Production of Metal-free Diamond Nanoparticles

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Supporting Information

This file contains extended data and figures for XPS measurements (Fig. S1, Table S1, Fig. S2, Fig. S3, Fig. S4).

**FIGURE S1. Survey XPS spectrum of pristine single crystal diamond (SC)**

XPS survey spectrum of the single crystal diamond sample before the milling process, and after a cluster argon ion cleaning. As expected, the only peaks detected are the carbon C1s and the oxygen O1s. The Si2p observed in the sample after tempered steel milling in figure 1b and 1c in the paper, was due to surface contamination and can be removed after an argon ion cleaning.
TABLE S1. Samples composition in atomic percentages

| Samples                          | Composition (%) | O1s/C1s ratio |
|----------------------------------|-----------------|---------------|
|                                  | C1s  | O1s  | N1s  | Fe2p | Si2p |               |
| Before Milling                   | 90.6 | 7.4  | 0.29 | -    | 1.60 | 0.08          |
| Before Milling (Ar. Cluster)     | 96.5 | 3.41 | -    | -    | 0.05 | 0.03          |
| After Milling (Temp. Steel)      | 27.5 | 40.1 | -    | 16.6 | 15.85| 1.45          |
| After Milling and cleaning (TS)  | 38.8 | 40.3 | -    | 0.20 | 20.6 | 1.03          |
| After Milling and cleaning (Si₃N₄) | 18.2 | 38.2 | 15.6 | -    | 28.1 | 2.09          |

Table S1. Composition of the different samples in atomic percentages.

The samples composition in atomic percentages as calculated from the XPS survey spectra (shown in the paper in figure 1).¹

It has to be noticed that these atomic percentages are calculated from XPS spectra taken in diamond nanoparticles and therefore the values for the atomic percentages are not as reliable as the ones taken in bulk diamond samples, due to differences in surface-volume ratios and consequently are just an indicator.

The as-received sample after a cluster argon ion cleaning shows the highest C1s content (96.5%) whereas the sample milled with silicon nitride shows the lower C1s content. After the tempered steel milling process, the C1s content decreases with the appearance of the Fe2p peak due to iron contamination produced during the milling. The iron content is reduced after the acid cleaning process. On the other hand, iron was not detected in the SC sample after silicon nitride milling.
FIGURE S2. High resolution XPS spectrum of Si2p peak

The high resolution XPS spectrum of the Si2p shows a clear shift of the Si2p peak for the silicon nitride and the tempered steel samples, which corresponds to different Si bonding species on the particles’ surface. The silicon nitride milled sample (shown in Figure S3 a)) shows two Gaussian peaks at 101.1 eV and at 102.4 eV, associated with the presence of silicon carbide (SiC) and silicon bonded to nitrogen respectively. For the sample milled with tempered steel, a single Gaussian like peak centred at 103 eV appears, attributed to silicon dioxide.²

Figure S2. Deconvolution of the Si2p peak for the samples milled with a) silicon nitride and b) tempered steel.
For the SC sample milled with silicon nitride (Figure S4 a)), the O1s peak can be deconvoluted with three Gaussians, centred at 531.1 eV, 532 eV and 535.8 eV. The first peak is associated with C=O bonds, the peak at 532 eV is due to C-O bonds and the peak at 535.8 eV can be attributed to carboxyl groups (COOH) or can also be due to atmospheric O₂ or CO₂ absorbed. The high resolution XPS spectrum of the O1s peak for the tempered steel sample can also be fitted with three Gaussians. The peak at 530 eV is associated with metal oxide bonds (Fe=O), the peak at 532 eV corresponds to organic bonds (C-O) and the peak at 533 eV can be attributed to hydroxyl (C-OH) compounds or SiO₂.
FIGURE S4. High resolution XPS spectrum of N1s peak

The XPS spectrum of the N1s peak, can be fitted with a single peak at 396.2 eV related to Si=N bond.

REFERENCES

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