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Presonication of nanodiamond hydrosols in radiolabeling by a tritium thermal activation method

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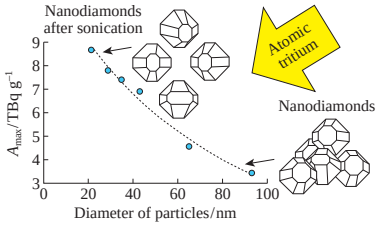
Specific radioactivity of tritium-labeled nanodiamonds obtained by a tritium thermal activation method can be increased by presonication only if this treatment reduces the diameter of nanodiamond aggregates in an aqueous suspension by a factor of 2 or more.



Nanodiamonds (NDs) are widely used.[1,2] Radioactive labeling is promising for visualizing nanoparticles in different systems.[3–5] Detonation NDs can be successfully labeled with tritium using either a tritium microwave plasma[6] or a tritium thermal activation method.[7] Here, we propose a method for improving the yield or radioactivity of labeled NDs obtained by the tritium thermal activation method. To this end, we tried to reduce the size of NDs aggregates in aqueous suspensions.

To study the influence of particle size in the hydrosols on the radioactivity of NDs,[†,8–10] we used ultrasonic treatment.[‡] Unlike other ND grinding techniques,[11,12] this approach does not lead to the introduction of additional impurities into the system, as confirmed by ICP AES analysis for metal impurities in NDs before and after sonication according to a published procedure.[13] The main impurities found in NDs after additional sonication were Na (0.9%), Si (0.8%), and Ti (0.3%), which are usual impurities in NDs,[15] while the starting material contained less than 0.1 % of these elements.

The second procedure reduced the average hydrodynamic diameters of hydrosol particles to 29±2, 43±2 and 21±6 nm for Sinta, SKN-100 and SKN-15 samples, respectively. The ζ-potentials were not changed after additional sonication.

The ND suspensions containing 0.17–0.6 mg of a solid phase were equally distributed on the walls of a reaction vessel used for tritium labeling and lyophilized.[§] The labeling procedure was described previously.[8] It was observed that the ratios between the final and initial radioactivity of additionally sonicated NDs were 55, 27 and 20% for Sinta, SKN-100 and SKN-15, respectively, while these values for the materials without additional sonication were 14, 11 and 15%, respectively. NDs subjected to the additional sonication formed targets with large holes that provide a more complete removal of water during lyophilization. Thus, we can suggest that short-term sonication prevents the strong agglomeration of NDs particles similar to the experiments with DMSO.[15] However, although the sonication results in a decrease in the agglomeration, it does not influence the specific surface area. SKN-30 and SKN-100 NDs possess a BET specific surface area of 280 m^2 g^{-1}. Thus, we believe that the pretreatment of NDs by sonication results in the better removal of adsorbed water impurities by lyophilization during the target preparation. Since water is a well-known acceptor of tritium atoms, additional sonication leads to a significant increase in the specific radioactivity of NDs (Figure 1).

The radioactivity data were analyzed using a model described previously,[16] according to which, the specific radioactivity (A) is described by the equation:

$$A = A_{max}[1 - \exp(-k_{eff}t)]. \quad (1)$$

† Commercial NDs from Sinta (Belarus) and aqueous ND suspensions from SKN (Russia) with average diameters of 100 and 15 nm were used, which are referred to as Sinta, SKN-100, and SKN-15, respectively. The NDs from Sinta were suspended in deionized water according to a procedure described previously.[8] The suspensions from SKN were used as received. The labeling was preceded by the characterization of all suspensions by dynamic light scattering on a Malvern Zetasizer Nano instrument (Malvern Instruments Ltd., UK) in accordance with published procedures.[9,10] The ζ-potentials of NDs were 27±5, 27±5 and 31±6 mV for Sinta, SKN-100 and SKN-15 samples, respectively. An average hydrodynamic diameter of particles in the suspensions determined by means of dynamic light scattering were 93±10, 65±6 and 35±4 nm for Sinta, SKN-100, and SKN-15, respectively.

‡ The first experiment was carried out using a Model 28-35 GRAD ultrasonic bath (Russia) for all of the hydrosols directly before target preparation during 20 min. The second procedure was performed on a UZDN-A ultrasonic disperser (Russia) with a titanium ultrasonic horn. A 10–20 cm^3 hydrosol portion with a concentration of 0.15 g dm^{-3} was sonicated for 2–6 min at an acoustic power of 30–60 W.

§ The reaction vessel with NDs was connected to a device designed for gaseous tritium and filled with a tritium–protium mixture to 1.3 Pa. Tungsten wire was electrically heated to 2000 K for 10 s. After that, the residual gas was pumped out, and the reaction vessel was filled with a new portion of tritium. The labeling procedure was repeated from 2 to 16 times. After the reaction, the residual gas was pumped out, the NDs were suspended in water, and their radioactivity was measured using a RackBeta 1215 scintillation spectrometer (LKB, Finland). To purify [^{3}H]NDs from labile tritium, the suspensions were evaporated and suspended in water once again. The evaporation/resuspension procedure was repeated until constant radioactivity .

Table 1 Maximum specific radioactivity (A_{max}) and effective rate constants of tritium bonding (k_{eff}) determined from equation (1).

NDs sample	Without sonication			Sonication		
	A_{max}/TBq g^{-1}	k_{eff}/s^{-1}	r	A_{max}/TBq g^{-1}	k_{eff}/s^{-1}	r
Sinta	3.4	0.015	0.938	7.8	0.020	0.984
SKN-100	4.5	0.025	0.988	6.9	0.062	0.947
SKN-15	7.4	0.033	0.697	8.7	0.041	0.991

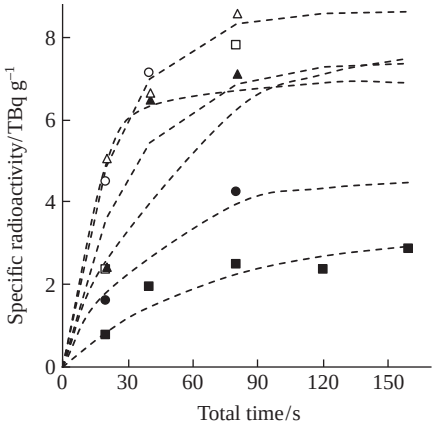


Figure 1 Dependence of the specific radioactivity of NDs on the total time of interaction with atomic tritium for targets prepared by ultrasonic treatment (open symbols) and initial ND hydrosols (black symbols). Samples: (squares) Sinta, (circles) SKN-100, and (triangles) SKN-15. Dashed line shows the result of calculations according to equation (1). Correlation coefficients (r) are summarized in Table 1.

Here, A_{max} is the limiting radioactivity, which is determined by the amount of active sites or positions available for tritium binding; k_{eff} is the effective rate constant of tritium bonding to carbon material; and t is the number of 10-s exposures multiplied to 10. Table 1 summarizes the calculated values of A_{max} and k_{eff}.

Note that, among the impurities in sonicated NDs, only titanium can form a hydride and thus enhance labeling efficiency. However, the calculations have shown that 0.3% Ti after the formation of titanium hydride (tritide) resulted in a radioactivity of 0.14 TBq per gram of NDs. Thus, such an amount of titanium contributes to the specific radioactivity, but it cannot increase the radioactivity by a factor of 3.

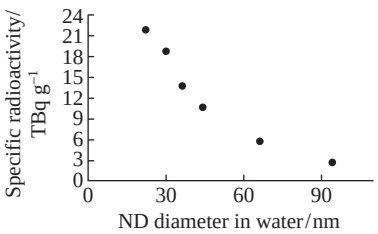


Figure 2 Dependence of the calculated maximum possible specific radioactivity (A_{max}) on the diameter of ND particles in aqueous suspensions.

Figure 2 shows the dependence of the calculated maximum possible specific radioactivity on the particle diameter of NDs in aqueous suspensions.

The parameter $A_{max}\,d$, where d is the particle diameter, should be a constant for the model of nanodiamond surface labeling. However, it is true only in the cases of NDs particles with diameters greater than 40 nm. In this case, the specific surface radioactivity is 0.15 TBq m^{-2}, which corresponds to 85 tritium atoms per nm^2. This concentration of hydrogen atoms on the surface is unattainable. Thus, we found that tritium in NDs occupied not only the surface of NDs aggregates but also pores, which are less than 20 nm in depth. Water molecules prevent the penetration of atoms into deep pores, resulting in an increase of labile radioactivity. More effective labeling becomes possible on the preliminary ultrasonication of aqueous suspensions due to a decrease in the particle size of NDs aggregates.

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