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Microwave-assisted purification of detonation nanodiamond

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ABSTRACT

In the present work microwave-assisted purification approaches for detonation nanodiamond (DND) are considered, and the resultant impurity content of purified DND revealed by direct ICP-MS and elemental analysis. A significant reduction in noncarbon contaminants as compared with detonation soot was achieved with resulting purity of 99.95%. Surface characterisation including scanning electronic microscopy, low temperature adsorption of nitrogen, acid–base potentiometric titration, zeta potential measurements and particle size distribution of the DND in suspensions revealed distinctive surface properties for each purified DND sample. Results highlight the suitability of the microwave purification approach using acid reagents, allowing nanodiamonds with different and reproducible surface properties to be produced or modified. Contamination effects from laboratory glassware used to store samples were carefully considered. Refined DND with impurity levels over two orders of magnitude lower than commercially available samples was prepared. The profile and concentration levels of residual impurities in purified samples of nanodiamond are discussed with identification of possible reasons for contamination.

1. Introduction

Carbon nanomaterials (and in particular nanodiamonds) have been an object of a growing scientific interest in recent decades [1]. Currently nanosized diamonds are widely produced through detonation transformation of powerful explosive composites having negative oxygen balance under conditions of high temperatures and pressures within closed chambers [2,3]. The detonation of such explosive charges surrounded by a non oxidising cooling media (gas, liquid, ice) leads to the formation of carbon phase (so called Diamond Soot — DS) containing nanosized diamond, graphitic carbon and inorganic constituents in different ratios [4,5]. The purity of detonation nanodiamonds (DND) is a key factor for their use in many areas including nanomedicine [6], drug delivery [7], bioimaging [4], and chromatography [8], so purification and purity of DND attract great interest amongst researchers in this field.

Detonation nanodiamond (DND) itself can be isolated from the DS and purified by using gas-phase or liquid-phase oxidative treatment [9–12]. The purification of DND is not a trivial task and no ideal method has been reported for complete removal of sp^2-bonded carbon. For example, gas-phase thermo-oxidative purification in air [12] can result in diamond mass loss and cannot totally remove metal admixtures, requiring subsequent treatment. A similar situation occurs when using ozone-enriched mixtures [9], where additional acid processing is required. DND reduction in hydrogen atmosphere at 500 °C for 5 h was also reported as a purification technique, but sp^2-carbon cannot be completely removed by this method [13]. However, no information on removal of metal impurities was provided by the authors. Another post production treatment involves the use of gaseous chlorine or carbon tetrachloride vapours [14], a process combining surface modification with metallic and Si-impurities removal under harsh conditions (723–1123 K).

The main advantage of the liquid-phase purification approach is the possibility for simultaneous removal of both graphitic carbon and metallic impurities. Liquid-phase treatment based on oxidative salt (either potassium dichromate [15] or permanganate [16]/acid mixtures) is probably the most commonly used type of DND-purification due to its simplicity. This approach can be performed even in small-scale laboratories, although potentially hazardous and expensive reagents are required; additionally the process outputs DND rich in metal contaminants. Oxidative purification using acids under elevated pressure and temperature is considered capable of producing nanodiamonds with low metal impurities [11]. At the same time the necessity for large and robust pressurised reactors constructed from titanium or niobium results in some inflexibility during the DND production process — few types of purified DND can be produced in large amounts. Recently a Russian team reported the use of a small 400 cm^3 titanium-walled autoclave for the laboratory scale digestion of DS with nitric acid at temperatures up to 523 K and concentrations reaching 57% [17]. Of course, in this case the application of some reagents

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is limited once again by the chemical resistance of internal walls of titanium reactors.

The other option for the purification of nanodiamonds from metal impurities is treatment with strong complexing agents. The use of 1-hydroxyethylidenediphosphonic acid (10% solution in water) for removal of iron and copper impurities was proposed [18]. Unfortunately no data on efficiency of such purification was provided [18]. The efficiency of six complexing agents including sodium 2,3-dimercaptopropanesulfonate (Unithiol), disodium dihydrogen ethylenediaminetetraacetate (EDTA), thiourea, potassium thiocyanate, dicyandiamide, and hexamethylenetetramine as 0.5–20% aqueous solutions for the removal of metal impurities was also checked [19].

A number of microwave-assisted approaches for the purification of mainly sp^2-nanocarbon structures have been reported in the literature [20]. A purely thermal approach has been described where microwave-assisted heating of carbon nanotubes (CNT) at a temperature of 125 °C dissociates and disperses “non-nanotube carbon” in an organic solvent (CH_2Cl_2) [21]. Another study describes treatment of CNT with nitric acid at a temperature of 160 °C in a closed reaction vessel using microwave irradiation [22]. Microwave assisted purification of CNT in closed vessel at 180 °C in presence of 20% hydrogen peroxide or HNO_3 has also been reported [23], revealing significant mass loss of CNT for the first option. A combined acid mixture of 3:1 H_2SO_4/HNO_3 with ultrasonication has been used to clean CNT from metal catalyst residues [24]. Purification, functionalisation and dispersion of CNT with acid mixtures and complexants have been reported [25].

Only a few papers report the direct DND-treatment using microwave energy. The microwave induced carboxylation of nanodiamonds has been considered [26]. An activation of the surface of nanodiamonds using mixture of 3:1 H_2SO_4/HNO_3 at 100 °C in a microwave reactor for 3 h before modification with poly(arginine) is described [27]. To the author's knowledge no study has focused on the microwave-assisted purification of detonation nanodiamond starting from the raw initial product, DS.

In the present paper the possibilities of microwave-assisted oxidative acid digestion for the purification of DND are considered. Seven different chemical compositions were tested under elevated pressure and temperature in reactors. Method efficiencies are assessed considering both the elimination of non-diamond carbon and/or metal impurities. Surface properties post-purification revealed variations depending on purification conditions. Furthermore, the application of microwave-assisted complexing agent treatment to highly purified DND further improved its purity. A recently reported direct inductively coupled plasma mass spectroscopic (ICP-MS) approach [5,28] was used for monitoring metal impurities of treated DND. Comparison with several previously investigated commercially available nanodiamond types [5] highlights the potential of the method.

2. Materials and methods

2.1. Materials

Diamond Soot (DS) was obtained from SRTI-BAS, Bulgaria, and YTM ARGE A.Ş., Istanbul, Turkey. DS type SRTI was synthesised using TNT/RDX charges with water coolant in 2 m^3 spherical blasting chamber, and represents a deep black powder with pH of 9.50 (in 1% aqueous suspension). DS type YTM was also synthesised using TNT/RDX charges with ice coolant in 5 m^3 spherical blasting chamber; and is a deep black coloured powder with pH of 9.43 (in 1% aqueous suspension). Milli-Q deionised water with resistivity 18.5 M Ω cm (at 298 K) was used throughout this work. All reagents used were of analytical grade quality: 95–97% H_2SO_4 and 48% HF, 70% HNO_3 (all from Chem-Supply, Gillman, SA, Australia), 37% HCl and 30% H_2O_2 (Merck, Kilsyth, Australia), 70% $HClO_4$ (Univar, Ingleburn, Australia), Na_2EDTA (Univar, Sydney, Australia) and 2,6-pyridinedicarboxylic (dipicolinic) acid (Sigma-Aldrich, Castle Hill, NSW, Australia).

2.2. Instrumentation

MLS-1200 MEGA Microwave Digestion System (Milestone Inc., Sorisole, Italy) with 6-position rotor was used for acid digestions of graphitic carbon from DS, and for the complexant-assisted post-purification refining. An ELEMENT 2 sector field ICP-MS spectrometer (Thermo Fisher, Bremen, Germany) was used for ICP-MS measurements, with direct introduction of the produced diluted suspensions (0.1 mg g^{-1}) to the instrument [21]. The elemental analysis for total N, C, H and S was determined using a Thermo Finnigan EA 1112 Series Flash Elemental Analyser (Thermo Scientific, Waltham, MA, USA). Samples were weighed using Sartorius SE2 ultra microbalance with an accuracy of 0.1 mg; combustion in ultrahigh purity oxygen together with V_2O_5 as a co-oxidant ensured fast and reliable oxidation of DND. BET surface determinations and pseudo-pore volumes were determined using low temperature nitrogen adsorption with a TriStar II analyser (Micromeritics, Norcross, GA, USA). High resolution images of the purified nanodiamond were acquired through Hitachi SU-70 field emission scanning electron microscope (FESEM; Hitachi High-Technologies Corp., Tokyo, Japan). Sonotrode type disintegrator MSE 10–75 MK2 and ultrasonic bath type Bransonic 5510E-DTH (Branson, Danbury, USA) were used for harsh and mild disintegration of DND suspensions. Zetasizer Nano ZS particle analyser (ATA Scientific, Taren Point, NSW, Australia) fitted with 632.8 nm red laser and 175° backscatter detection was used to estimate zeta (ζ)-potential and size parameters of derived samples. The pH-values of nanodiamond suspensions were adjusted using dilute solutions of sodium hydroxide and hydrochloric acid before injection into an electrophoretic cell. Titration results were derived using Metrohm Autotitrating 809 Titrando system fitted with 800 Dosino dosing unit (MEP Instruments Pty Ltd, Mitcham, Australia). Colorimetric measurement of the darkness of scanned images for purified and dried DND samples was done using Adobe Photoshop 6.0 for grayscale mode scans.

2.3. Sample preparation

2.3.1. Microwave digestion and refining

Seven different oxidative digestion mixtures and two complexing agents were applied (Table 1). Considering digestions loads from 0.60 to 1.20 g DS were mixed with corresponding mixture and agitated until fully suspended. Aliquots of the suspension were transferred to the specialised fluoropolymer vessels of MLS-1200 MEGA digestion system. Further amounts of HF and H_2O_2 (if necessary) were introduced immediately before capping the vessels. Working temperatures up to 533 K and pressures up to 1.1×10^7 Pa were used throughout the work. After digestion every sample suspension was washed repeatedly with deionised water until a pH of 4.0 or higher was reached.

For the deep purification procedures, two portions each of 0.50 g of the most refined nanodiamond type NSFPA-Pl-YTM were suspended in 30 g of 3.32% solution of Na_2EDTA, or of 0.50% (saturated) solution of dipicolinic acid. Ultrasonication was applied for 5 min to assist with the suspension process. After the microwave treatment suspensions were diluted to 100 mL with deionised water, decanted after settling, which was followed by three consecutive 1 L washings.

2.3.2. ICP-MS

Diluted and preliminary equalised to 0.1 mg g^{-1} aqueous suspensions of the corresponding DND were analysed directly using ICP-MS, according to the procedure described in [28]. The impurity content of the used primary DS was obtained as the sum of determined elementals in the decanted waste acid mixture after the digestion procedure, and that of corresponding DND after the consecutive washings, as described in [5]. Glass-related influence on the impurity levels of the suspensions (and separated supernatants) was monitored during storage in laboratory 20-mL borosilicate glass vials with intervals between from an hour to 15 days between measurements.