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Natural limit of the number of copper ions chemisorbed on the surface of a detonation nanodiamond

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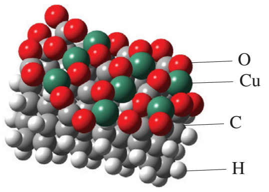
The upper limit of the amount of copper ions that can be grafted to the detonation nanodiamond surface has been calculated. A maximum of 34 wt% copper can be grafted to carboxylated and hydroxylated 5 nm nanodiamonds. The results of calculations have been compared with the experimental and published data.



The grafting of paramagnetic metal ions and chemotherapeutic molecular species to the surface of nanodiamonds is promising for a variety of applications in modern nanotechnology and medicine.[1–9] Functionalized diamond surfaces easy attach and adsorb metal ions, molecular species and even inorganic nanoparticles.[10–15] Detonation nanodiamonds (DNDs) with grafted double-charged copper ions have recently been reported.[16–21] Here, we analyze the natural limitations of DND surfaces for grafting copper atoms and compare the results of our calculations with our experimental findings and published experimental and theoretical data.

Detonation technique of nanodiamond preparation results in crystalline particles of size about 4-5 nm. To ease calculations, the shape of such particles is often assumed to be spherical, while detailed high resolution transmission electron microscopy studies indicated that single DND particles reveal faceting in the form of a truncated octahedron.[22] The most chemically active facets correspond to the (111) crystalline planes. A round 5 nm diamond particle with a density of 3.52 g cm^{-3} has a mass of 2.3×10^{-19} g and consists of ~11560 carbon atoms. The equivalent (having the same number of atoms) non-truncated octahedron shows eight (111) planes with the ribs of 5.18 nm long. In such a case, 1680 exterior carbon atoms located with a two-dimensional (2D) density of 1.81×10^{15} atom cm^{-2} on the (111) facets of this model nanoparticle reveal the up-standing σ-bonds with surface hydrogen, hydroxyl, carboxyl and other groups. These surface carbon atoms account for around 14.5% of the total number of carbons of the 5 nm DND particle, and they can be involved into ion grafting.

Metal cations are usually grafted to a diamond surface by the replacement of two hydrogen atoms of surface carboxyl groups by a copper ion using a wet chemistry method.[16–21] This issue was considered in detail in the framework of the density functional theory.[23] It was shown that the geometry of up-standing carboxyl groups implies two unique possibilities for the formation of surface chelates, which include $N/2$ or $N/3$ copper atoms for their maximal dense arrangement on a large surface cluster consisting of $2N$ carbon atoms (N up-standing positions). Since the energies of formation of these two types of surface chelates are comparable, one should assume their random arrangement with equal probability (50:50). This model yields $5N/12$ copper atoms for N up-standing positions on the (111) surface. In the case that all surface up-standing σ-bonds are saturated with hydroxyl groups, there is the only way of the formation of surface copper chelates with a slightly dense arrangement, $N/2$ Cu atoms for N up-standing positions. This approach uses a practically important non-wet chemical technology for grafting. Two sketches of a random arrangement of 7 copper atoms on a portion of diamond (111) surface consisting of 30 and 33 carbon atoms terminated from upside by 14 $–O^-$ or $–COO^-$ groups are shown in Figure 1 as an example. Covalent bonds between oxygen and copper atoms provide strong fixation of copper atoms on the surface. However, in any case, the actual coverage of the DND surface with copper embraces less than 50% of surface carbon atoms with up-standing σ-bonds. It means that a maximum of 1680 sp^3-C–COO^- or

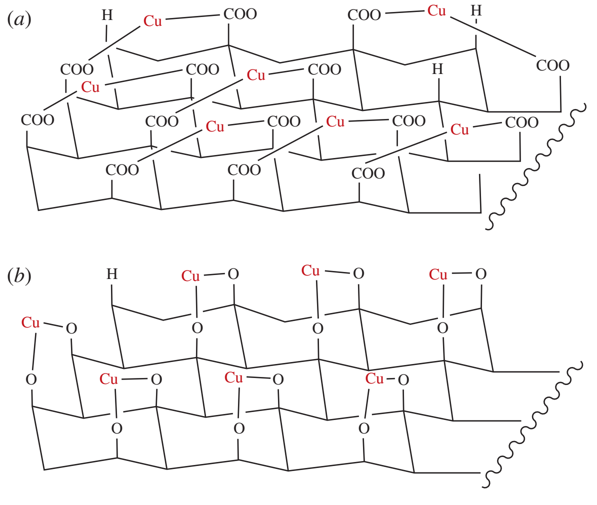


Figure 1 Dense arrangements of 7 copper atoms on a portion of the diamond (111) surfaces consisting of (*a*) 33 and (*b*) 30 carbon atoms terminated from upside by fourteen $–COO^-$ or $–O^-$ groups. For simplicity, some upstanding bonds on both panels are saturated by atomic hydrogen.

sp^3-C–O$^-$ sites on the surface of nanodiamond particle can be involved in bonding with copper and can therefore bind a maximum of 840 copper or other divalent paramagnetic ions. For the case of copper, this amount is

$$\frac{63.5\times 840}{63.5\times 840+12\times 11560}\approx 28\text{ wt\%}$$

(here, we neglect the weight of oxygen-containing surface groups in the denominator). Additional fixation of copper ions with somewhat stronger binding energies is represented by sp^3-C–COO$^-$ or sp^3-C–O$^-$ sites along the twelve ribs of octahedron. The amount of copper atoms fixed along these ribs may reach ~270 and increase our estimation up to ~34 wt%. Stable fixation of more than 34 wt% copper ions on the 5 nm DND particle is impossible. Therefore, the calculated coverage[21] of the DND surface with 4700 Cu^{2+} ions, which exceeds our estimate by a factor of 4.2 and allegedly results in the formation of nanodiamond particles encapsulated into copper shells, seems to be hardly realistic. Our estimations concern only Cu^{2+} ions that are directly bound by sp^3-C–COO$^-$ and sp^3-C–O$^-$ sites. However, the surface of diamond nanoparticles may accept an additional amount of copper in the form of Cu$^+$ ions and neutral copper atoms. The latter demonstrate a tendency to aggregate[†] and to form metal clusters consisting of dozens/hundreds of atoms that are weakly bound to the nanoparticle surface. In dry powder DND samples, these metal copper clusters are most probably localized within interparticle spaces.

On practice, the density of the surface carboxyl groups of commercial DND particles even subjected to the subsequent oxidation is relatively small. Therefore, only 2.4 wt% copper and 3.28 wt% gadolinium were grafted to the DND surface in our experiments using a wet chemistry method.[16–20] Obtaining higher concentrations was not possible due to particle coagulation and solid precipitation. The larger DND surface coverage with 7.5 wt% copper has recently been reported.[21] However, the XRD patterns[21] revealed Bragg reflections of the face-centered cubic copper lattice, which cannot result from separate copper atoms or copper monolayer. Herewith the XRD reflexes of copper are somewhat narrower than those of nanodiamond.[21] Based on these findings, we suggest that a more adequate model of the fabricated compound represents copper particles, whose size is comparable with or somewhat larger than that of DND grains, together with some amount of copper ions (much less than 7.5 wt%) grafted to the surface.

We note that a powerful tool for proving paramagnetic ion grafting to nanoparticle surfaces based on the analysis of ^{13}C and ^{1}H nuclear spin-lattice relaxation data has recently been developed. It allows distinguishing between grafted transition metal ions and those separated from the surface.[18–20] The matter is that the interaction of nuclear spins with 3*d*-electron spins of the transition metal ions affiliated to the DND surface creates an additional relaxation channel and results in the acceleration of relaxation. While when the metal ions are separated from the surface by >1 nm, their effect on relaxation is negligible because of the proportionality of the relaxation rate to the inverse sixth power of the distance between the nanoparticle and the paramagnetic ion. Thus, if the number of transition metal ions exceeds the above theoretical limit and ions are no longer grafted to the nanodiamond surface, the spin-lattice relaxation becomes ion density independent. This is also true for rare earth and other paramagnetic ions grafted to the surfaces of various carbon nanoparticles of different shapes and sizes.[20,24,25]

Thus, we conclude that the amount of copper ions grafted to the DND surface rises with the amount of surface carboxyl or hydroxyl groups. A maximum of 34 wt% Cu^{2+} ions can be grafted to carboxylated and hydroxylated single 5 nm nanodiamonds and probably only by methods of nonaqueous chemistry. Note that the DND surface carboxylation/hydroxylation should be preceded by a thorough purification of the diamond surfaces from sp^2 carbon atoms, which are formed on the real nanodiamond surface.

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References

1 *Detonation Nanodiamonds: Science and Applications*, eds. A. Vul' and O. Shenderova, Pan Stanford Publishing, Singapore, 2014.

2 V. N. Mochalin, O. Shenderova, D. Ho and Y. Gogotsi, *Nat. Nanotechnol.*, 2012, **7**, 11.

3 H. Man, J. Sasine, E. K. Chow and D. Ho, in *Nanodiamond*, ed. O. A. Williams, Royal Society of Chemistry, Cambridge, 2014, ch. 7, pp. 151–169.

4 Y. Liu, Z. Gu, J. L. Margrave and V. N. Khabashesku, *Chem. Mater.*, 2004, **16**, 3924.

5 A. M. Schrand, S. A. Ciftan Hens and O. A. Shenderova, *Crit. Rev. Solid State Mater. Sci.*, 2009, **34**, 18.

6 J. C. Arnault, in *Novel Aspects of Diamond: From Growth to Applications*, ed. N. Yang, Springer, Berlin, 2015, ch. 8, pp. 85–122.

7 M. Chen, E. D. Pierstorff, R. Lam, S.-Y. Li, H. Huang, E. Osawa and D. Ho, *ACS Nano*, 2009, **3**, 2016.

8 H. Huang, E. Pierstorff, E. Osawa and D. Ho, *Nano Lett.*, 2007, **7**, 3305.

9 M. Baidakova and A. Vul', *J. Phys. D: Appl. Phys.*, 2007, **40**, 6300.

10 M. Dubois, K. Guérin, N. Batisse, E. Petit, A. Hamwi, N. Komatsu, H. Kharbache, P. Pirotte and F. Masin, *Solid State Nucl. Magn. Reson.*, 2011, **40**, 144.

11 A. Peristyy, B. Paull and P. N. Nesterenko, *Adsorption*, 2016, **22**, 371.

12 G. P. Bogatyreva, M. A. Marinich, G. A. Bazalii and G. D. Il'nitskaya, *Nanosist. Nanomater. Nanotekhnol.*, 2010, **8**, 851 (in Russian).

13 T. A. Dolenko, S. A. Burikov, K. A. Laptinskiy, T. V. Laptinskaya, J. M. Rosenholm, A. A. Shiryaev, A. R. Sabirov and I. I. Vlasov, *J. Alloys Compd.*, 2014, **586**, S436.

14 N. Yang, F. Gao and C. E. Nebel, *Anal. Chem.*, 2013, **85**, 5764.

15 T. Plakhotnik, H. Aman, S. Zhang and Z. Li, *J. Phys. Chem. C*, 2015, **119**, 20119.

16 A. I. Shames, V. Yu. Osipov, A. E. Aleksenskiy, E. Osawa and A. Ya. Vul', *Diamond Relat. Mater.*, 2011, **20**, 318.

17 V. Yu. Osipov, A. E Aleksenskiy, A. I. Shames, A. M. Panich, M. S. Shestakov and A. Ya. Vul', *Diamond Relat. Mater.*, 2011, **20**, 1234.

18 A. M. Panich, A. I. Shames, O. Medvedev, V. Yu. Osipov, A. E. Aleksenskiy and A. Ya. Vul', *Appl. Magn. Reson.*, 2009, **36**, 317.

19 A. I. Shames, A. M. Panich, V. Yu. Osipov, A. E. Aleksenskiy, A. Ya. Vul', T. Enoki and K. Takai, *J. Appl. Phys.*, 2010, **107**, 014318.

20 A. M. Panich, A. I. Shames, N. A. Sergeev, V. Yu. Osipov, A. E. Alexenskiy and A.Ya. Vul', *J. Phys. Chem. C*, 2016, **120**, 19804.

21 K. Turcheniuk and V. N. Mochalin, *Carbon*, 2016, **109**, 98.

22 A. T. Dideikin, A. E. Aleksenskii, M. V. Baidakova, P. N. Brunkov, M. Brzhezinskaya, V. Yu. Davydov, V. S. Levitskii, S. V. Kidalov, Yu. A. Kukushkina, D. A. Kirilenko, V. V. Shnitov, A. V. Shvidchenko, B. V. Senkovskiy, M. S. Shestakov and A. Ya. Vul', *Carbon*, 2017, **122**, 737.

23 I. D. Gridnev, V. Yu. Osipov, A. E. Aleksenskii, A. Ya. Vul' and T. Enoki, *Bull. Chem. Soc. Jpn.*, 2014, **87**, 693.

24 A. M. Panich, A. I. Shames, M. I. Tsindlekht, V. Yu. Osipov, M. Patel, K. Savaram and H. He, *J. Phys. Chem. C*, 2016, **120**, 3042.

25 A. M. Panich and N. A. Sergeev, *Appl. Magn. Reson.*, 2018, **49**, 195.

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[†] The presence of Cu^{2+} ions on the DND surface was confirmed by EPR spectroscopy.[16,18,19] Subsequent EPR and magnetic susceptibility studies of Cu-grafted DND powders revealed that storage of these powders at ambient conditions for several months made some part of Cu^{2+} ions unobservable. The same occurred as a result of heat treatments at 110 °C. It indicates reduction of paramagnetic Cu^{2+} ions to the Cu$^+$/Cu^0 states with following aggregation of these species to neutral metallic clusters.