SUPPLEMENTARY INFORMATION

“Size and Purity Control of HPHT Nanodiamonds down to 1 nm”

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Comparison of (111) XRD peaks of DND and HPHT nanodiamonds of similar size distribution

Figure S1. Comparison of X-ray diffraction peak of (111) plane of MSY18-O3 (black) and DND-asrec nanodiamonds (red). The narrow blue line corresponding to diffraction angle of monocrystalline diamond is shown for comparison.

Figure S1 shows X-ray diffraction patterns ((111) plane) of DND-asrec and MSY18-O3 NDs in comparison with monocrystalline diamond standard. The peak of MSY18-O3 is more or less symmetrically broadened and the peak maximum matches that of monocrystalline diamond. In comparison, the peak of DND-asrec is obviously more broadened (asymmetrically) and its maximum is shifted to lower diffraction angles. The mean size values estimated from XRD by means of Scherrer equation are: 3.2 nm for DND-O and 7.2 nm for MSY18-O3. It is obvious that the size values obtained from XRD are underestimated for DNDs and overestimated for MSY nanodiamonds in contrast to AFM analysis which, in our opinion, provides values of very good accuracy, including size distribution. In addition, any size analysis of polydisperse nanoparticles by means of XRD is problematic due to the same reasons which are already mentioned in the discussion of Raman spectra, i.e. in addition to the size effect also inhomogeneous strain and crystal lattice imperfections contribute to the broadening and shift of the peaks in diffractograms.
AFM particle analysis of DNDs on Si substrate

The DNDs (detonation nanodiamond) deposited on Si substrate is shown in Figure S2a. It is obvious that except for several bigger clusters the main fraction is composed of single DNDs. The derived size distribution (Figure S2b) shows that the mean particle size of DNDs is ~4 nm.

![AFM topography image (1×1 μm²) of DNDs on Si substrate](a). Size distribution histogram derived from the AFM data showing mean particle size ~4 nm (b).

**Figure S2.** AFM topography image (1×1 μm²) of DNDs on Si substrate (a). Size distribution histogram derived from the AFM data showing mean particle size ~4 nm (b).

Comparison of STEM images of representative detonation and HPHT nanodiamonds

![Comparison of STEM images](a) Detonation nanodiamond, (b) HPHT nanodiamond.
Figure S3. STEM images of single DND (a) and HPHT (MSY18-O3) nanodiamond particle (b).

STEM images of representative DND (DND-asrec; 3.8 nm) and HPHT (MSY18-O3; 3.4 nm) nanodiamonds (NDs) are shown in the Figure S3. Despite both particles are crystalline there are several important differences between them. 1) The shape of the DND particle is slightly irregular and does not show any distinct facetting in contrast to the HPHT particle which appears as cuboctahedron formed by (111) and (100) planes. 2) There are obvious lattice defects and distortions mainly in the upper part of the DND particle in contrast to the HPHT particle which resembles nearly perfect crystal. 3) There is noticeable disordered in the outer region of the DND particle which is missing in the case of the HPHT particle.

Surface chemistry of MSY18 NDs as resolved by FTIR spectroscopy

![Figure S4](image)

Figure S4. Full range FTIR spectra (a) and 1000-2000 cm\(^{-1}\) region (b) of the MSY18 NDs before (MSY18-asrec) and after air-annealing at 450°C for 30 min (MSY18-O1), 60 min (MSY18-O2), 120 min (MSY18-O3) and at 500°C for 30 min (MSY18-O4).

Figure S4a shows full range Fourier-transformed infrared (FTIR) spectra characterizing surface functional groups of MSY18 NDs before and after air-annealing. For the MSY18-asrec,
the main features in the spectrum are related to O–H stretching (2500-3500 cm\(^{-1}\)) and bending (1625 cm\(^{-1}\)) vibrations from covalently attached functional groups and/or water adsorbed on the DNP\(\text{s}\) surface, and the C=O stretching at 1734 cm\(^{-1}\). This indicates a presence of carboxylic acid groups (1), (2) bonded to the amorphous non-diamond carbon shell and partially also to diamond cores. The carboxylic acid groups most probably results from wet chemical purification in strong acids such as sulphuric acid. A shoulder at 1590 cm\(^{-1}\) is ascribed to the presence of C=C symmetric stretching vibrations from the non-diamond phase which is detected also by other analyses. A very broad absorption feature at 800–1500 cm\(^{-1}\) is a combination of many overlapping peaks, which besides C–O–C stretching may include the O–H deformation, C–C stretching vibrations, peaks related to nitrogen defects, and other groups (1). In general the FTIR spectrum of the MSY18-asrec resembles that of graphene oxide where the main functional groups identified are carboxylic acid (–COOH), epoxy (C–O–C) and alcohol (–OH) groups (3), (4).

The FTIR spectra of annealed MSY18-O1 to O4 differ to some extent from the spectra of the MSY18-asrec. Most pronounced differences occur in the 1000-2000 cm\(^{-1}\) region as shown in Figure S4b.

First, the low-wavenumber shoulder (1590 cm\(^{-1}\)) of the 1625 cm\(^{-1}\) peak, which indicates the presence of C=C symmetric stretching vibrations from graphitic phase, is considerably decreased just after 30 min air-annealing at 450°C.

Second, the C=O peak position shifts from 1734 to 1790 cm\(^{-1}\) after the air-annealing. This indicates a change of the surface chemistry and along carboxyls also formation of anhydrides and lactones which shifts the carbonyl peak to higher frequencies/wavenumbers.

Third, in the FTIR spectra of all annealed nanoparticles MSY18-O1 to O4 the well resolved doublet bands centred in 1090-1287 cm\(^{-1}\) were observed. We assign them to symmetric (1090 cm\(^{-1}\)) and asymmetric (1305 cm\(^{-1}\)) C–O stretching vibrations from alcohol and carboxylic acid or carboxylic acid derivatives (anhydrides and lactones), respectively.

In addition, the band at 1462 cm\(^{-1}\), characteristic for air-annealed NDs (5) rises as the annealing progresses. Although origin of this band remains speculative it most probably originates from an oxygen containing moiety bonded to the diamond surface. Otherwise the spectra of all the air-annealed samples are very similar. Note that no trace of C–H groups (2800–3000 cm\(^{-1}\)) was detected in any of MSY18 sample.

The FTIR spectra of the DND-O and MSY18-O1 samples are compared in Figure S5. In the full range FTIR spectrum of the DND-O and MSY18-O1 samples (Fig. S5a) only the features related to OH stretching vibrations (2800-3700 cm\(^{-1}\)) and OH bending vibrations (~1625 cm\(^{-1}\)) are highlighted. It is obvious that both DND-O and MSY18-O1 exhibit the OH-related features which may be due to the adsorbed water together with OH bonds coming from the surface functional groups. The signal from OH bonds (~OH, C-O-H) is surprisingly higher in the case of
the MSY18-O1 nanoparticles, which is probably related to different quality of HPHT nanoparticles.

![FTIR spectra](image)

**Figure S5.** Full range (left) and 1000-2000 cm\(^{-1}\) region (right) FTIR spectra of MSY18-O1 and DND-O annealed at the same conditions (450°C, 30 min).

The FTIR data are well correlated well with Raman and XPS spectra showing clear differences between the as-received and air-annealed MSY18 nanoparticles. The Raman spectra indicate for instance the presence of the non-diamond phase (1590-1640 cm\(^{-1}\)) on the surface of MSY18-asrec, which decreases just after the short-term (30 min) air-annealing. Our results are in a good agreement with those reported by Mochalin et al. (6) regarding the air-annealing of DNDs at 425 °C and disappearance of the small broad C=C peak at 1600 cm\(^{-1}\) within 60 min. Ando et al. (2) proposed that the oxidation of DNDs is complete at 480 °C, and a decomposition of oxygen containing structures occurred above 480 °C. Jiang et al. (7) demonstrated the complete oxidation of DND nanoparticles at temperature of 500°C. A similar study on HPHT nanoparticles has been however missing so far. We observed only slight progression in the IR spectra of MSY18-O1 to O4 samples. It indicates that the air-annealing for 30 min is already sufficient to obtain oxidized NDs of high quality. It is in a good agreement with the XPS measurements indicating the similar surface chemistry of MSY18 NDs independent of annealing time (within the applied period).
Modified phonon confinement model (PCM)

In order to incorporate the particle size distribution, the PCM model was modified. The original PCM formula for the Raman intensity is

\[ I(\omega) \approx \int \frac{e^{-q^2L^2/4\pi}}{(\omega-\omega(q))^2+\gamma^2} dq \]  

(S1)

with \( L = LD / a \), where \( LD \) is the domain length, \( a \) the lattice constant (different for different crystallographic directions) and \( \gamma \) is the natural FWHM for a diamond crystal including instrumental broadening. A disadvantage of this formula is that it is not normalized, i.e. the integral intensity is dependent on \( L \). We have found that the formula can be modified as

\[ I(\omega) = \frac{\Gamma L^3}{K} \int \frac{e^{-q^2L^2/4\pi}}{(\omega-\omega(q))^2+\gamma^2} dq \]  

(S2)

with \( K \sim 275.7 \text{ cm}^{-1} \), to approximately fulfill the condition for unit peak area,

\[ \int_0^{\infty} I(\omega) d\omega = 1. \]  

(S3)

In the approach of Ager (8), the phonon dispersion \( \omega(q) \) was averaged from the measured phonon density of states as

\[ \omega(q) = A + B\cos(q\pi) \]  

(S4)

with \( A = 1241.25 \) and \( B = 91.25 \). Yoshikawa (9) used \( A = 1193.75 \) and \( B = 139.25 \) and in addition, they replaced the natural linewidth by

\[ \Gamma = a + \frac{b}{L} \]  

(S5)

where the constants \( a,b \) were fitted to the Raman spectra of selected grains fractions. This was, however, done for particles up to 500 nm.

Osswald (10) used the formula (S1) with the dispersion \( \omega(q) \) fitted as a polynomial with parameters specific of each of the selected 7 phonon modes \((\Lambda_1, \Lambda_3, \Delta_2, \Delta_5, \Sigma_1, \Sigma_2, \Sigma_3)\). The intensity of each mode and \( L \) for each mode were fitted to the measured Raman spectra. In our approach, we used the formula (S2) and assumed that the line broadening is given solely by varying \( L \) and dispersion \( \omega(q) \) for the 7 phonon modes, i.e. the \( \Gamma \) was constant and equal to our measured FWHM of the reference diamond single crystal \((8.6 \text{ cm}^{-1})\). The composite function with the incorporated particle size distribution fulfilling the condition (S3) is

\[ I(\omega) = \frac{1}{7} \sum_{i=1}^{M} \sum_{k=1}^{N} P_i f_{i,k}(\omega, L_i, \Gamma, \omega_k(q)) \]  

(S6)
where \( P_i \) is the volumetric fraction of DNP of size \( LD_i \) out of \( M \) sizes evaluated by AFM and

\[
 f_{i,k}(\omega) = \frac{\Gamma L_i^3}{k} \frac{e^{-q^2 L_i^2}}{4 \pi q^2} \int \frac{dq}{(\omega - \omega_k(q))^2 + \frac{\Gamma^2}{4}} \tag{S7}
\]

with \( L_i = D_i / a_k \) where \( D_i \) is the particle diameter, \( a_k \) is the lattice constant corresponding to specific phonon mode (0.206 nm for \( \Lambda \) modes, 0.357 nm for \( \Delta \) modes, and 0.252 nm for \( \Sigma \) modes. We found that including the equation (S4) did not substantially improve the fit. Moreover the shape of the MSY-01 diamond Raman peak can be reproduced very well even without any fitting, just with the given parameters.

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