**Electronic Supplementary Information:** 

## In situ simultaneous reduction-doping route to synthesize hematite/Ndoped graphene nanohybrids with excellent photoactivity

Yun-Pei Zhu,<sup>a</sup> Tie-Zhen Ren<sup>b</sup>, Yu-Ping Liu<sup>a</sup> and Zhong-Yong Yuan<sup>\*a</sup>

<sup>a</sup> Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), College of Chemistry, Nankai University, Tianjin 300071, China. Fax: +86 22 23502604; Tel: +86 22 23509610; E-mail: <u>zyyuan@nankai.edu.cn</u>.

<sup>b</sup> School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China.

## **Experimental Section.**

## Materials

Graphite powder was purchased from Aladin Ltd. Hydrogen peroxide ( $H_2O_2$ , 30 wt%), ferric chloride (FeCl<sub>3</sub>), sulfuric acid ( $H_2SO_4$ , 98 wt%), potassium permanganate (KMnO<sub>4</sub>), sodium nitrate (NaNO<sub>3</sub>), sodium sulfate (NaSO<sub>4</sub>), hexamethylenetetramine (HMT) and phenol were obtained from Tianjin Guangfu Chemical Co. All chemicals and reagents are of analytical reagent grade and used without further purification. Deionized water was used in the whole experiment.

**Synthesis of GO.** GO was synthesized by the modified Hummers method.[W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.] In a typical method, 0.5 g of graphite powder along with 0.5 g of NaNO<sub>3</sub> was suspended in 23 mL of concentrated  $H_2SO_4$ . It was allowed to stir for 15 min, and the suspension was transferred to an ice bath, followed by slow addition of 4 g of

KMnO<sub>4</sub> till the solution of the color changes to purple-green. It was then placed in a water bath to maintain the temperature around 40 °C. Afterwards, it was allowed to stir for 90 min, followed by addition of 50 mL of deionized water, and again stirred for 20 min. About 6 mL of 30%  $H_2O_2$  was added slowly to produce a golden-brown solution. A 50 mL portion of deionized water was then added to it, and the resultant solution was centrifuged and washed several times with deionized water to adjust the pH to 6. Finally, the obtained product was dried at 80 °C for 24 h.

**Preparation of hematite/N-doped graphene (HNG) hybrid.** Typically, 30 ml of 2.5 mg ml<sup>-1</sup> GO was dispersed in deionized water under ultrasound for 2 h. Then 7 ml of 1.2 mmol L<sup>-1</sup> FeCl<sub>3</sub> and 10 ml of 4 mmol L<sup>-1</sup> HMT solution were added in a sequence under stirring. After 30 min of stirring, the mixture was transferred into a Teflon-lined autoclave, and heated at 145 °C under autogenous pressure for 24 h. The resultant sample, abbreviated as HNG for hematite/N-doped graphene, was washed with water and ethanol alternatively, and then dried. N-doped graphene (NG) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were also prepared via the similar route but without FeCl<sub>3</sub> and graphene, respectively. By increasing the concentration of HMT to 4.2 mmol L<sup>-1</sup>, Fe<sub>3</sub>O<sub>4</sub>/NG could be successfully synthesized through the same procedure.

**Preparation of hematite/graphene (HG) composite material.** For comparison, the hematite/nondoped graphene (HG) composite was synthesized in the absence of HMT. In a typical run, 30 ml of 2.5 mg ml<sup>-1</sup> GO was dispersed in deionized water under ultrasound for 2 h. 7 ml of 1.2 mmol L<sup>-1</sup> FeCl<sub>3</sub> was added slowly into the GO suspension. After the obtained suspension was aged for 24 h at 60 °C, the sample was separated by centrifuging and washed with water and ethanol, followed by the reduction of GO using sodium borohydride as a reducing agent.

**Characterization.** X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus diffractometer with Cu K<sub>a</sub> radiation ( $\lambda = 1.5418$  Å) operated at 40 kV and 40 mA. Scanning electron microscopy (SEM) was carried out on a Joel JSF-7500L at an acceleration voltage of 5.0 kV. Transmission electron microscopy (TEM) was carried out on a Jeol JEM 2100F at 200 kV. N<sub>2</sub> adsorption-desorption isotherms were recorded on a Quantachrome NOVA 2000e sorption analyzer at liquid nitrogen temperature (77 K). The samples were degassed at 100 °C overnight prior to the measurement. The surface area was obtained by the multipoint Brunauer-Emmett-Teller (BET)

method. X-Ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD (delay line detector) spectrometer equipped with a monochromatic Al  $K_{\alpha}$  X-ray source (1486.6 eV). The XPS survey spectra were recorded with a pass energy of 160 eV, and high-resolution spectra with a pass energy of 40 eV. Binding energies were calibrated by using the containment carbon (C 1s 284.6 eV). Raman spectra was obtained on Thermo-Fisher Scientific DXR spectrometer with 514 nm wavelength incident laser light. Fourier transform infrared (FT-IR) spectra were measured on a Bruker VECTOR 22 spectrometer with KBr pellet technique, and the ranges of spectrograms were 4000 to 400 cm<sup>-1</sup>.

Photocurrent measurement was performed via a conventional electrochemical cell consisting of a prepared electrode, a platinum wire as a counter electrode, and a Ag/AgCl reference electrode. The resultant cell was filled with an aqueous solution of 0.1 M Na<sub>2</sub>SO<sub>4</sub>. Typically, the working electrode was prepared as follows: 0.05 g of the prepared materials, acetylacetone (0.2 ml), and trace of distilled water and ethanol were blended in a mortar to get a homogeneous mixture, which was then dip-coated onto a 1.5 cm  $\times$  3 cm fluorine-doped tin oxide (FTO) glass electrode. Electrodes were dried in air at 180 °C for 6 h, and then stored in dark for photoelectrochemical measurements. The electrochemical impedance spectroscopy (EIS) was performed applying sinusoidal perturbations of 5 mV at the frequency range from 0.1 to 10<sup>5</sup> Hz. All the photoelectrochemical tests were carried out on a Zennium (Zahner, German) workstation.

**Photocatalytic tests.** The photoefficiency of all synthesized catalysts was tested toward degradation of phenol under visible radiation. In a typical run, 25 mg of photocatalyst with 100 mL of 5 mg L<sup>-1</sup> phenol solution was taken in a 100 mL closed Pyrex flask. The solutions were exposed to visible light irradiation under ambient conditions. After irradiation, the suspension was centrifuged at a given time interval and the concentration of the supernatant solution was analyzed quantitatively at 504 nm using a SP-722 spectrophotometer.



Fig. S1 Photos of the GO and NG suspensions.

In fact, the suspension of NG in aqueous solution was considerably stable, and no obvious precipitation could be observed even after 4 months. However, for the HNG nanohybrid, it showed up in the form of black precipitation after mild hydrothermal treatment.



Fig. S2 TEM images of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (a) and Fe<sub>3</sub>O<sub>4</sub>/graphene nanocomposites (b).



Fig. S3 (a) SEM image of GO and (b, c) TEM images of NG.



Fig. S4 N<sub>2</sub> adsorption-desorption isotherm of the HNG, NG and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials.



Fig. S5 Wide-angle XRD pattern (a) and FT-IR spectrum (b) of the magnetite/NG nanohybrid.



Fig. S6 Digital photographs of separation of magnetite/NG from water solution under an external magnetic field.



Fig. S7 (a) Photocurrent-potential curves and (b) photocurrent response signals of the synthesized materials under visible light irradiation.



Fig. S8 EIS spectra of the HNG and HG composite materials.

EIS is a powerful strategy to evaluate the internal resistances for the charge transportation processes and thus to investigate the electrochemical properties of the composite materials [*J. Mater. Chem. A*, 2013, **1**, 9853]. The diameter of the semicircles in the high frequency region reflects the electron-transfer resistance. The observed semicircle radii of HNG are smaller as compared to that of HG composite material, signifying the charge transfer resistance decreased after the introduction of nitrogen species into the graphene framework.