

Electronic Supplementary Information (S)

Roles of quaternary N in N-doped graphene-Fe₂O₃ nanocomposites as efficient photocatalysts for CO₂ reduction and acetaldehyde degradation

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Experimental-S

1. Synthesis of materials

Nanocrystalline α -Fe₂O₃ (F) was synthesized by a phase-separated hydrolysis-solvothermal method.¹⁶ In a typical procedure, n-butyl alcohol as organic solvent and hydrated ferric nitrate (Fe(NO₃)₃ • 9H₂O) was used as a iron source. 10 mL of 5% ammonia solution was poured into a 50 mL TefLon-lined autoclave and a weighing bottle (10mL) which containing a solution of 0.8 g Fe(NO₃)₃ • 9H₂O dissolved in 8 mL n-butyl alcohol was placed in the autoclave with as a supporter between the autoclave bottom and the weighing bottle. Then, the system was maintained at 140°C for 6h. After cooling to room temperature, several times washed with ethanol and then washed with deionized water, and dried, nanocrystalline Fe₂O₃ was obtained.

Graphene (G) was prepared by the introduction of aqueous FeCl₂ to the active carbon and stirred for 10 h in nitrogen environment, followed by carbonization at 1100 °C for 30 min under the same environment and finally treated by 10% hydrochloric acid at 90 °C for 8 h.¹⁷

The N doped graphene was synthesized via a one-pot hydrothermal process using the equal amount of urea (200:1 for the mass ratio of urea to graphene) as the origin of the doped N in the presence of a graphene-dispersed solution (1g/L) at different temperatures (160°C, 180°C, 200°C, 220°C and 240°C).¹⁶ For the obtained NG, XNG is defined, in which X means the hydrothermal temperature.

The naocomposites between 3% (in mass) N-doped graphene and Fe₂O₃, named as XNG-F, were successfully fabricated via a simple wet chemical process.¹⁶ In a typical reaction, for each

sample 1.0 g of nanocrystalline α -Fe₂O₃ was taken and mixed with 30 mg of G (or NG) in a 50% ethanol solution under stirring for 3 h, followed by drying at 80 °C and finally calcined at 400 °C for 2 h.

2. Characterization of Materials

In order to investigate crystalline structures, raman spectra were recorded on a Jobin Yvon HR800 micro-Raman spectrometer with 457.9 nm laser, and the laser intensity at the sample was kept below the threshold for any laser-induced changes in the Raman spectra and electrical transport characteristics. The compositions and elemental chemical states of the samples were examined by X-ray photoelectron spectroscopy (XPS) using a Kratos-Axis Ultra DLD apparatus with an Al (mono) X-ray source, and the binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV). X-ray powder diffraction (XRD) measurements of all the samples were carried out with a Rigaku D/MAX-A powder diffractometer, using CuK α radiation with wavelength (λ) equal to 0.154056 nm. An accelerating voltage of 30 kV and emission current of 20 mA were employed. The UV-vis diffuse reflectance spectra (DRS) of the samples were measured by a Shimadzu model UV-2550 spectrophotometer. The electron micrographs were taken on a JEOL JEM-2010 transmission electron microscope (TEM) operated at 200 kV.

The steady-state surface photovoltage spectroscopy (SS-SPS) and time-resolved surface photovoltage (TR-SPV) responses were measured with the home-built apparatuses that have been described in detail elsewhere.¹⁹ The SS-SPS instrument was a home-built apparatus equipped with a lockin amplifier (SR830) synchronized with a light chopper (SR540). The powder sample was sandwiched between two ITO glass electrodes, which was arranged in an atmosphere controlled container with a quartz window, and monochromatic light was obtained by passing light from a 500 W xenon lamp (CHF XQ500W, Global xenon lamp power) through a double prism monochromator (SBP300). The TR-SPV measurement was performed with a self-assembled device in air atmosphere at room temperature, in which the sample chamber was connected to an ITO glass as the top electrode and to a steel substrate as the bottom electrode, and a 10 μ m thick mica spacer was placed between the ITO glass and the sample to decrease the space charge region at the ITO-sample interface. The samples were excited by a 532 nm-laser radiation with 10ns

pulse width from a second harmonic Nd: YAG laser (Lab-130-10H, Newport, Co.). The laser intensity was modulated with an optical neutral filter and measured by a high-energy pyroelectric sensor (PE50BF-DIF-C, Ophir Photonics Group). The TR-SPV signals were registered by a 1 GHz digital phosphor oscilloscope (DPO 4104B, Tektronix) with a preamplifier.

3. Photoelectrochemical (PEC) and electrochemical measurements

For the synthesis of film electrodes, conductive fluorine-doped tin oxide (FTO)-coated glasses were used as substrates. Prior to use, the FTO glasses were washed with deionized water under sonication for 30 min and then washed with ethanol followed by deionized water and finally dried at 450 °C for 30 min. For F, G-F, and NG-F films, the corresponding pastes were prepared as follows: 0.5 g of the resulting powder was dispersed in 2 mL of isopropyl alcohol under continuously stirring, and then 0.3 g of Macrogol-6000 was introduced to the obtained mixture, followed by an ultrasonic process for 10 min and then treated by magnetic stirring for 30 min. Finally, 0.15 mL of acetylacetone was added, and the mixture was kept under vigorous stirring for 2 days, which led to the paste formation. The films were prepared by the doctor blade method, and Scotch tape was adopted as the spacer. After it was naturally dried, the film was calcined at 450 °C for 30 min and then cooled to room temperature. Finally, the film was cut into 1.0×2.5 cm² pieces, The working geometric surface area of nanocomposites was 0.5 cm × 0.5 cm where as the remaining area was covered with epoxy resin.

PEC experiments were performed in a quartz cell using a 500 W xenon light with a stabilized current power supply as the illumination source and 1 M NaOH solution was used as an electrolyte. The as-prepared films were used as working electrodes illuminated from the FTO glass side, whose illumination area was about 0.5×0.5 cm². A platinum plate (99.9%) was used as the counter electrode, and a saturated KCl Ag/AgCl electrode (SSE) was used as the reference electrode. All the potentials in this work were referred to SSE at 298 K, and applied potentials were controlled by a commercial computer-controlled potentiostat (AUTOLAB PG STAT 101). High-purity N₂ gas was employed to bubble through the electrolyte before and during the experiments. For comparison, the related current was also measured in the dark. In addition, electrochemical O₂ or CO₂ reduction experiments were carried out in the dark. High-purity O₂ or CO₂ gas was employed to bubble through the electrolyte before and during the experiments.

4. Evaluation of photocatalytic activities for CO₂ reduction and for acetaldehyde degradation

In the photocatalytic reduction of CO₂, for each experiment, 0.1g powder sample was dispersed in water (2 ml) contained in a cylindrical steel reactor with 100 ml volume and having area 3.5cm². A 300W Xenon arc lamp was used as the light source for photocatalytic reaction. High purity CO₂ gas was passed from water and followed into the reaction setup for reaching ambient pressure. The used photocatalyst was allowed to equilibrate in the CO₂/H₂O system for 1 hour. During the irradiation, about 0.5 ml of gas production was taken from the reaction cell at given time interval for subsequent concentration analysis of CO as the main one by using a gas chromatograph (GC-2014 with TCD detector; Shimadzu Corp., Japan).

Photocatalytic activities of the samples were evaluated by degrading gas-phase acetaldehyde. The light source was a 150 W spherical xenon lamp (XQ150/150 W, Warren Bulb Factory, Shanghai) with an emitting spectrum similar to sunlight, and a light filter was used between the light source and the reactor to cut off UV light (<420 nm) in all photocatalytic experiments. In the gas-phase acetaldehyde degradation experiment, 0.1 g of sample powder was put into a Pyrex glass cylindrical reactor with a diameter of 7.0 cm and effective volume of 640 mL. A premixed gas containing 810 ppm of acetaldehyde, 20% O₂, and 80% N₂ was introduced into the reactor. The concentration of acetaldehyde for every 20 min time interval was measured with a gas chromatograph (GC- 2014, Shimadzu) equipped with a flame ionization detector.

5. Measurement of temperature-programmed desorption for CO₂ and O₂

Temperature-programmed desorption (TPD) for desorption CO₂ were performed in a conventional apparatus by Chemisorption Analyzer, tp 5080 Chemisorb which equipped with a thermal conductivity detector (TCD). About 50mg samples were preheated to 300 °C to remove the moisture for 1 hour and then cool down to room temperature under by an ultra-high-pure He flow rate of 30 ml min⁻¹. The highly pure CO₂ gas was introduced in a constant temperature of 30 °C under flow rate 30 ml min⁻¹ for 60 minutes. The excess weak physically adsorbed CO₂ was removed by exposed with ultra-high-pure He at 30 °C for 60 minutes. Then heated to 700 °C with the heating rate of 10 °C min⁻¹ under pure He. The desorbed O₂ was analyzed by Chemisorption Analyzer, tp 5080 Chemisorb.

O₂-TPD curves were recorded using a home-built facility, as described previously.¹⁷ The O₂-TPD was also measured using a home-built apparatus. Sample powder (50 mg) was pretreated in a Pyrex tube (i.d. 6 mm) at 270 °C for 30 min by an ultra-high-pure He flow, and then the temperature was cooled to room temperature. For O₂ adsorption saturation, the sample was continuously blown with ultra-high-pure O₂ for 90 min at room temperature. After O₂ adsorption, the sample was flushed in ultra-high-purity He flow to remove the physically adsorbed O₂ on the powders. An O₂-TPD profile of the sample was recorded by increasing the temperature from 30 to 600 °C at a heating rate of 10 °C min⁻¹ under 20 mL min⁻¹ of ultra-high-purity He flow. The desorbed O₂ was analyzed by a gas chromatograph (GC-2014, SHIMADZU) with a TCD detector.

Figures-S

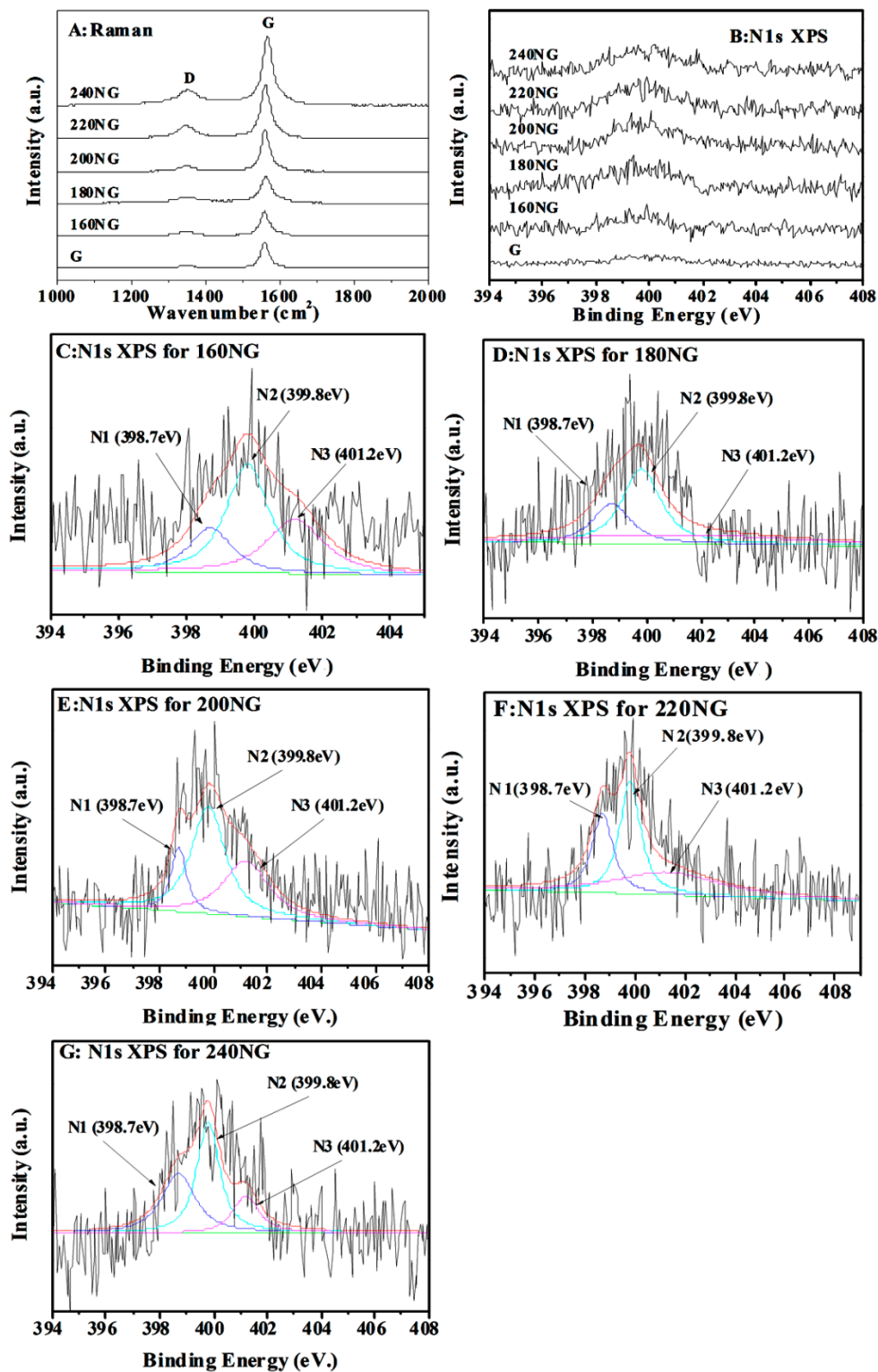


Figure S1 Raman spectra (A), N1s XPS spectra of N-doped graphenes (B), and the XPS-peak-differentiation-imitating analyses of N1s for all the NG samples (C, D, E, F, and G).

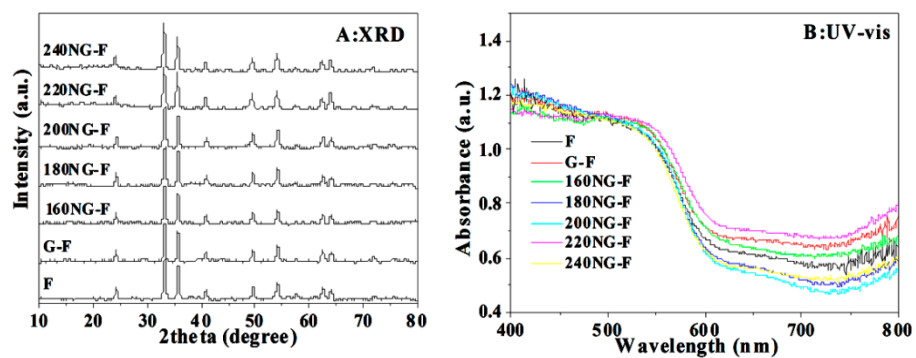


Figure S2 XRD patterns (A) and Uv-Vis absorption spectra (B) of different nanocomposites.

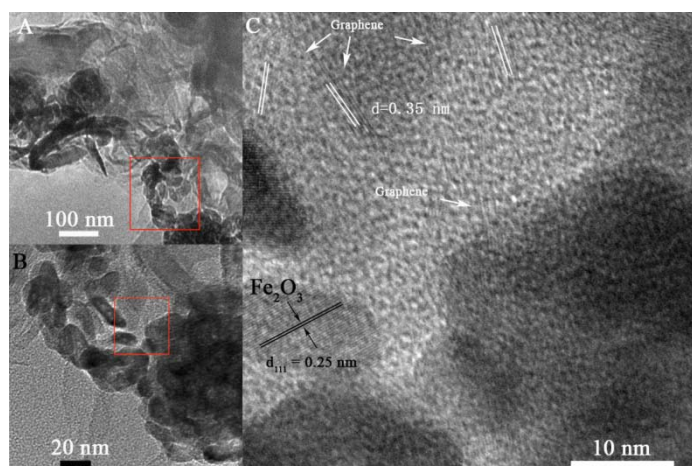


Figure S3 TEM images of 220NG-F (A) and (B), with an area-selected HRTEM (C).

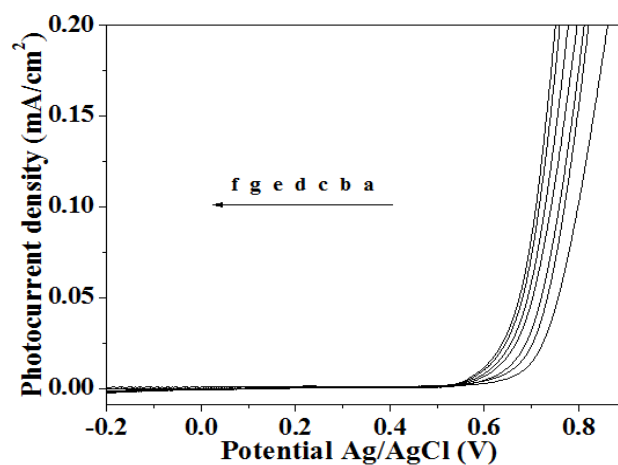


Figure S4 I-V curves of F, G-F and different NG-F samples in the dark. {a: Fe_2O_3 (F), b: graphene-coupled F (G-F), c: 160NG-F, d: 180NG-F, e: 200NG-F, f: 220NG-F, and g: 240NG-F}.

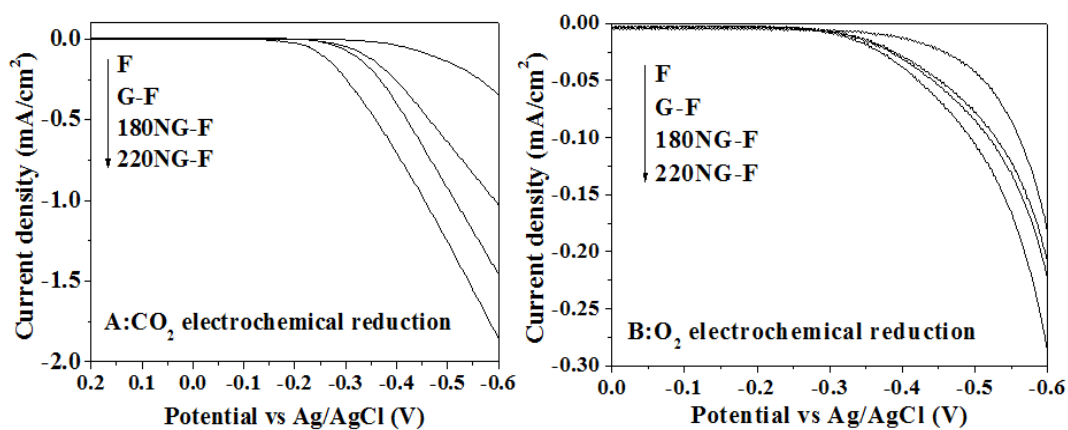


Figure S5 Curves of electrochemical reduction of CO_2 (A) and O_2 (B) on F, G-F, and different NG-F samples