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Electronic Supplementary Information

Enhanced photocatalytic activities by net-like hematite nanoparticle/graphene oxide composite

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Experimental

Graphene (99.0%) used in this work were purchased from Nanjing XFNano Material Tech Co., Ltd, and its thickness and length are 0.8 nm and 0.5–2 μm, respectively. Other analytical reagents were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (Tianjin, China) and used without further purification.

Preparation of G/β-FeOOH nanocomposites

Typically, 8.0 g of $Fe(NO_3)_3 \cdot 9H_2O$ (98.5%) was dissolved in 600 mL of deionized water (DI water), and then 20 mg of graphene was added into the solution. After sonication for 5 min, this solution above was kept at 50°C for 3 h under stirring. The precipitate was filtered off, washed with distilled water and absolute ethanol, and dried at 60°C for 8h.

Preparation of net-like hematite nanoparticle/graphene oxide composite

G/β-FeOOH nanocomposites were annealed at 500°C for 0.5, 1 and 2 h with a heating rate of 2°C $min^{-1}$and thencooled naturally.

Preparation of photoelectrodes

50 mg of sample was dispersed in 0.5 mL of terpineol (99.5%) under vigorously stirring for 24 h. The terpineol suspension was coated onto fluorine-doped tin oxide (FTO) glass substrates (Heptachroma) using the doctor blading technique with Scotch tape as the spacer. After they were dried at 60°C, the photoelectrodes were calcined in nitrogen at 450°C for 30 min and then cooled to room temperature. Finally, the FTO was connected with a copper wire by silver conducting paste and the remaining area was covered by epoxy resin.

Characterization

The morphology and the size of the synthesized samples were characterized by SEM JEOL-JSM-6700F, and TEM JEOL 2010. The crystal structures of the samples were determined by XRD (Rigaku D/max 2550 V, Cu Kα radiation). XPS measurements were carried out using a spectrometer with Al Kα radiation (K-Alpha, Thermofisher Co.). Nitrogen adsorption-desorption isotherms were obtained on a Micromeritics TriStar II 3020 porosimeter at 77 K. All samples were outgassed at 100°C for 4 h under vacuum prior to measurements. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. ICP mass spectrometry were measured by Thermo iCAP 6000 ICP-MS. Element iron was analyzed from ICP experiments. We deduced the weight percent of hematite in the composite and obtained the GO contents by removing the content of hematite. For precise measurement, the sample was heated at 100°C for 5 min in N_2 to remove the adsorbed water in the sample. UV-vis absorbance measurement was conducted, where $BaSO_4$ was used as a blank and diffuse reflectance spectroscopes were collected. The absorbance data was calculated according to the Kubelka-Munk function, $f(R)=(1-R)^2/(2R)$, where R= reflectance with the reflectance at 1000 nm set at 100%.

Photocatalytic oxygen evolution measurement

A 300 W solar simulator (SolarEdge700, Xe) was used as the light source. The illumination intensity was 100 mW cm^{-2}. In a typical photocatalytic experiment, 50 mg photocatalysts and 300 mg $Na_2S_2O_8$ (99.0%) sacrificial electron acceptors were dispersed in 100 mL DI water. Prior to irradiation, the flask was evacuated down to 5 torr and purged with helium gas. The temperature inside the flask was maintained at about 5°C by cooling water circulator. All the measurement conditions for oxygen production were kept the same to guarantee the received results are comparable. The air-tight irradiation system connects a vacuum pump and a gas chromatograph (Techcomp GC7900) with the sample flask to quantify the amount of gas evolved, using area counts of the peaks and the identity of the gas from the calibrated carrier times. In order to evaluate background O_2 formation, irradiation of sodium persulfate (UV/vis) for 5 hours without Fe_2O_3 catalyst produced O_2 just barely above the detection limit (~ 0.2 μ mol).

Photoelectrochemical (PEC) Measurement

Using a CHI electrochemical station (660D), we conducted PEC measurement in a three-electrode configuration with the as-prepared photoanodes as the working electrode, a platinum plate (99.9%) as the counter electrode, and a saturated KCl Ag/AgCl electrode (SSE) as the reference electrode. A 500 W xenon light (TrusTech) with a stabilized current power supply employed as the solar simulator whose illumination intensity was adjusted to 100 mW/cm^2 was applied to illuminate the photoelectrodes. An aqueous solution of 1.0 M NaOH with a pH of 13.6 was used as an electrolyte. The solution was bubbled for 20 min with high-purity N_2 before measurement. In a typical experiment, the potential was linearly swept from 0.6 V to 1.6 V vs RHE at a rate of 10 mV/s. The measured potential vs Ag/AgCl was converted into the potential vs RHE according to the Nernst equation, $E_{RHE} = E_{Ag/AgCl} + 0.059pH + E°_{Ag/AgCl}$, where E_{RHE} is the potential vs RHE, $E°_{Ag/AgCl}$=0.1976 V at 25°C, and $E_{Ag/AgCl}$ is the measured potential vs Ag/AgCl. Electrochemical impedance spectroscopy (EIS) measurements were performed by applying sinusoidal perturbation of 10 mV with a bias of 1.25 V vs. RHE at the frequency ranging from 0.1 Hz to 100 kHz under illumination (AM 1.5G, 100 mW/cm^2).

Table. S1 Lattice parameters* of NHG1 and Standard (JCPDS no. 33-0664).*Standard uncertainties are given in parentheses.

Sample	lattice parameters (Å)	
	a	*c*
NHG1	5.043 (0.003111*)	13.80263 (0.007592*)
Standard values	5.0356	13.7489

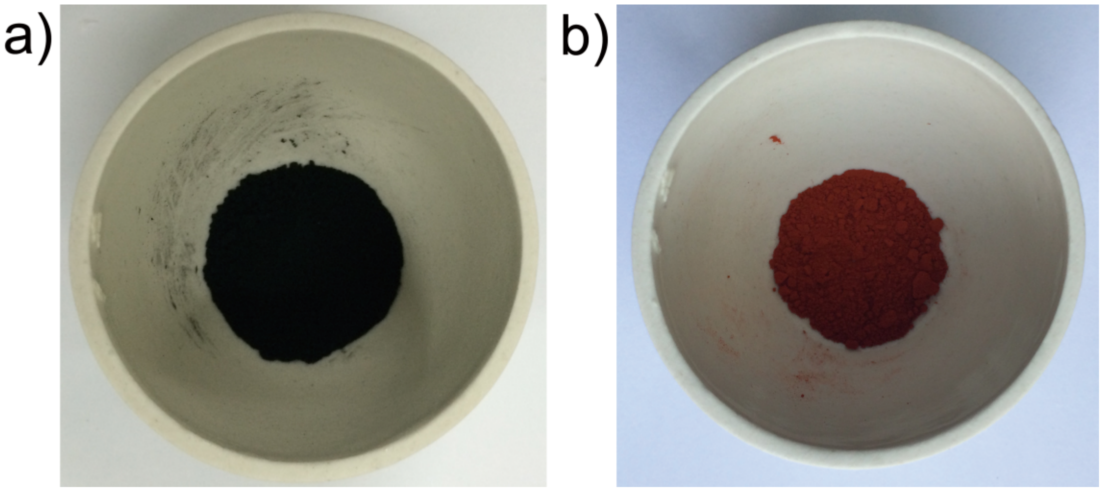

Fig. S1 Photographies of a) sample before annealing, b) sample after annealing.

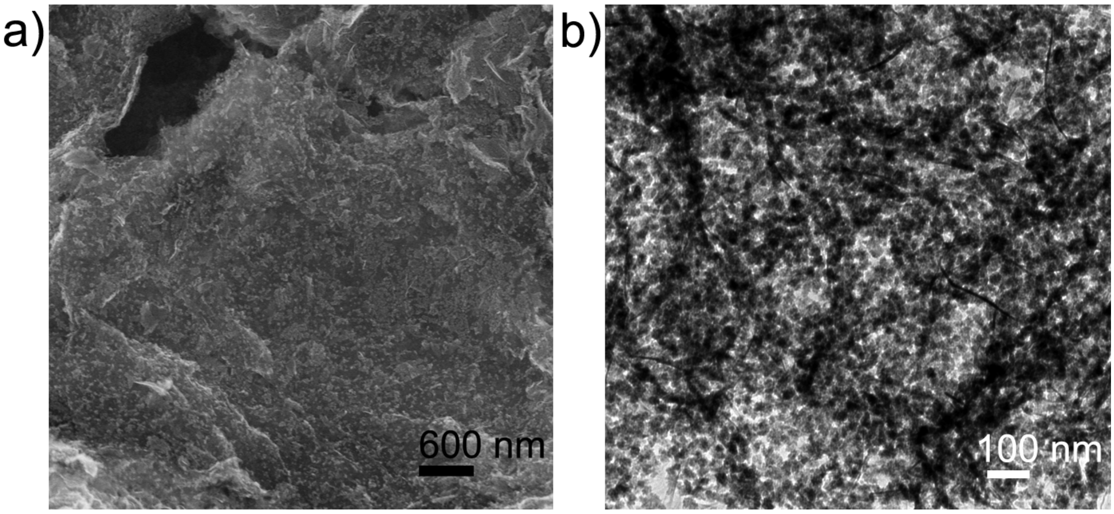

Fig. S2 a) SEM and b) TEM images of G/β-FeOOH nanocomposites.

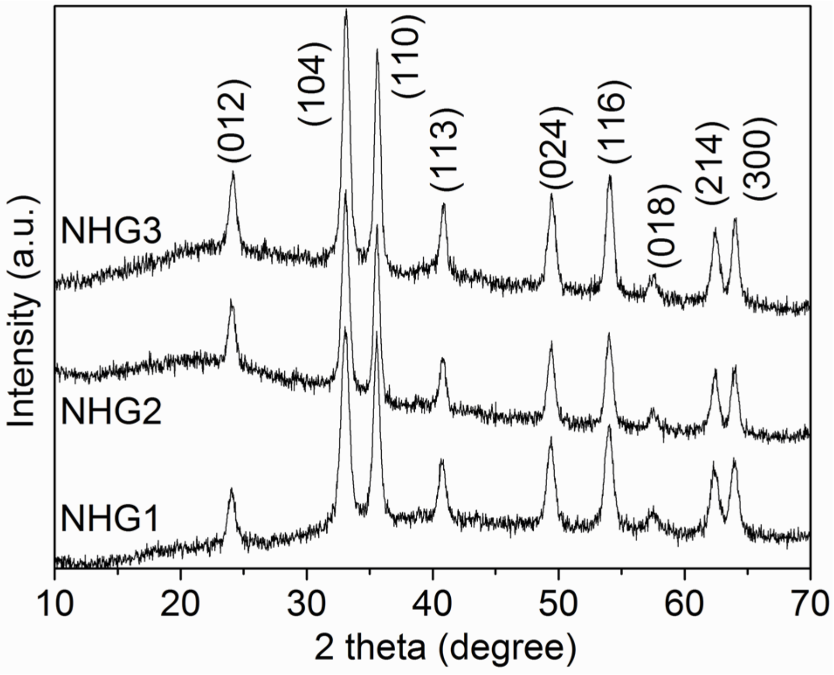

Fig. S3 XRD pattern of NHGs.

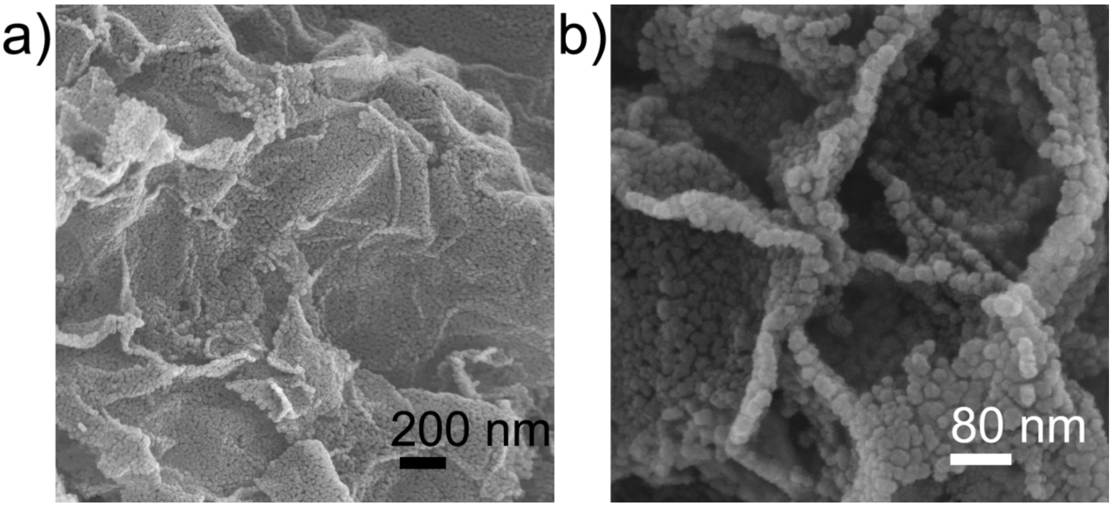

Fig. S4 SEM images of a) NHG1 and b) NHG3.

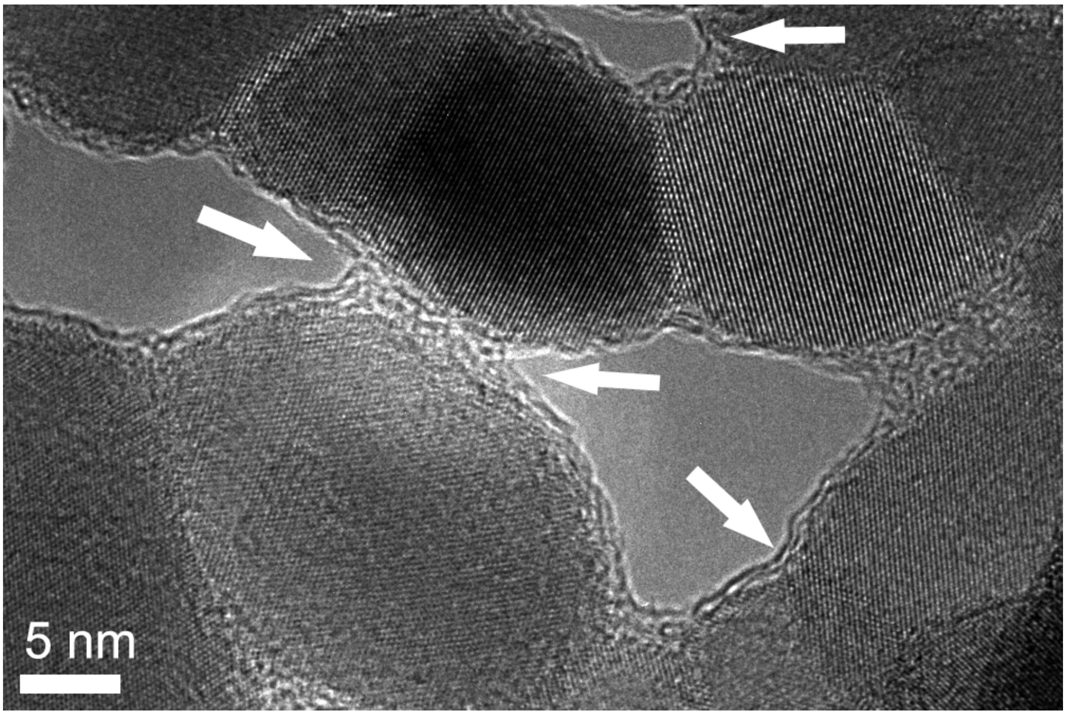

Fig. S5 High resolution TEM image of NHG2

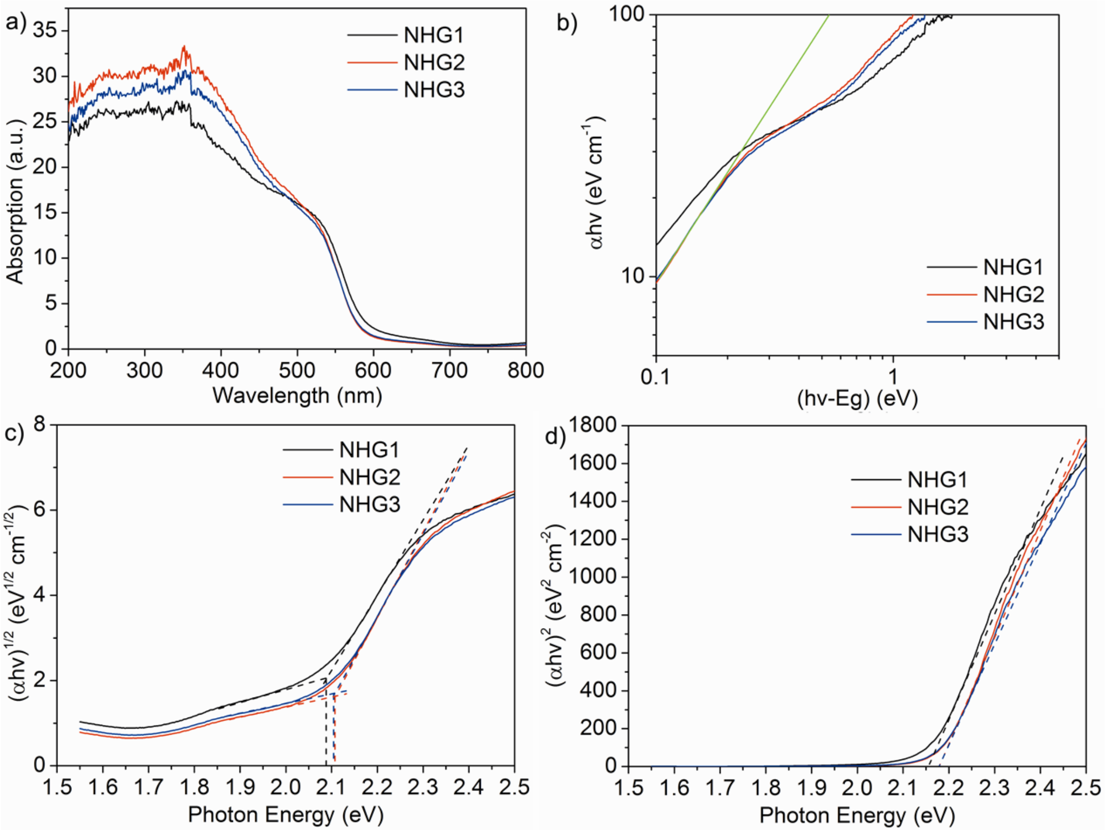

Fig. S6 a) UV-Vis absorption spectra of NHGs, b) Test for nature of electronic transition on absorption edge of NHGs, Tauc plots evaluating the optical band gap for c) the indirect case and d) the direct case.

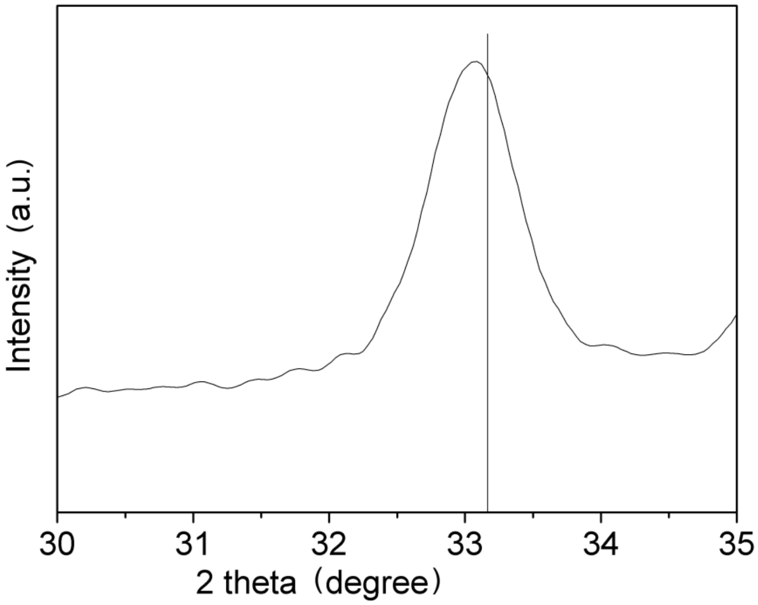

Fig. S7 Enlarged profile of the (104) diffraction patterns of NHG1.

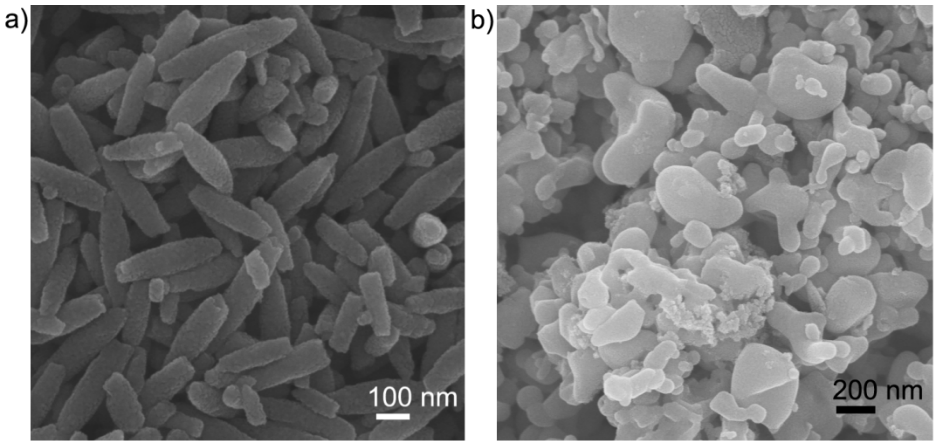

Fig. S8 SEM image of a) α-Fe_2O_3 nanorods and b) commercial α-Fe_2O_3

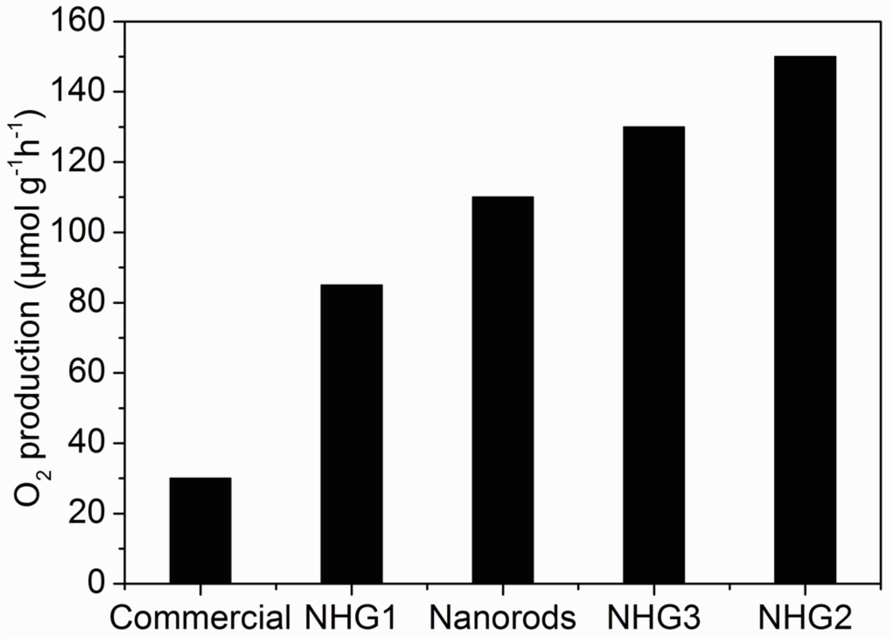

Fig. S9 Comparison of O_2 evolution of different samples

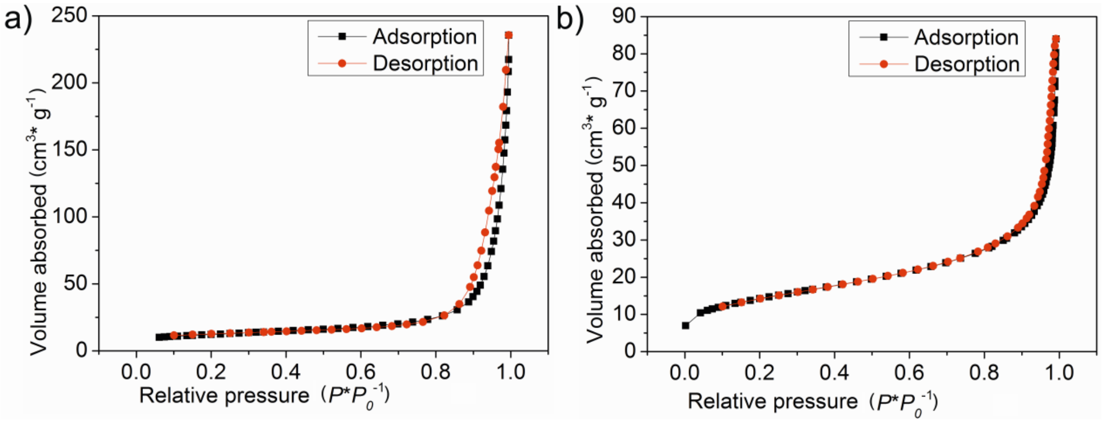

Fig.S10 a)Nitrogen adsorption and desorption isotherms measured at 77 K for NHG2 and the specific surface area is 41.7 m²/g, b)Nitrogen adsorption and desorption isotherms measured at 77 K for α-Fe_2O_3 nanorods and the specific surface area is 49.9 m²/g, which was calculated using the Brunauer-Emmett-Teller (BET) method.

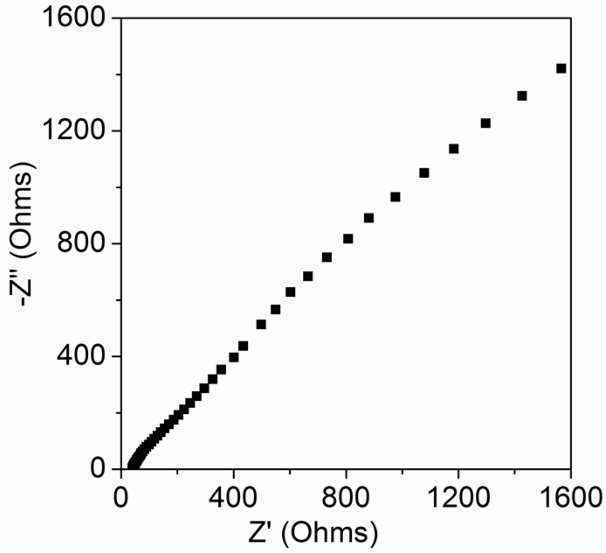

Fig. S11 EIS of α-Fe_2O_3 nanorods photoelectrode

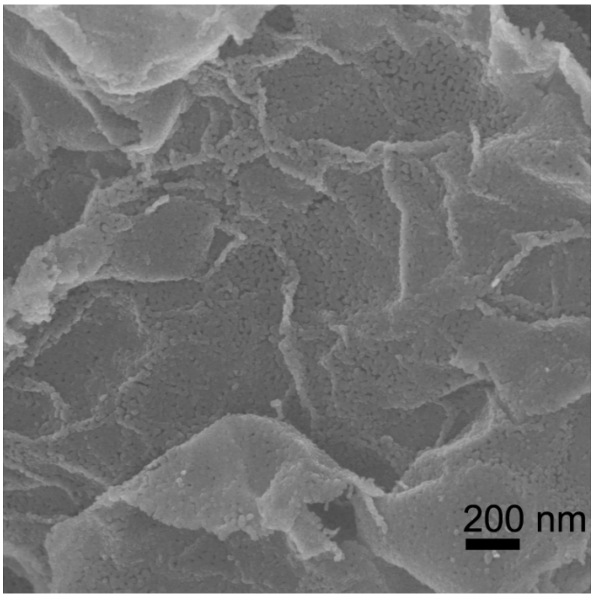

Fig. S12 SEM image of NHG2 after the photocatalytic water oxidation test.

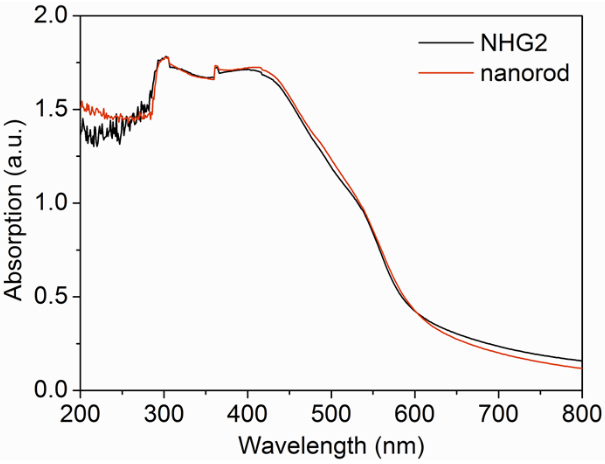

Fig. S13 The absorption spectra of NHG2 and nanorod photoelectrodes