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Gadolinium ion bonding on the surface of carboxylated detonation nanodiamond in terms of magnetochemistry and density functional theory

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Contents

S1. General information and Experimental Procedures

DND surface was functionalized by Gd^{3+} 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 Gd^{3+} cations just after adding the certain amount of 0.3 wt.% water solution of gadolinium nitrate $Gd(NO_3)_3 \times 6H_2O$ into suspension and subsequent agitation and stirring. The details of procedure were described earlier in Ref.S1. As a precursor DND suspension we used the suspension ND-5-nm-N-H_2O (concentration 10 mg/ml) from Adamas-Nanotechnologies, Inc. (US). It was diluted in two times by distilled deionized water for all other subsequent works.

After the end of DND functionalization by Gd^{3+} ions the colour of DND suspension was changed from black to gray and slow sedimentation of coarse and fine DND particles occurred (Figure S1). After that the obtained suspension was subjected to intensive centrifugation at 13000 rpm and the sedimented product from the bottom was dried. The images of modified suspensions before and after the centrifugation are shown in Figure S2. The pellets were dried in secondary vacuum at ~50ºC. The yield of final product was about ~60 mg.

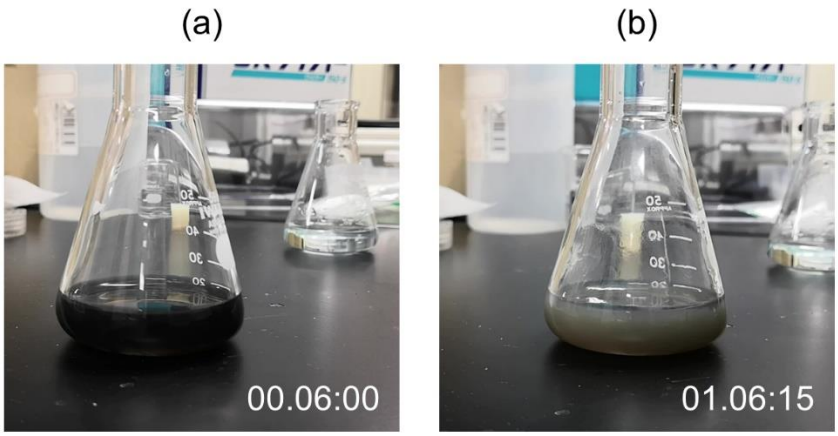

Figure S1. The images of water suspension of DND before (a) and ~1 min after its mixing with certain amount of 0.3 wt.% water solution of gadolinium nitrate (b).

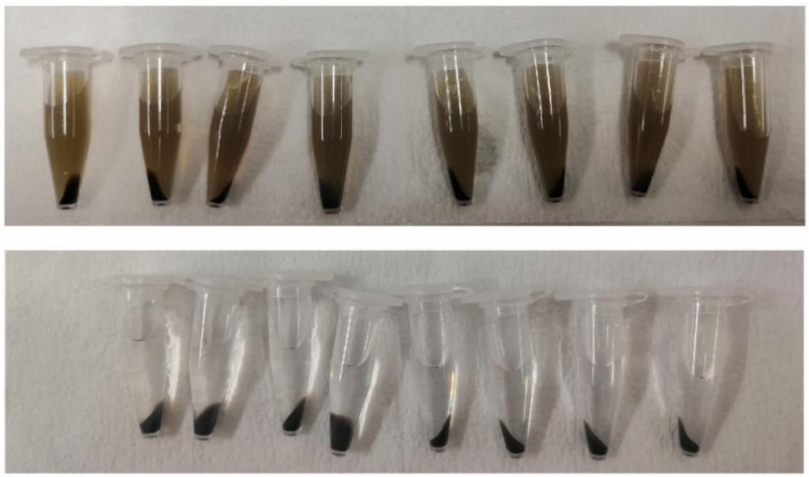

Figure S2. The images of metal-modified water suspension of DND before (a) and after the centrifugation (b).

S2. Analytical data and Formulas

Magnetisation of DND sample grafted by gadolinium ions is a sum of three component:

$$M(H) = \chi_o H + M_{\mathrm{DND}}^{S_1=1/2} + M^{Gd} = \chi_o H + N_{s_1} g S_1 \mu_B B_{S=\frac{1}{2}}(H) + N_{s_2} g S_2 \mu_B B_{S=\frac{7}{2}}(H)$$

where χ_o – core diamagnetic susceptibility of carbon atoms, H- magnetic field, N_{s_1}- concentration of interior S_1=1/2 paramagnetic species inside the DND particles, N_{s_2} – concentration of exterior gadolinium S_2=7/2 ions grafted on the surface of DND particles, S_1 and S_2 – spin values for paramagnetic species related with own interior defects inside DND particles and exterior Gd ions, μ_B – Bohr magneton, $B_{S=\frac{1}{2}}(H)$ and $B_{S=\frac{7}{2}}(H)$ – Brillouin functions for the ensembles of spins with spin values ½ and $^7/_2$. $g \approx 2$ is a g-factor (Lande factor) for both paramagnetic species S_1=1/2 and S_2=7/2. Brillouin function for the both groups of spins is defined by the next expression [S2]:

$B_s = \frac{2S+1}{2S}\coth\frac{(2S+1)x}{2} - \frac{1}{2S}\coth\frac{x}{2}$, where S is a spin value and variable x equals $x = g\mu_B H/k_B T$. Here k_B is a Boltzmann constant and T is a temperature. At T = 2 K both Brillouin functions show the impressive saturation trends. The saturation trend is more featured for higher spin values.

The amount of gadolinium cations may be evaluated from the third component in *M(H)* after subtraction the contributions from diamagnetism of carbon matrix and paramagnetism of own carbon-inherited defective species: $M^{Gd}(H) = M(H) - \chi_o H - M_{\mathrm{DND}}^{S_1=\frac{1}{2}}(H)$. For doing this operation correctly we used the next parameters for DND: χ_o = - 4.32×10^{-6} emu mol^{-1}, N_{S_1} = 7.57 ×10^{20} spin mol^{-1}. Such procedure gives very fine results for own magnetization of Gd^{3+} ions on the DND surface at T=2 K.

References

[S1] V.Yu. Osipov, A.E. Aleksenskiy, K. Takai and A.Y. Vul`, *Phys. Solid State*, 2015, **57**, 2314 (*Fiz. Tverd. Tela*, 2015, **57**, 2245).

[S2] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, Heidelberg, 1986.