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Supporting Information

Efficient and highly selective boron-doped carbon materials-catalyzed reduction of nitroarenes †

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Materials

Nitrobenzene (99%) were purchased from Aladdin Reagent Co. Ltd., Shanghai, China. Hydrazine monohydrate (85%), and ethanol (AR), were supplied by China Medicine Group Shanghai Chemical Reagent Company. Boric oxide (~1um, 99.99 %, S_{BET}=16 m^2 g^{-1}), boron powder (99.99 %), boron nitride (1~2 um, 99.9 %, S_{BET}=22 m^2 g^{-1}), boric carbide (1~10um, 98 %, S_{BET}=18 m^2 g^{-1}) were obtained from Aladdin Co. Carbon nanotubes (CNTs) were bought from Shandong DazhanTechnology Ltd. and were further treated with water-diluted HCl (volume ratio is 1:1) before use. Purified ultra-dispersed nanodiamond (UDD) was supplied from Beijing Grish Hitech Co. (China), produced by detonation and followed by acid washing. The noncombustible contaminations were tested by an inductively coupled plasma emission spectrometer and included Fe < 50 ppm, Cr < 10 ppm, Al < 50 ppm, Cu < 10 ppm, Mg < 10 ppm, Ti < 10 ppm, and Ca <50 ppm. The average particle size was about 5 nm. Boric acid (H_3BO_3) (Aladdin Co. high purity, 99.999 %) was chose as the dopant. The B-OLC samples were produced by the following procedures: (1) The mixtures with 8 wt %, 15 wt %, 25 wt % boric acid and ultra-dispersed nanodiamond (UDD) were produced by manual mixing for 1 h and then the samples were thermally treated from 25 °C to 100 °C at a very slowly heating rate of 0.5 K•min^{-1} in a furnace under argon atmosphere, respectively. (2) The obtained mixtures were further annealed at 1500 °C for 30 min at a heating rate of 5 K•min^{-1} in a furnace under argon atmosphere. The final samples were labelled by B-OLC-1, B-OLC-2 and B-OLC-3, respectively. The B-CNTs samples were obtained by the same approach, and the starting material was acid-treated CNTs. The final samples were assigned to B-CNTs-1, B-CNTs-2 and B-CNTs-3, respectively. Pristine OLC and CNTs were prepared by annealing the UDD and acid-treated CNTs at 1500 °C for 30 min. B-CNTs-2-P was synthesized by annealing the mixture of 15 wt% boric acid and CNTs without acid-treated at 1500 °C for 30 min. CNTs-P was obtained by annealing the CNTs without acid-treated at 1500 °C for 30 min as reference.

Characterization

High-resolution transmission electron microscopy (HRTEM) images were achieved on a FEI Tecnai G2 F20 microscope. The X-ray photoelectron spectroscopy (XPS) spectra was recorded on an ESCALAB 250 XPS system with a monochromatized Al Ka X-ray source. Raman spectra of samples on SiO_2/Si were performed with a LabRam HR800 spectrometer and a He/Ne laser at 532 nm (50×objective) was selected as the excitation source. Moreover, the laser power and exposure time were kept well to avoid the damage of samples and the heating effects.

The nitroarenes reduction reactions were carried out in a 25 ml round-bottom flask containing a certain amount of catalyst, 1.23 g of nitrobenzene and 1.5~4.0 equivalent of hydrazine monohydrate. The reaction solution was sampled periodically and analyzed using gas chromatography (Agilent 7890A).

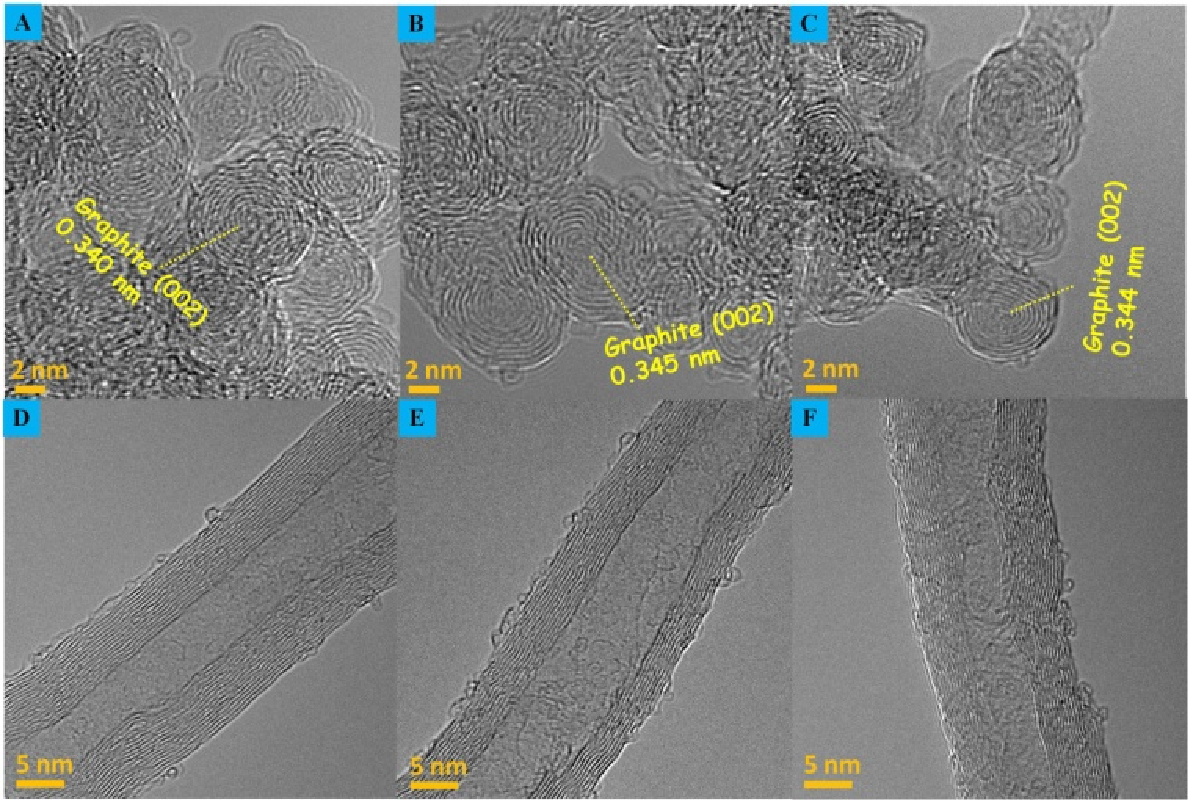

Fig. S1 HRTEM images of (A) pristine OLC, (B) B-OLC-2, (C) B-OLC-3, (D) pristine CNTs, (E) B-CNTs-2 and (F) B-CNTs-3 samples.

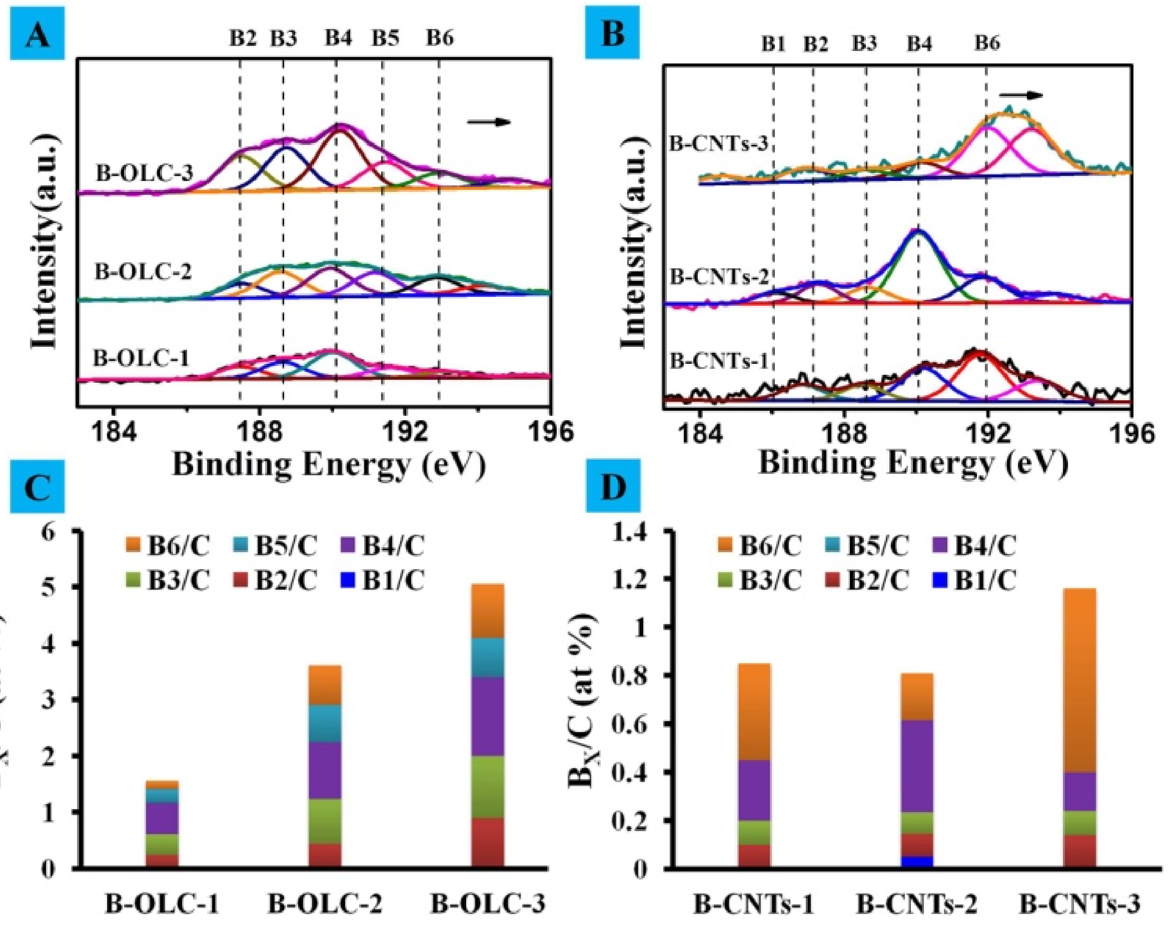

Fig. S2 XPS B1s spectra of (A) B-OLC and (B) B-CNTs samples. Bx/C distribution diagram of (C) B-OLC and (D) B-CNTs samples. The XPS spectra were divided by fitting the peak maximum within ±0.15 eV and applying a full width at half-maximum (FWHM) of 1.4-1.6 eV.

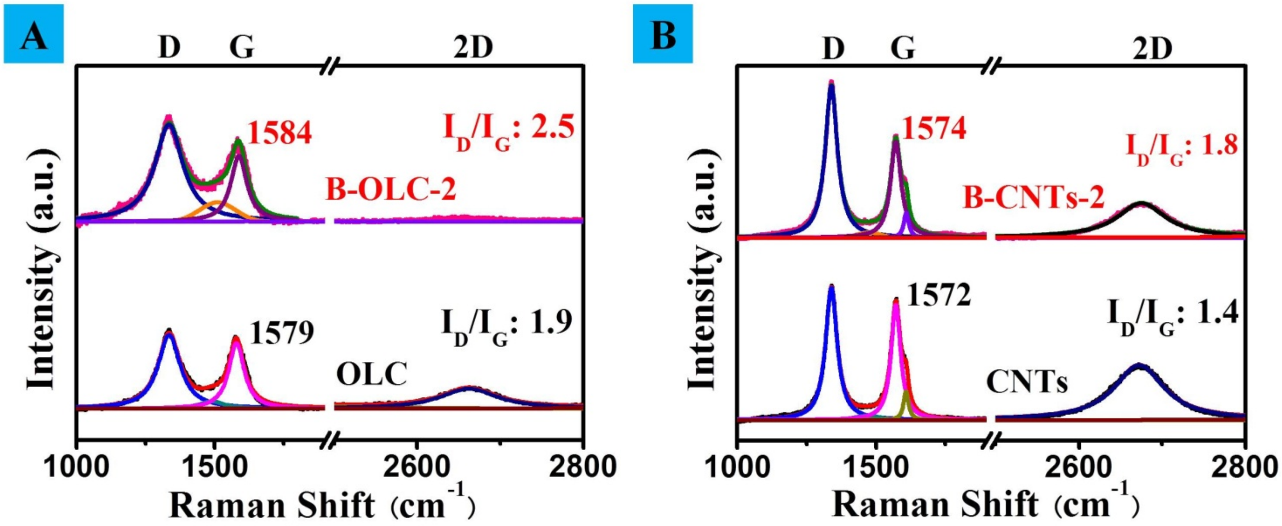

Fig. S3. (A) and (B) The deconvolution of the first- and second-order for Raman spectra of the B-OLC-2 and B-CNTs-2 samples using a He-Ne laser (λ=532 nm), respectively.

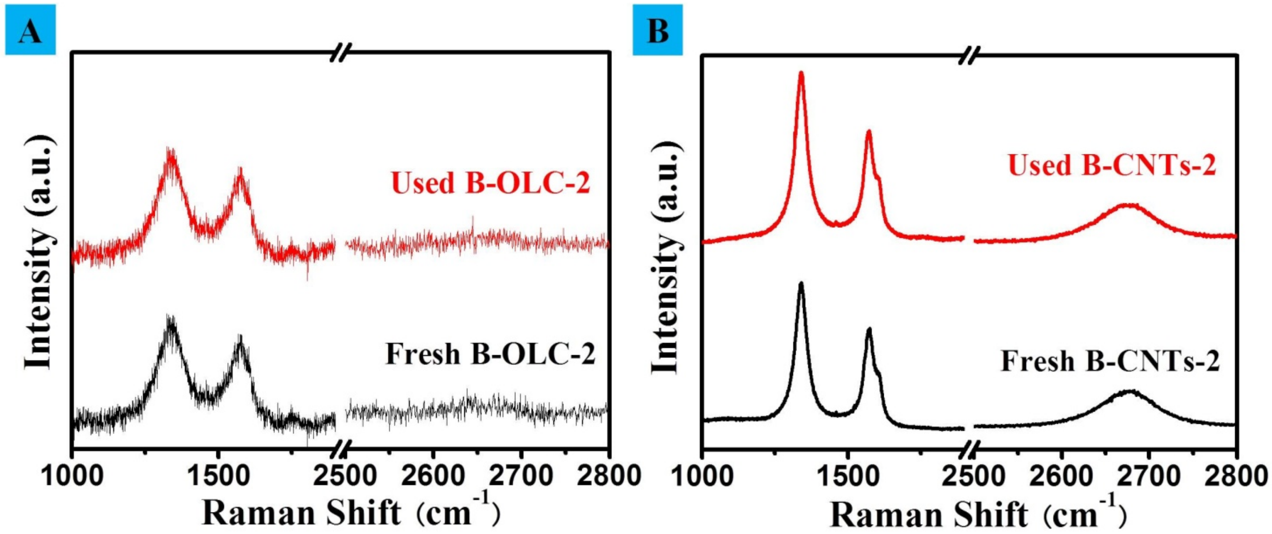

Fig. S4. (A) Raman spectra of fresh B-OLC-2 and used B-OLC-2 (after ten cycles). (B) Raman spectra of fresh B-CNTs-2 and used B-CNTs-2 (after ten cycles).

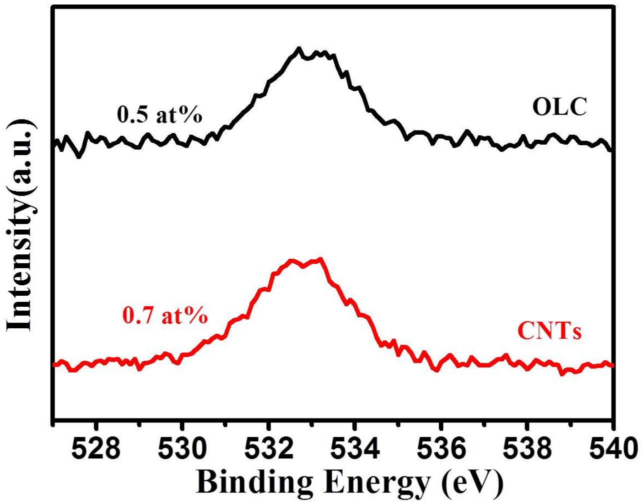

Fig. S5. XPS O1s spectra of pristine OLC and CNTs.

Table S1. Catalytic activity of different catalysts for the nitrobenzene reduction[a].

Entry	Catalyst	S_{BET} (m^2 g^{-1})	Normalized Value (m^2)[e]	Con. (%)	Sel. (%)
1	----	----	----	4.8	95.6
2[b]	B-OLC-2	400	0.8	23.2	97.3
3[c]	B-CNTs-2	179	0.716	31.8	98.1
4[d]	B	----	----	5.0	95
5[d]	B_2O_3	16	0.64	5.1	96.1
6[d]	BN	22	0.88	5.3	95.5
7[d]	B_4C	18	0.72	5.4	96.5

[a] Reaction condition: 10 mmol (1.23 g) substrate, 1.5 equiv N_2H_4, 100 °C, 4 h. [b] 2 mg catalyst. [c] 4 mg catalyst. [d] 40 mg catalyst. [e] The normalized value = specific surface area(m^2/g)×catalyst mass (g)