**Electronic supplementary materials** *Mendeleev Commun.*, 2022, **32**, 132-135

# Magnetic resonance tracking of copper ion fixation on the surface of carboxylated nanodiamonds from viewpoint of changes in carbon-inherited paramagnetism

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## Contents

## S1. General information and Experimental Procedures

DND surface was functionalized by $Cu^{2+}$ ions in water suspension of DND. It was done through the ion exchange reaction between the protons of carboxyl groups located on the DND surface and $Cu^{2+}$ cations just after adding the certain amount of 0.3 wt.% water solution of copper nitrate $Cu(NO_3)_2 \times 3H_2O$ into 0.5 wt.% water suspension of DND and subsequent agitation and stirring. The details of procedure were described earlier in Ref.S1. We also used a similar technique to modify the surface of DND particles with gadolinium ions.[S2] As a precursor DND suspension we used the suspension ND-5-nm-N-$H_2O$ (concentration 10 mg/ml) from Adamas-Nanotechnologies, Inc., Raleigh, NC, USA (Figure S1, left). A feature of this suspension is the use of zirconium dioxide balls for grinding DND and subsequent preparation of a stable suspension of 5-nm particles. It was diluted in two times by distilled deionized water for all other subsequent works. As copper nitrate trihydrate (M=241.60), we used a high-purity product (Figure S1, right) from Fujifilm Wako Pure Chemical Corporation (Osaka, Japan).

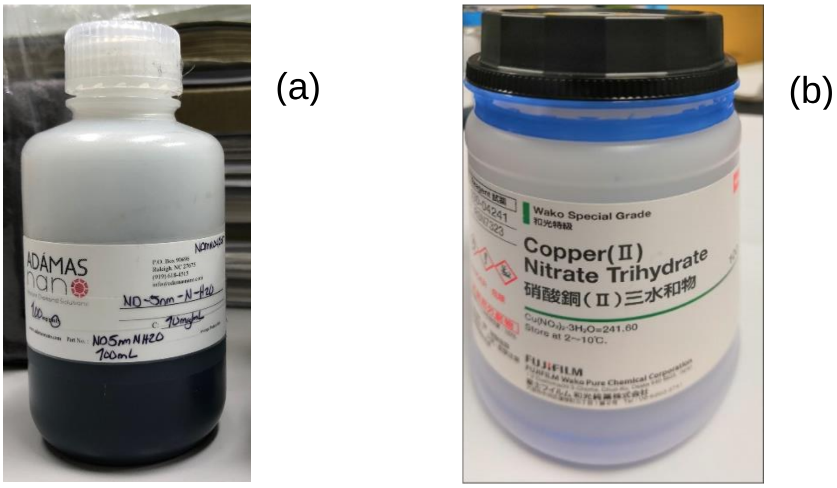

**Figure S1.** Industrial precursors used to prepare DND particles modified with copper ions: water suspension of DND (a), copper nitrate trihydrate (b).

After agitation and stirring the obtained suspension was subjected to intensive centrifugation at 13000 rpm and the sedimented product from the bottom was dried. The scheme of modification of the surface of DND particles with copper ions, specially adapted for readers, is shown in Figure S2. Images of the suspension after mixing with a nitrate solution and stirring, and then after centrifugation are shown in Figure S2 (e, f). It is important to note that the process of functionalization of DND particles with copper ions is accompanied by a change in the color of the suspension from the initial deep black to gray. This is a specific marker of the passage of the ion exchange reaction and the fixation of metal ions in chelate positions between carboxyls. The pellets were dried in secondary vacuum at ~50$^{o}$C. The yield of final product was about ~60 mg. The last panel (g) in Figure S2 shows an image of a dry copper-modified product in a 4 mm diameter quartz EPR tube.

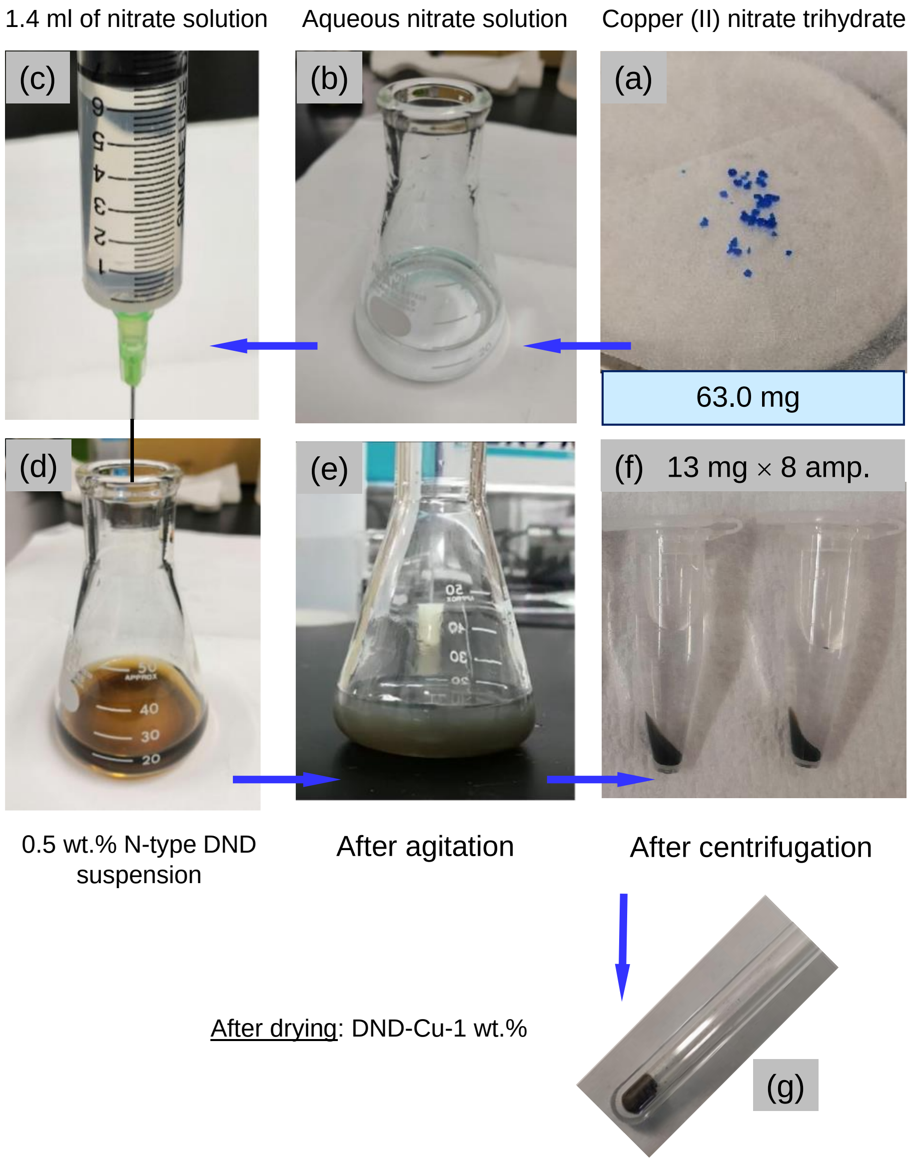

**Figure S2**. Illustrative diagram of the modification of DND particles with bivalent copper ions. Stages: weighing a sample of copper nitrate trihydrate, (b) preparation of a nitrate solution of a given concentration, (c), (d) - adding several milliliters of nitrate solution to a 0.5 wt.% DND suspension, (e) - agitation and stirring of the mixture, (f) - centrifugation with sedimentation of a solid component, (g) - obtaining a dry product intended for magnetic research.

## S2. Characterization

### S2.1 *Electron paramagnetic resonance*

X-band EPR spectra were studied at the Ioffe Institute. For each sample, when it was loaded into a microwave cavity, a new clean quartz tube with an outer diameter of 4 mm was used. The samples were repeatedly measured under different conditions for recording the spectra for 6 months. All measurements were taken at room temperature. The spectra recorded at different times were compared with each other in order to confirm the stability of the EPR characteristics and the absence of degradation of the $Cu^{2+}$ subsystem after synthesis.

*Spectrum splitting procedure*. As an example, consider the procedure for splitting the EPR spectrum into components for sample D2. The EPR spectrum of sample D2 is presented in Figure S3 in integral representation (after single integration of the experimentally measured spectrum with respect to the variable magnetic field).

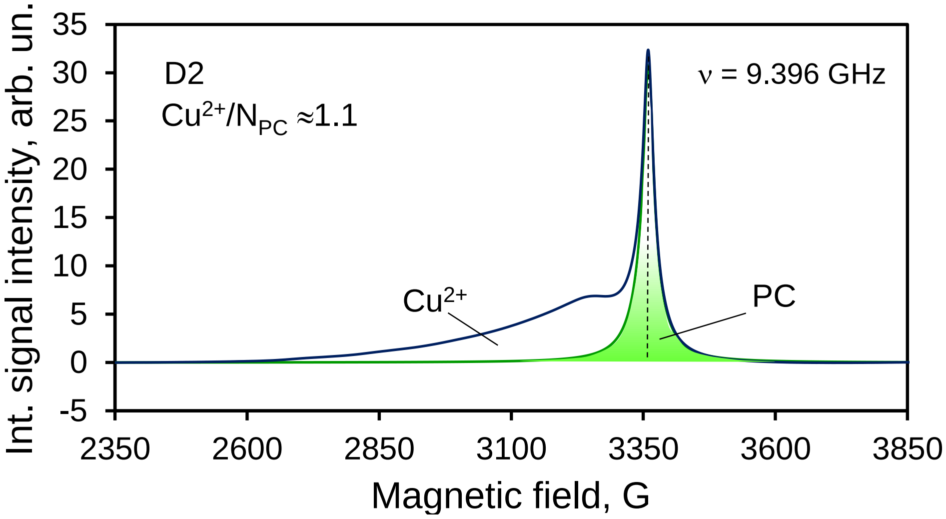

**Figure S3.** EPR spectrum of sample D2 after integration over the variable H (magnetic field) in the range 2350-3850 G, showing contributions from $Cu^{2+}$ ions (open area) and the DND matrix itself (shaded in green). $T = 293$ K. Microwave frequency – 9.397±0.001 GHz.

More precisely, Figure S3 shows the total consolidated EPR signal from all types of spins obtained after numerical integration of the primary signal of the first derivative of absorption ($dA/dH$) in a wide range of magnetic fields from 2350 to 3850 G. A flat even background in the regions <2500 G and >3650 G allows one to well determine the base zero level and thereby separate the signals from the DND carbon matrix proper and copper ions, and metrologically accurately estimate the contribution to the total signal from copper ions per unit mass of carbon or the total number of spins in the diamond matrix. On the integrated EPR spectrum in Figure S3, a relatively narrow EPR signal from the DND is specially highlighted in green, which is a superposition of two Lorentzian contours of different widths. It is easily identified due to the large amplitude of the resulting signal with $g = 2.0027$ from defects in the diamond matrix. From the integrated EPR spectrum D2 in Figure S3, it can be seen that the contributions to the integrated intensity of the EPR signal from $Cu^{2+}$ spins $^{1}/_{2}$ and spins $^{1}/_{2}$ of the diamond matrix are approximately the same, and to correctly determine the proportion of the former, it is necessary to subtract the EPR signal of the diamond matrix from the total consolidated signal. Subtraction of the narrow DND EPR signal (two Lorentzian contours L1, L2) from the integral spectrum made it possible to accurately determine the EPR signal from $Cu^{2+}$ in the integral representation, and thereby estimate the relative concentration of copper ions in all samples of the series. Difference EPR spectra of bivalent copper ions for samples D1-D3 are shown in Figure S4 in integral representation. Each of them was obtained by direct subtraction of the EPR signal of the diamond matrix from the integral EPR spectrum of the corresponding sample. Noteworthy is the feature at H = 3360.7 G. It is located at the edge of the descending high-field slope of the spectrum and is possibly associated with some additional signal of unknown origin or an artifact of numerical processing. The latter is clearly seen in the direct differentiation of the integral EPR spectra D1-D3. The *g*-factor of this signal is 2.0030 (after correcting the magnetic field values). Note that in Figure S4 the horizontal axis shows the uncorrected value of the magnetic field obtained from the Hall sensor, and for precision calculations, the field was corrected by 8.28 G downward when using a powder EPR standard with a *g*-factor of 2.0024. The spectra in Figure S4 are not reduced to the unit weight of the powders, but are normalized to the total number of 1/2 spins ($N_{PC}$) in the diamond matrix, i.e. on the intensity of the narrow main EPR signal with a *g*-factor of 2.0027 from a group of spins located in diamond particles.

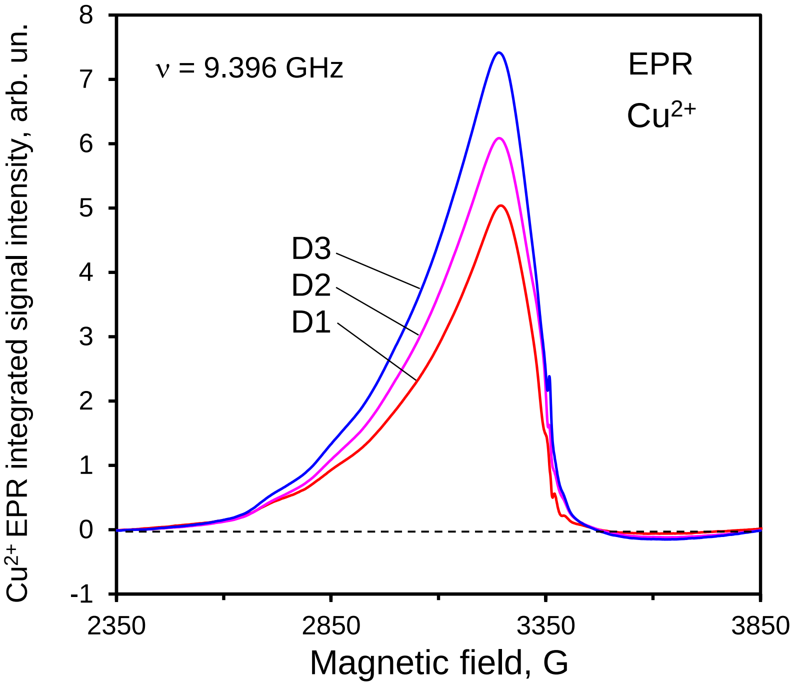

**Figure S4.** Integral, obtained after mathematical processing, EPR spectra of $Cu^{2+}$ ions adsorbed on DND particles for samples D1-D3. Microwave frequency: 9.396 GHz. Temperature T=293 K. Before processing, the original spectra were recorded with the following parameters: microwave power - 2 mW, magnetic field modulation - 1 G, single spectrum recording time 90 sec, number of signal accumulations - 6. The subtracted EPR signal from the diamond matrix was represented as the sum of two Lorentzian contours of different widths with approximately the same *g*- factors.

For these three spectra, the ratio of the numbers of spins in both spin groups $[Cu^{2+}]/N_{PC}$ varies from 0.91 to 1.34. As this ratio increases, the widths of the Lorentz contours *L1* and *L2* increase as shown in Figure S5. As can be seen from Figure S5, the broad Lorentzian component of the EPR signal (*L*2) is more sensitive to the amount of ionic copper on the surface. The reason for this is that the *L*2 component is caused by paramagnetic centers of shallow (0.76 nm) occurrence, and the narrow component *L*1 is caused by paramagnetic centers located deeper (~1.1 nm). The broadening mechanism is a dipole-dipole interaction between the spins of both groups - copper spins and spins in a diamond lattice.

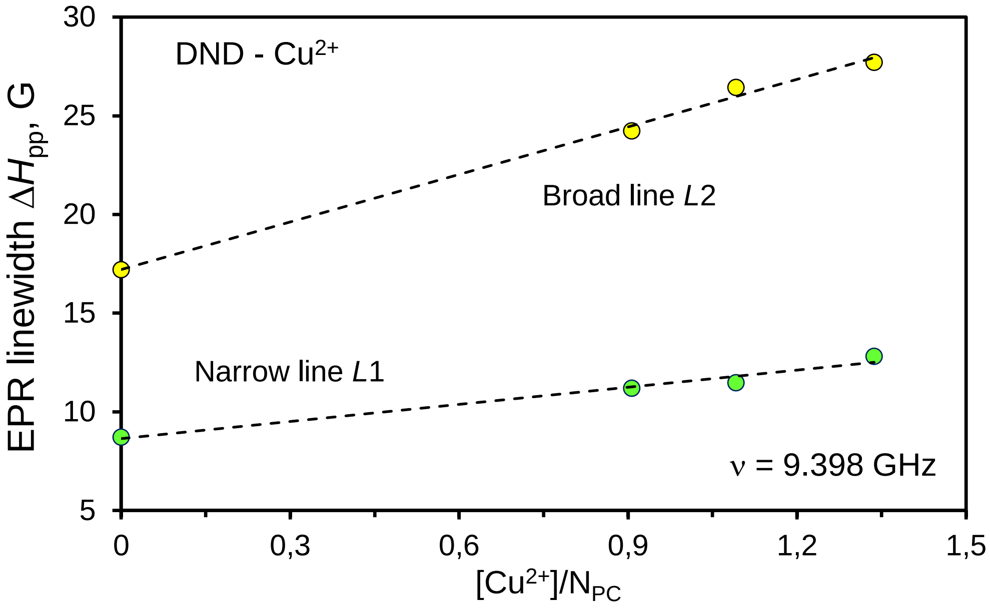

**Figure S5.** Dependences of the widths of the narrow (*L*1) and broad (*L*2) Lorentzian components of the main EPR signal ($g$=2.0027) of the DND on the relative content of paramagnetic copper on the particle surface.

Here we should also note the following about the used DND precursor. Of the foreign elements in the DND precursor, only zirconium was found (in addition to natural impurities of nitrogen and oxygen). Its presence is due to the use of grinding balls made of zirconium dioxide in the production technology of a 5-nm DND suspension and a small amount of their traces (micro-fragments) in the final product. Since the $Zr^{4+}$: $[Kr]5s^0 4d^0$ ions in stoichiometric $ZrO_2$ have zero magnetic moment, they should not affect the observability of the EPR spectra. Here we also neglect the influence of paramagnetic defects in pure zirconium dioxide, namely: $Zr^{3+}$ ions, yielding an axial signal ($g_{\parallel} = 1.958$ and $g_{\perp} = 1.979$) and oxygen monovacancies. No specific EPR signals with a $g$-factor $g < 2$ located in the high-field wing of the main EPR signal of the DND were found.

### S2.2 *X-ray photoelectron spectroscopy*

The XPS spectra of the original unmodified DND-*ini* and samples D1 and D3 were studied using equipment from the Hosei University and the Research Park of Saint-Petersburg State University. To study D1 and D3, a complex spectrometer Thermo Fisher Scientific Escalab 250Xi was used. Aggregates of nanoparticles D1 and D3 were deposited in a thick layer on a silicon substrate from aqueous-alcoholic suspensions of the corresponding powder samples. The survey XPS spectra of samples DND-*ini* 5-nm and D3 are shown in Figure S6 a,b together with the fragments of the spectra of the peaks C1s, N1s, Cu2p and Zr3d for sample D3 (panels c,d,e,f). The spectrum of O1s in high resolution is not shown here. The relatively large heights of the O1s peaks in both survey spectra (Figure S6 a, b) indicate a high concentration of oxygen-containing groups on the surface of 5-nm DNDs that can bind metal ions. After the addition of ionic copper, the intensity of the O1s peak in the XPS spectrum for D3 practically does not change, but new weak peaks appear in the spectrum at 930-960 eV associated with the Cu2p signal (Figure S6 b,e).

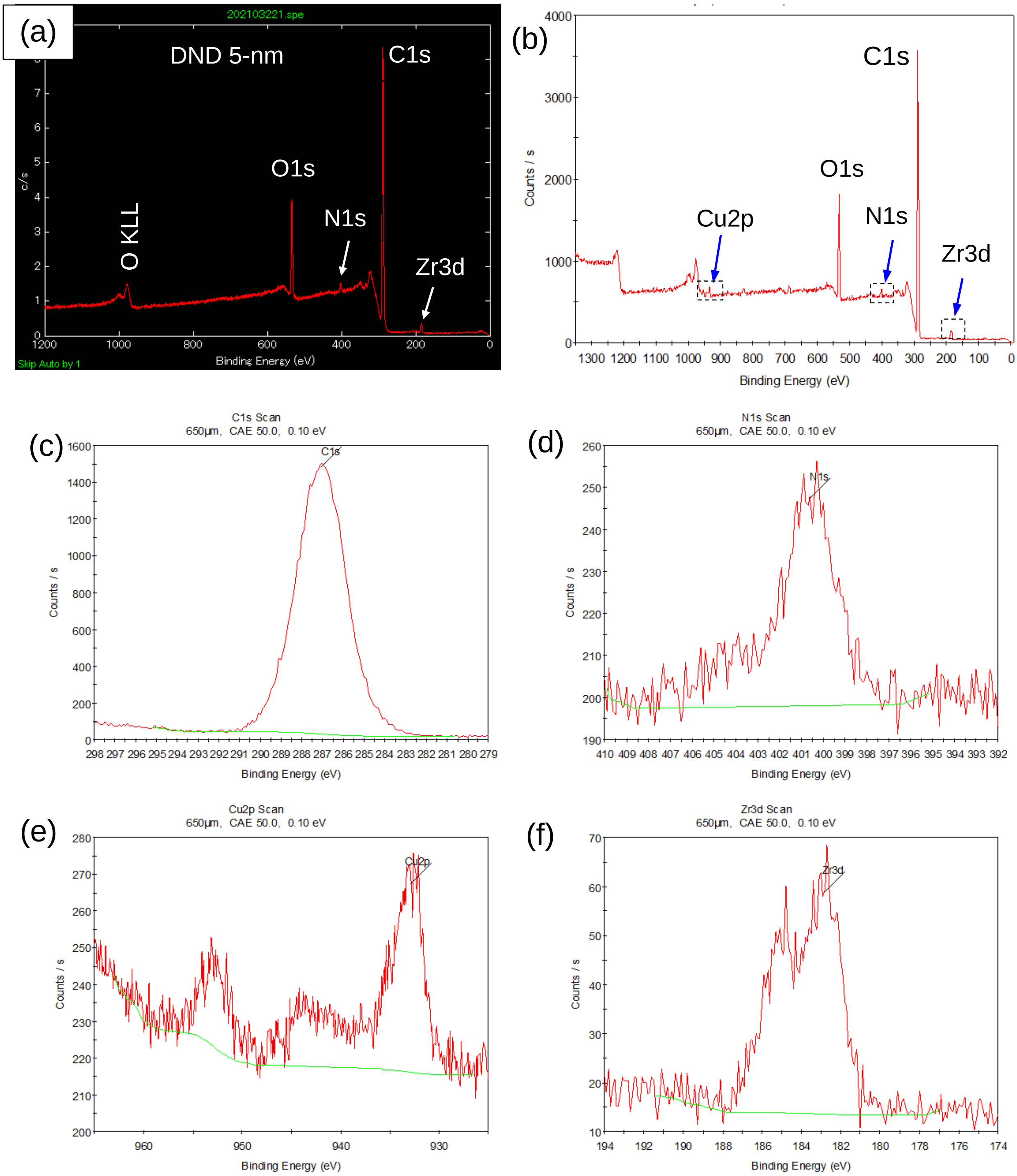

**Figure S6.** The survey XPS spectra of samples DND-*ini* (a) and D3 (b) together with detailed spectra of peaks C1s (c), N1s (d), Cu2p (e) and Zr3d (f) for sample D3. Copper content: 2.28 wt.%.

It is very useful to compare the details of individual lines in the XPS spectra from elements C, O, N in 5-nm DND with those for DND aggregates studied in Ref. S3. The high-energy wing (B.E. above 402 eV) of the N1s signal, extending along the energy scale by ~6 eV, as in the Ref. S3, is associated with surface nitrogen-oxygen groups, and the main central peak (at ~400.5 eV) with impurity nitrogen atoms in the *sp*$^3$ covalent lattice of diamond. The concentration of such nitrogen in DND exceeds 2 at.%. Data on the content of individual elements in samples D1 and D3 are shown in Table S1. They were obtained from the analysis of the XPS spectra of samples D1 and D3.

**Table S1.** Elemental composition of samples D1 and D3 for the first five elements most prevalent in them.

| | Sample D1 | | | Sample D3 | | |
|---|---|---|---|---|---|---|
| Element and level | Content, at. % | Content, wt. % | $ZrO_2$-corrected content, wt. % | Content, at. % | Content, wt. % | $ZrO_2$-corrected content, wt. % |
| C1s | 84.69 | 78.40 | 81.006 | 83.74 | 76.62 | 79.448 |
| O1s | 12.62 | 15.58 | 15.227 | 13.14 | 16.03 | 15.661 |
| N1s | 2.05 | **2.21** | 2.288 | 2.27 | **2.42** | 2.513 |
| Cu2p | 0.29 | **1.42** | 1.479 | 0.47 | **2.28** | 2.378 |
| Zr3d | 0.34 | **2.39** | - | 0.38 | **2.64** | - |
| | 99.99% | 100% | 100% | 100% | 100% | 100% |

According to XPS, for sample D3, the copper content is 0.47 at% or ~2.3 wt%. This corresponds to 54 copper atoms on one DND particle 5 nm in size. This is 1.5-1.6 times more than the value determined by the SEM-EDX method. At the same time, according to the EPR data, the [$Cu^{2+}$] / $N_{\mathrm{PC}}$ ratio is 1.34. Since the concentration of PC in DND is ~1300 ppm, the number of $Cu^{2+}$ ions in one DND particle of 5 nm in size is **20**. Hence it follows that the amount of ionic bivalent copper on the DND surface is about ~37% of the total number of deposited copper, or the XPS method gives the data are 1.5-1.6 times higher. It seems that at least 45% of copper is on the surface of DND particles in a non-paramagnetic state (in neutral clusters or in a +1 charge state).

At the same time, we should note that the XPS spectra of both the original DND-*ini* sample and doped D1-D3 contain Zr3d peaks at ~183-185 eV (Figure S6a,b). The weight content of zirconium, estimated from the intensity of this peak, is ~2.39 wt% or 0.34 at% (for D1). The slightly increased oxygen content in D1 and D3 is due to oxygen from the $ZrO_2$ oxide phase. The fourth and seventh columns of Table S1 show the corrected data for the elemental composition of D1 and D3 as a result of subtracting the percentage of zirconium and oxygen in units of atomic percent.

A strong argument confirming the correctness of all our quantitative XPS data is the almost identical presence of zirconium from the parasitic $ZrO_2$ phase in all samples, estimated from the area of the weak peak at 184 eV from the Zr3d level.

### S2.3 *Energy dispersive X-ray analysis*

Energy Dispersive X-Ray (EDX) analysis was carried out using a JEOL JSM-6390 scanning electron microscope (JEOL Ltd., Japan) equipped with an attached EDX spectroscope (analyzer) Oxford Instruments INCA x-act (UK). Elemental composition information was obtained by analyzing the powder surface on a conductive substrate. Data were analyzed from 5-6 surface areas and averaged.

Figure S7 shows the EDX spectra of sample D3 from an area with a local copper content of 1.43 wt% (0.29 at%). The oxygen content is 9.38 at%. Possibly 0.48 at% of oxygen is part of zirconium oxide. This means that the content of atomic oxygen bound to the surface (about 8.9 at.%) is approximately 30 times higher than the amount of atomic copper. It can be assumed that the number of copper atoms on the surface is only 7.5 times less than the number of pairs of carboxyl groups chelating doubly charged cations. According to the maximum estimate, taking into account the surface oxygen content of 8.9 at%, there can be about 255 such pairs of $COO^-$ groups for a 5-nm particle, and the particle can potentially bind up to two hundred copper atoms. It follows from the EDX measurements that only 33 copper atoms are located on the particle surface. This value is close to the data obtained by the EPR method.

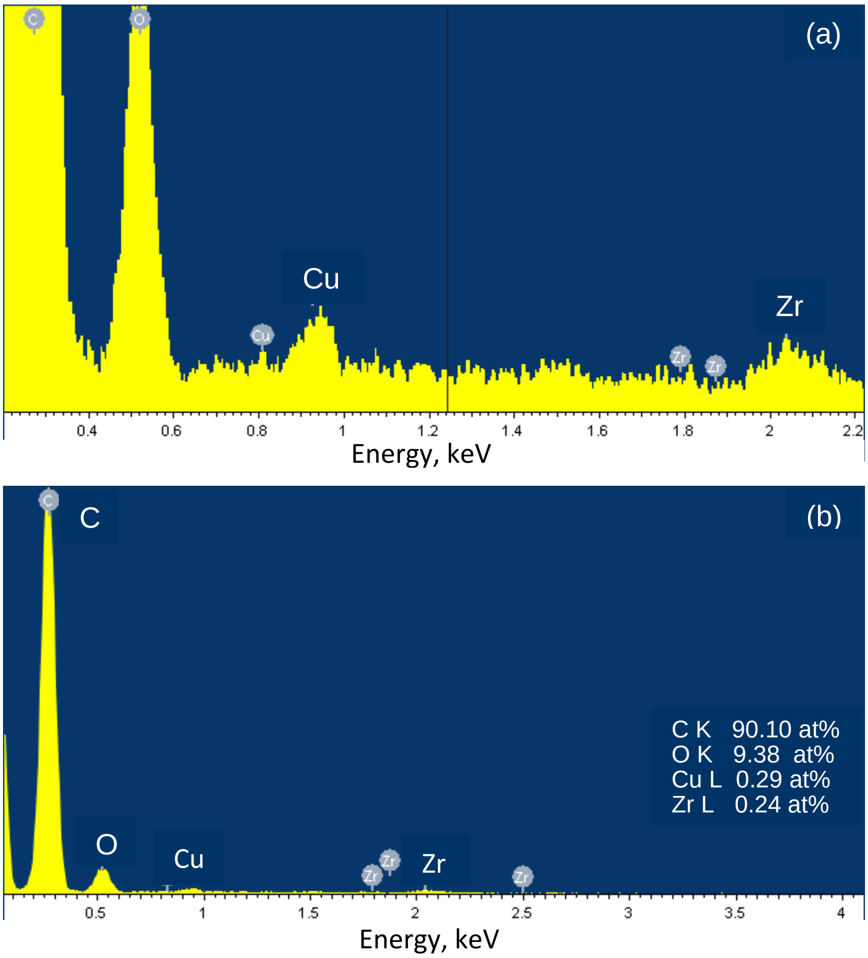

**Figure S7.** The EDX spectra of sample D3 taken from one of the local areas with a size of 100 × 100 microns, presented both in an overview form (bottom) and in an enlarged form in the energy range up to 2.2 keV (top). Copper and zirconium signals are clearly visible on the top panel. The copper content is 0.29 at%.

## S3. Formulas

For a 5-nm diamond particle of a quasi-spherical shape and a density of 3.52 g·cm$^{-3}$, we have the following relations between the concentrations of spins in units of *spin·g$^{-1}$*, *ppm* and *spins per particle*.

$$N\ [ppm] = 2 \times 10^{-17}\ N\ [spin \cdot g^{-1}]$$

$$N\ [spin\ per\ particle] = 2.304 \times 10^{19}\ N\ [spin \cdot g^{-1}]$$

$$N\ [ppm] = 10^{4}\ N\ [at.\%]$$

The concentration of paramagnetic spins (or copper ions) is here determined by normalizing the total number of spins ½ (or Cu$^{2+}$ ions) to the weight of the carbon matrix or the equivalent number of carbon atoms. Here, the mass of a 5-nm particle is assumed to be 2.304×10$^{-19}$ grams. Such a particle consists of 11520 carbon atoms. For example, the spin concentration of intrinsic paramagnetic centers of DNDs 6.3×10$^{-19}$ spin·$g^{-1}$, estimated by magnetometry methods, corresponds to a value of ~1260 ppm or ~14.5 spins per particle. In turn, a copper concentration of 0.47 at% (according to XPS) corresponds to ~54 copper atoms per 5 nm particle.

## References

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