High Graphite N Content in Nitrogen-Doped Graphene as an Efficient Metal-free Catalyst for Reduction of Nitroarenes in Water

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1. General Information

$^1$H NMR spectra are recorded on JNM-LA300FT-NMR (300 MHz, 400 MHz) spectrometers. $^1$H NMR spectra are reported as follows: chemical shift in ppm ($\delta$) relative to the chemical shifts of CDCl$_3$ at 7.26 ppm and CD$_3$OD at 3.33 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

2. Mechanism study for the reduction of nitroarenes

0.5 mmol p-nitrochlorobenzene (40 mg) was moved into a reactor together with 2 mg NG-1 and 1 ml water at room temperature. The mixture was stirred for 1-2 min for thoroughly mixing. 5 equiv. of NaBH$_4$ (1.25 mmol/mL) 2mL was added dropwise into the above solution under magnetic stirring at room temperature. After reacting for 0.5 hour, the sample was dissolved in ethyl acetate and analyzed by GC-MS. The initial temperature of the column was 70 °C held for 1 min and was programmed to 300 °C at 15 °C/min, then held for 15 min at 300 °C, the sample injection volume was 2 μL. Helium was used as carrier gas at a flow rate of 1.1 mL/min on split mode (1:50).

3. Computational details

All the electronic structure and energy calculations were carried out by the spin-polarized density functional theory (DFT) using the Vienna ab initio simulation package (VASP).$^{1-4}$ PAW potentials were used to describe ion cores and valence electrons interactions.$^{5,6}$ The adopted exchange-correlation functional is the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof.$^7$ A kinetic energy cut off of 350 eV was used with a plane-wave basis set. The integration of the Brillouin zone was conducted using a 5×5×1 Monkhorst-Pack grid.$^8$ All atoms were fully relaxed and optimized until the force was converged to 0.05 eV/Å and the total energy was converged to 1.0×10$^{-5}$ eV/atom.

Four kinds of nitrogen doped graphene (NG), graphitic N, pyridinic N, pyrrolic N, and pyridinic N oxidized, were established based on the 4 × 4 single layer graphene, armchair and zigzag ribbons. The structures were designed according to previous reference.$^9$ The periodical graphene slab 9.86 Å × 8.60 Å in size was used. The edge graphene ribbon was prepared with the size of 20 Å × 8.60 Å. To avoid the image
interactions sufficiently large vacuum of 15.0 Å has been taken along the z-axis.

The adsorption energy ($E_{\text{ads}}$) of nitrobenzene was defined as follows:

$$E_{\text{ads}} = E_{\text{substrate+nitrobenzene}} - E_{\text{nitrobenzene}} - E_{\text{substrate}} \quad (1)$$

where $E_{\text{substrate+nitrobenzene}}$, $E_{\text{nitrobenzene}}$, and $E_{\text{substrate}}$ are corresponding to the total energies of a nitrobenzene molecule and four NG substrates, a gas phase nitrobenzene, and an isolated substrate, respectively. A negative value indicates an exothermic chemisorption.
4. The GC-MS spectra of reduction reaction intermediate products

Fig. S1 The GC-MS spectra of reduction reaction intermediate products.
5. A proposed reaction mechanism for NG catalyze reduction of nitroarene

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\text{Fig. S2 Schematic of the proposed reaction pathway for nitroarenes reduction}
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6. Spectroscopic data of the products:

**Aniline hydrochloride (Table 3, entry 1)^10**

\[
\text{Cl-} \text{NH}_2 \text{HCl}
\]

\[^{1}H\text{ NMR (400 MHz, CD}_3\text{OD)} \delta 7.57-7.52 (m, 3H), 7.44 (d, J = 8.8 Hz, 2H).\]

**4-Chloroaniline (Table 3, entry 2)^11**

\[\text{Cl-} \text{NH}_2\]

\[^{1}H\text{ NMR (400 MHz, CDCl}_3\text{)} \delta 7.10 (d, J = 8.4 Hz, 2H), 6.33 (d, J = 8.4 Hz, 2H), 3.66 (s, 2H).\]

**4-Bromoaniline hydrochloride (Table 3, entry 3)^10**
4-Iodoaniline hydrochloride (Table 3, entry 4)

4-Methylaniline hydrochloride (Table 3, entry 5)

4-Nitroaniline (Table 3, entry 6)

4-Aminophenol hydrochloride (Table 3, entry 7)

4-Methoxyaniline hydrochloride (Table 3, entry 8)

4-Amino-benzoic acid hydrochloride (Table 3, entry 9)
$\text{HOOC-} \text{NH}_2\text{HCl}$

$^1\text{H NMR (300 MHz, CD}_3\text{OD) } \delta 8.16 (d, J = 8.7 \text{ Hz}, 2\text{H}), 7.48 (m, J = 8.7 \text{ Hz}, 2\text{H}).$

4-Aminobenzonitrile (Table 3, entry 10)

$\text{N}=\text{C-} \text{NH}_2\text{HCl}$

$^1\text{H NMR (400 MHz, CD}_3\text{OD) } \delta 7.76 (d, J = 8.8 \text{ Hz}, 2\text{H}), 7.30 (d, J = 8.8 \text{ Hz}, 2\text{H}).$

References

3. $^1$H NMR charts of the products:

Aniline hydrochloride (Table 3, entry 1):

![Aniline hydrochloride NMR chart](image)

4-Chloroaniline (Table 3, entry 2):

![4-Chloroaniline NMR chart](image)
4-Bromoaniline hydrochloride (Table 3, entry 3):

4-Iodoaniline hydrochloride (Table 3, entry 4)
4-Methylaniline hydrochloride (Table 3, entry 5)

4-Nitroaniline (Table 3, entry 6)
4-Aminophenol hydrochloride (Table 3, entry 7)

4-Methoxyaniline hydrochloride (Table 3, entry 8)
4-Amino-benzoic acid hydrochloride (Table 3, entry 9)

4-Aminobenzonitrile (Table 3, entry 10)