

Electronic Supplementary Information

Experimental methods

Materials

Ferric trichloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), hydrochloric acid (HCl, 36.5–38%), sodium hydroxide (NaOH) and potassium hydroxide (KOH) were purchased from Chengdu Kelong Chemicals (Chengdu, China); ethanol, acetone, dichloromethane (CH_2Cl_2), sodium nitrate (NaNO_3) were obtained from Tianjin Fuyu Fine Chemical Co., Ltd (Tianjin, China); Cetylpyridinium chloride monohydrate (CPC) was purchased from Sigma-Aldrich (St Louis, MO, USA); Titanium sheet (0.2 mm thick) was purchased from Qingyuan Metal Materials Co., Ltd (Xingtai, China), All the chemicals were of analytical-reagent grade and used without further purification. Double distilled water was used in the whole experiment.

Synthesis of N-CDs

N-CDs were synthesized at room temperature according to previous report.¹ Briefly, 20 mL NaOH (2.0 M) was added into CPC aqueous solution (30 mM, 200 mL) at room temperature, and the color of the mixture solution turned from colourless to light yellow and then to wine red as the reaction time proceeded. The solution changed to be turbid after 12 h, and then 50 mL of CH_2Cl_2 was added to transfer the N-CDs to the bottom organic layer due to their hydrophobicity. After several wash and separations with water to remove the uncarbonizing CPC, the N-CDs dispersed in CH_2Cl_2 were vacuum-dried at 45°C and then redispersed in ethanol to prepare N-CDs ethanol solutions with different concentration. The prepared N-CDs ethanol solutions were stored at 4 °C before use.

Synthesis of $\alpha\text{-Fe}_2\text{O}_3/\text{Ti}$ and N-CDs@ $\alpha\text{-Fe}_2\text{O}_3/\text{Ti}$

α -Fe₂O₃/Ti was hydrothermally synthesized.² In a typical synthesis, Ti sheets were sonicated in acetone, ethanol and deionized water for 10 min, respectively. Then, such Ti sheets were vertically put into a teflon-lined stainless autoclave with an aqueous solution containing 0.15 M FeCl₃•6H₂O and 1 M NaNO₃ at pH 1.5, followed by a thermal treatment at 95 °C for 4 h. The resulting Ti with β -FeOOH precursor was then rinsed with deionized water three times for complete removal of the residual salts and then transformed into α -Fe₂O₃ nanorods array after annealing at 550 °C in a furnace for 2 h.

N-CDs@ α -Fe₂O₃/Ti was obtained by immersing above α -Fe₂O₃/Ti in a N-CDs ethanol solution for a period of time, which was then dried in an oven at 80 °C for 2 h.

Characterization

TEM measurements were made on a JEOL JEM-2010 transmission electron microscope (TEM, Tokyo, Japan) with an accelerating voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were taken by a Kratos XSAM 800 spectrometer (Manchester, U.K.) using monochromated Al K α as the excitation source. A Hitachi U-2900 UV–vis spectrophotometer (Tokyo, Japan) was used to measure the UV–vis adsorption spectra. Fluorescence measurements were carried out on a Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan). The morphologies of all samples were characterized with a Hitachi S-4800 ultra-high resolution field emission scanning electron microscope (FESEM; Tokyo, Japan) and. X-ray diffraction (XRD) patterns were recorded using a Rigaku Spider X-ray diffractometer (Tokyo, Japan) with a Cu K α X-ray source. UV-visible diffusion reflectance spectra were measured on a Shimadzu UV-3600 spectrometer (Japan) by using BaSO₄ as reference.

Photoelectrochemical measurements

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using α -Fe₂O₃/Ti or N-CDs@ α -Fe₂O₃/Ti as the working electrode, a platinum wire as the counter electrode and a Ag/AgCl as the reference electrode. The EIS measurements were performed in the frequency range of 0.01Hz–100 kHz at open circuit potential under both dark and illuminated conditions with an AC voltage amplitude of 10mV. The potentials reported in this work were calibrated to RHE, using the following equation: E (RHE) = E (Ag/AgCl) + (0.197 + 0.059 pH) V. The area of the photoanode exposed to the electrolyte was 1 cm², set by silicon rubber. For light measurements, the light source was a 300 W xenon lamp (Perfect Light, PLS-SXE300) with an AM 1.5 filter. The output power was adjusted to 100 mW cm⁻². All experiments were carried out at room temperature (~25 °C).

Incident photon-to-current conversion efficiencies (IPCE) were calculated from chronoamperometry measurements using a PerfectLight omni3005 monochromator (PerfectLight, Beijing). The light power was measured with a silicon photodetector (HAMAMATSU, S1337). The IPCE values were calculated using the following equation

$$\text{IPCE} = (1240 \times J) / \lambda \times P$$

where J is the measured photocurrent density (mA cm⁻²) and P is the incident light power density (mW cm⁻²) for each wavelength λ (nm).

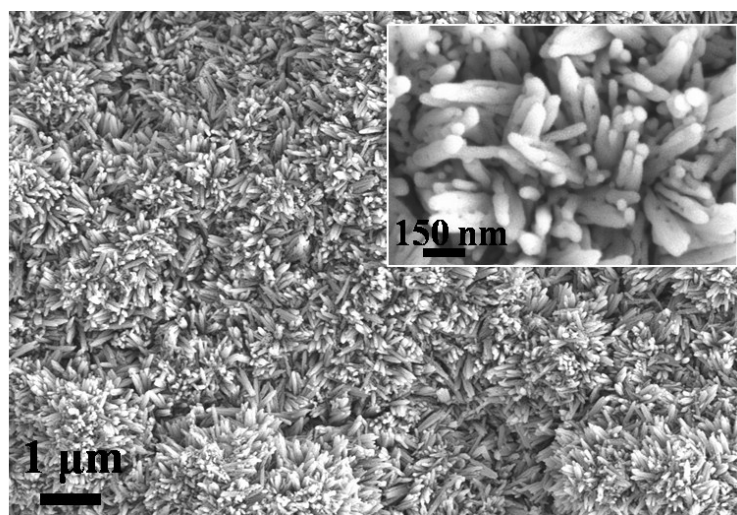


Fig. S1. SEM images of α -Fe₂O₃ nanorods array.

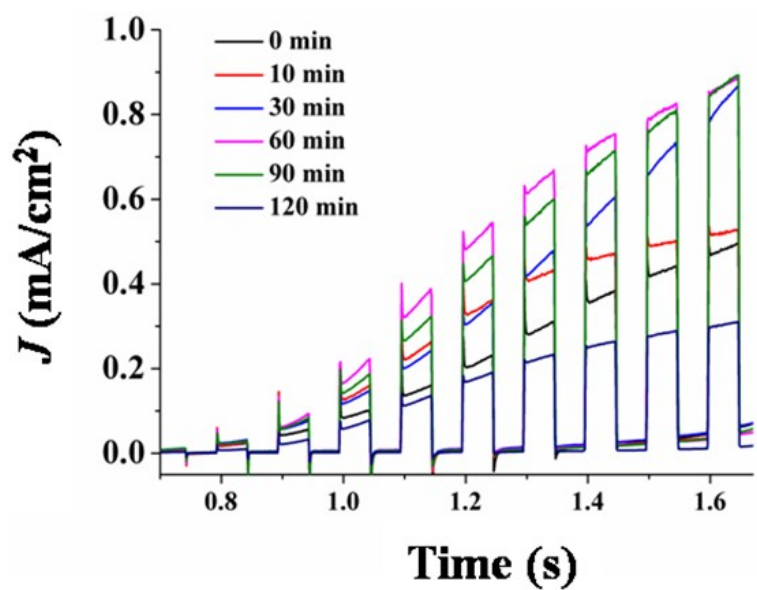


Fig. S2. Photoresponse of N-CDs@ α -Fe₂O₃/Ti electrode prepared by immersing α -Fe₂O₃/Ti in N-CDs ethanol solution (1 mg mL⁻¹) with different time (0-120 min).

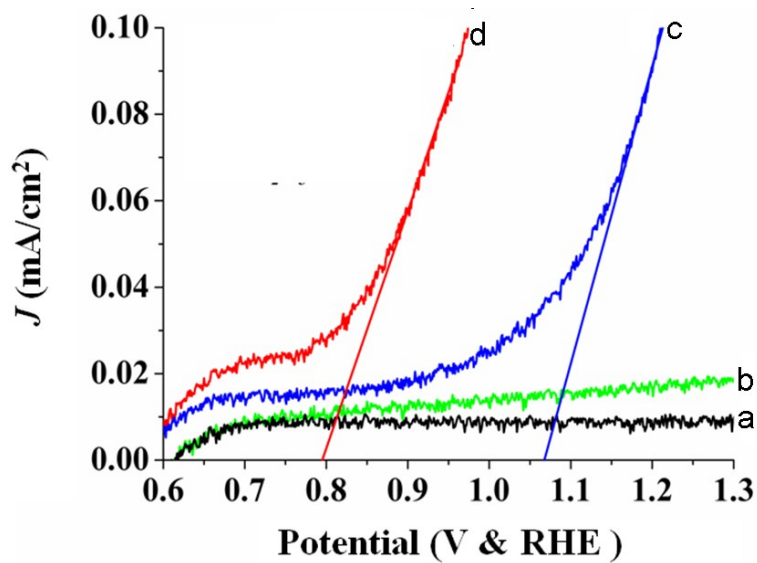


Fig. S3. Local magnified linear sweep voltammetry curves of $\alpha\text{-Fe}_2\text{O}_3/\text{Ti}$ (a, c) and N-CDs@ $\alpha\text{-Fe}_2\text{O}_3/\text{Ti}$ (b, d) photoanodes under dark (a, b) and illumination (c, d) conditions.

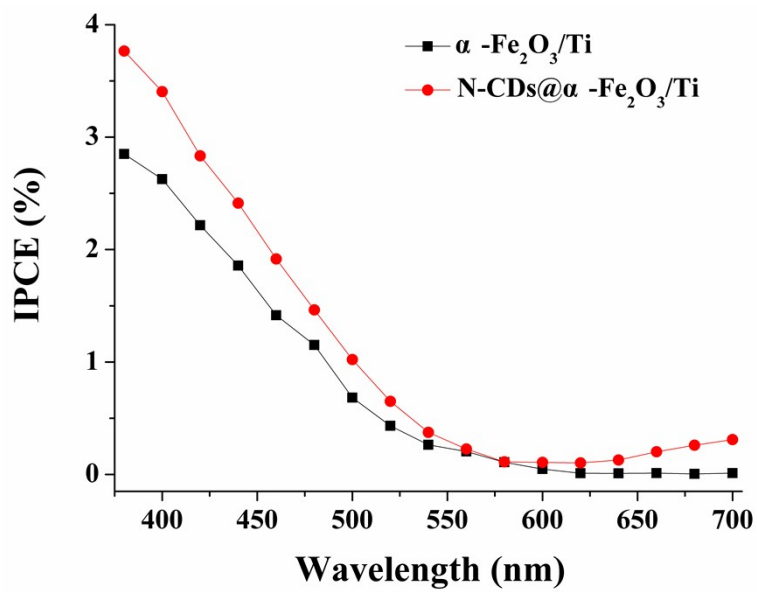


Fig. S4. Incident photon-to-current conversion efficiency (IPCE) of α -Fe₂O₃/Ti and N-CDs@ α -Fe₂O₃/Ti photoanodes under illumination at 1.23V (vs. RHE).

References

- 1 B. Zheng, T. Liu, M. C. Paa, M. Wang, Y. Liu, L. Liu, C. Wu, J. Du, D. Xiao and M. M. F. Choi, *RSC Adv.*, 2015, **5**, 11667.
- 2 P. Jiang, Q. Liu, Y. Liang, J. Tian, A. M. Asiri and X. Sun, *Angew. Chem., Int. Ed.*, 2014, **53**, 12855.