:Fe₂O₃ and (c) Ge: Fe₂O₃



Figure S5. TEM image of NiFeOOH/Ti-Ge:Fe₂O₃

In order to clearly see the thickness (about 3 nm) of the NiFeOOH co-catalytic layer, NiFeOOH was electrodeposited for 20 cycles by CV to ensure the thickness of cocatalytic layer outside the Ti-Ge:Fe₂O₃ recognizable.



 $Figure \ S6. \ Hydrophilicity \ tests \ of \ bare \ Fe_2O_3, \ Ge: Fe_2O_3, \ Ti: Fe_2O_3, \ Ti-Ge: Fe_2O_3 \ and \ NiFeOOH/$

Ti-Ge:Fe₂O₃



Figure S7. (a) UV-vis absorption spectra and (b) Localized magnification of UV-vis absorption spectra of bare Fe₂O₃, Ge:Fe₂O₃, Ti:Fe₂O₃ and Ti-Ge:Fe₂O₃



Figure S8. Raman spectra of bare Fe₂O₃, Ge:Fe₂O₃, Ti:Fe₂O₃ and Ti-Ge:Fe₂O₃



Figure S9. Measurement of LSV curves of Ti:Fe₂O₃ in GeO₂ solution with different impregnation

times



Figure S10. Measurement of LSV curves of Ti-Bi:Fe₂O₃, Ti-Ca:Fe₂O₃ and Ti-Ru:Fe₂O₃



Figure S11. (a-d) Linear-sweep voltammograms chop of Fe₂O₃, Ge:Fe₂O₃, Ti:Fe₂O₃ and Ti-Ge:Fe₂O₃ photoanodes; (e) Transient photocurrent density curves of Fe₂O₃, Ge:Fe₂O₃, Ti:Fe₂O₃ and Ti-Ge:Fe₂O₃ photoanodes at 1.23V vs RHE.



Figure S12. Photoluminescence (PL) spectroscopy of Fe₂O₃, Ge-Fe₂O₃, Ti:Fe₂O₃ and Ti-Ge:Fe₂O₃

photoanodes.



Figure S13. (a-d) Voltammograms of bare Fe₂O₃, Ge:Fe₂O₃, Ti:Fe₂O₃ and Ti-Ge:Fe₂O₃ photoanodes at various scan rates (20-100 mV s⁻¹) and (e) ECSA evaluation (Capacitance of double layer, Cdl).



Figure S14. (a) Open circuit potential (OCP) measurements of the photoanodes and (b) OCP measurements under both dark and light conditions (points marked with dark and light, respectively).



Figure S15. Mott-Schottky diagrams of bare Fe₂O₃, Ge:Fe₂O₃, Ti:Fe₂O₃ and Ti-Ge:Fe₂O₃ photoanodes



Figure S16. (a) Surface charge densities bare Fe_2O_3 , $Ge:Fe_2O_3$, $Ti:Fe_2O_3$ and $Ti-Ge:Fe_2O_3$ photoanodes and (b) Built-in electric field intensities (Built-in electric field value is calculated from the surface photovoltage value and the surface charge density) of bare Fe_2O_3 , $Ge:Fe_2O_3$, $Ti:Fe_2O_3$ and $Ti-Ge:Fe_2O_3$



Figure S17. XPS spectra of (a) Fe $2p_{1}$ (b) O $1s_{1}$ (c) Ni_ (d) Ge 2p and (e) Ti 2p of

NiFeOOH/Ti-Ge:Fe₂O₃ photoanodes



Figure S18. (a) J-V curves of Ti-Ge: Fe₂O₃ and NiFeOOH/Ti-Ge: Fe₂O₃; (b) ABPE curves; (c)
IPCE curves; (d) Separation efficiency of bulk phase charges; (e) Surface charge injection
efficiency and (f) Nyquist plots under 1.23 V vs RHE of NiFeOOH/Ti-Ge: Fe₂O₃



Fig. S19 XPS spectra of (a) Fe, (b) Ge and (c) Ti elements after Ar⁺ plasma etching; (d) Fe and(e) Ge elemental ratios at different etching times for Ge:Fe₂O₃.

etching for different times					
Metal ratio (at.%)					
	Fe	Ge	Ti		
Etching Time (s)					
0	69.66	28.31	2.03		
50.25	74.71	23.19	2.10		
100.35	78.10	19.99	1.91		
150.56	80.02	18.19	1.79		
200.94	81.84	16.36	1.80		

Table S1 The metal ratio extracted from survey XPS spectra of Ti-Ge: Fe $_2O_3$ after Ar+ plasma

Table S2 Impedance curves measured at 1.23 V vs RHE under illumination. The fitting results using the equivalent model for EIS measurements

Sample	$R_{s}\left(\Omega ight)$	Error (%)	$R_{ ext{trap}}\left(\Omega ight)$	Error (%)
Bare Fe ₂ O ₃	30.34	5.9515	2177	5.6904
Ge:Fe ₂ O ₃	52.95	0.75195	488	3.5158
Ti:Fe ₂ O ₃	51.15	0.9391	250.1	1.0056
Ti-Ge: Fe ₂ O ₃	40.45	0.97795	131.4	2.0945
NiFeOOH/Ti-Ge: Fe ₂ O ₃	42.31	1.2716	106	2.9562

Sample	Efb (V vs RHE)	N_d (cm ⁻³)	
Bare Fe ₂ O ₃	0.52	$6.38*10^{17}$	
Ge:Fe ₂ O ₃	0.47	$1.96^{*}10^{18}$	
Ti:Fe ₂ O ₃	0.38	$7.6^{*}10^{18}$	
Ti-Ge: Fe ₂ O ₃	0.37	$1.16^{*}10^{19}$	

Table S3 Flat band potential and carrier density of each $\mathrm{Fe_2O_3}$ base photoanode

Table S4 Comparison of our photoanode to other hematite-based photoanodes

Photoanodes	Photocurrent (mA cm ⁻² Onset potential (V		Ref.
	@1.23V vs RHE)	vs RHE)	
NiOOH/FeOOH/Ti-Pt:Fe ₂ O ₃	2.81	0.6	1
Ce _x PO ₄ /P-Fe ₂ O ₃	1.23	/	2
Fe ₂ O ₃ :Ti/ZnFe ₂ O ₄	0.26	0.9	3
Ni ₂ P/Ta:α-Fe ₂ O ₃	2.98	0.67	4
grad-P:Fe ₂ O ₃ /Co-Pi	2.0	/	5
Li@a-Fe ₂ O ₃	0.75	0.68	6
Nb,Sn:Fe ₂ O ₃ @FeNbO ₄ /FTO	2.71	/	7
Ge-Fe ₂ O ₃	0.92	/	8
Ti-Fe ₂ O ₃	0.66	/	9
Nb,Zr-Fe ₂ O ₃	2.05	/	10
F-Zr:Fe ₂ O ₃ /FTO	1.91	/	11
NiFeO _x @Ti:Si-Fe ₂ O ₃	2.62	0.70	12
NiFeOOH/Ti-Ge: Fe ₂ O ₃	2.92	0.68	This work

Reference

- Z. Zhong, G. Zhan, B. Du, X. Lu, Z. Qin, J. Xiao, Design of Ti-Pt Co-doped a-Fe₂O₃ photoanodes for enhanced performance of photoelectrochemical water splitting, *J. Colloid Interface Sci.*, 2023, 641, 91-104
- 2 X. Bu, Y. Gao, S. Zhang, Y. Tian, Amorphous cerium phosphate on P-doped Fe₂O3 nanosheets for efficient photoelectrochemical water oxidation, *Chem. Eng. J.*, 2019, **355**, 910-919.
- 3 C. Miao, S. Ji, G. Xu, G. Liu, L. Zhang, C. Ye, Micro-Nano-Structured Fe₂O₃:Ti/ZnFe₂O₄ Heterojunction Films for Water Oxidation, *ACS Appl. Mater. Interfaces*, 2012, **4**, 4428-4433.
- 4 X Cao, P Wen, R Ma, Y Liu, S Sun, Q Ma, P Zhang, Y Qiu, Ni₂P nanocrystals modification on Ta:α-Fe₂O₃ photoanode for efficient photoelectrochemical water splitting: In situ formation and synergistic catalysis of Ni₂P@NiOOH cocatalyst, *Chem. Eng. J.*, 2022, **449**, 137792.
- 5 Z. Luo, C. Li, S. Liu, T. Wang, J. Gong, Gradient doping of phosphorus in Fe₂O₃ nanoarray photoanodes for enhanced charge separation, *Chem. Sci.*, 2017, **8**, 91-100.
- 6 J. Cai, L. Xu, X. Tang, L. Kong, J. Wang, R. Wang, X. Li, Q. Xie, K. Mao, H. Pan, Role of lithium doping on α-Fe₂O₃ photoanode for enhanced photoelectrochemical water oxidation, *J. Alloy. Compd.*, 2022, **915**, 165349.
- 7 H. Zhang, Y. K. Kim, H. Y. Jeong, J. S. Lee, A Few Atomic FeNbO₄ Overlayers on Hematite Nanorods: Microwave-Induced High Temperature Phase for Efficient Photoelectrochemical Water Splitting, ACS Catal., 2019, **9**, 1289-1297.
- 8 L. Zhao, J. R. Xiao, H. L. Huang, Q. Y. Huang, Y. C. Zhao, Y. D. Li, Enhanced efficiency of hematite photoanode for water splitting with the doping of Ge, *Int. J. Hydrogen Energ.*, 2018, 43, 12646-12652.
- 9 Z. Yu, L. Chen, L. Luo, R. Huang, Z. Tang, P. Xiao, Y. Zhang, Combining bulk charge transport and surface charge transfer to design titanium-doped hematite homojunction photoanodes, J. Phys. Chem. C, 2022, **126**, 4296-4305.
- 10 L. K. Dhandole, T. S. Koh, P. Anushkkaran, H. S. Chung, W. S. Chae, H. H. Lee, S. H. Choi, M. Cho, Enhanced charge transfer with tuning surface state in hematite photoanode integrated by niobium and zirconium co-doping for efficient photoelectrochemical water splitting, *Appl. Catal. B-Environ*, 2022, **315**, 121538.