Materials Chemistry and Physics 173 (2016) 325–332

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

On the nature of fibres grown from nanodiamond colloids

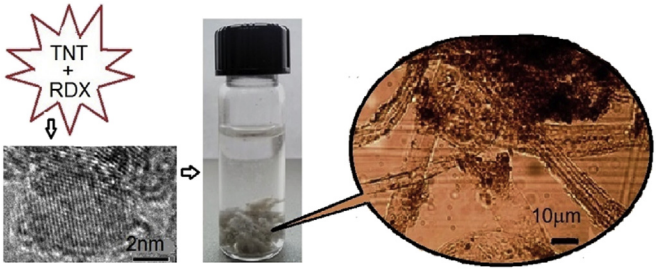
Stepan S. Batsanov [a, *], Dmitry L. Guriev [a], Sergey M. Gavrilkin [a], Katherine A. Hamilton [b], Keith Lindsey [b], Budhika G. Mendis [c], Helen J. Riggs [d], Andrei S. Batsanov [d]

[a] National Research Institute of Physical-Technical Measurements, Moscow Region, Russia
[b] School of Biological and Biomedical Sciences, Durham University, Durham, UK
[c] Physics Department, Durham University, Durham, UK
[d] Chemistry Department, Durham University, Durham, UK

HIGHLIGHTS

- Entangled fibres slowly grow in dilute (~0.1%) colloids of nanodiamond in water.
- Refractive index (~1.56), electron microscopy and CHN analysis indicate nanodiamond dispersed in organic matter.
- Explanation: nanodiamond grains help the growth of fungi which assemble them.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 August 2015
Received in revised form
19 January 2016
Accepted 6 February 2016
Available online 20 February 2016

Keywords:
Nanostructures
Biomaterials
Electron microscopy
Optical microscopy
Optical properties

ABSTRACT

Contrary to earlier assumptions, the fibres spontaneously forming in aqueous colloids of detonation-produced nanodiamond (ND), do not consist purely of ND particles but are agglomerates of the latter with water and/or soft matter of biological (probably fungal) origin, as shown by elemental analysis, IR and Raman spectroscopy, X-ray diffraction, optical refractometry, optical and electron (TEM and ESEM) microscopy, as well as biological staining tests.

1. Introduction

Nanodiamond(ND) particles of 4–5 nm size, produced in bulk quantities by detonation of explosives with negative oxygen balance [1], form colloidal dispersions in water (NDW) [2] which are essential in the manufacturing of ND and in most of its applications, especially biomedical, e.g. drug delivery [3]. The stability *vs* coagulation of NDW is thus extremely important. The propensity for coagulation varies widely, depending on the surface modification of ND and therefore, on the history of its synthesis and purification [4], and is not yet fully understood.

As a part of our ongoing studies of NDW [5], in the present work we investigate the earlier reports that microscopic fibres, assumed to be diamond nano-wires with very high length-to-thickness ratio (aspect ratio), can form from NDW.

* Corresponding author.
E-mail address: batsanov@mail.ru (S.S. Batsanov).

http://dx.doi.org/10.1016/j.matchemphys.2016.02.019
0254-0584/

Here, two distinct cases must be considered. Belobrov in 1996 and Koscheev in 1999 observed spontaneous formation from NDW (especially in the presence of salts) of fibres, entangled 'felt-like'. Their results were never published in peer-reviewed journals but reported in an unpublished DSc thesis [6] and an interview to a popular-scientific journal [7] (both in Russian). They became widely known through citation in influential reviews [8] and [4], respectively. Unfortunately, neither report contained any details, apart from optical and electronic microscopy images of the fibres. Later we obtained similar fibres [5a] and recorded their X-ray diffraction pattern and IR spectra. On the other hand, Dai et al. obtained rectangular-shaped microfibres with aspect ratio of over 1000 on the boundary of a drying drop of NDW on a slide [9].

Fibrous shapes are surprising, as ND has cubic crystal symmetry and no apparent source of directed, one-dimensional interactions. It has been suggested that ND particles possess dipole moment which disappears on aggregation [8], that different crystal faces of an ND particle acquire opposite electric charges, the electrostatic attraction between which holds the fibres together [10]. Another model emphasized Van der Waals interactions between diamond faces [11]. While these models can explain self-assembly of *ideal* nano-sized crystal of diamond (though hardly predict the formation of micron- or even mm-long fibres), they are hardly applicable to *real* ND particles. The latter usually have quasi-spherical shape and no properly formed crystal faces. Furthermore, they are never pure diamond, nor even pure *carbon*. The diamond core is always surrounded by a shell of amorphous carbon and then by H atoms and/or various functional groups (e.g. OH, carboxyl, etc.) terminating the surface [1,3,4,8]. Indeed, it can be argued that impurities are indispensable for the diamond core's stability [12]. Furthermore, none of the previous researchers in fact analysed the chemical composition of the fibres – they were only *assumed* to consist entirely of ND.

In view of these problems, as well as prospective utility of ND wires as electrochemical bio- and gene-sensing platforms [13], we systematic studied the origin, composition and properties of these supposed 'nano-diamond fibres' (NDF).

2. Experimental section

2.1. Characterization

Elemental analysis was performed using Carlo Erba 1106 analyser. TEM studies were carried out on a JEOL 2100 F field emission gun transmission electron microscope (microscope voltage 200 kV), the sample being deposited on a holey carbon grid. ESEM experiment in environmental mode was carried out on an XL30 ESEM® TMP instrument with the sample cooled on a Peltier stage. Energy-dispersive X-ray data were recorded on an Oxford Instruments EDX spectrometer. IR spectra were obtained with a Perkin Elmer Spectrum One instrument in the disturbed full inner reflexion mode using Universal ATR Accessory (520–4000 cm^{-1}); a powder sample was pressed against the diamond window of the accessory. The Raman scattering and photoluminescence experiments were carried out on a Horiba LabRAM HR 800 spectrometer; the samples were places on Si substrate and excited using Ar^+ laser (λ = 488 nm, 350 MW, 1 × 1 μm focal spot). ESR spectra were recorded on a modernised RE-1306 instrument. Refractive indices (n_D) were measured by the immersion method at λ = 589 nm [14]. Staining of the samples was carried out using either aniline blue or lactophenol cotton blue, according to previously published techniques [15,16].

2.2. Preparation of the colloids

1 g of ND powder (specific surface area of 310 m^2 g^{-1} by BET method) prepared and purified as described earlier [5b], was thoroughly ground in an agate mortar (to break up larger agglutinations of ND particles down to 2–10 μm size) and stirred with 150 ml of high-purity water. The mixture was homogenised in an ultrasonic bath for 1 h, then left until solid residue stopped precipitating and the solution became clear; this stage takes from several days to several weeks depending on the initial dispersion state of ND. The clear solution was syringed off and further cleared by centrifugation (at 15,000 rpm); the final concentration of ND in such solution was *ca.* 0.01 wt%. Suspensions of orthorhombic sulphur, graphite and amorphous boron in water were prepared similarly from commercial materials with mean particle sizes of 0.2 μmin their colloidal suspensions, as verified by dynamic laser scattering using Fritsch Analyzette 22 instrument. Teflon vials were used for all experiments and storage, because we found colloids and slurries ofND to erode glassware, whether abrasively or chemically.

3. Results and discussion

Lacking the exact protocols or spontaneous NDF growth from earlier works [6,7], we allowed 50 samples of aqueous ND colloids to evaporate slowly at room temperature under atmospheric air, at various rates ranging from several days to several months. After approximately tenfold decrease of the NDW volume, i.e. when ND concentration reached *ca.* 0.1 wt%, spherical particles of *ca.* 10 μm size emerged, which then coagulated into larger quasi-spherical clusters of the order of 100 μm, see Fig. 1(a). Simultaneously with this, agglomerates of entangled light-brown or grey fibres, on the order of 1 μm thick and up to 1 mm in length, emerged and ultimately grew to several mm or up to 1 cm in diameter, see Fig. 1(b–d). At this stage, the coagulated product was clearly visible to naked eye, Fig. 2(a). Remarkably, the fibres always emerged within the volume of NDW, rather than on the walls of the vial, where crystallisation usually starts. In two cases, we observed fibres of rather different appearance, green or bright red colour, which evolved on the surface of the liquid and clearly resembled mould infestation, Fig. 2(b). This induced us to explore the possibility that NDF can be of biological nature (*vide infra*) [17].

Freshly filtered-off (without drying) NDF gave a rather featureless X-ray diffraction pattern [5a] (Fig. S1). After drying and compaction, it was possible to discern broad Bragg reflections of ND (Fig. S2) but no other. Elemental analysis (Table 1) of the NDF samples dried in air at room temperature for 2 h (**1**) and for 4 h (**2**), or at 60 °C for 1 h (**3**) and for 2 h (**4**), revealed a substantial presence of N and H, a steady relative increase of the carbon content (in the succession **1** < **2**<**3** < **4**) on drying, and a decrease of the balance. The latter is presumably mostly oxygen, whether from water, surface-terminating groups of ND particles, or other sources. However, energy-dispersive X-ray (EDX) spectra showed, besides C, N and O, small but significant presence of Si, Na, K and Ca (see Fig. S3). Chemical analysis also revealed sample **1** to contain ca. 0.6% of Si, which contaminated the original ND powder due to well-known ability of powerful shock-waves to extract Si from the steel walls of the explosion chamber [18]. Ignoring these admixtures, the composition of NDF can be roughly approximated as listed in Table 1.

Inspecting samples **1**, **3** and **4** under a high-magnification polarising microscope, we found the fibres to comprise agglomerates of dark brown particles linked by transparent nearly-colourless chords (Fig. 3), which we studied by optical refractometry. Typically, the refractive index (n) of chords averaged 1.56 ± 0.01 and