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Supporting Information

Insights into surface chemistry and electronic properties of sp^2 and sp^3-hybridized nanocarbon materials for catalysis

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Experimental Section

Materials

Purified ultra-dispersed nanodiamond (ND) was bought from Beijing Grish Hitech Co. (China), produced by detonation and purified by acid washing; the average particle size is ~5 nm. The noncombustible contaminations were tested by an inductively coupled plasma optical emission spectrometer (ICP-OES) and included Fe < 50 ppm, Cr < 10 ppm, Al < 50 ppm, Cu < 10 ppm, Mg < 10 ppm, Ti < 10 ppm, and Ca <50 ppm. Graphene (GR, 99%) was supplied by Tanmei Ltd, Co. (China). Multi-walled carbon nanotubes (MWCNTs) was purchased from Shandong DazhanTechnology Ltd. and was further treated with water-diluted HCl (volume ratio is1:1) before use.

Samples preparation

900BND, 1100BND and 1300BND with graphite-like shell structures were produced by annealing purified ND at 900, 1100 and 1300 °C for 4 h in argon atmosphere, respectively. Similarly, OLC can be prepared by annealing ND at 1500 for 30 min in an Ar atmosphere. Both GR and MWCNTs were treated by HCl for 24 h to wash the residual metals.

Characterization

High-resolution transmission electron microscopy (HRTEM) was conducted on a FEI Tecnai G2 F20 microscope and electron energy-loss spectra (EELS) were recorded by a Gatan GIF 963 spectrometer. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 XPS system with a monochromatized Al K-alpha X-ray source. N_2 adsorption-desorption was carried out on the Micromeritics ASAP2020 setup and analyzed applying Brunauer-Emmett-Teller (BET) theory. Raman spectra of samples on SiO_2/Si were collected 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 maintained low to avoid local damage of samples by the heating. The electrical conductivity of all the samples was operated on a conventional four probe system. UPS spectra are obtained at room temperature using a He discharge lamp (He I: hv=21.22 eV). The samples were biased by about 6 V during the work function measurements to accelerate the low energy secondary electrons (SE) and nickel metal was used as reference.

The work function (Φ) =21.22 eV-$|E_{SE}-E_F|$, where E_F was the Fermi edge. The valence band edge was calculated by the cross-over point between tangent of photoemission spectra and X axis.

Catalytic activity testing

The 2,3,6-trimethylphenol oxidation reactions were carried out in 48 ml round-bottom flask containing a certain amount of catalyst, substrates and oxidant. A certain amount of ethylbenzene as an internal standard was added in the reaction solution after reaction. And then, the reaction solution was sampled periodically and analyzed using gas chromatography with a HP-5 column (Agilent 7890A). Conversion, yield, and selectivity for the oxidation of 2,3,6-trimethylphenol to target products were defined as follows:

Conversion (%)= $[(C_0 - C_r)/C_0] \times 100$

Yield (%)= $C_p/C_0 \times 100$

Selectivity (%)=$[C_p/(C_0 - C_r)] \times 100$

where C_0 is the initial concentration of 2,3,6-trimethylphenol, and C_r and C_p are the concentration of reactants and products, respectively, at a certain time after the reaction.

Similarly, the nitrobenzene reduction reactions were carried out in a 25 ml round-bottom flask containing 25 mg catalyst, 10 mmol (1.23 g) of nitrobenzene and 6.0 equivalent of hydrazine monohydrate. The reaction solution was sampled periodically and analyzed using gas chromatography (Agilent 7890A).

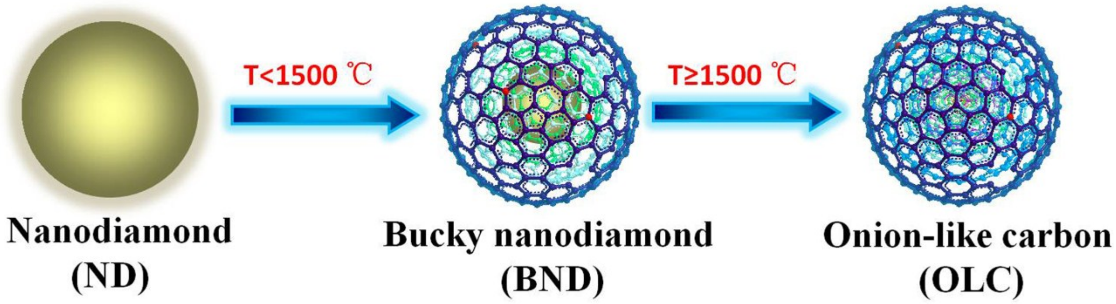

Figure S1. The phase transformation of ND to BND and OLC. The surface of BND and OLC should be rather irregular sp^2 carbon fragments, although multiple perfect graphitic shells were displayed for simplicity.

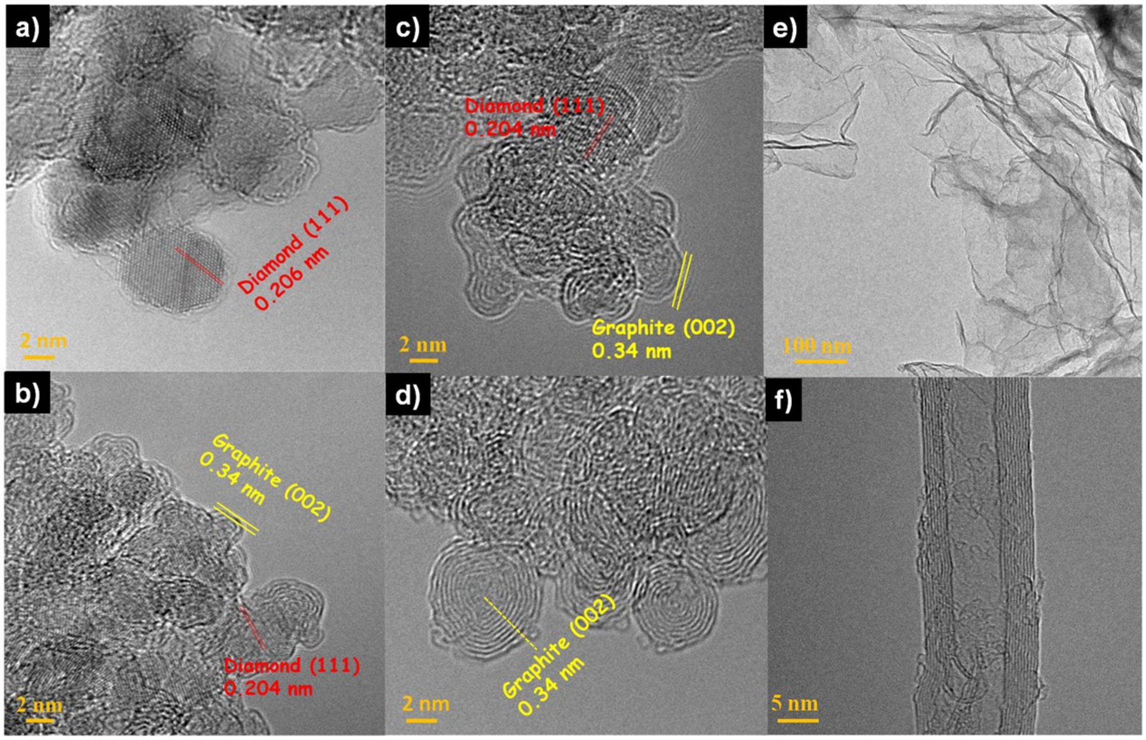

Figure S2. HRTEM images of ND (a), 900BND (b), 1100BND (c), OLC (d), GR (e) and MWCNTs (f) .

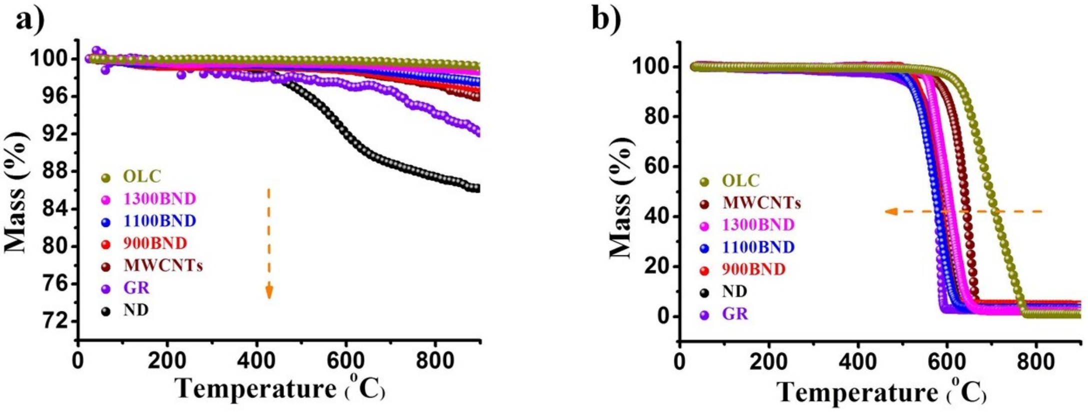

Figure S3. TG spectra of various carbon materials in different atmospheres, a) Ar, b) Air.