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Transition metal atoms grafted on the nanodiamonds surface: identification and guest–host spin–spin interactions

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S1. General information and some technological details

The main experiments described in this work were obtained for the DND surface functionalized with Cu^{2+} ions in an aqueous DND suspension. For this, a 0.5 wt% aqueous suspension of DND and a solution of copper nitrate $Cu(NO_3)_2 \times 3H_2O$ were mixed. The details of the procedures for mixing the solutions, recovering the modified solid component, and drying it have been described in our recent article [S1]. As a precursor DND suspension we used the suspension ND-5-nm-N-H_2O from Adamas-Nanotechnologies, Inc., Raleigh, NC, USA. Product number: Sigma-Aldrich, # 900180 (monodispersed nanodiamond particles 5 nm avg. part. size (DLS), 10 mg/mL in H_2O, carboxylated). It is a stable suspension of 5-nm diamond particles with a negative zeta potential (around -35 mV) at pH ~7. It was diluted in two times by distilled deionized water for all our works. An image of 6 ml of Adamas-Nanotech's original suspension diluted in half in a plastic syringe is shown in Figure S1(*a*). In turn, the DND-Cu powder deposited from the modified suspension is shown in Figure S1(*b*).

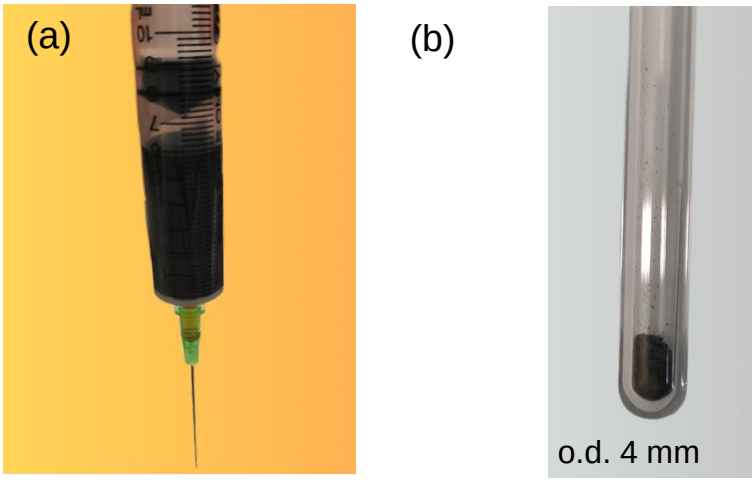

Figure S1. A doubly diluted suspension of DND particles from Adamas Nanotech. Inc, drawn into a plastic syringe (a), intended for subsequent modification with ionic copper, and a powder of DND-Cu particles precipitated by centrifugation from such a modified suspension (b).

The infrared absorption spectrum of a DND-Cu sample with a copper content of more than 1 wt% is shown in Figure S2. It is typical for nanodiamonds from a single-particle aqueous suspension of DND, prepared by processing the initial factory product (aggregates of DND particles) in air at a temperature of 420–430 °C. It is noteworthy that the absorption peak from nitrate ions at 1384 cm^{-1} is practically absent in the spectrum, which indicates that the ion exchange reaction of Cu^{2+} with protons of carboxyl groups has completely passed, and that there is no sorption of nitrate ions on the surface of DND particles.

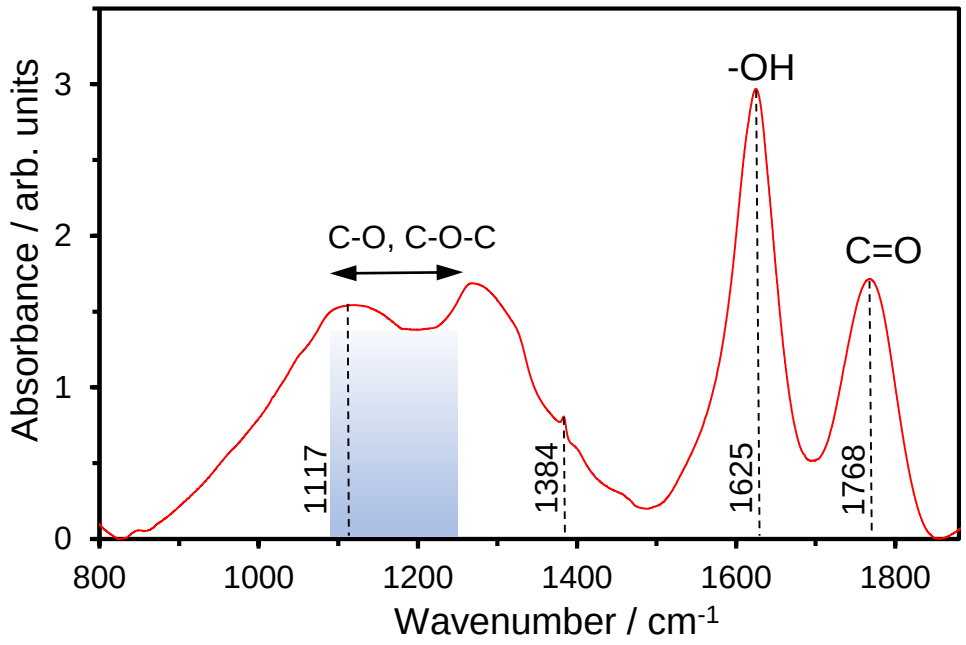

Figure S2. IR absorption spectrum of a DND-Cu powder with a copper content of 1.3 wt%, taken by pressing the powder into a spectroscopically pure potassium bromide matrix.

The corresponding link to the website of the manufacturer of DND precursor suspension with catalog number ND5nmNH2O100ml is below:

https://adamasnano.com/assets/dnd-suspensions-product.pdf

Product information is also available on the seller's website:

https://www.sigmaaldrich.com/RU/en/technical-documents/technical-article/materials-science-and-engineering/biosensors-and-imaging/monodispersed-nanodiamonds-applications

We also used a similar technique to modify the surface of DND particles with gadolinium Gd^{3+} ions. The corresponding procedure has been described in Ref. **S2**. But in this case, a suspension of carboxylated 5-nm diamond particles from another source (Ioffe Institute, St. Petersburg, Russia) was used. The suspension was made on the basis of specially treated DND powder produced by the Joint-Stock Company "SKTB Technolog" (St. Petersburg).

S2. Formulas

For a 5-nm diamond particle of a quasi-spherical shape with a density similar to that of a bulk diamond, we have the following relations between the concentrations of spins in units of $spin \cdot g^{-1}$, *ppm* and *spins per particle*.

$$N\ [ppm] = 2 \times 10^{-17}\ N\ [spin \cdot g^{-1}]$$
$$N\ [spin\ per\ particle] = 2.304 \times 10^{-19}\ N\ [spin \cdot g^{-1}]$$

The formulas are written in the following approximations: the molar mass of carbon is 12 g/mol, the Avogadro number is rounded to the first two significant digits, the weight of the powder is considered equal to the weight of the diamond particles (crystalline phase) with their surrounding molecular functional shells. The weight of the metal phase is neglected at a powder doping level of less than 3 wt%. The concentration in units of $spin \cdot g^{-1}$ is obtained by dividing the total number of analyzed spins (for example, $^1/_2$ spins) in the system by the weight of the carbon matrix. The mass of a 5-nm particle is assumed to be 2.304×10^{-19} grams (the weight of ~11500 carbon atoms). Since DND powder weighed in air can contain water adsorbed from the ambient air in an amount of up to 8-10 wt%, the inaccuracy in determining the mass of the solid part of the powder is a source of error in the spin concentration in units of $spin \cdot g^{-1}$. This remark mainly refers to the value of N_{PC}, i.e. the concentration of intrinsic spins of diamond particles, determined from measurements of the magnetization of the powder at low temperatures in a vacuum.

References

[S1] V. Yu. Osipov, N. M. Romanov, I. E. Suvorkova, E. V. Osipova, T. Tsuji, Y. Ishiguro and K. Takai, *Mendeleev Commun.*, 2022, **32**, 132.

[S2] V. Yu. Osipov, A. E. Aleksenskiy, K. Takai and A.Y. Vul', *Phys. Solid State*, 2015, **57**, 2314 (*Fizika Tverdogo Tela*, 2015, **57**, 2245).