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Supporting information for

TiO₂/Graphene/NiFe-Layered Double Hydroxide Nanorod Arrays Photoanode for Efficient Photoelectrochemical Water Splitting

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Experimental Details

Preparation of α-Fe₂O₃ nanowire arrays: The α-Fe₂O₃ nanowire arrays were prepared by a simple hydrothermal method.¹ Typically, 1.6 g of FeCl₃·6H₂O and 3.4 g of NaNO₃ were dissolved in 40 ml of deionized water. The pH of the as-obtained solution was adjusted to 1.5 with hydrochloric acid (6 M) under stirring. The resulting solution was then transferred to a Teflon-lined stainless steel autoclave. One piece of cleaned FTO glass substrate (2 cm × 5 cm) was placed at an angle against the wall of the reactor with the conducting side facing down. The hydrothermal growth was carried out at 100 °C for 6 h. After cooling down to room temperature, the FTO substrate was withdrawn, rinsed extensively with deionized water, and dried at 60 °C in air. The as-obtained film was then treated with a programmed annealing in air at 550 °C for 4 h follow by 700 °C for 0.5 h.

Preparation of WO₃ nanowire arrays: The WO₃ nanowire arrays were prepared by a previously reported hydrothermal method.² Firstly, a seed layer of WO₃ was deposited on FTO glass by spin-coating of a solution prepared by dissolving 1.25 g of H₂WO₄ and 0.5 g of poly(vinyl alcohol) (PVA) in 17 ml of 30 wt. % H₂O₂, followed by a 500 °C annealing for 2 h in air. A H₂WO₄ solution was prepared by dissolving 1.25 g of H₂WO₄ into 23 ml of deionized water by adding 17 ml of 30 wt. % H₂O₂ with heating at 95 °C under stirring. The resulting clear solution was diluted to 0.05 M using deionized water. The solution for the growth of nanowire array was obtained by adding 6 ml of H₂WO₄ solution (0.05M), 1 ml of hydrochloric acid (6 M), and 5 ml of deionized water into 20 ml of acetonitrile. This solution was then transferred to a Teflon-lined stainless steel autoclave. The FTO glass substrate with a WO₃ seed layer was placed at an angle against the wall of the reactor with the conducting side facing down. The hydrothermal growth was carried out at 180 °C for 6 h. After cooling down to room temperature, the substrate was withdrawn, rinsed extensively with deionized water, and dried at 60 °C in air. The resulting film was further annealed in air at 500 °C for 1 h.

Oxygen detection: The measurement of the photoelectrochemically generated O_2 was carried out in a home-made airtight transparent electrochemical cell using a three-electrode configuration connected with the electrochemical workstation (CHI 660C, CH Instruments Inc., Shanghai). The geometrical area of these NAs electrodes was 1 cm × 3 cm. PEC water splitting measurements were performed in a Na₂SO₄ aqueous solution (0.5 M, 128.5 ml) using bulk electrolysis method at 0.6 V *vs.* SCE

under an illumination of 150 W Xe lamp (100 mW cm⁻²). The headspace volume was measured to be 74.3 ml. Prior to the measurement, the electrolyte was thoroughly degassed by purging argon for 30 min. The formation of O_2 was detected by injecting the gas in the reactor headspace into a gas chromatograph (GC-7890II; Techcomp. Co., Ltd.) equipped with a semicapillary column and a thermal conductivity detector. The total O_2 production includes the O_2 amount in the headspace calculated by the ideal gas law and the dissolved O_2 in the electrolyte calculated by the Henry's Law.

Calculation of the electrochemically active surface area (ECSA): To obtain the ECSA, the double-layer capacitance (C_{dl}) was measured by cyclic voltammetry (CV) in a non-Faradaic region of 0.3–0.5 V vs. SCE at scan rates of 20, 50, 100, 150, 200, 250, and 300 mV s^{-1.3–6} The charging current difference (ΔI) between the anodic (I_a) and cathodic charging current (I_c) in the middle of the potential window was plotted against the scan rate, and the linear slope is twice of C_{dl} . The ECSA is calculated from C_{dl} according to the equation:

$$ECSA = C_{dl} / C_s \tag{1}$$

where C_s is the specific capacitance of the sample (the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions). However, it is not practical for most electrodes for the synthesis of smooth and planar surface to measure C_s and to estimate ECSA. The commonly used C_s values are those measured for a variety of metal electrodes in acidic and alkaline solution.^{3–6} Unfortunately, the electrolyte used in this configuration is a neutral Na₂SO₄ aqueous solution, which has not been used for the measurement of C_s . Considering the test conditions in this system, the C_s of FTO substrate in 0.5 M Na₂SO₄ electrolyte was measured for the calculation of ECSA. *Calculation of the charge separation and charge injection efficiency*: Photocurrent density arising from PEC water oxidation can be described by the following equation:^{7,8}

$$J_{H2O} = J_{absorbed} \times P_{charge separation} \times P_{charge injection}$$
(2)

Where $J_{absorbed}$ is the photocurrent density resulting from the complete conversion of the absorbed irradiation,⁹ which is a constant with fixed semiconductor photocatalyst and illumination source; $P_{charge separation}$ is the charge separation yield of the photogenerated charge carriers; $P_{charge injection}$ is the charge injection yield from electrode to electrolyte, which presents the efficiency of water oxidation process. This equation reflects the energy losses in different reaction steps of PEC water oxidation. To obtain detailed information for the efficiencies in each process, a hole scavenger was added into the electrolyte to eliminate the energy loss in the surface water oxidation process (charge injection) due to its fast hole capture kinetics, which indicates a charge injection efficiency of 100%. By this way charge separation efficiency can also be determined. Herein, we choose a widely used hole scavenger Na₂SO₃ for this investigation. As mentioned above:

$$J_{Na2SO3} = J_{absorbed} \times P_{charge separation}$$
(3)

Therefore, the charge separation and charge injection efficiency can be calculated by:

$$P_{\text{charge separation}} = J_{Na2SO3} / J_{absorbed} \tag{4}$$

$$P_{\text{charge injection}} = J_{H2O} / J_{Na2SO3}$$
(5)

Herein, TiO₂ is the only semiconductor photocatalyst in these four photoanodes (TiO₂, TiO₂/NiFe-LDH, TiO₂/rGO, and TiO₂/rGO/NiFe-LDH). Therefore, $J_{absorbed}$ for these photoanodes was calculated to be 1.87 mA cm⁻² under a 100 mW cm⁻² Xe lamp irradiation.⁹

Computational Details

Model construction: The model of rutile TiO₂ is $2 \times 2 \times 2$ in the *a*-, *b*- and *c*-direction, with 16 Ti atoms and 32 O atoms in the supercell. The supercell rGO shows a chemical formula of C₃₂H₂O₄. The hydroxyl, carbonyl and ketone groups are included in model rGO. The model of NiFe-LDH is built with the space group of $r^{3}m$. The supercell of NiFe-LDH is $3 \times 3 \times 1$ in the *a*-, *b*- and *c*-direction. Nine nitrate anions are added in the interlayer space.

Computational method: All the calculations were performed using the CASTEP code in the Materials Studio, version 6.1 software package (Accelrys software inc., San Diego, CA).¹⁰ The DFT calculations were performed using a plane wave implementation at the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) level.¹¹ Spin-polarized DFT + U theory is applied to correct the well-known DFT self-interaction errors for the strongly correlated electrons in the first-row transition metal ions (Ni²⁺, Fe³⁺ and Ti⁴⁺ here). In this work, the values of *U*-*J* (*U*_{eff}) is 3.8 eV for Ni²⁺, 4.3 eV for Fe³⁺ and 3.0 eV for Ti⁴⁺, respectively.^{12,13} The DFT dispersion correction is performed with the Tkatchenko-Scheffler method to describe the noncovalent forces, such as hydrogen bonding and van der Waals interactions. The Broyden-Fletcher-Goldfarb-Shanno algorithm is used to search the potential energy surface during optimization. The structure optimization is based on the following points: (1) an energy tolerance of 1×10^{-5} eV/atom; (2) a maximum force tolerance of 0.03 eV/Å; (3) a maximum displacement tolerance of 1×10^{-3} Å. A Fermi smearing of 0.1 eV and Pulay mixing are used to ensure the fast convergence of the self-consistent electron density.

For the calculation of band structure of TiO_2 and NiFe-LDH, the Γ -point-centered k-point meshes used for the Brillouin zone integrations are $3 \times 3 \times 1$ k-points.

The binding energy between TiO_2 and NiFe-LDH is calculated with equation (6):

$$E_{\rm B} = E_{\rm TiO_2/rGO/NiFe-LDH} - E_{\rm TiO_2/rGO} - E_{\rm NiFe-LDH}$$
(6)

Similarly, the binding energy between TiO_2 and rGO is calculated with equation (7):

$$E_{\rm B} = E_{\rm TiO_2/rGO/NiFe-LDH} - E_{\rm TiO_2/NiFe-LDH} - E_{\rm rGO}$$
⁽⁷⁾

Supplementary Figures and Tables



Fig. S1 Tapping-mode atomic force microscopy (AFM) topographic image and the height profile of graphite oxide (GO).



Fig. S2 The EDX spectra and corresponding elemental contents of (A, B) TiO_2 , (C, D) $TiO_2/NiFe-LDH$, (E, F) TiO_2/rGO , and (G, H) $TiO_2/rGO/NiFe-LDH$ NAs.



Fig. S3 Raman spectrum of rGO prepared by thermal reduction of GO using the same condition for TiO_2/GO NAs.



Fig. S4 Plot of $(\alpha hv)^2$ vs. hv of TiO₂ NAs corresponding to its UV-Vis diffuse-reflectance spectrum for the determination of the direct bandgap.



Fig. S5 Time-resolved photoluminescence (PL) spectra of TiO_2 , $TiO_2/NiFe-LDH$, TiO_2/rGO , and $TiO_2/rGO/NiFe-LDH$ NAs, respectively.

Table S1. Fluorescence lifetime parameters obtained from the time-resolved PL spectra with

 triple-exponential fitting

Samples	$ au_1$	A_1	$ au_2$	A_2	$ au_3$	A_3	<7>	~2
	(ns)	(%)	(ns)	(%)	(ns)	(%)	(ns)	χ-
TiO ₂	0.77	49.12	4.54	31.06	31.63	19.83	8.06	1.167
TiO ₂ /NiFe-LDH	0.84	25.15	5.58	21.87	38.87	52.98	22.02	1.081
TiO ₂ /rGO	0.75	16.23	6.62	20.47	42.98	63.30	28.68	1.014
TiO ₂ /rGO/NiFe-LDH	0.81	13.79	6.04	18.44	39.57	67.78	28.05	1.073

Table S2. A comparison study of the $TiO_2/rGO/NiFe-LDH$ photoanode in this work and previously reported TiO_2 -based photonaodes toward PEC water splitting in neutral medium.

Photoanode material	Photocurrent density	Light intensity	Testing condition	Referenc e
NiCr-TiO ₂ -P	0.94 mA cm ⁻² at 1.23 V <i>vs.</i> RHE	100 mW cm ⁻²	0.1 M PBS (pH 7) 10 mV s ⁻¹	14
Disordered surface layer modified TiO ₂ nanorod arrays	1.18 mA cm ⁻² at 1.23 V <i>vs</i> . RHE	100 mW cm^{-2}	$\begin{array}{l} 0.5 \ M \ Na_2 SO_4 \ (pH \ 6.8) \\ 50 \ mV \ s^{-1} \end{array}$	15
TiO ₂ /BaTiO ₃ core/shell nanowires	~1.3 mA cm ⁻² at 1.23 V <i>vs</i> . RHE	100 mW cm ⁻²	0.5M phosphate buffer (pH = 7)	16
GO-decorated TiO ₂ nanorod arrays	0.767 mA cm ⁻² at 1.23 V <i>vs.</i> RHE	100 mW cm ⁻²	Potassium phosphate-buffered 0.5 M Na ₂ SO ₄ (pH 7.0) 10 mV s ⁻¹	17
Selectively exposed (101) crystal faceted TiO ₂ thin film	0.13 mA cm ⁻² at 0.65 V Ag/AgCl	100 mW cm ⁻²	$0.5 \text{ M Na}_2 \text{SO}_4 \text{ (pH} = 6.8)$ 20 mV s ⁻¹	18
Co-Pi modified TiO ₂ nanowire array	~0.47 mA cm ⁻² at 1.23 V <i>vs.</i> RHE	100 mW cm^{-2}	0.1 M potassium phosphate electrolyte (pH = 7) 25 mV s ⁻¹	19
Co-Pi decorated TiO ₂ @g-C ₃ N ₄ nanorod arrays	1.6 mA cm ⁻² at 1.23 V vs. RHE	100 mW cm^{-2}	$0.10 \text{ M Na}_2\text{SO}_4 \text{ (pH} = 6.8)$ 10 mV s^{-1}	20
3D ZnO/TiO ₂ /FeOOH nanowire arrays	1.59 mA cm ⁻² at 1.8 V <i>vs</i> . RHE	100 mW cm ⁻²	$0.5 \text{ M Na}_2 \text{SO}_4 \text{ (pH} = 7)$	21
MnO_x/TiO_2 nanotube arrays	1.56 mA cm ⁻² at 1.23 V <i>vs.</i> RHE	100 mW cm^{-2}	$0.5 \text{ M Na}_2\text{SO}_4 \text{ (pH} = 6.8)$ 10 mV s^{-1}	22
Carbon nitride quantum dots modified TiO ₂ nanotube arrays	1.34 mA cm ⁻² at 0.3 V vs. Ag/AgCl	100 mW cm ⁻²	$\begin{array}{l} 0.1 \ M \ Na_2 SO_4 \ (pH \ 6.0) \\ 20 \ mV \ s^{-1} \end{array}$	23
BiVO ₄ /Graphene/TiO ₂ nanocomposite thin film	~0.13 mA cm ⁻² at 0.8 V vs Ag/AgCl	100 mW cm ⁻²	$0.1 \text{ M K}_2 \text{SO}_4 \text{ (pH} = 6.7)$	24
N^+ ion irradiated TiO_2 thin films	0.6 mA cm ⁻² at 0.8 V <i>vs</i> . SCE	100 mW cm ⁻²	0.5 M Na ₂ SO ₄	25
AZO/TiO ₂ /Au nanocones arrays	1.1 mA cm ⁻² at 1.23 V vs. RHE	100 mW cm ⁻²	$0.1 \text{ M Na}_2 \text{SO}_4 \text{ (pH} = 6.8)$	26
TiO ₂ /rGO/NiFe-LDH NAs	1.736 mA cm ⁻² at 1.23 V <i>vs</i> . RHE	100 mW cm ⁻²	0.5 M Na ₂ SO ₄ (pH 6.8) 10 mV s ⁻¹	This work



Fig. S6 SEM images of TiO_2/rGO samples with different spin-coating cycles of rGO: (A) TiO_2/rGO -1, (B) TiO_2/rGO -3, (C) TiO_2/rGO -5, (D) TiO_2/rGO -10, (E) TiO_2/rGO -15, and (F) TiO_2/rGO -20.



Fig. S7 EDX spectra and corresponding elemental contents of (A) $TiO_2/rGO-1$, (B) $TiO_2/rGO-3$, (C) $TiO_2/rGO-5$, (D) $TiO_2/rGO-10$, (E) $TiO_2/rGO-15$, and (F) $TiO_2/rGO-20$.



Fig. S8 (A) Current-voltage (*J*-V) curves, (B) charge separation efficiency vs. potential curves, and (C) charge injection efficiency vs. potential curves of TiO_2/rGO -x samples with different spin-coating cycles of rGO.



Fig. S9 SEM images of TiO₂/rGO/NiFe-LDH NAs with different loading amount of rGO: (A)

TiO₂/rGO-3/NiFe-LDH, (B) TiO₂/rGO-5/NiFe-LDH, and (C) TiO₂/rGO-10/NiFe-LDH.



Fig. S10 SEM images of $TiO_2/rGO/NiFe-LDH$ NAs with different electrodeposition time: (A)

10 s, (B) 25 s, and (C) 50 s.



Fig. S11 (A) Large-scale SEM image of TiO_2/rGO NAs; (B) and (C) SEM images of TiO_2/rGO -cover NAs; (D) EDX spectrum and corresponding elemental contents of TiO_2/rGO -cover NAs.



Fig. S12 (A) Current-voltage (*J*-V) curves, (B) charge separation efficiency *vs.* potential curves, and (C) charge injection efficiency *vs.* potential curves of TiO_2 , TiO_2/rGO , and TiO_2/rGO -cover NAs, respectively.



Fig. S13 A comparison between the IPCE and the oxygen production quantum efficiency of $TiO_2/rGO/NiFe-LDH$ NAs.



Fig. S14 The measured *I-t* curves at an applied potential of 0.6 V for TiO_2 , $TiO_2/NiFe-LDH$, TiO_2/rGO , and $TiO_2/rGO/NiFe-LDH$ NAs with a geometric area of 3 cm².

Table S3. Total oxygen production (μ mol) and corresponding faradaic efficiency (shown in the bracket) of TiO₂, TiO₂/NiFe-LDH, TiO₂/rGO and TiO₂/rGO/NiFe-LDH NAs in five-cycle chronoamperometry measurement.

Sample	Cycle number							
	1	2	3	4	5			
TiO ₂	25.3(99%)	25.0(98%)	25.0(99%)	24.4(97%)	24.4(99%)			
TiO ₂ /NiFe-LDH	31.7(98%)	31.1(97%)	30.5(98%)	29.5(97%)	29.6(98%)			
TiO ₂ /rGO	38.3(92%)	37.9(92%)	37.7(93%)	36.5(92%)	35.5(91%)			
TiO ₂ /rGO/NiFe-LDH	46.4(97%)	45.6(99%)	46.1(96%)	47.6(97%)	46.8(97%)			



Fig. S15 C 1s XPS spectra of (a) TiO_2/rGO NAs, (b) TiO_2/rGO NAs after 5 h chronoamperometry measurement, (c) $TiO_2/rGO/NiFe$ -LDH NAs, and (d) $TiO_2/rGO/NiFe$ -LDH NAs after 5 h chronoamperometry measurement.



Fig. S16 CV curves measured in a non-Faradaic region of 0.3-0.5 V at various scan rates for (A) TiO₂, (B) TiO₂/NiFe-LDH, (C) TiO₂/rGO, and (D) TiO₂/rGO/NiFe-LDH NAs with a geometric area of 3 cm², respectively.



Fig. S17 Charging current differences ($\Delta I = I_a - I_c$) measured at 0.4 V plotted against scan rate for TiO₂, TiO₂/NiFe-LDH, TiO₂/rGO, and TiO₂/rGO/NiFe-LDH NAs, respectively. I_a and I_c are the anodic and cathodic current, respectively, and the linear slope is twice of the double-layer capacitance (C_{dl}).



Fig. S18 Double-layer capacitance (C_{dl}) measurements for determining the specific capacitance (C_s) of FTO substrate from cyclic voltammetry (CV) in 0.5 M Na₂SO₄: (A) CV curves measured in a non-Faradaic region of 0.3–0.5 V at various scan rates, (B) Charging current density differences ($\Delta J = J_a - J_c$) measured at 0.4 V plotted against scan rate. J_a and J_c are the anodic and cathodic current density, respectively, and the linear slope is twice of the C_s .

As shown in Fig. S13, C_{dl} is calculated to be 17.58, 18.02, 20.38 and 21.20 µF for TiO₂, TiO₂/NiFe-LDH, TiO₂/rGO and TiO₂/rGO/NiFe-LDH, respectively. The specific capacitance (C_s) of FTO substrate is calculated to be 5.70 µF cm⁻² (Fig. S14).



Fig. S19 (A) Chronoamperometry measurement of TiO₂/rGO/NiFe-LDH NAs at 0.6 V for 3 h,
(B) current-voltage (*J-V*) curves of TiO₂/rGO/NiFe-LDH NAs before and after this 3 h test,
(C) SEM image and (D) EDX spectrum and corresponding elemental contents of TiO₂/rGO/NiFe-LDH NAs after 3 h chronoamperometry measurement.



Fig. S20 (A) *J-V* curves of Fe₂O₃, Fe₂O₃/LDH, Fe₂O₃/rGO, and Fe₂O₃/rGO/NiFe-LDH NAs; (B) *J-V* curves of WO₃, WO₃/LDH, WO₃/rGO, and WO₃/rGO/NiFe-LDH NAs.



Fig. S21 *J-V* curves of (A) TiO_2 , (B) $TiO_2/NiFe-LDH$, (C) TiO_2/rGO , and (D) $TiO_2/rGO/NiFe-LDH$ NAs in 0.5 M Na₂SO₄ and 0.1 M Na₂SO₃ electrolyte, respectively.



Fig. S22 The optimized geometries of (A) TiO₂, (B) rGO, and (C) NiFe-LDH, respectively.



Fig. S23 The band structure of TiO_2 . The blue dashed line represents the Fermi level.



Fig. S24 The band structure of NiFe-LDH. The blue dashed line represents the Fermi level.



Fig. S25 The work function of TiO_2 . The red dashed line represents the vacuum level and the blue dashed line represents the Fermi level.



Fig. S26 The work function of NiFe-LDH. The red dashed line represents the vacuum level and the blue dashed line represents the Fermi level.

The work function of TiO₂ and NiFe-LDH is 5.620 eV and 4.646 eV, respectively. Thus the energy of CBM and VBM, E_{CBM} and E_{VBM} , are obtained with equation (8) and (9):

$$E_{CBM} = -W + 0.5E_g \tag{8}$$

$$E_{VBM} = -W - 0.5E_g \tag{9}$$



Fig. S27 The optimized geometry of TiO_2/rGO .



Fig. S28 The optimized geometry of TiO₂/NiFe-LDH.

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