

Reduced Graphene Oxide as Catalyst for Hydrogenation of Nitrobenzene

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Experimental Section

Materials

Expanded graphite (63.6 m²/g) was purchased from Beijing Invention Biology Engineering & New Material Co., Ltd. and pyrolytic GO which have a high surface area (423.6 m²/g) was prepared by quickly heating GO in hydrogen atmosphere. GO was prepared from natural flake graphite by Hummers' method. Colloidal dispersions of graphene oxide sheets in water at a concentration of 5 mg/ml were obtained. After sonication, 400 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 according to a modified Wallace's method. 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 308 K for 2 h, the black solid was milled into a fine powder before being used as catalyst.

Catalytic evaluation

Typically, nitrobenzene (0.5 g), RGO (0.01 g) and hydrazine hydrate (2 ml) and water (1.5 ml) were added in turn into a 50 ml round-bottom flask. The mixture was heated to a designated temperature under a water-cooled condenser and kept at that temperature for a period of time. Upon completion of the reaction, 5 ml of ethanol was added through the condenser and a homogeneous solution was obtained. After removal of the catalyst, the solution was diluted to exactly 25 ml in a volumetric flask. 100 μ l of reaction mixture was diluted to 1 ml by acetonitrile/water (volume ratio 60:40) and analyzed by Agilent HPLC 1200 using a C-18 column. The isolated product was also checked by ¹H NMR and ¹³C NMR to confirm its structure. The whole reaction process was monitored with an *in-situ* ¹³C NMR experiment. The reaction mixture was put into a glass NMR tube equipped with a polymer pipe condenser. After loading into the NMR machine, the temperature of the tube reactor was controlled by a temperature programmer. The ¹³C NMR measurements were made during the temperature ramp or at different reaction times at 100.6 MHz with high-power proton decoupling using a 2-ms pulse and 2-s repetition time. For each ¹³C NMR spectrum, 1600 free induction decays were accumulated with an average recording time of 90 min. A tab stop has been set in the style to allow for easy indenting of text (although the first paragraph and paragraphs that follow headings should not be indented).

Characterization

Scanning electron microscopy (SEM) images of samples were obtained on a FEI Quanta 200F field emission electron microscope operated at 30 kV. RGO were directly glued onto a conductive film pasted onto the specimen holder while graphene solution samples were spin-coated on silicon wafers and then pasted onto the specimen holder by a conductive film. The sample (prepared with graphene solution, as with the SEM study) was also examined by atomic force microscopy (AFM, VEECO Digital Instruments NanoMan). Solid-state ¹³C MAS NMR spectra were recorded on a Varian Infinityplus-400 spectrometer equipped with a 4-mm MAS probe. All ¹³C MAS NMR spectra were recorded at 100.5 MHz with the samples spun at 13 kHz. X-ray diffraction (XRD) patterns were

collected on a Rigaku D/MAX 2500 diffractometer with Cu K α radiation ($\lambda=1.5418$ Å) using a generator voltage of 40 kV and a generator current of 200 mA. The scan speed and step size were 5°/min and 0.02°, respectively. X-ray photoelectron spectroscopy (XPS) which used Mg K α radiation (1253.6 eV) with a power of 200 W and pass energy of 50.0 eV was also used to characterize these solid samples. All samples were pressed into a slice and pasted onto a specimen holder with conductive film. Raman experiments were carried out on a LabRam I confocal microprobe Raman instrument (Dilor, France) at a laser power of around 7 mW.

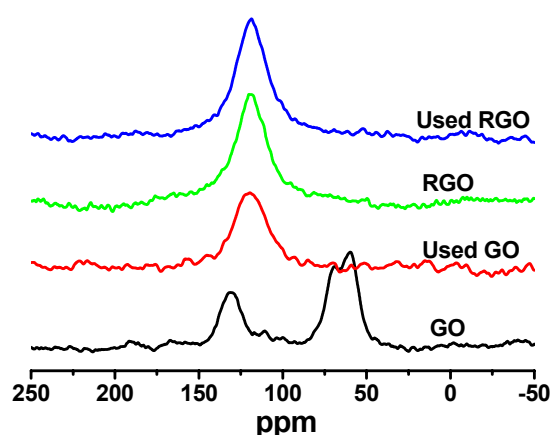


Figure S1. ^{13}C MAS NMR spectra of GO, RGO catalysts and their corresponding used catalysts.

^{13}C MAS NMR was used to characterize the groups on these carbon materials. The same shifts of RGO, used RGO and used GO indicate that the three materials have similar chemical structure.

XRD patterns of natural flake graphite(NG), graphite oxide(GO), reduced graphene oxide(RGO) catalyst, used RGO catalyst (once) and used GO catalyst (once) are shown in Fig. S2. NG has a very intense and narrow peak at $2\theta=26.5^\circ$ caused by reflection on the (002) planes of well-ordered graphene with 0.34 nm spacing. When natural flake graphite was completely oxidized to GO, the basal spacing between the (002) planes increased from 0.34 nm to about 0.7 nm, which was signified by a new broad peak at $2\theta=12.1^\circ$ replacing the peak at $2\theta=26.5^\circ$. It was found that a broad peak formed at $2\theta=25.1^\circ$ after the GO was reduced by hydrazine hydrate. This indicates the removal of large number of oxygen-containing groups and the formation of much more disordered graphene sheets^{1,2}. In addition, the used GO and used RGO catalysts have similar diffraction patterns with the native RGO, indicating that these catalysts, at working conditions, have almost the same structure.

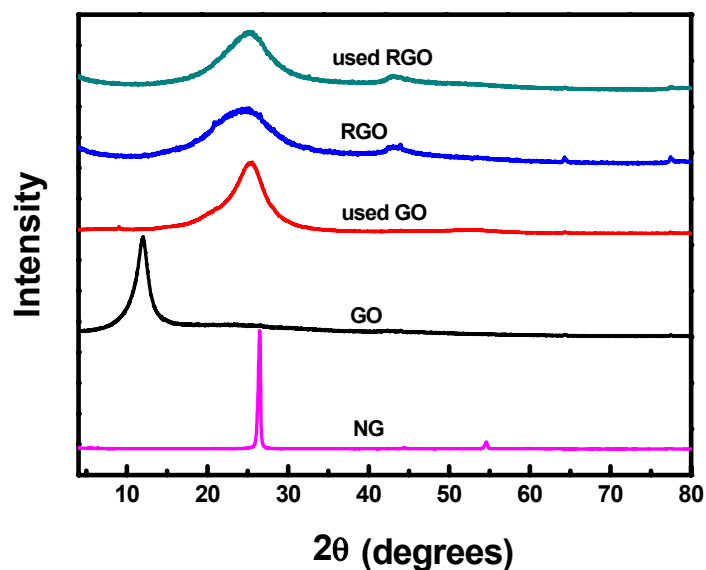


Figure S2 X-ray powder diffraction patterns of natural flake graphite(NG), graphene oxide(GO), reduced graphene oxide(RGO), used GO, and used RGO catalyst.

Raman spectroscopy is usually used to characterize carbon materials. Fig. S3 clearly indicates that GO, RGO, used RGO and used GO are more amorphous than natural flake graphite. NG has a prominent G band at 1581 cm^{-1} which is assigned to the first-order scattering of the E_{2g} modes. In the Raman spectrum of GO, the D band at 1355 cm^{-1} becomes more intense and the broadened G band is shifted to 1599 cm^{-1} due to the destruction of conjugated system in graphite. After GO was reduced to RGO, the D band became narrower and more prominent whilst the G band shifted from 1599 cm^{-1} to 1590 cm^{-1} because large numbers of sp^3 carbon were reduced to sp^2 carbon.

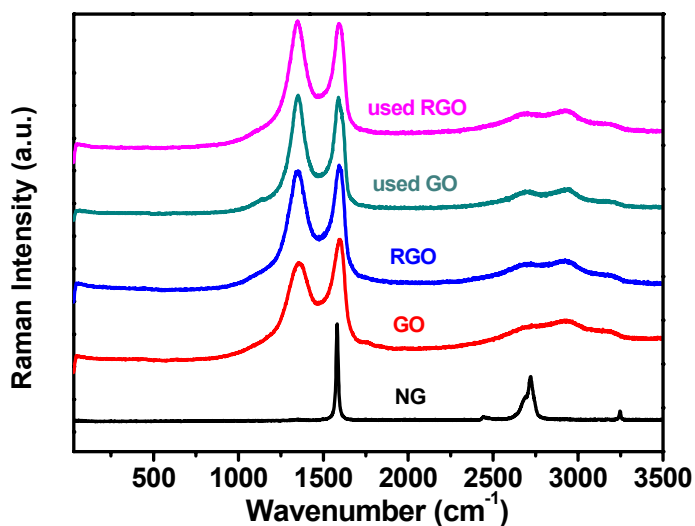


Figure S3 Raman spectra of NG, GO, RGO, used GO and used RGO catalyst.

Powder samples were pressed into slices and dried at room temperature *in vacuo* prior to XPS testing.

The C1s XPS spectrum of GO shows that, beside the band of aromatic C-C bonds at BE=284.6 eV, there is a very broad peak ranging from 286 to 290 eV, indicating a considerable degree of oxidation and the presence of different oxygen-containing groups. This is in good agreement with the ^{13}C MAS NMR results (see Fig. S1). However, C1s XPS spectra of RGO, used RGO catalyst and used GO show almost identical features with that of NG, which demonstrated the aromatic nature of graphene-like material. The broadened peak shape of graphene catalyst, used graphene catalyst and used graphene oxide (Fig. S4) indicate that these materials have a much more disordered structure than graphite.

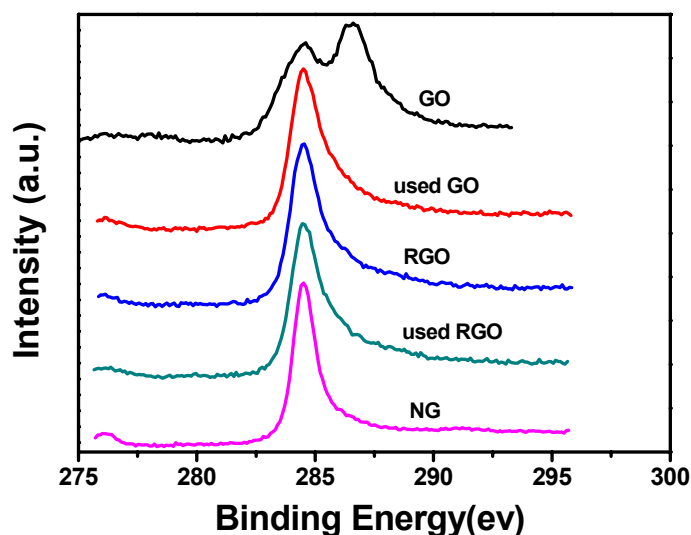


Figure S4 XPS spectrum of NG, GO, RGO, used RGO and used GO.

Effects of residual manganese in RGO and larger surface area

ICP results indicate that a small quantity of manganese remained in RGO (Mn: 0.47%) and GO (Mn: 0.29%) because a mass of potassium permanganate were used as oxidant. In order to exclude the effect of residual manganese left in RGO, the catalysts of carbon black supporting different amount of MnSO_4 were prepared and tested in reduction of nitrobenzene under same condition. The results illustrate that manganese has no catalytic activity for this reaction (Table 1). In addition, GO and RGO with lower content of manganese (RGO (Mn: 0.0090%) and GO (Mn: 0.0024%)) were prepared through intensively washing products with hydrogen peroxide and water. No decreasing catalytic activity was observed when the RGO and GO with lower manganese content was used as catalyst (Table S1). The results illustrate that manganese species has no obvious catalytic activity for this reaction.

Table S1. Hydrogenation of nitrobenzene catalyzed by carbon black containing different amount of manganese^[a].

Entry	Catalyst	Yield (%) ^[b]
1	Carbon black (0.49% Mn)	1.8
2	Carbon black (0.97% Mn)	3.5
3	Carbon black (1.33% Mn)	1.8
4	Carbon black (3.83% Mn)	1.7
5	Carbon black (5.85% Mn)	2.2
6	GO (0.0024% Mn)	88.0
7	RGO (0.0090% Mn)	89.0

^[a] Reaction conditions: 0.5 g nitrobenzene, 2 mL hydrazine hydrate, 1.5 mL water, 0.010 g catalyst, reflux, 4 h.

^[b] The products were detected by HPLC.

^[c] Reaction conditions: 0.5 g nitrobenzene, 2 mL hydrazine hydrate, 0.010 g catalyst, reflux, 4 h.

The results of nitrogen adsorption experiment illustrate that RGO has larger BET surface area than GO and carbon black (Table S2). In order to clarify whether the large surface area of carbon materials is essential for catalytic activity in this reaction, active carbon with larger BET surface area (1060 m²/g) was used as catalyst to catalyze the reaction in same condition. Only 15.4% yield of aniline was achieved. Therefore, residual manganese in RGO and larger surface area have no crucial function for catalytic activity.

Table S2. The BET surface area of different carbon materials used in our experiments.

Carbon black (m ² /g)	Graphene oxide (m ² /g)	Reduced graphene oxide (m ² /g)	Natural graphite (m ² /g)	Active carbon (m ² /g)	Expanded graphite (m ² /g)	Pyrolytic GO (m ² /g)
62.5	26.8	456.9	-	1060.0	63.6	423.6

DFT calculation

The activation of the N=O bonds and the subsequent removal of oxygen by a reduction agent are the critical steps in the nitrobenzene hydrogenation reaction. To check whether graphene is able to promote the activation of the N=O bonds, DFT calculations of the molecular geometry and conformation change,

with or without graphene as catalyst, were conducted. A finite model, $C_{36}H_{16}$, was used to represent a single layer of graphene (Fig. S5a; the hydrogen atoms were used to terminate the open ends to avoid dangling bonds). It is possible that edge carbon sites without the protection of terminal hydrogen atoms exist. They will react with nitrobenzene molecules ($PhNO_2$) to form a six-member-ring intermediate through the formation of two C–O bonds. As a control, we have also investigated the geometries of the free nitrobenzene (Fig. S6) and the nitrobenzene molecule reacting with three-layer and five-layer graphene possessing edge carbon sites in each middle sheet (Fig. S7). During the optimization, all the atoms in the single-layer model and the atoms in the middle sheets of three-layer and five-layer models were allowed to fully relax.

Gradient-corrected density functional calculations were carried out on an SGI O2 workstation, using the DMOL3 software in CERIUS 2 (version 4.2) of MSI (CERIUS 2, Version 4.2, DMOL 3, Molecular Simulations, Inc., 2000.). In the calculations, the numerical orbitals of a DND basis set (double-numerical basis functions supplemented by polarization functions) were employed. This basis is comparable in its quality to Gaussian 6-31G** sets. Exchange and correlation interactions were described with the Becke-Perdew functional. The self-consistent-field parameters were set in such a way that the total energy converged to 1×10^{-5} Hartree.

It is clear from Figs. S5–S7 that the N=O bond was activated with the bond length elongated after reacting with graphene. For single-layer graphene, the average lengths of the N=O bonds changed from 1.24 Å for free nitrobenzene to 1.49 Å after reacting with the zigzag edge of graphene. This strongly suggests that the zigzag edge of graphene has a very high chemical reactivity, which is in accordance with recent theoretical reports^{3,4} and our experimental observation. In addition, we need to point out that for few-layer graphene (three-layer or five-layer in the present case), although it is not as active as one-layer graphene, the N=O bonds were still activated as indicated by the elongated average bond lengths.

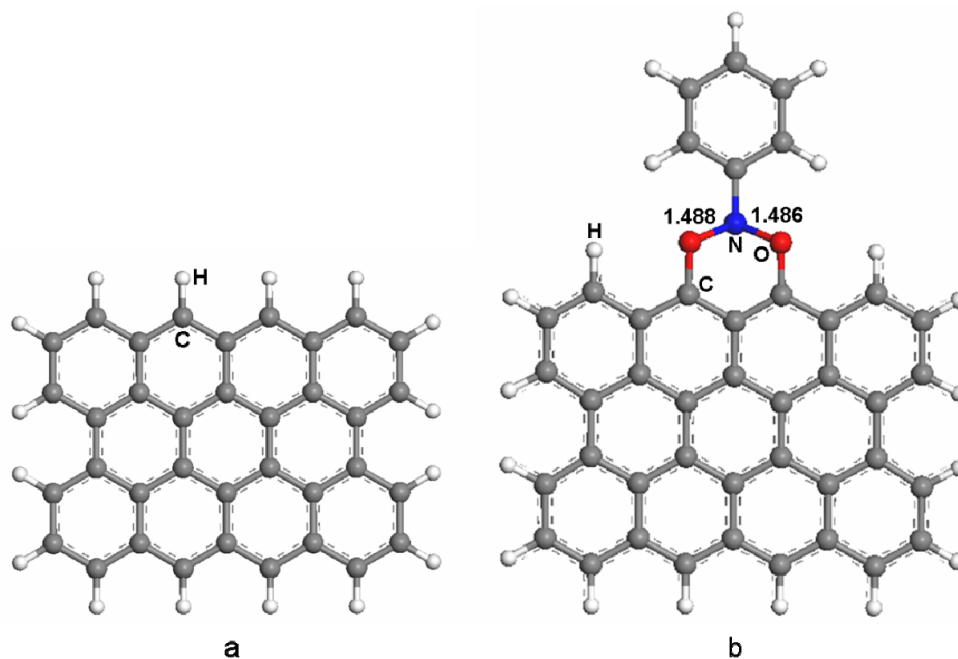


Figure S5. (a) Structure of defect free one-layer graphene; (b) The optimized structure of the nitrobenzene molecule reacting with one-layer graphene through two C–O bonds.

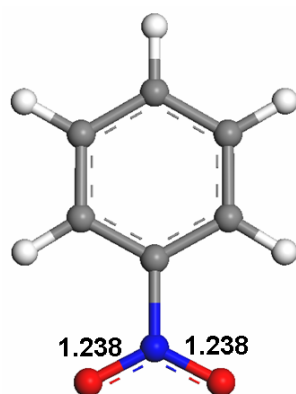


Figure S6. The optimized structure of the nitrobenzene molecule.

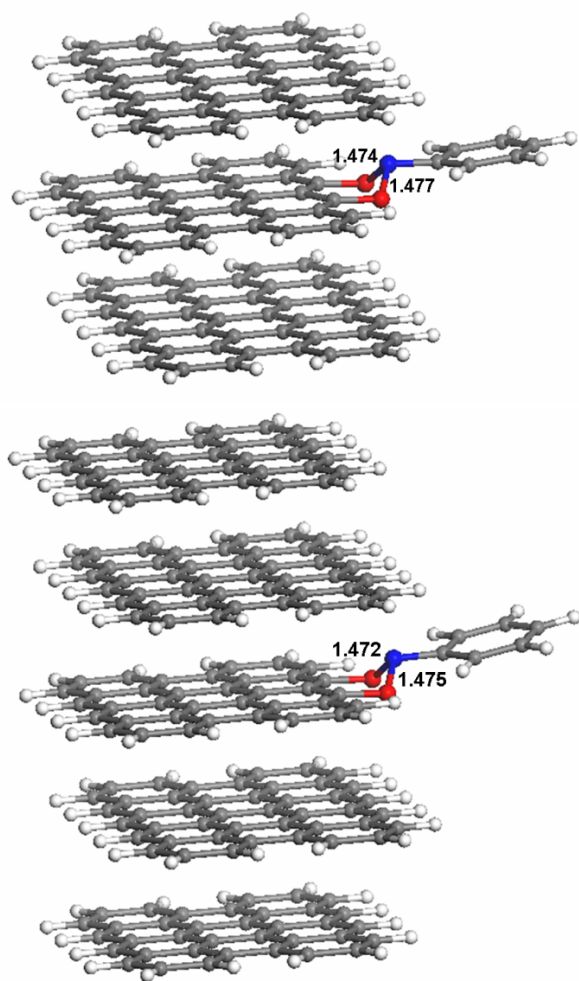


Figure S7. Optimized structures of the nitrobenzene molecule reacting with three-layer and five-layer graphene possessing edge carbon sites in each middle sheet. (the numbers in the figure has a unit of Å)

References

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