Supplementary Information

Nanodiamond as Photocatalysts for Reduction of Water and Graphene Oxide

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Experimental

Acid purification, oxygenation, and hydrogenation of ND. Nanodiamonds (99 % purity, specific surface area of 300 m^2/g, and *ca.* 5 nm diameter), synthesized by the detonation of carbon-containing explosives, were purchased from JSC Diamond Center, Russia. The acid purification was achieved by refluxing the NDs in a 3:1 mixture of HNO_3/H_2SO_4 for 2 hrs and dried in a vacuum oven. This acid-purified ND (PND) was oxidized by heating at 400 °C under air in a furnace for 2 hrs, and was described as oxygenated ND (OND).[1] The PND was hydrogenated by heating in H_2 gas flow at 800 °C for 2 hrs, to remove oxygen functionalities from the surface, thus forming hydrogenated ND (HND).

Photoreduction of GO and synthesis of ND-RGO composites. GO was synthesized from graphite by following a modified version of Hummers' exfoliation method.[2] About 10 mg of GO and 50 mg of ND were suspended in distilled water (10 mL) after 30 min of sonication. The solution was placed in a reaction vessel equipped with a typical 2-inch dia. quartz optical widow. The photocatalytic reduction of GO was performed under 532 nm Nd-YAG laser pulse irradiation (20 mJ/pulse, 10 Hz, 10 ns pulse width). After 30 min of irradiation, the products were centrifugally precipitated, washed, and vacuum dried at 80 ^{o}C for 12 hrs. To obtain the chemically reduced form, the as-synthesized GO was reduced in 50% hydrazine solution at 100 °C for 1 day.

Characterization. The products were characterized by field-emission transmission electron microscopy (FE TEM, FEI TECNAI G2 200 kV and Jeol JEM 2100F) and high-voltage transmission electron microscopy (HVEM, Jeol JEM ARM 1300S, 1.25 MV). UV-visible-NIR absorption spectroscopy (Varian, Cary 1000) and IR spectroscopy (Thermo Scientific Nicolet iS10 FT-IR spectrometer) were also employed to characterize the products. Raman spectroscopy measurements were performed on a Raman microscope (HR-800, HORIBA Jobin Yvon) by using a 514.5 nm laser radiation with a power of 0.7 mW and 1s integration time.

Measurements of photocatalytic H_2 generation. A total of 100 mg of the PND (or HND, OND) was suspended in distilled water (100 mL) or an aqueous solution containing 30 wt. % methanol, under 30 min of sonication. The solution was placed in a reaction vessel equipped with a typical 2-inch dia. quartz optical widow. The photocatalytic degradation of water or methanol aqueous solution was performed under 532 nm laser irradiation (10-100 mJ/pulse). Recycled degradation data was noted by using HND. After each run, we precipitated the catalysts and added fresh water to achieve the same initial concentration.

The gas chromatography (GC) measurements were performed to detect H_2 on a GC (Young Lin ACME 6100) equipped with a pulsed discharge detector (VICI, Valco Instruments Co., Inc.) and a column (RESTEK-5A 80/100) with a length of 1.8 m and I.D. of 2 mm. The temperatures of the detector, injector port, and column were 100, 100, and 40 ºC, respectively.

Fabrication of ND-RGO assembled electrodes by using dielectrophoresis (DEP) technique. Photolithography was used to deposit the Ti (20 nm)/Au (80 nm) film electrode structure onto a Si substrate with a 1-µm-thick thermally grown SiO_2 layer, by sputtering using a patterned mask. The gap distance between the electrodes was 2 µm. The ND-RGO (or RGO) was dispersed in isopropyl alcohol (IPA), and a drop (0.2 µL) of IPA suspension was then dropped between the electrodes on the substrate. An alternating electric field of 10 kHz with a peak-to-peak voltage of 5 V was applied between the electrodes for 1 min. AFM (Park System XE100) confirmed that the ND-RGO composite sheets between the electrodes had an average thickness of 10 nm. The devices were heat-annealed at 300 °C for 1 min.

Photocurrent measurement. We measured the electrical characteristics of photodetector devices on the probe station with parametric test equipment (Agilent E5270A) at room temperature. A constant light intensity of 20 mW from a 514 nm Ar ion laser was used as the light source.

References:

1. S. Osswald, G. Yushin, V. Mochalin, S. O. Kucheyev and Y. Gogotsi, Control of sp^2/sp^3 Carbon Ratio and Surface Chemistry of Nanodiamond Powders by Selective Oxidation in Air. *J. Am. Chem. Soc.* 2006, **128**, 11635.
2. W. S. Hummers, Jr. and R. E. Offeman, Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* 1958, **80**, 1339.

Fig. S1 HRTEM images of the (a), (b) ND before irradiation, (c), after irradiation; (d) GO. The corresponding fast Fourier-transform (FFT) images, generated by using Digital Micrograph GMS 1.4 software (Gatan Inc.), are displayed in the inset. The distance between adjacent (111) planes (d_{111}) of the ND was 2.1 Å, which was close to the value of bulk diamond (JCPDS card no. 79-1467; cubic $a = 3.517$ Å).

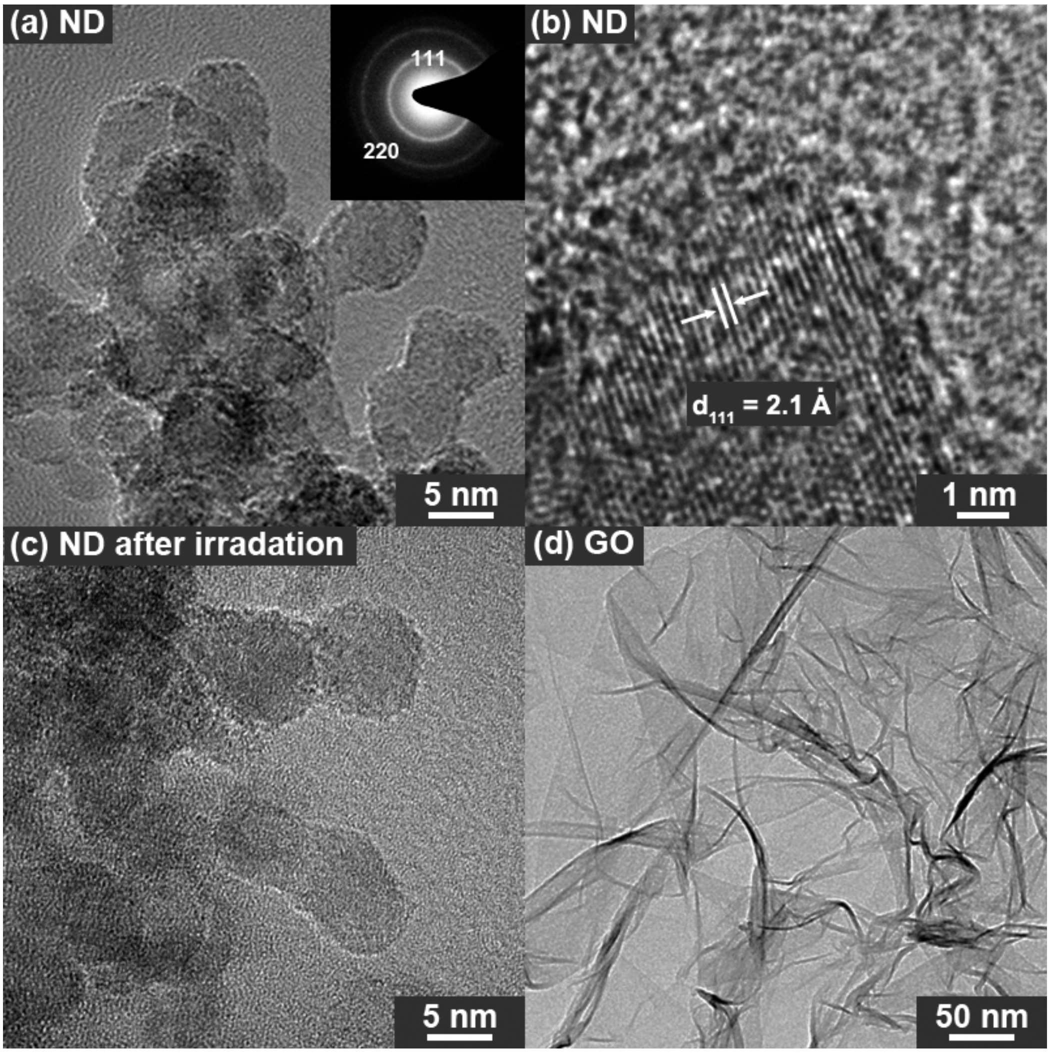

Fig. S2 IR spectra of the pristine (ND), acid-purified (PND), oxygenated (OND), and hydrogenated ND (HND), before and after 3 hrs of laser irradiation. The peak at 3420 cm^{-1} is assigned to the O-H stretching vibration modes in alcoholic or carboxylic groups. The peaks at 2960, 2925, and 2855 cm^{-1} are assigned to the C-H stretching vibration modes. The peak at 1780 cm^{-1} of OND (before irradiation) is assigned to the C=O stretching vibration modes in coupled carboxylic groups (-COOH).[1] The peak at 1640 cm^{-1}, is attributed mainly to the bending of O-H or conjugation of C=O with C=C bond. The peak at 1330 cm^{-1} of HND (before irradiation) might be associated with the characteristic vibrational modes resulting from the interaction between O-H bending and ester C-O stretching vibration modes. The peak at 1120 cm^{-1} could be originated from the C-C-O stretching in unsaturated O-H groups. Before the laser irradiation, the OND contains a large amount of the C=O bonds, which is mainly different from the PND and HND. However, such C=O stretching vibration mode disappears after the laser irradiation. Both OND and HND exhibited common enhancement in the peaks related with the C-H and O-H bonds, at 1640 and 1120 cm^{-1}, respectively, resulting in the nearly similar IR spectrum after the laser irradiation.

References:

1. T. Jiang and K. Xu, FTIR Study of Ultradispersed Diamond Powder Synthesized by Explosive Detonation. *Carbon* 1995, **33**, 1663.
2. S. Osswald, G. Yushin, V. Mochalin, S. O.Kucheyev and Y. Gogotsi, Control of sp^2/sp^3 Carbon Ratio and Surface Chemistry of Nanodiamond Powders by Selective Oxidation in Air. *J. Am. Chem. Soc.* 2006, **128**, 11635.

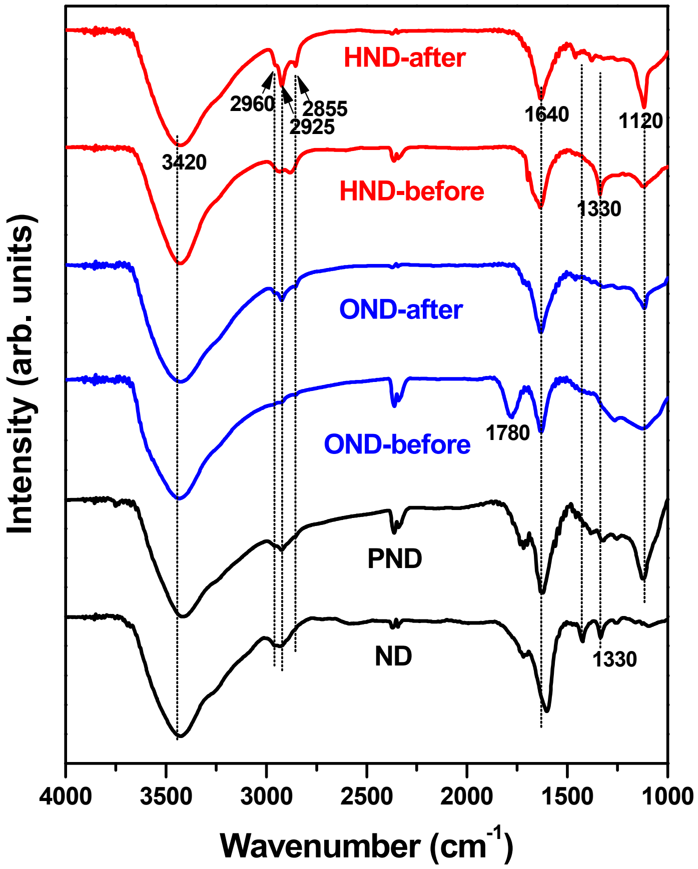
HND-after
2960
2925
2855
1640
1120
3420
HND-before
1330
OND-after
OND-before
1780
PND
ND
1330
Intensity (arb. units)
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm^{-1})

Fig. S3 Raman spectra of the pristine (ND), acid-purified (PND), oxygenated (OND), and hydrogenated ND (HND). Excitation wavelength was set to 514.5 nm Ar ion laser. The C-C *sp*^{3} peak of the ND appears at ~1325 cm^{-1} and the *sp*^{2} peaks at ~1600 cm^{-1} (G band).[1] The peak at 1340 cm^{-1} (D band) originated from the defective *sp*^{2} bonding structures. The spectrum of PND and HND shows the larger D band as compared with the OND, probably due to the C-H and/or O-H on surface.[2] The shoulder at 1240 cm^{-1} and blue-shift G band (1635 cm^{-1}) of OND may be due to the formation of C=O, as suggested by Osswald *et al.*[3] The laser irradiation induces the broader D and G band for all the ND's, resulting from an increase in the H-containing bonds.

References:

1. A. C. Ferrari and J. Robertson, Raman Spectroscopy of Amorphous, Nanostructured, Diamond-like Carbon, and Nanodiamond. *Phil. Trans. R. Soc. Lond. A* 2004, **362**, 2477.
2. K. B. Holt, C. Ziegler, D. J. Caruana, J. Zang, E. J. Millán-Barrios, J. Hu and J. S. Foord, Redox Properties of undoped 5 nm Diamond Nanoparicles. *Phys. Chem. Chem. Phys*. 2008, **10**, 303.
3. S. Osswald, G. Yushin, V. Mochalin, S. O.Kucheyev and Y. Gogotsi, Control of sp^2/sp^3 Carbon Ratio and Surface Chemistry of Nanodiamond Powders by Selective Oxidation in Air. *J. Am. Chem. Soc.* 2006, **128**, 11635.

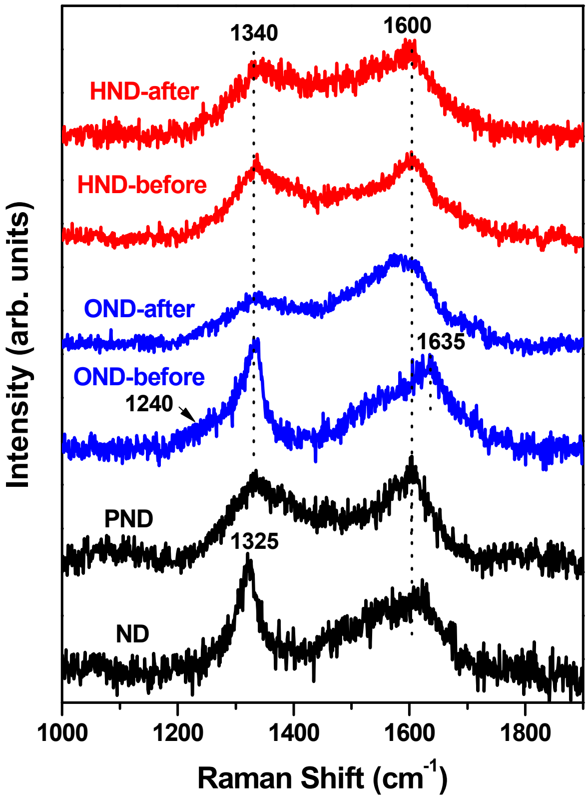

Fig. S4 UV-visible absorption spectrum of the PND, OND, and HND. The spectra were measured in reflection geometry by using the powders. The HND exhibited a larger absorption over the visible range, when compared to the PND and OND, which is probably associated with their surface C-H bonds.[1] Photograph shows the PND, OND, and HND dispersed in water. The HND shows a slightly darker color than the PND and OND.

1. A. E. Aleksenskiĭ, V. Yu. Osipov, A. Ya. Vul', B. Ya. Ber, A. B. Smirnov, V. G. Melekhin, G. J. Adriaenssens and K. Iakoubovskii, Optical Properties of Nanodiamond Layers. *Phys. Solid State* 2001, **43**, 145.