

Graphite oxide as an efficient and durable metal-free catalyst for aerobic oxidative coupling of amines to imines

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Electronic Supplementary Information

Experimental Details

I. Catalytic materials

High purity graphite powder (99.9995%; 200 mesh) was provided by Alfa Aesar. Multiwall carbon nanotubes (MWCNTs) with diameter 30-50 nm and activated carbon (AC) were supplied by Chengdu Organic Chemical CO., LTD (COCC). Au/TiO₂ (type A, lot no. Au/TiO₂ no. 02-1) was supplied by the World Gold Council (WGC). All other reagents, H₂SO₄ (95 – 98%), KMnO₄, H₂O₂ (30 wt. %) were of analytical grade and were used as received.

Synthesis of graphite oxide (GO): GO was synthesized by a modified Hummers method.^[S1,S2] Briefly, 2 g of as-received graphite powders was stirred in concentrated H₂SO₄ (46 mL) at room temperature, and NaNO₃ (1.0 g) was added. After over continuous stirring for over 2 h, the mixture was cooled to 0 °C and KMnO₄ (6 g) was slowly added to the suspension with vigorous stirring. The rate of addition was controlled to prevent the rapid rise in the temperature of the suspension (should be < 10 °C). After removal of the ice-bath, the mixture was stirred at room temperature for 1 h. Then the temperature of above suspension was brought to 35 °C, where it was maintained for 3 h. Then distilled water (92 mL) was slowly added to the reaction vessel. The diluted suspension was stirred for an additional 15 min and further diluted with distilled H₂O (280 mL) and then H₂O₂ (20 mL, 30 wt.% solution) was added. After filtered and washed with 5 % HCl aqueous solution, the remaining suspension was transferred to dialysis tubes (MW cutoff 6000 – 9000). Dialysis was carried out for 5 days, and then the wet form of GO was separated by centrifugation. The gel-like material was vacuum-dried (60 °C) to give a fine dark brown powder (BET surface area ~ 69 m² g⁻¹).

Preparation of hydrazine-reduced graphene oxide (RGO): After sonication, a 200 mL GO solution (5 mg/mL) was transformed *in situ* into graphene under stirring by adding 2 mL hydrazine hydrate (50%) and 5 mL ammonia solution (25%) into the solution. Solid graphene samples were obtained by filtrating the solution of RGO through a membrane filter. After washing with deionized water (20 mL) three times and drying in vacuum at 60 °C for 2 h.

II. Catalytic activity measurements

General procedure for aerobic oxidative coupling of amines: Catalytic experiments were performed in a batch autoclave reactor (10 mL). In a typical reaction, benzylamine (5 mmol, 0.536 g) was put into the reactor with the catalyst (50 wt % loading, 0.268 g). The mixtures were magnetically stirred (800 rpm) at 100 °C under molecular oxygen atmosphere for the required time. After the reaction, the catalyst was removed by filtration, extracted with acetonitrile and the combined organic solutions concentrated under reduced pressure. Anisole was used as an external standard for the determination of conversion level. The products were analyzed by a GC-17A gas chromatograph equipped with a HP-FFAP column (30 m×0.25 mm) and a flame ionization detector (FID). For isolation, the combined organic layer was dried over anhydrous Na₂SO₄, concentrated, and purified by silica gel column chromatography.

Recovery and reuse of GO: The reusability of the catalyst was tested for the oxidation of benzylamine. In this case, the reaction mixture was filtered at the end of the reaction, washed with acetonitrile (5 mL), dried at 120 °C for 2 h. Then the catalyst was reused for a subsequent run with fresh benzylamine without any further treatment.

III. Characterization

Elemental analysis: Residual metallic impurities contained in the as-synthesized GO samples were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

Transmission electron microscopy (TEM): TEM measurements were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the

samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator.

X-ray diffraction (XRD): XRD patterns were collected on a Rigaku D/MAX 2500 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) using a generator voltage of 40 kV and a generator current of 200 mA. The scan speed was 4°/min and the scan range was from 5° to 45°.

Fourier transform infrared spectroscopy (FT-IR): The FTIR spectra were recorded by a Nicolet Avatar-360 FT-IR spectrometer equipped with a DTGS detector, in the range 400– 4000 cm^{-1} , by applying an optical resolution of 4 cm^{-1} . The samples were investigated by using the KBr pellet technique.

X-ray photoelectron spectroscopy (XPS): The spectra were obtained on a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The pressure in the analysis chamber was kept below 10^{-7} Torr. The excitation source was the Mg K α line ($h\nu = 1253.6 \text{ eV}$, 300 W). The binding energy was referenced to the C 1s line at 284.6 eV.

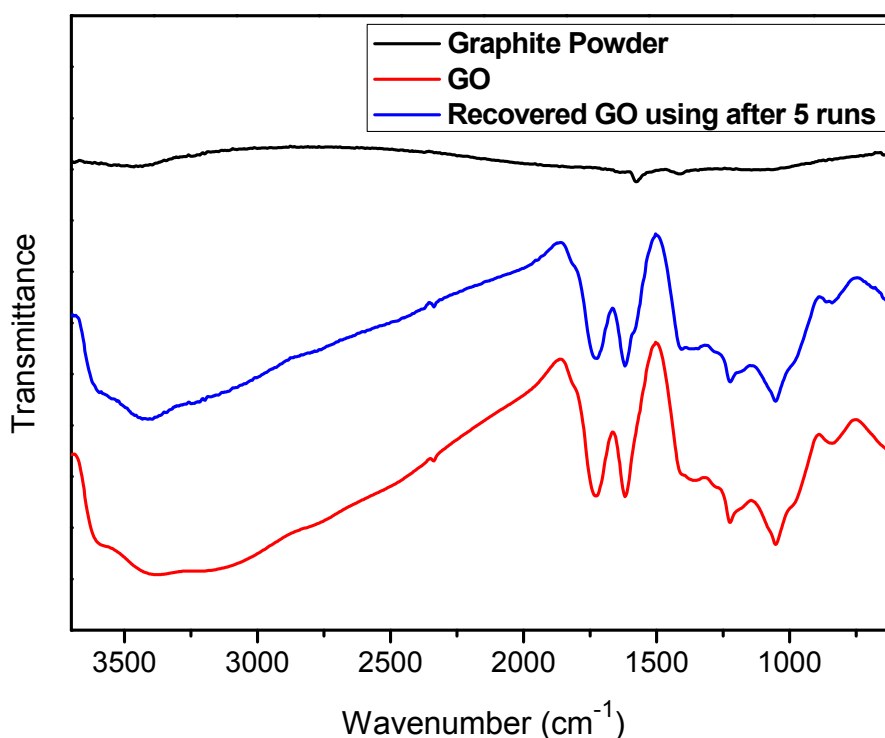


Fig. S1: FTIR Spectra of natural graphite powder, fresh GO and recovered GO sample using after five runs.

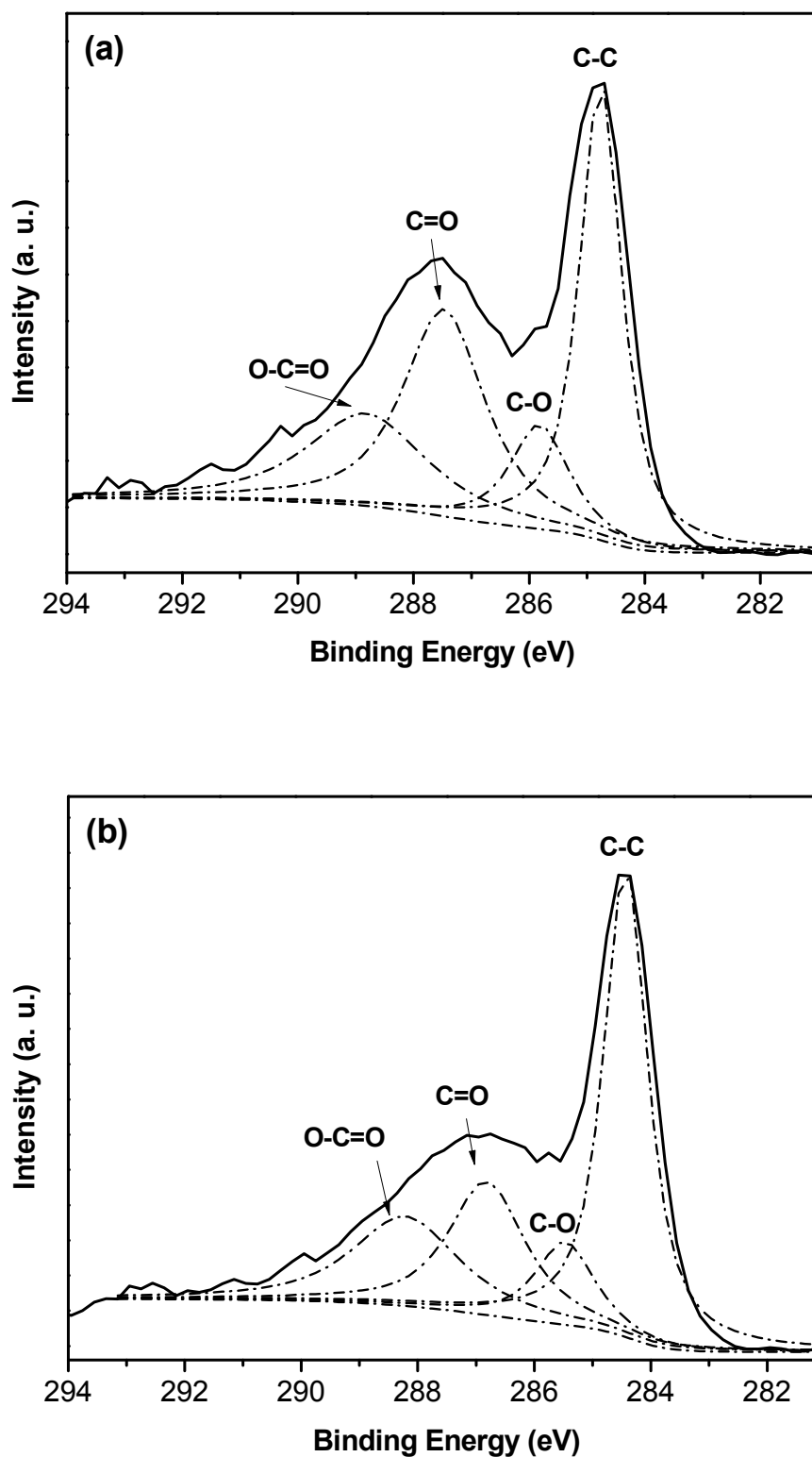


Fig. S2: XPS spectra for C 1s peak of (a) GO, (b) recovered GO using after five runs, which confirmed that the C 1s peak consisted of four different oxygen bearing functional groups: sp^2 carbon (284.5 eV), C-O (286.6 eV), C=O (287.9 eV), O-C=O (289.0 eV).

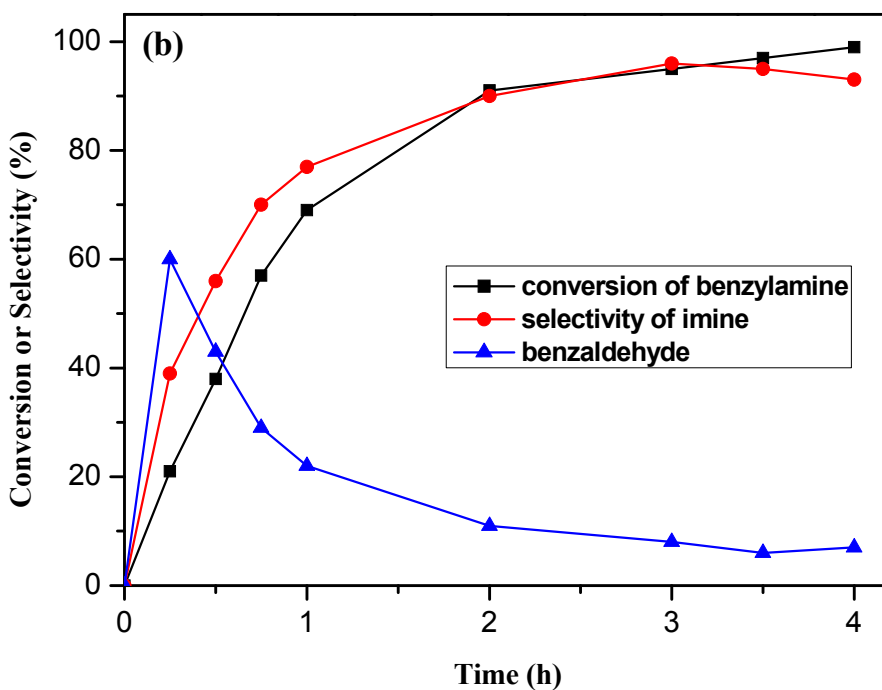
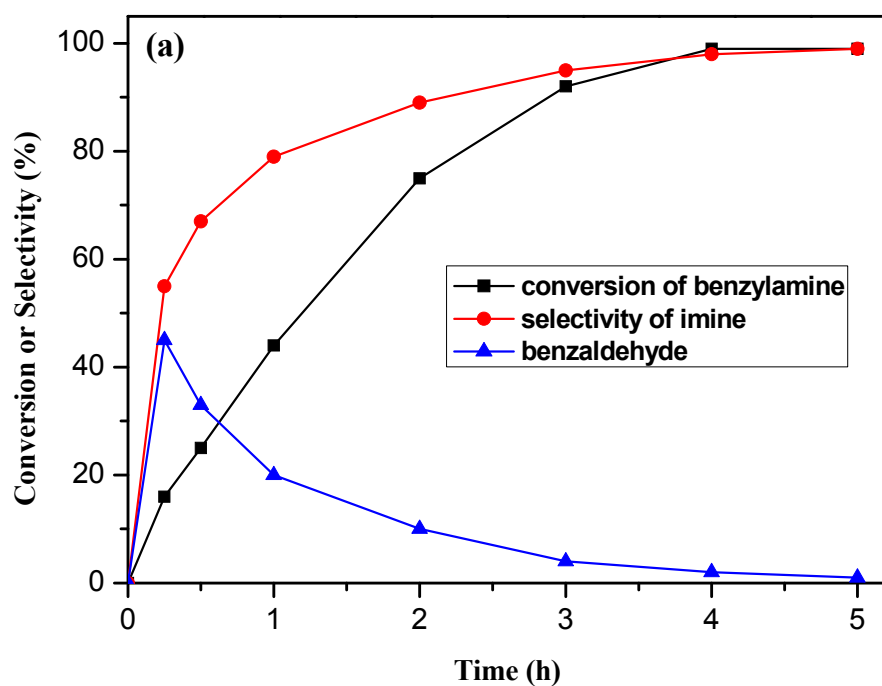


Fig. S3: Temporal reaction profiles of benzylamine oxidation catalyst by GO. Reaction conditions: 5 mmol benzylamine, 50 wt.% loading GO (0.268 g), 100 °C, 5 atm O₂, (a) without H₂O, (b) with 1 mmol H₂O.

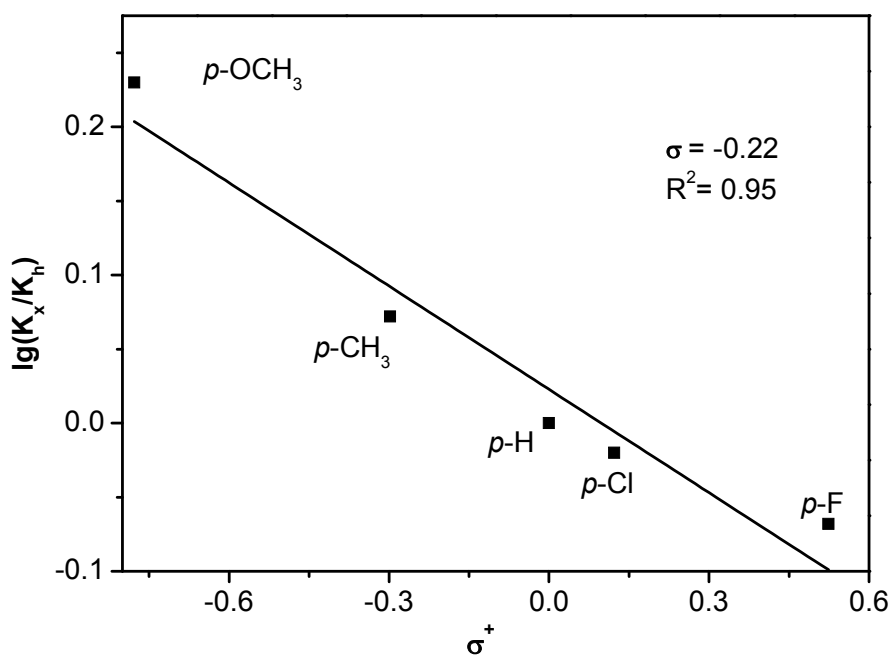


Fig. S4: Hammett plots for the competitive oxidation of *para*-substituted benzylamines with oxygen using GO. The ratio of $\log(k_x/k_h)$ was obtained by the conversion with reaction time of 10 min. A reasonable linearity between the $\log(k_x/k_h)$ values and the Brown–Okamoto constant (σ^+) parameters was obtained, thereby suggesting that the reaction proceeds via the intermediacy of a carbocationic species.^[S3]

References:

- [S1] W. S. Hummers Jr. and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- [S2] A. Lerf, H. He, M. Forster and J. Klinowski, *J. Phys. Chem. B*, 1998, **102**, 4477.
- [S3] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 1958, **80**, 4979.