



Novel synthesis and properties of hydrogen-free detonation nanodiamond

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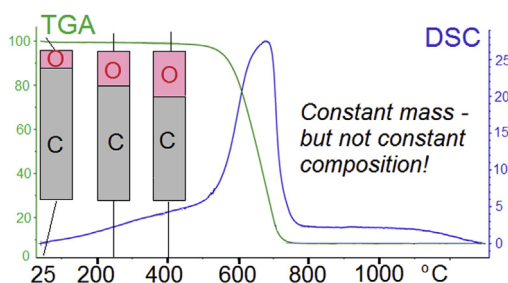
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HIGHLIGHTS

- Detonating pure RDX yields hydrogen-free nanodiamond prospective for neutron optics.
- Larger particles than ordinary nanodiamond.
- Enigmatic oxidation without apparent weight loss.

GRAPHICAL ABSTRACT



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ABSTRACT

Practically hydrogen-free nanodiamond (HFND), a prospective neutron-optical material, was prepared (in up to 3% yield) by detonating pure or graphite-doped RDX in an ice shell and comprehensively characterized by elemental analysis, X-ray diffraction, TEM, SAED, EELS, Raman and IR spectra, ESR, DSC/TGA, and specific-surface (BET) determination. The primary diamond grains are larger (15–16 nm) than in ordinary nanodiamond from RDX/TNT blends (ca. 5 nm) but smaller than in HFND from benzotrifuroxan (27 nm), with electron spins distributed in volume. HFND is much less hygroscopic and more prone to oxidation than ordinary nanodiamond. When heated in air up to 400°C, HFND shown a drastic increase of oxygen/carbon ratio without an apparent loss of mass. The mechanism of hydrogen non-contamination (through segregation of detonation gases) and particle growth is discussed.

1. Introduction

Different allotropic forms of nanocarbon [1] attract intense interest and find a widening variety of applications, due to their multifunctional properties. Thus, composites involving graphitic-type (sp^2 -C) nanophases, such as carbon black [2], nanotubes [3–6] and 2D-carbon flakes [7] are prospective for catalytic, optoelectronic, gas-sorption and ion-scavenging applications, thermally reduced graphene for copolymer building blocks [8] and graphene quantum dots for photo-luminescence

and supercapacitance devices [9]. On the other hand, nanodiamond (ND) particles (sp^3 -C) [10,11] which are now industrially produced [12] at low cost by detonation of high explosives, have actual and potential applications ranging from drug delivery to quantum computers, besides more conventional uses, such as abrasive materials. Another prospective area is ‘neutron optics’. ND is the most efficient reflector of very cold neutrons (VCN) in their entire energy range, due to fortunate combination of physical parameters: the size of nanoparticles is comparable with the VCN wave length, they provide high

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neutronoptical potential and low neutron absorption [13–15]. The energy of a cold neutron can be further reduced on interaction with ultracold ND [13]. Thus the density of VCN can be increased by many orders of magnitude, with exciting methodical results. Unfortunately, ND usually contains up to 1% of hydrogen, most of which cannot be removed by degassing, thermal treatment, etc. Large inelastic scattering by ^1H makes it a most unwelcome impurity, causing large loss of neutrons and much devaluing ND as a neutron-optics material [15], while its isotopic replacement with deuterium is very difficult. Therefore it is highly desirable to prepare intrinsically hydrogen-free ND (HFND).

The formation of ND, both chemically and physically, is a far-from-equilibrium, multi-stage process of great complexity, still imperfectly understood [12,16–21]. Indeed, the very appearance of condensed carbon is a challenge to the canonical theory of the plane wave steady detonation process [22]. Two conditions are considered indispensable: the explosive having negative oxygen balance (OB), i.e. an excess of carbon over oxygen, and suitable thermodynamic parameters on the Chapman–Jouguet (CJ) plane [23–25], i.e. the surface where the reacting gases just reach sonic velocity as the chemical reaction (and energy release) is essentially complete. These parameters, temperature T_{CJ} and pressure P_{CJ} , depend on the detonation velocity W_d , hence on the composition, structure and porosity of the explosive. Industrially, ND is usually prepared by detonating RDX (hexogen, $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$) blended in various proportions with trinitrotoluene (TNT, $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$). Formation of ND requires $T_{\text{CJ}} > 3000\text{ K}$ and $P_{\text{CJ}} > 30\text{ GPa}$ and begins with nucleation (near the CJ plane) of carbon nanoclusters from supersaturated carbon vapour. During the subsequent isentropic expansion of the detonation products, these clusters coagulate into nanodroplets of carbon, which crystallize and grow in the diamond structure, as at these conditions (3400–2900 K, 16.5–10 GPa) nanodiamond is thermodynamically more stable than graphite [17]. As the opposite is true at lower pressures, the products must be cooled rapidly to the temperature where thermodynamic favourability of the diamond→graphite conversion is nullified by its high kinetic barrier. This is achieved by allowing the detonation gases to expand into large volume of a blast chamber and/or by surrounding the charge with a shell of ice or liquid water (the so-called ‘wet method’) which both reduces the temperature and extends the duration of high pressure. Then the post-explosion soot is treated by oxidizing acids (HClO_4 , HNO_3 /oleum, *aqua regis*, etc.) or by ozone to eliminate the graphitic phase.

This scheme has many caveats. OB is conventionally calculated assuming only H_2O , N_2 and CO_2 as gaseous products, but in fact the reaction is often incomplete and yields CO. It was therefore suggested [26] that the $\text{OB} < 0$ condition is not enough and the carbon/oxygen atomic ratio must exceed 1, in which case pure RDX should not yield ND. Homogenous nucleation model fits awkwardly with highly non-homogenous nature of post-detonation media. On nanoscale, both the melting conditions and the equilibrium between graphite and diamond are different from those of the bulk phases (to which the conventional phase diagram refers!), but even for the latter the melting conditions of diamond are debatable. Carbon coagulation being exothermic, the droplets can become much hotter than the detonation products themselves; CJ plane is not easy to define for multistage reaction. The experimental studies, difficult due to extreme rapidity of the reactions, aimed primarily at increasing the yield of ND, and therefore paid relatively little attention to the fate of impurities. Thus, to our knowledge, there has been no inquiry whether the hydrogen contamination comes from the explosive(s), the coolant or even the oxidizing solution.

Recently, we prepared HFND by detonation of a hydrogen-free explosive, benzotrifuroxan (BTF, $\text{C}_6\text{N}_6\text{O}_6$) [27]. (Interestingly, Titov et al. used the same explosive in 1993 [28] and probably obtained HFND without recognizing it, as neither elemental analysis nor chemical properties of the ND product were reported.) However, the synthesis of BTF [29] is expensive, and the yield of HFND from it is low (ca. 5%). Therefore in the present work we developed a technique of preparing HFND from cheap mass-produced explosives. In the process, we

clarified some general aspects of ND synthesis and comprehensively characterized the physico-chemical properties of HFND, which differ substantially from those of ND prepared conventionally from RDX/TNT blends.

2. Experimental part

Commercial RDX was obtained from the Altay Federal Scientific-Industrial Centre (Biysk, Russia), BTF from the Soyuz Federal State Unitary Enterprise (Moscow Region, Russia), carbon black (particles size ca. 200 nm, elemental analysis: C, 97.51; N, 0.19; H, 0.35%) from the Technical Carbon Co (Yaroslavl, Russia), synthetic μm -sized diamond powder from Euro Superabrasives Ltd (Darlington, UK).

Detonation experiments used a cylindrical explosive charge assembled of 10 pressed disks, 8.8 mm thick and 20.1 mm in diameter, enclosed in an ice shell and detonated in a nitrogen-filled steel chamber. The recovered soot was refluxed with concentrated perchloric acid to remove the graphitic component and then repeatedly refluxed with fresh portions of boiling de-ionized water until approximately neutral reaction, whereupon ND was precipitated from colloidal solutions by centrifugation (at 15,000 rpm) and dried in air at 200 °C until constant weight. The explosive charge consisted either of pure commercial RDX or of RDX doped with 5% of graphitic carbon black, yielding ND products 1 and 2, respectively. BTF-derived HFND 3 [27] and ordinary ND 4 [30] were prepared as described earlier and purified identically to 1 and 2. Teflon and (for centrifugation) nalgene vessels were used throughout, to exclude contamination by silica from glassware.

CHN analysis was carried out on a freshly calibrated Carlo Erba 1106 automatic analyzer [31]; samples were burnt under flow of oxygen at 1050°C (1800°C at the moment of flash), the combustion products (N_2 , CO_2 , H_2O) were chromatographed in a flow of He gas. The X-ray diffraction patterns were recorded on a modernized DRON powder diffractometer (Cu-K α -radiation, $\lambda = 154.18\text{ pm}$). Grain sizes, τ , were calculated using Scherrer equation

$$\tau = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

where $K = 0.94$ and β is the peak half-width in radians. The total particle sizes D were estimated from the observed specific surface area S and density ρ (hence $V = 1/\rho$), assuming spherical particle shapes, as

$$D = \frac{V}{S} = \frac{\pi D^3/6}{\pi D^2} = \frac{6}{\rho S} \quad (2)$$

Specific surfaces were measured on a Gemini VII 2390 V1.02t instrument (Micromeritics Instrument Co) by N_2 gas adsorption at 77.3 K, using an adaptive rate and static volumetric technique. Samples were dried and degassed at 200°C, then kept under vacuum for 12 h before being weighed and analysed; the data were processed using Brunnauer-Emmett-Teller (BET) model. Densities of HFND powders were measured by liquid picnometry in toluene. ESR spectra were recorded using the State Standard Instrument in National Research Institute of Physical-Technical Measurements (Russia) with the signal modulation of 0.5 Gs. IR spectra were recorded on Perkin Elmer Spectrum One and Universal ATR Accessory instrument by the method of full internal reflection. Raman spectra were recorded using a Horiba Jobin-Yvon LabRamHR, equipped with a 532 nm laser, and calibrated against Si line (520 cm^{-1}). DSC/TGA measurements were carried out using a NETZSCHSTA 409 PC/PG instrument, heating rate 10 K/min.

TEM and SAED experiments were performed on a JEOL 2100 F field emission gun instrument (microscope voltage 80 kV). The solution containing nanodiamond was sonicated and deposited on a holey carbon grid. Energy-dispersive X-ray spectra were recorded on an Oxford Instruments EDX spectrometer. EELS spectrum was recorded on Gatan Tridiem instrument, including spectrum imaging in scanning TEM (STEM) mode [32].

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