Electronic Supplementary Information for

Facile synthesis of nitrogen doped reduced graphene oxide as a

superior metal-free catalyst for oxidation

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Experimental Section

Preparation of GO: Graphene oxide (GO) was prepared by a modified Hummers' method [1]. Graphite powder (GP) was oxidized by concentrated H_2SO_4 and KMnO₄, followed by H_2O_2 treatment. The obtained GO was separated by a centrifuge and washed by HNO₃/deionized water for several times. Lastly the GO was made from gels and dispersion by drying in air at 418 K and grinded finely.

Preparation of G-N: 1.0 g of GO and 1.0 g of ammonium nitrate (Warning: mass production needs to be aware of its explosive/hazardous nature) were dissolved in 50 mL of ethanol, and the mixed solution was stirred for 30 min. Then solution temperature was increased to 50 $^{\circ}$ C to evaporate ethanol whilst stirring. The dried mixture was then put into a furnace for calcination at 350 $^{\circ}$ C for 1 h at a heating rate of 5 $^{\circ}$ C/min. The sample was then washed by ethanol once and by ultrapure water for three times. After drying in an over at 80 $^{\circ}$ C overnight, the nitrogen doped rGO (G-N) was obtained.

Preparation of G-N-B and G-N-P: G-N-B was prepared same as the preparation of G-N exception for the addition of certain amount of ammonium pentaborate octhydrate in the mixed solution at first step. G-N-P preparation followed the same

procedure with ammonium phosphate monobasic as phosphorus precursor.

Preparation of Co₃O₄: The nanostructured Co₃O₄ was prepared by a hydrothermal method [2]. Co(NO₃)₂• $6H_2O$ (5 mmol) and Co(NH₂)₂ (25 mmol) were dissolved in 50 mL of DI water with stirring. The mixed solution was then transferred to a 125 mL of Teflon-lined stainless steel autoclave, and put into an oven with heating at 10 °C for 5 h. The precipitate was collected, washed and dried at 80 °C over night. The dried powder was then annealed at 400 °C for 4 h, then the nanosized spinel Co₃O₄ was obtained.

Preparation of MnO₂: Typically, MnSO₄•H₂O (0.008 mol) and an equal amount of ammonium persulfate ((NH₄)₂S₂O₈) were put into distilled water at room temperature to form a homogeneous solution, which was then transferred into a 40 mL Teflon-lined stainless steel autoclave, sealed and maintained at 140 °C for 12 h. [3] After the reaction was completed, the resulting solid product was filtered, washed with distilled water to remove ions possibly remnant in the final products, and finally dried in air.

Characterization: X-ray diffraction (XRD) patterns were obtained on a Bruker D8-Advaneed X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å), at accelerating voltage and current of 40 kV and 40 mA, respectively. Raman spectra were recorded on an ISA (Dilor) dispersive Raman spectrometer with argon ion 514 nm lasers. Scanning electron microscopy (SEM) was performed on a Zeiss Neon 40EsB FIBSEM. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were operated on a JEOL JEM-1010 microscope and a JEOL JEM-2100 microscope, respectively. The atomic force microscopy (AFM) measurements were done using a Digital Instruments Dimension 3100 scanning probe microscope system with Nanoscope V6.13 control software (Veeco, Santa Barbara, CA). The Brunauer-Emmett-Teller (BET) surface area and pore size distribution were evaluated by nitrogen sorption at -196 °C using a Quantachrome Autosorb AS-1. All samples were degassed at 100 °C for 4 h prior to the adsorption experiments. The SSA and pore volume were obtained by applying the BET equation and $p/p^0 = 0.95$ to the adsorption data, respectively. The pore size distribution was obtained by the Barrett-Joyner-Halenda (BJH) method. Chemical states were analysed by X-ray photoelectron spectroscopy (XPS) using Thermo Escalab 250 with a monochromatic Al Ka X-ray source. All binding energies were calibrated by the C 1s peak at 284.6 eV arising from adventitious carbon. [4]

Catalytic oxidation of phenol solutions: The catalytic oxidation of phenol was employed to probe the efficiency of activation of potassium peroxymonosulfate (using OXONE, 2KHSO₅•KHSO₄•K₂SO₄ from Aldrich). The reactions were carried out in a 500 mL reactor containing 20 ppm of phenol solution. The reactor was attached to a stand and dipped into a water bath with a temperature controller (25 °C). A catalyst sample 0.2 g/L was firstly added to the solution and stirred for 10 min. Then OXONE

(2.0 g/L) was added to the mixture to start the reaction. The pH of reaction solution was not adjusted, and was about 6.5 at first, then decreased to 2-3 due to the influence from oxidation and oxidation processes. At each time interval, 1 mL of solution was withdrawn by a syringe and filtered by 0.45 μ m Millpore film. The filtered solution was injected into a high performance liquid chromatography (HPLC) vial which was filled with 0.5 mL of methanol as a quenching reagent. Phenol solutions were measured by a HPLC (Varian) with a C-18 column. After reaction, the spent catalysts were recovered from the reaction mixture by filtration and treated by water washing, ultrasonic washing or thermal treatment and dried at 80 °C for repeated uses. The adsorption tests were performed without addition of PMS.



Fig. S1 XRD patterns of Co₃O₄ and MnO₂.



Fig. S2 SEM images of (a) Co_3O_4 and (b) MnO_2 .



Fig. S3 TEM and HRTRM images of G-N.



Fig. S4 AMF image of G-N sample and the estimation of layers based of single layer thickness of 0.38 nm [5].



Fig. S5 N₂ adsorption isotherm curves of rGO and G-N.



Fig. S6 Pore size distribution of rGO, G-N, and G-N-B.



Fig. S7 XPS B1s spectrum of G-N-B.



Fig. S8 XPS C 1s spectra of rGO, G-N and G-N-B.



Fig. S9 Effect of phosphor modification on phenol degradation.



Fig. S10 Effect of treatment methods of used catalysts on their phenol degradation at second runs.

References

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