

Noncovalent bonding of copper atoms to the nitrogen-containing sites of hydrogenated diamond surfaces

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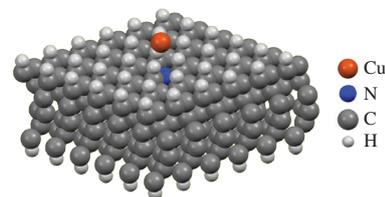
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We demonstrate that isolated copper atoms can be bound to the four-coordinated surface nitrogen sites of a diamond lattice fully terminated by atomic hydrogen. This bonding is related to the ability of surface nitrogen sites to donate unpaired electrons (from an antibonding orbital) to third alien surface agents.



Nanodiamonds with a mean size of <10 nm are very promising for their use in biotechnology and delivery of water-insoluble therapeutics^{1–4} or as carriers for platinum group metal nanocatalysts.⁵ This is related to the presence of oxygen-containing (mainly carboxyl and hydroxyl) functional groups on their surface capable of binding various atomic groups, large-scale molecules, metal cations and clusters of dozens of metal atoms.^{6–8} Nanostructures based on carbon allotropes may contain exterior and interior impurities depending upon the synthesis method and the subsequent treatment.⁹ Only some of them, for example, detonation nanodiamonds (DNDs) with a mean size of ~5 nm, can be heavily doped with appropriate interior impurities without losses in their mechanical properties and changes in morphology. Such diamond nanoparticles contain up to 2.5–2.7 at% nitrogen distributed more or less homogeneously in the covalent lattice of diamond cores, but enriched at defect regions like stacking faults.^{10,11} Turner *et al.*^{10,11} also concluded that the embedded nitrogen predominantly occurs in the diamond lattice as NN dimers (A centers) or isolated neutral or positively/negatively charged nitrogen *sp*³-coordinated impurities (C centers). The presence of interior nitrogen inside the DND particles was also assumed by Kulakova.¹² Here we consider nitrogen sites on/under the surface of DND particles in case of the surface fully terminated by atomic hydrogen. The amount of surface carbon atoms with up-standing σ -bonds in a round 5 nm diamond particle consisting of ~11000 carbon atoms is about ~1300 and the amount of nitrogen atoms laying on or within a thin (one lattice constant) surface layer may even achieve ~110.[†] Such a huge number of nitrogen in the undersurface layer may provide weak fixation of anions and cations on the diamond surface through the ability of nitrogen sites to donate or accept electrons to/from the third atomic agents disposed no more than 2 nm from them. Usually, an electron from the antibonding orbital of

nitrogen atom in the diamond lattice can easily overcome a distance of 1–2 nm through tunnelling. The barrier for tunnelling from a bulk site to the surface is about 2 eV through the specific position of donor levels of nitrogen sites in the diamond bandgap. The shorter a distance from these nitrogen atoms (C or A centers) to the diamond surface, the higher a probability for them to be involved in the chemical bonding of some agents coming close to the surface *via* long-range Coulomb forces. Thus, the potential reactivity and functionality of nitrogen-rich diamond nanoparticles is very high, and it may be used for special purposes.

In this research, we used commercial suspensions of extra purified DNDs with surface hydrogen terminated or functionalized by oxygen-containing groups. The surface of DND particles was chemically modified with copper according to a published procedure.^{13,14} Preliminary experiments demonstrated that some copper atoms can be bound with the nitrogen-rich surface of DND particles completely terminated by atomic hydrogen, and these copper adatoms are fairly stable. The status of the H-terminated DND surface was confirmed both by IR spectroscopy [wide strong absorption bands related to *sp*³-CH and *sp*³-CH₂ bonds (2800–3010 cm⁻¹)] and the analysis of gases released after sample heating to 1000 °C. The presence of about 20–22% of Cu²⁺ ions on the H-terminated DND surface was confirmed by electron paramagnetic resonance (EPR) and low temperature magnetometry similarly to the data obtained earlier.^{15,16} In case of copper on the H-terminated DND surface, the broadening of an EPR line ($g = 2.0027$) related to interior paramagnetic centers in DND is smaller by a factor of 4.6 than that for the same amount of copper attached to the carboxylated DND surface.[‡] Thus, at least only one fifth of all chemisorbed copper adatoms is fixed on the nanoparticle surface in the Cu²⁺ state with spin half ($S = 1/2$). This is because the mechanism of dipole–dipole EPR line broadening through exterior paramagnetic copper is

[†] Based on published data,¹¹ we assumed that nitrogen centres were distributed homogeneously within the diamond nanoparticles. The number of nitrogen sites within a one lattice constant layer from the surface was about one hundred.

[‡] About 25 spins half ($S = 1/2$) of Cu²⁺ lead to broadening the width of EPR line of carboxylated DND on ~0.345 mT similar to published data.¹⁶

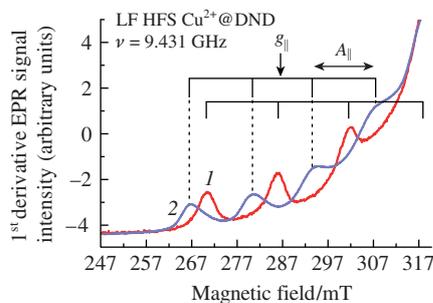


Figure 1 LF HFS components of EPR spectra of Cu^{2+} ions on (1) H-terminated and (2) carboxylated DND surface. Shifting the positions of LF HFS components to higher magnetic fields means the change of Cu^{2+} coordination from 4O to another one related with surface nitrogen sites. The main highly intensive EPR line ($g = 2.0027$, $\Delta H_{pp} = 0.86$ mT) related with interior paramagnetic centers in DND and g_{\perp} component of Cu^{2+} ions EPR signal (above 320 mT) are not shown for simplicity. The most high field component ($n = 4$) of hyperfine pattern of g_{\parallel} component of Cu^{2+} EPR signal for H-terminated surface is not well observable on the highly raising background above 314 mT.

not essential for such H-terminated DNDs functionalized by copper. Low field (LF) components[§] of hyperfine structure (HFS) of EPR spectrum of mononuclear axially distorted Cu^{2+} ion complexes are presented in Figure 1 for both H-terminated and carboxylated DND surfaces. Shifting the positions of all LF HFS g_{\parallel} -components of Cu^{2+} EPR spectrum for H-terminated surface by ~ 3.7 – 7.8 mT to higher magnetic fields and an increase in the value of A_{\parallel} by $\sim 15\%$ mean that Cu^{2+} ions are coordinated on the surface in another manner with the probable participation of nitrogen sites like $2\text{N}2\text{O}^{\parallel}$ and 4N (rather than 4O as for a carboxylated surface). At the same time, according to the experimental results, the most part of copper atoms occurring on the H-terminated diamond surface are not in the Cu^{2+} state with $S = 1/2$ but in another EPR-silent state, probably, close to the +1 charged or neutral or even -1 charged. *A priori* the type of chemical bonding between the copper atom and H-terminated diamond surface was not clear because of the absence of any theoretical support. Here, we analyze the types of chemical bonding between isolated copper atoms and a nitrogen-containing diamond surface terminated by hydrogen atoms.

We used the density functional theory (DFT) as implemented in the pseudopotential code SIESTA.¹⁷ The calculations were performed using the generalized gradient approximation (GGA-PBE) with spin polarization¹⁸ and implementation of the correction of van der Waals forces.¹⁹ During the optimization, the ion cores were described by norm-conserving nonrelativistic pseudopotentials²⁰ with cut off radii of 1.14, 1.25, 1.20 and 2.15 a.u. for C, N, H, and Cu metal, respectively, and the wave functions were expanded with localized orbitals and double- ζ basis set for hydrogen and a double- ζ plus polarization basis set for other species. Full optimization of the atomic positions was performed. Optimization of the force and total energy was performed with an accuracies of 0.04 eV \AA^{-1} and 1 meV, respectively. All of the calculations were carried out with an energy mesh cutoff of 360 Ry and a k-point mesh of $8 \times 6 \times 4$ in the Monkhorst–Pack scheme.²¹ For the modeling of the surface of nanodiamonds, we used a slab of four layers of carbons passivated from both sides by hydrogen atoms [Figure 2(a)] corresponding to the diamond

[§] Four components characterizing the principal g_{\parallel} and A_{\parallel} parameters of $^{63}\text{Cu}^{2+}/^{65}\text{Cu}^{2+}$ ($I = 3/2$) spectra with $g_{\parallel} = 2.347 \pm 0.005$, $A_{\parallel} = 13.7 \pm 0.17$ mT (for carboxylated surface) and laying on the left wing of DND EPR spectrum at $\nu = 9.43$ GHz.

[¶] In practice, the additional O-coordination is provided by oxygen atoms of adsorbed water molecules if DND powder is storing under ambient conditions.

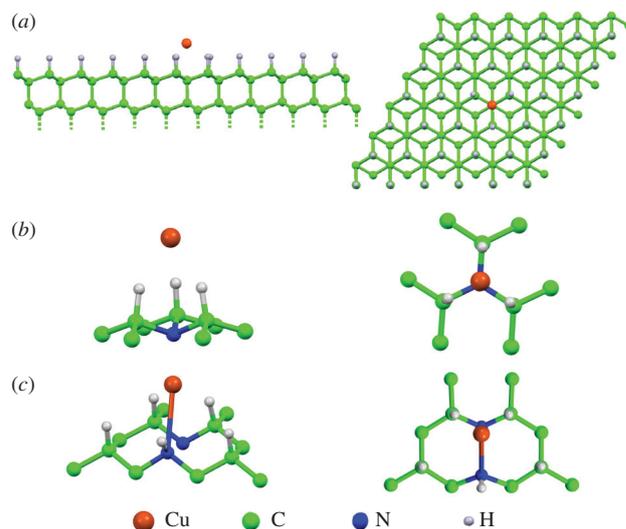


Figure 2 Optimized atomic structures a–c of (a) the upper part of diamond slab with copper adatom and (b), (c) the parts of the system in the vicinity of copper impurity, respectively. Left, side view; right, top view.

(111) surface. Since the exact atomic structure of the source of copper on the surface is unknown, we could only evaluate the relative stability of copper adatom. We used the absolute energy of copper atom on the perfect H-terminated surface [Figure 2(a)] as a reference ($E_{\text{surface}}^{\text{ref}}$). The relative binding energy was calculated as $E(\text{Cu}) = E(\text{Cu@surface}) - E_{\text{surface}}^{\text{ref}}$. A decrease in the energy of copper atom (its down shifting to the lower states on the energy scale) corresponds to the stabilization of a substrate–adatom bond.

We considered the adsorption of a copper adatom both on the perfect hydrogenated (111) surface of diamond and on the analogous surface with defects such as missing hydrogen atom (hydrogen vacancy) and nitrogen centres. The calculations demonstrated that, in the presence of a single carbon or nitrogen atom non-passivated by hydrogen on the surface, only the trivial formation of covalent copper–carbon or copper–nitrogen bonds occurs. Three other possible configurations correspond to the fixation of copper atoms by nitrogen sites without covalent bonds formation (Figure 2, Table 1). The first configuration (a) [Figure 2(a)] is on the perfect fully hydrogenated diamond surface with electronic charge transfer ($0.095e$) from substrate to adatom. Another two structures (b, c) related with substitutional nitrogen sites [Figure 2(b), (c)] are energetically favourable.

These configurations are noncovalent with bonding of ionic type between copper atom and underlying nitrogen site. In configuration b [see Figure 2(b)], the binding energy $\Delta E = 3.39$ eV is higher than that for two reference cases where a copper atom is covalently bound to a hydrogen non-terminated sp^3 C- or sp^3 N-site (sp^3 C–Cu and sp^3 N–Cu).^{††} The distance between the Cu atom and the (111) diamond plane is larger in noncovalent bonding ($h = 2.85$ \AA vs. 2.05 and 2.10 \AA for covalent cases sp^3

Table 1 Calculated relative binding energies of copper atom (ΔE), distances between copper and nearest carbon or nitrogen atom (d), the heights of copper adatom above the utmost plane of carbon atom (h), changes in the Mulliken occupancy of copper adatom (Δe , in electrons), and magnetic moments (m_{Cu}) on copper for three non-chelate configurations a–c shown in Figure 2.

Configuration	$\Delta E/\text{eV}$	$d/\text{\AA}$	$h/\text{\AA}$	$\Delta e/e^-$	m_{Cu}/μ_B
a	0.00	2.53	2.05	0.095	0.869
b	–3.39	3.20	2.85	0.472	0.000
c	–0.86	3.02	2.37	0.181	0.745

^{††} The corresponding binding energies are 3.13 eV (sp^3 C–Cu) and 1.42 eV (sp^3 N–Cu). Figures for these configurations are not shown.

C–Cu and sp^3 N–Cu, respectively), however bonding is more robust. This is because the excessive charge about half an electron ($\Delta e = 0.472e$) jumps from the substitutional nitrogen site laying on the substrate to the Cu atom. The Cu atom is a true anion in this case with the probable electronic configuration $3s^23d^{10}4s^2$, and the corresponding magnetic moment is zero. Thus, this configuration is responsible for magnetically silent copper. The underlying nitrogen site losses an electron and becomes non-paramagnetic. An analogous situation occurs in configuration c [see Figure 2(c)], where a Cu atom is bound by two neighbouring N sites (A center). The copper atom accepts a smaller electronic charge of 0.181e from the substrate, and it has an essential but slightly reduced magnetic moment (0.745 μ_B). It is closer to the surface ($h = 2.37$ Å) than in the previous case. The binding energy $\Delta E = 0.86$ eV in this case is slightly smaller than that for a reference situation.^{‡‡} Note that the above charge transfer is a new type of chemical noncovalent ionic bonding between the impurity site in a solid (diamond) donating an electronic charge and an outside isolated atom or molecule near the surface accepting this charge similar to the weak chemical bonding between molecular dioxygen and the zigzag graphene edge.²²

In conclusion, a new protocol has been proposed for non-covalent fixation of copper atoms on the H-terminated diamond surface containing nitrogen defects which is directly responsible for appearance of magnetically silent ‘latent’ copper. This work opens the new way for surface modification of the DND particles by metal atoms *via* their bonding with surface sp^3 N-sites terminated by atomic hydrogen. The binding energy may be enough high in this case for stable long-term fixation metal anions on the DND surface. This method can find applications in biomedicine and biotechnology. Further progress will be related with taking into account the molecular environment of isolated metal atoms, which comprises at least few water molecules.

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^{‡‡} The corresponding scheme ‘surface A-center–Cu’ is not presented here. Binding energy and distance h are 1.17 eV and 1.81 Å, respectively, in this case.

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