Supplementary Information

On the Relation between Chemical Composition and Optical Properties of Detonation Nanodiamonds

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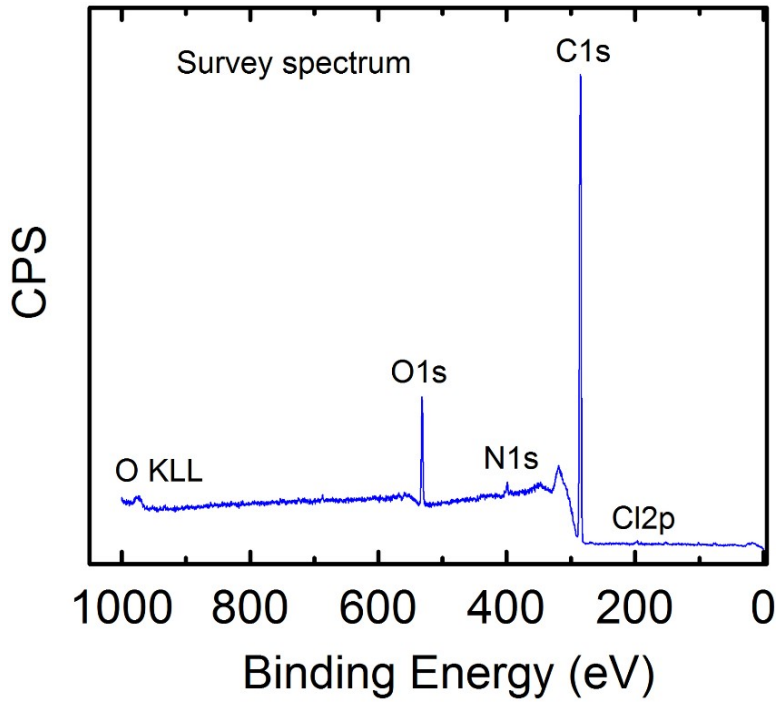

Figure S1.

XPS survey spectrum of DND sample showing presence of C, O, N and traces of Cl.

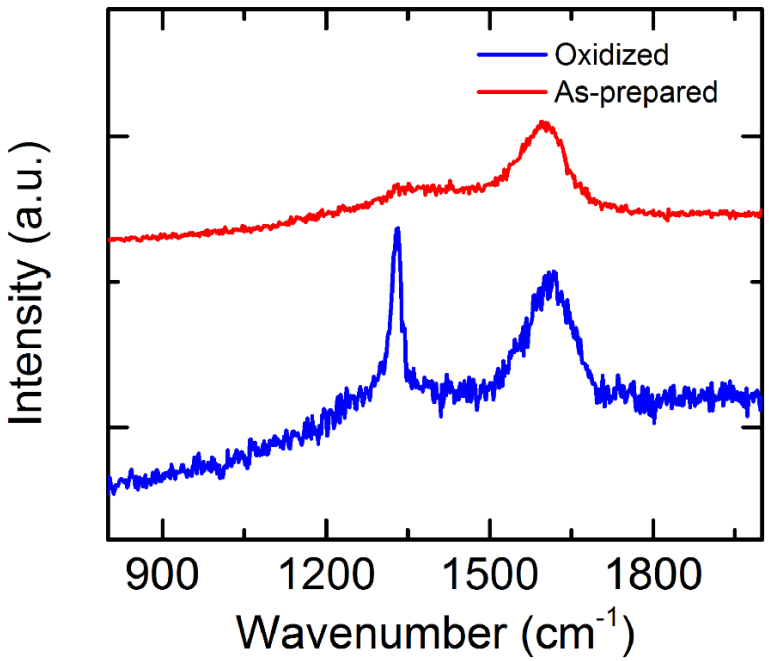

Figure S2.

Raman spectra for the as-prepared (red) and oxidized (blue) cases. Pronounced features are observed in the spectra after shell is removed via oxidation. The feature at 1330 cm^{-1} related to the diamond core gets enhanced relative to the graphite related G-band around 1600 cm^{-1}, as a result of oxidation (blue).(1, 2)

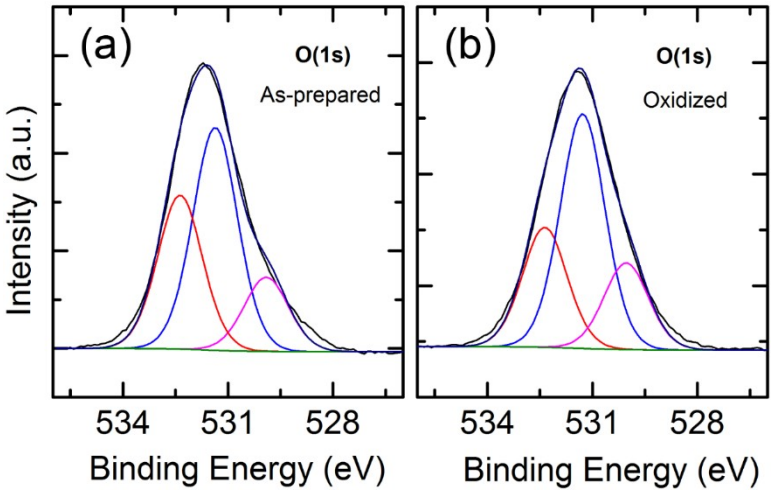

Figure S3.

O (1s) XPS spectra for (a) as-prepared DNDs, and (b) oxidized.

Sample	C(%)			N (%)				O(%)
	Total	sp^3	sp^2	Total	N_{sp^3}	N_{sp^2}	N_{sp^3}/N_{sp^2}	
Oxidized	84.0	45.2	14.8	1.1	0.9	0.2	3.8	14.8
As-prepared	91.1	34.9	42.1	1.8	1.5	0.4	3.7	7.1

Table SI1.

Relative atomic concentrations for the as-prepared and oxidized samples as measured by XPS.

Temperature (°C)	C(%)			N (%)				O(%)
	Total	sp^3	sp^2	Total	N_{sp3}	N_{sp2}	N_{sp3}/N_{sp2}	
Room T	94.4	37.4	35.9	1.4	1.1	0.3	3.0	4.2
200	95.2	38.6	26.3	1.5	1.1	0.4	3.2	3.3
350	96.6	49.4	4.7	1.4	1.1	0.3	3.4	2.0
500	97.4	50.1	3.8	1.4	1.1	0.3	3.8	1.1
700	98.3	55.2	11.3	1.5	1.1	0.3	3.3	0.3
850	98.8	44.1	22.8	1.2	1.0	0.2	5.7	0.0
1000	98.8	39.2	29.9	1.2	1.0	0.2	5.4	0.1

Table SI2.

Relative atomic concentrations of the C, N and O species in the as-prepared DND film at each cycle of thermal annealing, as obtained from XPS.

Discussion

Sequential heating of the as-prepared DNDs was carried out by passing a direct current through the sample in UHV in steps. This was done in an attempt to systematically control the nitrogen and oxygen content of the DNDs along with the sp^2 shell. As the temperature is ramped up in steps, the DNDs begin to lose the sp^2 content. This was accompanied by a decrease of nitrogen, N_{sp^2} and oxygen. A decrease in O suggests that oxygen primarily resides in the graphitic shell of the as-prepared DNDs. At higher temperatures however, the sp^3 core begins to graphitize leading to an increase in the overall sp^2 content. At sufficiently high temperatures, O

vanishes. This experiment suggests that since the sp2 content changes in an incommensurate manner, it might not be possible to systematically control the N and O content in the DNDs along with the sp^2 content.

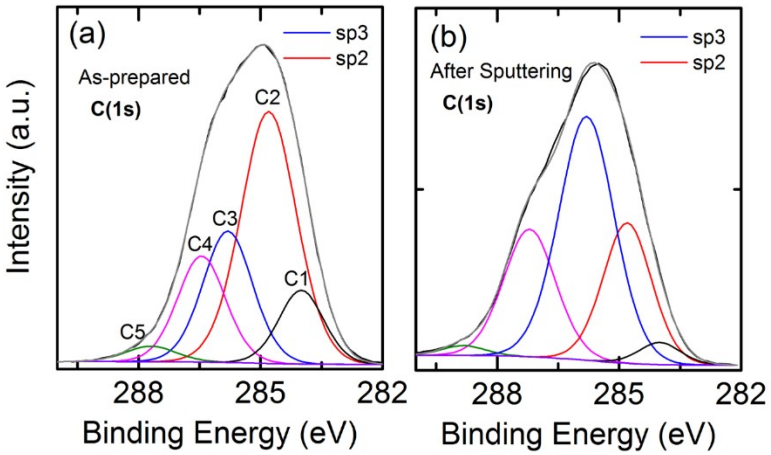

Figure S4.

C (1s) XPS spectra for (a) as-pre pared and (b) Ar^+-sputtered DNDs.

Discussion

The C1s XPS spectra of as-prepared DNDs and after depth profiling are shown in Fig. S4(a) and (b) respectively. In general, the carbon-nitrogen bonding structure can be very complex as both the atoms can be bonded to each other in a large number of ways.(3) The following factors can influence the energy spectra of these systems: the coordination structure of the atom, the atom type distribution and bond length distribution around the atom, and the coordination structure of the nearest neighbor atoms.**(4)** The starting point of C1s peak fitting is based on the results of TGA and the TEM analyses

that suggest the presence of sp^2 and sp^3 C species and consistent with the literature reports.(5) Based on this, peak fitting is performed by fitting five components: C1–C5 (Fig.S4(a,b)). C2 centered at 284.8 eV and C3 centered at 285.8 eV are attributed to C atoms solely bonded to carbon neighbors, as in graphite/amorphous and diamond-like carbon, respectively. When carbon is bonded to nitrogen a shift towards higher binding energies is expected due to the higher electronegativity of nitrogen. Therefore C4 (286.5 eV) and C5 (287.7 eV) can be attributed to various C–N bonds. The exact position and intensity of the C4 and C5 peaks, however, is somewhat uncertain, as the physisorbed water/hydroxyls and organic adsorbates (carboxyl groups) C–O and C=O bonds that are generally detected around the same binding energies might result in multiple overlapping of the components and make it heavily convoluted. The C4 peak can presumably be assigned to C in a nitrile group.(6) C1 (283.8 eV) has been assigned to the nitrogen induced fullerene-like defects in the DND graphitic shells.(6,7) Although the C1s remains quite convoluted but an overall decrease of the sp^2 graphitic carbon content starting from ~36% in the as-prepared sample to ~20% after sputtering is apparent (see Supplementary Table SI3 below).

Sputtering cycle	C(%)			N (%)				O(%)
	Total	sp^3	sp^2	Total	N_{sp3}	N_{sp2}	N_{sp3}/N_{sp2}	
As-is	93.6	36.9	36.0	1.4	1.0	0.4	2.9	5.0
1	92.8	33.3	36.5	1.5	1.1	0.4	2.7	5.6
2	94.3	47.9	13.7	1.4	1.1	0.3	4.0	4.3
3	94.5	42.8	20.7	1.2	1.0	0.2	4.9	4.3
4	94.5	47.9	12.4	1.4	1.1	0.2	4.5	4.1
5	94.7	45.4	11.0	1.3	1.1	0.2	5.3	4.0
6	94.8	42.5	19.6	1.4	1.1	0.2	4.8	3.9

Table SI3.

Relative atomic concentrations of the C, N and O species in the DND film at each cycle depth profiling, as obtained from XPS. Each cycle involved 3 minutes of ion bombardment.

References

1. Smith BR, Gruber D, Plakhotnik T. The effects of surface oxidation on luminescence of nano diamonds. Diamond and Related Materials. 2010;19(4):314-8.
2. Chung PH, Perevedentseva E, Cheng CL. The particle size-dependent photoluminescence of nanodiamonds. Surface Science. 2007;601(18):3866-70.
3. Titantah JT, Lamoen D. Carbon and nitrogen 1s energy levels in amorphous carbon nitride systems: XPS interpretation using first-principles. Diamond and Related Materials. 2007;16(3):581-8.
4. **Lu Y-G, Turner S, Verbeeck J, Janssens SD, Haenen K, Van Tendeloo G. Local bond length variations in boron-doped nanocrystalline diamond measured by spatially resolved electron energy-loss spectroscopy. Applied Physics Letters. 2013;103(3):032105.**
5. Osswald S, Yushin G, Mochalin V, Kucheyev SO, Gogotsi Y. Control of sp2/sp3 Carbon Ratio and Surface Chemistry of Nanodiamond Powders by Selective Oxidation in Air. Journal of the American Chemical Society. 2006;128(35):11635-42.
6. Barinov A, Malcioğlu OB, Fabris S, Sun T, Gregoratti L, Dalmiglio M, et al. Initial Stages of Oxidation on Graphitic Surfaces: Photoemission Study and

Density Functional Theory Calculations. The Journal of Physical Chemistry C. 2009;113(21):9009-13.

7. Susi T, Kaukonen M, Havu P, Ljungberg MP, Ayala P, Kauppinen EI. Core level binding energies of functionalized and defective graphene. Beilstein Journal of Nanotechnology. 2014;5:121-32.