

Supporting information

Defective graphene@diamond hybrid nanocarbon material as effective and stable metal-free catalyst for acetylene hydrochlorination

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Experimental

Materials

Purified ultradispersed nanodiamond was purchased from Beijing Grish Hitech Co. (China), produced by detonation and followed by acid washing. All materials except nanodiamond were analytical grade and used without further purification.

Preparation of the materials

Nanodiamond powders were annealed in argon flow ($100 \text{ ml}\cdot\text{min}^{-1}$) for 4 h at 900 and 1300 °C, respectively, and then cooled down to ambient temperature in argon.

Measurement of catalytic activity

The catalytic performance was investigated using a fix-bed glass reactor (i.d. of 20 mm). Acetylene (99.9% purity) was passed through concentrated sulfuric acid solution to remove the trace impurities, and hydrogen chloride gas (99.9% purity) was dried using 5A molecular sieves. Acetylene ($5.0 \text{ mL}\cdot\text{min}^{-1}$) and hydrogen chloride ($5.5 \text{ mL}\cdot\text{min}^{-1}$) were introduced into a heated reactor containing catalyst (1.0 mL) through a mixing vessel via calibrated mass flow controllers, giving a C_2H_2 gas hourly space velocity (GHSV) of 300 h^{-1} at 220 °C. The pressure for acetylene and hydrogen chloride is 0.1 MPa and the feed volume ratio of $V_{\text{HCl}}/V_{\text{C}_2\text{H}_2}$ is 1.2. The microreactor was purged with nitrogen to remove water and air before the reaction. The reactor effluent was passed through an absorption bottle containing a sodium hydroxide solution to remove the unreacted hydrogen chloride. The gas mixture was analyzed using a GC-1690F gas chromatograph (GC) equipped with FID detector.

Characterizations

Nitrogen sorption isotherms were determined at -196 °C by a Quantachrome Autosorb-IQ instrument in static measurement mode. Before the measurement, the samples were degassed at 300 °C for 8 h. The pore size distribution of the carbon materials was determined by the BJH method based on desorption branch. X-ray powder diffraction (XRD)

measurements were performed using a Rigaku D/Max-2500/pc powder diffraction system using Cu K α radiation (40 kV and 100 mA) over the range $10^\circ \leq 2\theta \leq 80^\circ$.

High resolution Transmission electron microscopy (HRTEM) was performed on a Philips-FEI Tecnai G2 F30 S-Twin electron microscope with a field emission gun as the source of electrons operated at 300 kV. The samples were mounted and ultrasonically dispersed in ethanol, and then a few droplets of the suspension were deposited on a copper grid coated by a holey carbon film, followed by drying at ambient conditions.

X-ray photoelectron measurements were conducted on a Kratos AXIS Ultra DLD instruments using 300W Al K α radiation and C1s peak at 284.6 eV as the internal standard. Raman spectroscopy was performed on powder samples using a HORIBA LabRam HR Raman spectrometer with 532 nm excitation wavelength.

TPD of various carbon materials was performed on samples (100 mg) in a vertically positioned quartz tubular reactor. The samples were annealed under argon at 110 °C for 1 h and then were swept in a flowing argon stream (30 mL/min) until the baseline no longer fluctuated. After the samples were cooled to room temperature, they were heated from 50 to 850 °C with a rate of 10 °C/min. The desorption products of CO ($m/z = 28$) and CO $_2$ ($m/z = 44$) were identified and quantified by an on-line Hiden gas analyzer (QIC 20).

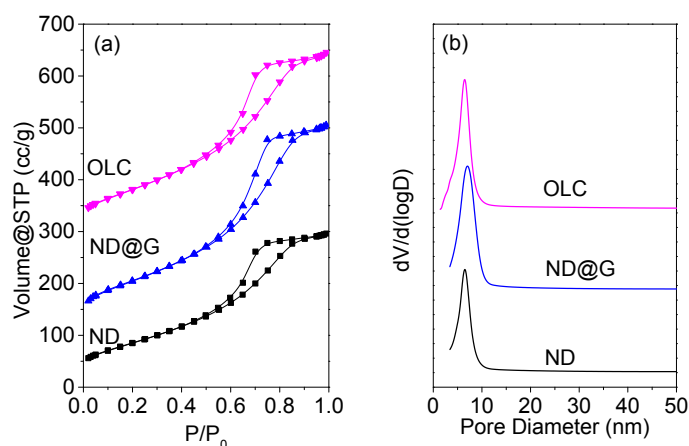


Figure S1 Nitrogen adsorption isotherms (a), pore size distributions (b) of various carbon materials.

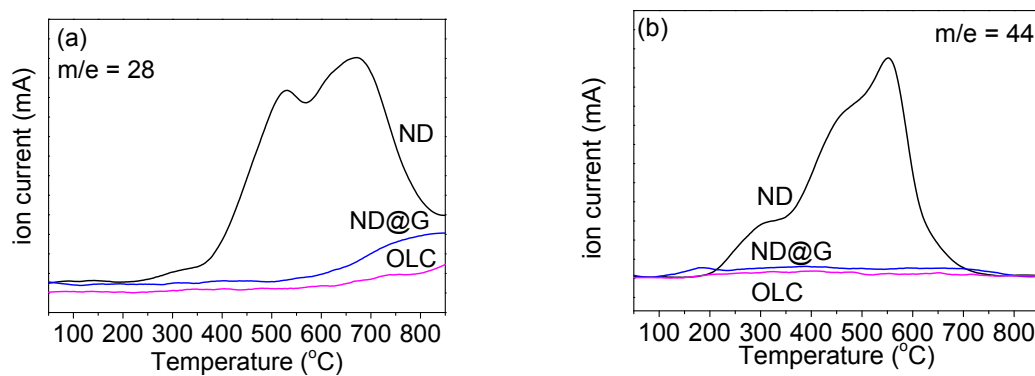


Figure S2 TPD profiles of various carbon materials in argon at a heating rate of 10 °C min⁻¹, (a) CO, m/z = 28; (b) CO₂, m/z = 44.

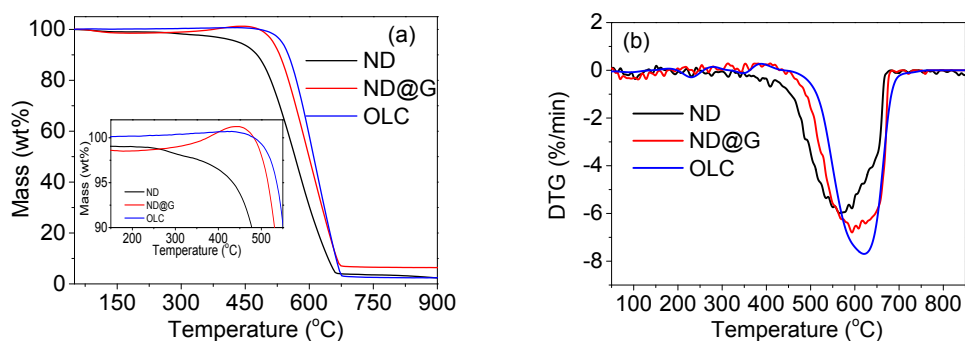


Figure S3 O₂-TG and DTG profiles of various carbon materials.

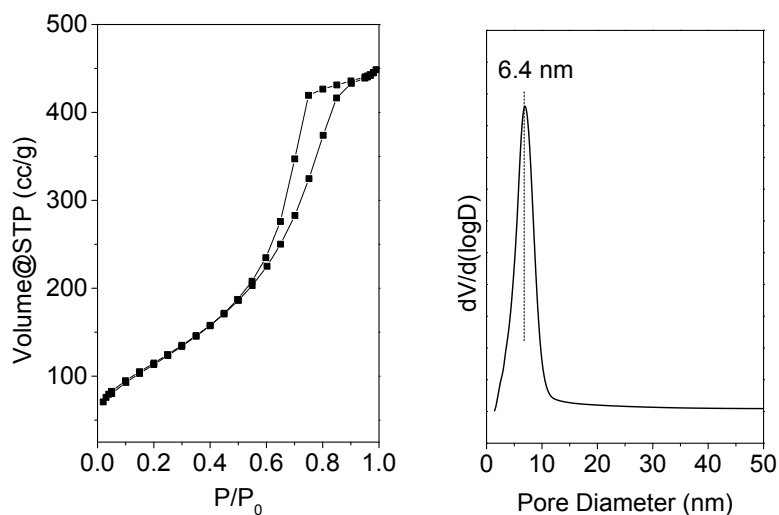


Figure S4 Nitrogen adsorption-desorption isotherms (a), pore size distributions (b) of ND@G catalyst used for 200 h.

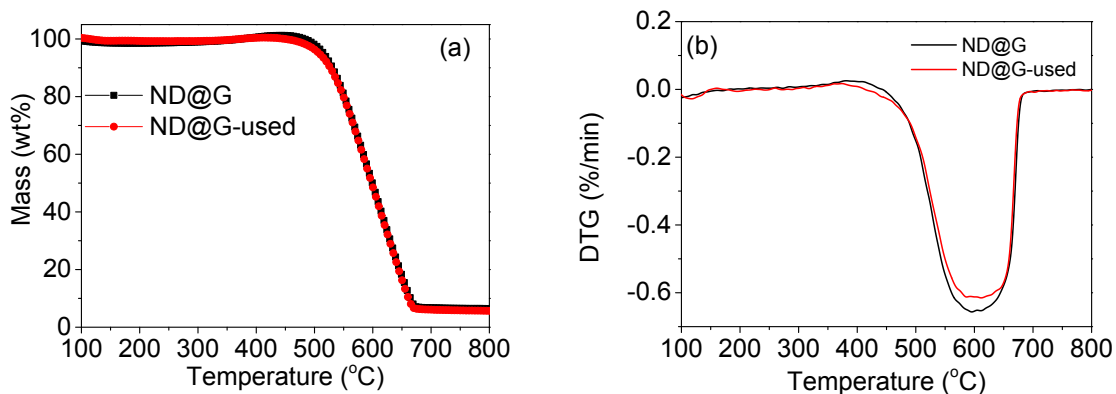


Figure S5 Air-TG and DTG profiles of various fresh ND@G and ND@G catalyst used for 200 h.

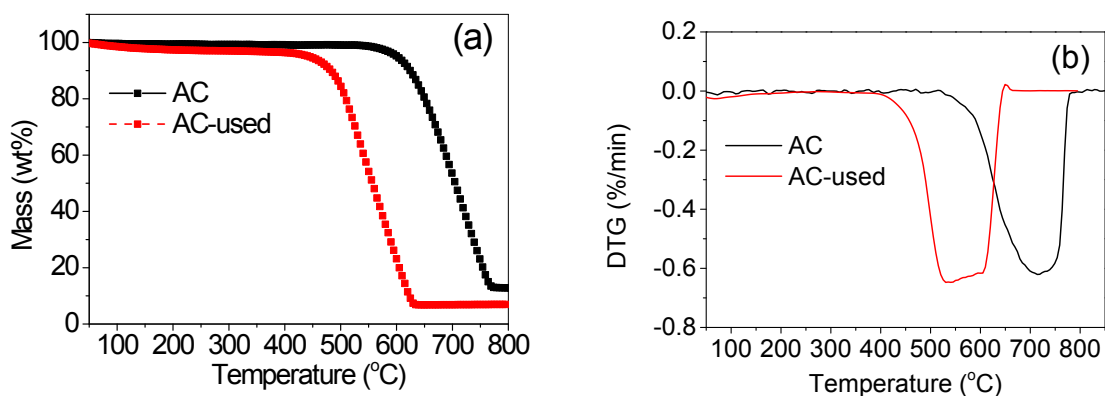


Figure S6 Air-TG and DTG profiles of various fresh AC and AC catalyst used for 50 h.

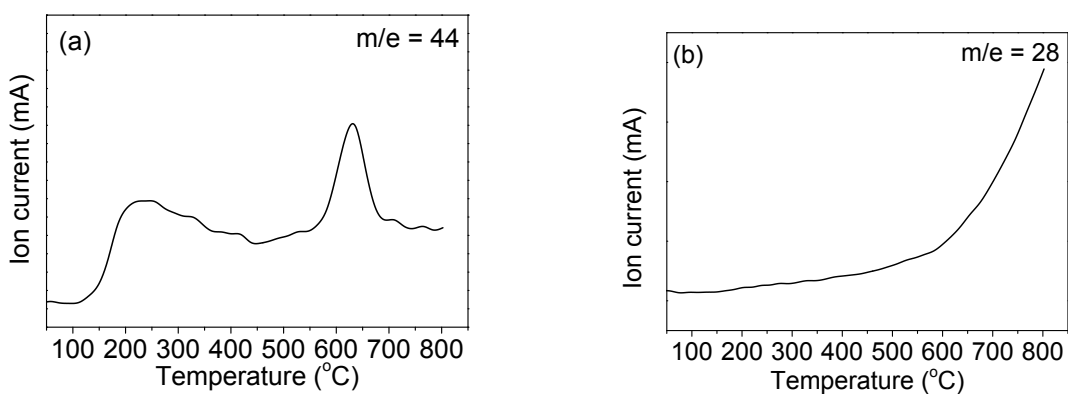


Figure S7 TPD profiles of AC in argon at a heating rate of 10 °C min⁻¹, (a) CO, m/z = 28; (b) CO₂, m/z = 44.

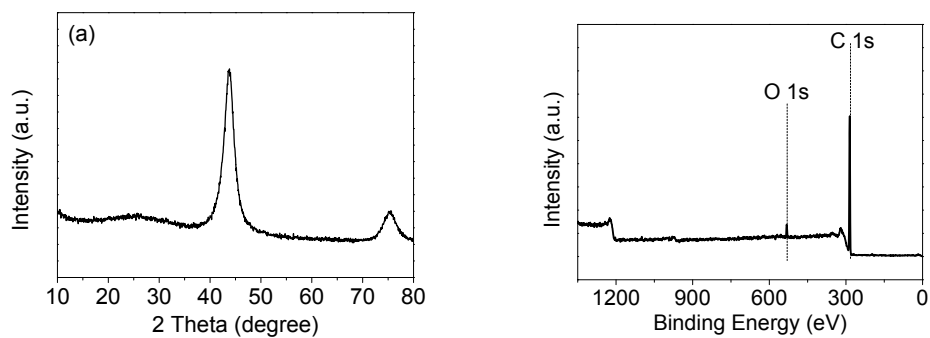


Figure S8 XRD patterns (a) and XPS analysis (b) of the ND@G catalyst used for 200 h.

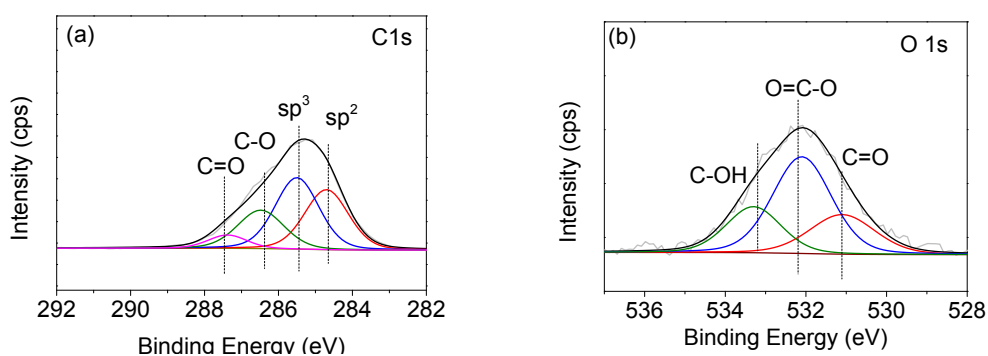


Figure S9 Deconvolution of C 1s (c) and O 1s (d) XPS spectra of the ND@G catalyst used for 200 h.

Table S1 O₂-TG analyses of various carbons.

Samples	Wight gain between 200-450 °C (wt%)
ND	-5.45
ND@G	+2.75
OLC	+0.52