



HAL
open science

Facile characterization of metallic impurities in detonation nanodiamonds through selective combustion using standard techniques

Killian Henry, Mélanie Emo, Sébastien Diliberto, Sebastien Hupont, Jean-Charles Arnault, Hugues Girard, Marc Dubois, B. Vigolo

► To cite this version:

Killian Henry, Mélanie Emo, Sébastien Diliberto, Sebastien Hupont, Jean-Charles Arnault, et al.. Facile characterization of metallic impurities in detonation nanodiamonds through selective combustion using standard techniques. *Diamond and Related Materials*, 2023, 140 (Part A), pp.110466. 10.1016/j.diamond.2023.110466 . hal-04227808

HAL Id: hal-04227808

<https://hal.univ-lorraine.fr/hal-04227808v1>

Submitted on 4 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Facile characterization of metallic impurities in detonation nanodiamonds**
2 **through selective combustion using standard techniques**

3

4 Killian Henry^{1,2}, Mélanie Emo¹, Sébastien Diliberto¹, Sébastien Hupont¹, Jean-Charles
5 Arnault³, Hugues A. Girard³, Marc Dubois², Brigitte Vigolo^{1,*}

6

7 1 Université de Lorraine, CNRS, Institut Jean Lamour, UMR 7198, allée André Guinier
8 54000 Nancy, France

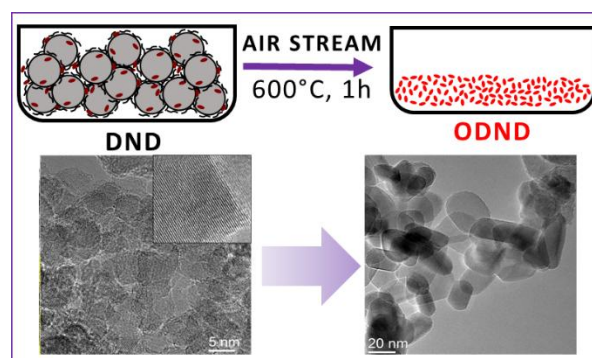
9 2 Université Clermont Auvergne, CNRS, ICCF UMR 6296, 24 av. Blaise Pascal, F-63178
10 Aubière, France

11 3 Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif sur Yvette, France

12 * Corresponding author e-mail: Brigitte.Vigolo@univ-lorraine.fr

13

14 Keywords: nanodiamonds ; metallic impurities ; impurity traces ; standard techniques ;
15 selective combustion



16 **Graphical abstract**

17

18 **Abstract** Detonation nanodiamonds are sp^3 carbon nanomaterials with narrow diameter
19 distribution. They have high potential of application in various fields like nanomedicine,

20 advanced composites and lubricants, photocatalysis. Detonation nanodiamonds unfortunately
21 contain metallic and inorganic impurities of diverse nature which can act as “Trojan horses”
22 and even at weak content, they can significantly impact the nanodiamonds efficiency and the
23 searched performances. Detection and quantification as well as subsequent removal of these
24 impurities is highly difficult due to the lack of tools available by scholars. In this work, we
25 propose a useful approach to detect and identify the inorganic impurities in detonation
26 nanodiamonds. Our method which consists in a selective combustion of the nanodiamonds
27 results in concentrating these impurities is a one-step and simple method. This approach,
28 transferable to other kinds of carbon nanomaterials, is proved to be a valuable way allowing
29 analysis of detonation nanodiamonds by standard characterization techniques such as X-ray
30 Photoelectron Spectroscopy, Fourier Transform Infra-Red and Raman spectroscopies or
31 Powder X-Ray Diffraction, available in any material science laboratory.

32

33 **1 Introduction**

34 After their confidential synthesis in the 1960s, detonation nanodiamonds (DNDs) have
35 become fascinating nanomaterials over the world in the last thirty years. The detonation
36 process is a powerful technique to produce NDs in high amount with a narrow distribution
37 size and of rather high crystallinity [1]. Typically, DNDs are synthesized from mixtures of
38 cyclotrimethylene trinitramine (RDX) and trinitrotoluene (TNT) leading to detonation
39 reaction; high pressure and temperature allow then the formation of nanometric diamond
40 crystallites. DNDs combine excellent thermal, mechanical and optical properties as well a
41 high and chemically modifiable surface area [2–4]. DNDs are considered as ideal materials
42 for applications over broad fields such as field emission, molecular sensing, heterogeneous
43 catalysis... [5–9]. Their development for bioapplications such as cancer therapy,
44 antimicrobial systems or drug delivery has increased in recent years. [10–18] Their use to

45 develop new slow neutron reflectors is another emerging research activity [19,20]; they have
46 the potential to achieve a breakthrough in condensed matter since they could provide the
47 unique technology to perfectly reflect slow neutrons. Pure DNDs could allow elastic or quasi-
48 elastic scattering due to their low velocity and low thermal (cold) character making them
49 particularly of great interest for study of condensed matter like colloids, biological molecules,
50 polymers etc...

51 Unfortunately, DNDs contain a variety of inorganic impurities under the form of traces with a
52 total content up to 2 - 3 wt.% [20–22]. Their origin is multiple: the reactor corrosion due to
53 the harsh conditions during the detonation synthesis, the post-synthesis treatments for their
54 separation from the other carbonaceous by-products and their post-synthesis purification
55 [23,24]. These impurities, especially heavy metals, can have a negative impact on the DND
56 properties to be exploited and they lead to non-desired and non-controlled effects:
57 radioactivity through neutron interaction, toxicity by release into bodies, non-controlled
58 optical phenomena...

59 The complete removal of these undesired metallic impurities within DNDs is currently not
60 possible with efficacy [25–27]. Their detection by standard characterization techniques is
61 impossible because of the weak content of each noncarbon impurity (below the Limit Of
62 Detection, LOD). This difficulty renders it all the more difficult to develop efficient and
63 simple purification approaches. It is as well important to note that each manufacturer or
64 supplier has its own method of synthesis and post-purification, resulting in impurities of
65 different natures and contents. There are multiple analytical methods suitable for direct
66 identification of elemental impurities such as X-ray fluorescence (XRF), atomic absorption
67 spectroscopy (AAS) or inductively coupled plasma-optical emission spectroscopy (ICP-
68 OES),[24,28] but only a few techniques are sensitive enough to quantify ultra-traces of
69 elements like in DNDs: inductively coupled plasma-mass spectrometry (ICP-MS) [22,23],

70 neutron (NAA) and prompt-gamma activation analyses (PGAA)[20,21]. Unfortunately, such
71 equipment are seldom available in common material research laboratories especially for
72 neutron activation based methods since they belong to large scientific instruments. It clearly
73 appears there is a need of developing a simple approach allowing a facile detection and
74 identification of the noncarbon byproducts in DNDs.

75 In this work, we propose to concentrate the inorganic part from DND samples by selectively
76 burning off the DNDs. These residues can be then characterized by means of standard
77 techniques whereas they fall below the LOD in the starting DNDs. Our approach, inspired
78 from the core principle of elemental analysis techniques [22–24], proposes a simple method
79 which allows to clearly identify the inorganic elements in DNDs and also the compounds
80 (nature and crystalline phase) belonging to the DNDs. The proposed approach consists of
81 thermally gasified the DND samples under air at 600°C, just above their combustion
82 temperature. During the DND's combustion process, the metal-based impurities possibly
83 undergone an oxidation reaction and their amount is finally substantially increased in the
84 outcome ashes. Their analysis is consequently strongly facilitated. Furthermore, this
85 treatment can be easily used by any scholars. We clearly show in this work that such method
86 allows to overcome the long-term issue of detection and identification of the inorganic
87 compounds in DNDs by standard characterization techniques: like X-ray diffraction (XRD),
88 X-ray photoemission spectroscopy (XPS), Fourier Transform InfraRed (FTIR) and Raman
89 spectroscopies. The proposed approach provides a universally accessible tool for the
90 determination of the main DND's impurities and their relative quantification. The resulting
91 better knowledge of DNDs is useful for developing efficient purification methods and can
92 boost future applications of DNDs.

93

94 2 Experimental Section

95 2.1 Sample preparation

96 The used DNDs were provided by the Federal State Unitary Enterprise (FSUE) “Russian
97 Federal Nuclear Center – Academician E.I. Zababakhin All-Russian Research Institute of
98 Technical Physics” (RFNC-VNIIF institute, Snezhinsk, Russia). The production followed the
99 Technical Regulation TY 2-037-677-94, where the DNDs were synthesized using a 60/40
100 mixture of TNT/RDX, and washed multiple times by acids. According to the RFNC-VNIIF
101 institute, this procedure leads to nanoparticles with a mean diameter of 4-5 nm.

102 For the selective combustion of DND sample, approximately 1 g of the as-received powder
103 was placed in a quartz boat then transferred into a quartz tube inside a tubular furnace. A
104 pump was fixed to one extremity of the tube to provide an air flow of around 100 mL/min.
105 The powder was therefore heated under air at 600 °C for one hour (10 °C/min), and then
106 cooled under ambient conditions until reaching room temperature. The outcome sample was
107 referred to as ODND. Since the content of the inorganic impurities (after oxidation) are
108 around 1.8 wt.% (Figure 1f, insert), 1 g of starting DNDs gives rise to around 180 mg of
109 residues which generates a sufficient quantity for several characterizations such as FTIR,
110 Raman spectroscopy, XPS and Transmission Electronic Microscopy (TEM) since for each of
111 them only less than 10 mg of sample are required.

112

113 2.2 Structural characterization

114 Powder XRD (PXRD) investigation was performed on a Bruker D8 advance diffractometer,
115 in the Bragg-Brentano geometry with a Cu-source ($\lambda_{\text{Cu}} = 1.54060 \text{ \AA}$) equipped with a fast 1D
116 LynkEye detector. Phase identification was performed using the Diffrac.Eva software V6.

117 The thermogravimetric analysis (TGA) was carried out using a Setaram Setsys evolution
118 1750 Thermal Gravimetric Analyzer. After loading the DND powder (around 10 mg) in an

119 alumina crucible, temperature was raised up to 900 °C under dry air at 5 °C/min with a
120 flowrate of 20 mL/min. For the cooling, the rate was of 20 °C/min.

121 For TEM and High Resolution TEM (HRTEM) analysis, DNDs were dispersed in ethanol
122 under sonication during 15 min. One droplet of the DND dispersion was deposited on a 200-
123 mesh-size holey carbon grid provided by Delta Microscopies. The TEM observations were
124 carried out using a JEOL JEM-ARM 200F Cold FEG apparatus equipped with a spherical
125 aberration (Cs) probe corrector working at an accelerating voltage of 200 kV. For the sake of
126 representativity of the sample, at least 50 images obtained at different locations on the sample
127 were taken. In the TEM figures shown in the paper, representative images of DNDs are
128 selected. Electron energy loss spectroscopy (EELS) and energy dispersive X-Ray
129 spectroscopy (EDX) experiments were performed in scanning transmission electron
130 microscopy (STEM) mode, as well as the high angle annular dark field (HAADF) images. X-
131 maps and spectra were recorded on a Jeol spectrometer (SDD, Jeol DRY SD 30 GV). For
132 EELS measurements, the spectrometer was set to an energy dispersion of 0.25 eV/channel to
133 collect C-K, N-K, O-K, Cr-L_{2,3} and Fe-L_{2,3} edges.

134 FTIR spectrometry was performed using a Nicolet 6700 FT-IR (Thermo Scientific)
135 spectrometer. Spectra were recorded in attenuated total reflectance (ATR; diamond crystal)
136 mode using 100 scans and a resolution of 2 cm⁻¹.

137 The microRaman spectroscopy study was performed with a LabRAM HR 800 micro-Raman
138 spectrometer. For the phase study for the ODND sample, a Torus diode laser with a
139 wavelength of 532 nm provided by Laser Quantum was used. The energy received by the
140 sample is around 4 mW/cm² at full power.

141 XPS spectra were collected on a Kratos Axis Ultra (Kratos Analytical, UK) spectrometer
142 equipped with a monochromatic Al K α (1486.6 eV). All spectra were recorded at a 90°
143 takeoff angle. The high-resolution regions were acquired with 0.1 eV step and 20 eV pass

144 energy (instrumental resolution better than 0.5 eV). For the analysis, the powders were fixed
145 onto a copper scotch tape. Curve fitting was performed using a combined Gaussian and
146 Lorentzian line profile after Shirley's background subtraction by Casa XPS software.

147 Regarding ICP-MS the quadrupole ICP-MS is an iCAPQ (ThermoElectron) classically
148 equipped with a cyclonic glass nebulization chamber (tuned in high matrix mode, with a
149 dwell time set to 40 ms) and a nanoparticle glass nebulizer (Glass Expansion). A collision
150 cell is used to avoid molecular ions that could be formed in the argon plasma. Samples are
151 analyzed by external calibration in the range 5 to 150 ppb. All dilutions are performed by
152 weight. Barium, copper, aluminum, iron, zinc, calcium, sodium and lead standards solution
153 are obtained by dilution from a SPEX CertiPrep Claritas and 2 % hydrochloric acid purified
154 by sub-boiling distillation. Samples are constantly placed inside an ultrasonic bath.

155

156 **3 Results and Discussion**

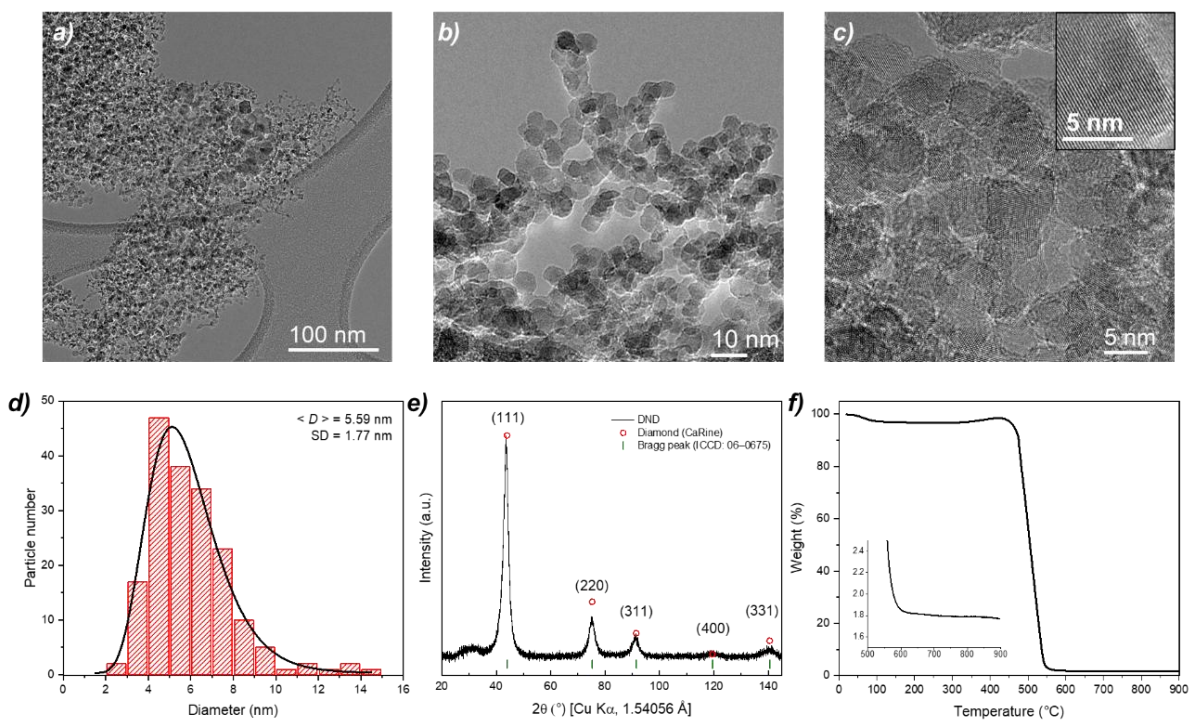
157 **3.1 Concentration of inorganic impurities by selective combustion of DNDs**

158 TEM observations show DNDs aggregates or chaplets of several hundreds of nm in size
159 (Figures 1a-1b), as typically observed for the NDs synthesized by the detonation method
160 [29–32]. An example of HRTEM image is depicted in Figure 1c. The insert exhibits lattice
161 planes of the DNDs, showing the crystallized structure of the material [29,33,34]. The size
162 distribution, over a total of 183 nanoparticles measured, follows a log normal distribution
163 behavior centered around 5.6 ± 1.8 nm, which is in agreement with the mean diameter of
164 4-5 nm given by the supplier (Figure 1d).

165 PXRD pattern of the studied DNDs exhibits the five reflections expected for the diamond
166 phase in the ICCD database (PDF#06-0675): (111) at 42° , (222) at 75° , (311) at 90° , (400) at
167 120° and (331) at 140° . By applying the Scherrer law on the (111) peak, a value of 4.2 nm

168 was found for the crystallite size, which is in accordance with the TEM analysis. The
 169 experimental diffractogram of DNDs (black) matches quite well with the XRD pattern
 170 simulated with CaRine software (red). The broad peak observed from 20-40° seems to belong
 171 to the (002) reflection of a sp^2 layers surrounding the DND particles [35–37], as suggested on
 172 upper left particle in Figure 1c.

173 Figure 1f exhibits the thermogram performed under air of the raw DNDs. After dehydration
 174 of the DNDs at around 120 °C, the major weight loss around 500°C corresponds to the DND
 175 complete combustion. Above 600 °C, the total amount of the inorganic impurities present in
 176 DNDs is around ~ 1.8 wt.% (inset Figure 1f). Those which are not already of an oxidized
 177 form have undergone an oxidation during TGA under air, which is confirmed by the weight
 178 gain observed in the 300-425 °C range.

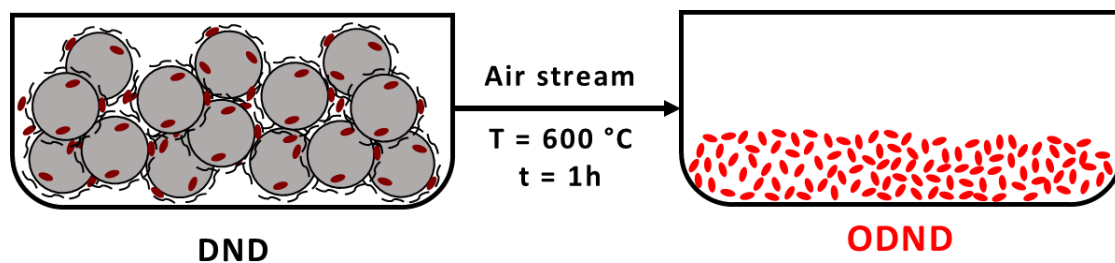


179
 180 **Figure 1** a)-b) TEM images of detonation nanodiamonds at different magnifications and c)
 181 HRTEM image of the same sample, insert: zoom-in on a ND particle. d) Size distribution of
 182 DND with a log normal distribution function (black curve), calculated based on 183 particles.
 183 The mean diameter is note $\langle D \rangle$, while the standard deviation is abbreviated SD. e) PXRD

184 pattern (Cu, 1.5406 Å) of as-received DND. The black line is the experimental pattern, the
185 red circles are the simulated pattern for diamond, based on CaRine software, green bars
186 indicate the position of (hkl) planes from the ICDD #06-0675 file. f) Thermogram of DND
187 under dry air. The insert is a zoom in the high temperature range showing the remaining mass
188 after the complete consumption of the DNDs.

189

190 Figure 2 illustrates the developed selective combustion of detonation nanodiamond method.
191 Temperature is raised up to above the DND burnt off (*i.e.* 600°C) determined from TGA
192 (Figure 1f) and the remaining inorganic impurities are thus naturally concentrated.



193

194 **Figure 2** Selective combustion of the detonation nanodiamonds leading to the outcome
195 ODND sample. DNDs are represented as grey solid circles surrounded by some graphite
196 layers (in black) and inorganic impurities (in brown). The resulting ashes (ODND) are
197 displayed in red.

198

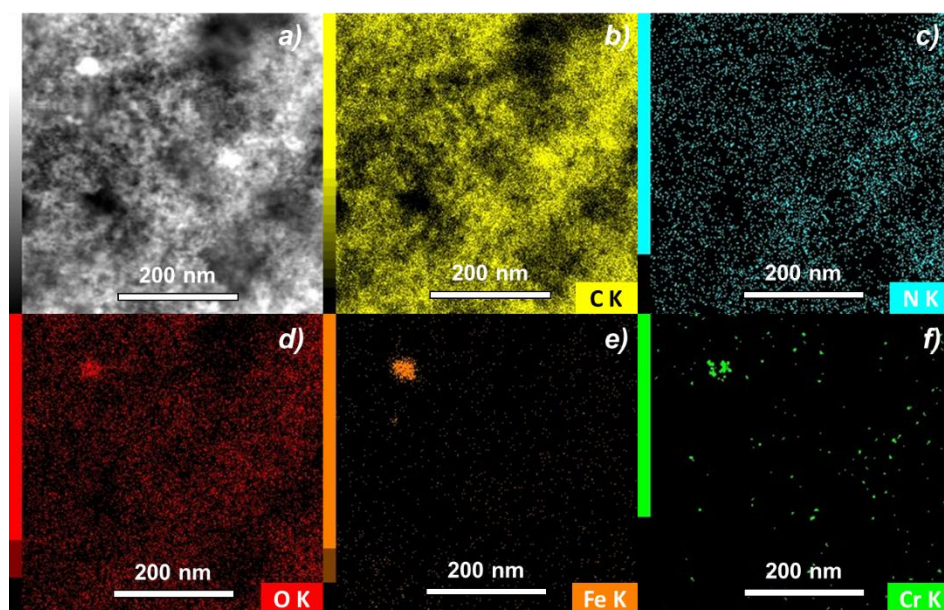
199 3.2 Determination of the main impurities in DND and ODND

200 The inorganic impurities (total amount of ~ 1.8 wt.%) present in the raw DND powder have
201 many origins and they are of numerous natures. Their detection is consequently a tricky task
202 since their respective content is below the LOD of most of the standard characterization
203 techniques. Thanks to local techniques such as EDX and EELS analysis, some impurities,
204 certainly those being present at the highest concentration in DNDs, could be detected.

205 Although local, such scrutinized investigation is required before quantitative analysis by
206 using ICP-MS which is indeed not possible in a blind manner.

207 **3.2.1 The main inorganic impurities in DNDs**

208 The TEM observation of inorganic impurities in DND was made possible by the use of high
209 angle annular dark field (HAADF) images in scanning mode. Thus, EDX spectroscopy
210 analyses were performed to determine the elemental composition of these particles. Also,
211 X-maps were acquired to localize precisely the inorganic elements. In Figure 3a, two brighter
212 spots are visible in the HAADF STEM, one is constituted of carbon (Figure 3b), while the
213 upper left particle is composed of two metallic elements: iron and chromium (Figures 3e-3f).
214 Also, oxygen is localized in the upper left particle, presuming a Cr/Fe-oxide based particle
215 (Figures 3d-3f). The size of the observed particles in DND is typically of 30-40 nm. A
216 complementary EELS experiment was carried out in another region and signals of O K-edge,
217 Cr and Fe L-edges were recorded, together with C and N K-edges (Figure S1, Supporting
218 Information). By investigated other areas of the DND sample, different particles were found
219 with distinct compositions (Figure S2, Supporting Information): one is composed of O, S and
220 Ba, while the other is constituted of O, Si, K, Cr and Fe. The fact that chromium and iron
221 were found in multiple particles seems to further confirm their distribution in the whole
222 sample as the main impurities. Also, a large particle constituted of Si and O was observed
223 (Figure S3, Supporting Information), probably originating from fragments of laboratory
224 glassware used for the purification of DND.



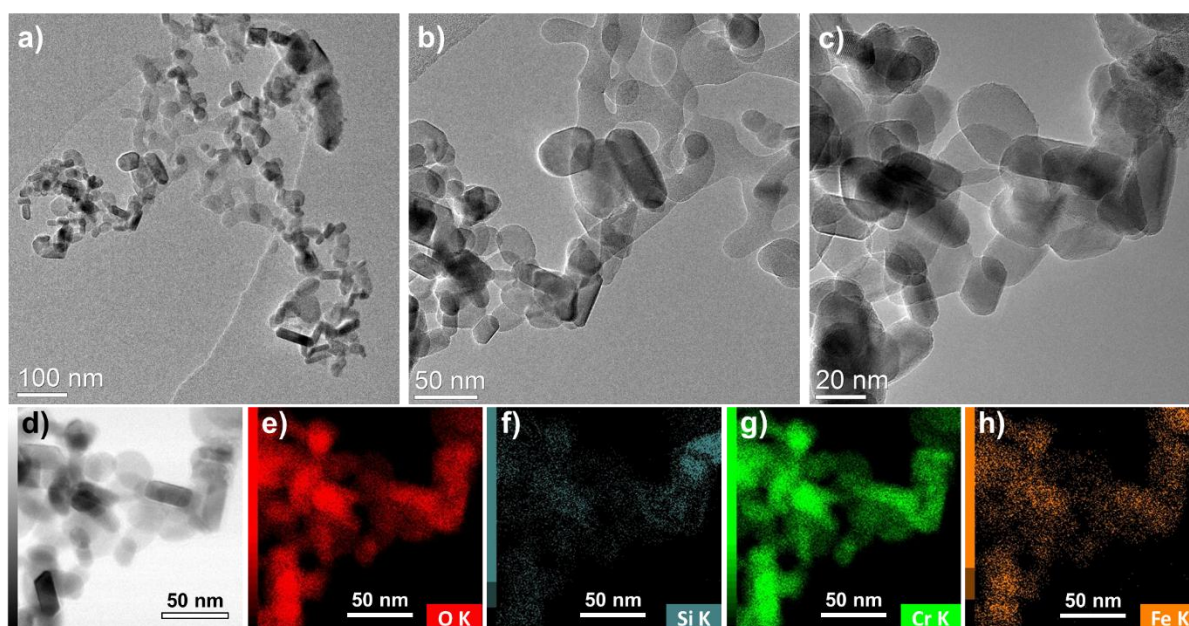
225

226 **Figure 3** a) High angle annular dark field (HAADF) STEM image of a selected area of the
 227 as-received DND, and b-f) corresponding EDX spectroscopy elemental mappings. Carbon
 228 signal is shown in yellow (b), nitrogen in light blue (c) and oxygen in red (d). Iron (e) and
 229 cobalt (f) are respectively represented by orange and green colors.

230

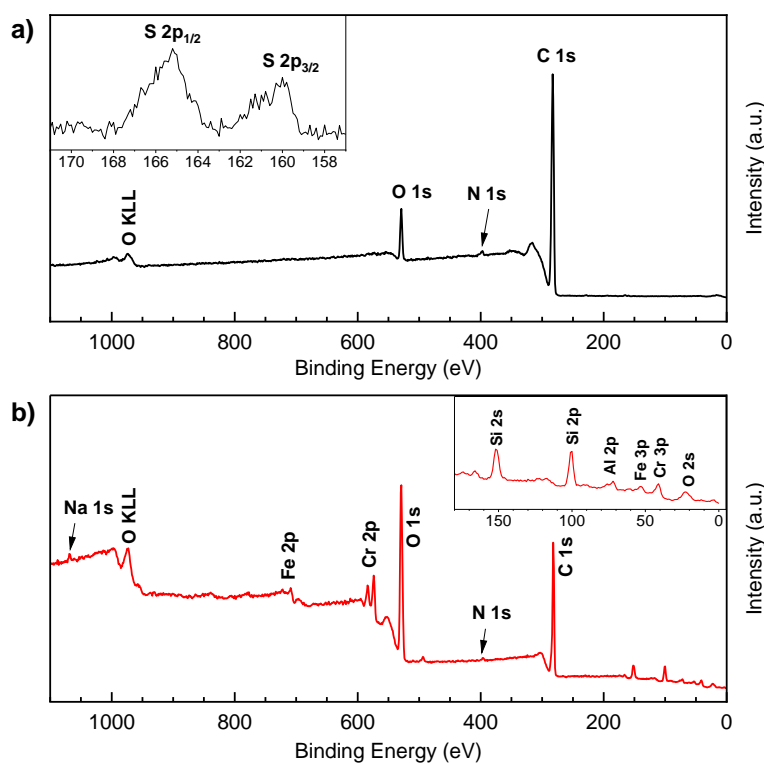
231 3.2.2 Determination of elements as impurities in ODND by local and bulk analysis

232 By TEM, the outcome residues appear as several spherical and elongated particles (Figures
 233 4a-4c and Figures S5-S6, Supporting Information) of a size typically in the 20-40 nm range
 234 (Figure S4, Supporting Information) in agreement with the non-carbon particle size observed
 235 in DND sample (Figure 3). From the TEM observations made on several zones of the ODND
 236 sample and the analysis of 50 micrographs, no nanodiamond was noticed. By EDX
 237 spectroscopy elemental mapping, silicon, chromium and iron could be detected in agreement
 238 with DND analysis. Cr and Fe are most often localized within the same particles (Figure 4
 239 and Figure S5, Supporting Information) and in some areas, chromium oxides are found
 240 without presence of iron (Figure S6, Supporting Information). Aluminum and titanium were
 241 as well detected (Figures S5 and S6, Supporting Information).



242
 243 **Figure 4** a-c) TEM images of ODND at different magnifications. d) corresponding bright-
 244 field STEM image of c). e-h) EDX spectroscopy elemental mapping of O-, Si-, Cr- and Fe K-
 245 edges, respectively.

246
 247 To confirm the presence of the above listed elements, a XPS analysis of DND and ODND
 248 powders was performed, and shown in Figure 5. In DNDs (Figure 5a), only C, N, O and S
 249 could be observed, while for ODND (Figure 5b) a few metallic elements were seen: Na, Al,
 250 Si, Cr and Fe. The observed elements are in good agreement with EDX study above (Figure
 251 4, Figures S4 and S5, Supporting Information). The fact that no traces of Ti was detected in
 252 the XPS spectrum of ODND could signify its content is very weak. For Na, since the TEM
 253 analysis is a local technique, observations were certainly done in the areas where it is not
 254 present.



255

256 **Figure 5** XPS survey scans of a) DND and b) ODND.

257

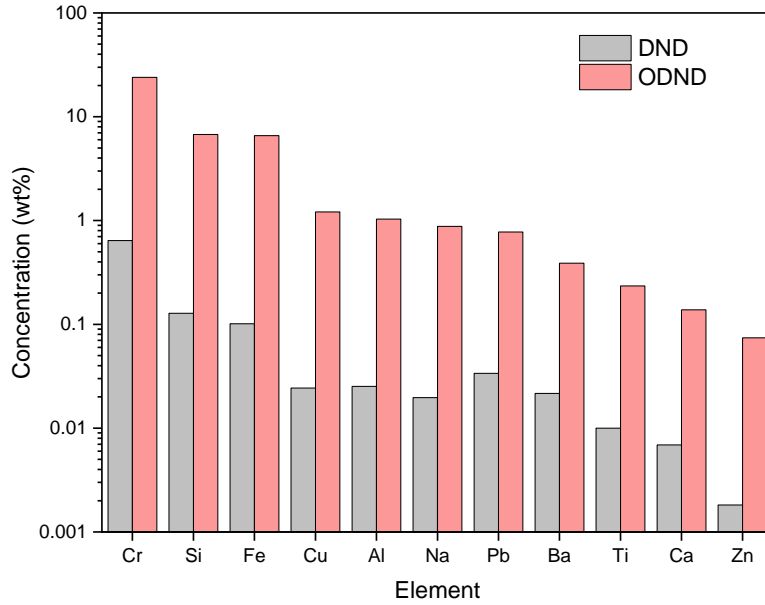
258 To summarize from local (EDX spectroscopy) and bulk techniques (XPS), Si, Cr and Fe may
 259 be considered as the main metallic elements in DND. Na, Al and Ti seem to be present in
 260 weaker amount.

261

262 3.2.3 Reliability of the selective combustion of nanodiamonds approach

263 Analysis from ICP-MS, shown below in Figure 6, provides the contents of the main
 264 heteroelements present in both DND and ODND samples. In agreement with EDX
 265 spectroscopy analysis, ICP-MS shows that Si, Cr and Fe are the main impurities in the DND
 266 sample. Cu, Al, Na, Pb, Ba, Ti and Ca are at least 5 times less concentrated than the three
 267 main elements. Zn is present as traces in DND (2.10^{-3} wt.%).

268



269

270 **Figure 6** ICP-MS elemental analysis of DND (grey) and ODND (red). The detected elements
 271 are as function of their concentration in weight percent. For visibility purposes, a log-scale
 272 was used.

273

274 Table 1 gives the content of the main elements in DND and ODND. The corresponding ratios
 275 of each element with respect with Cr, the main impurity found, fall in the same range for both
 276 samples, proving that ODND provides a reliable insight of the metallic impurities of DND.
 277 These latter concentrated in the thermally treated DNDs make possible their further detection
 278 and analysis by standard techniques, as shown in the following.

279 The impurities in DND samples supplied by the RFNC-VNIIF institute were investigated by
 280 other techniques, such as NAA [20], and AES [38], with the need of ICP-MS [23], and are in
 281 good agreement with Table 1.

282

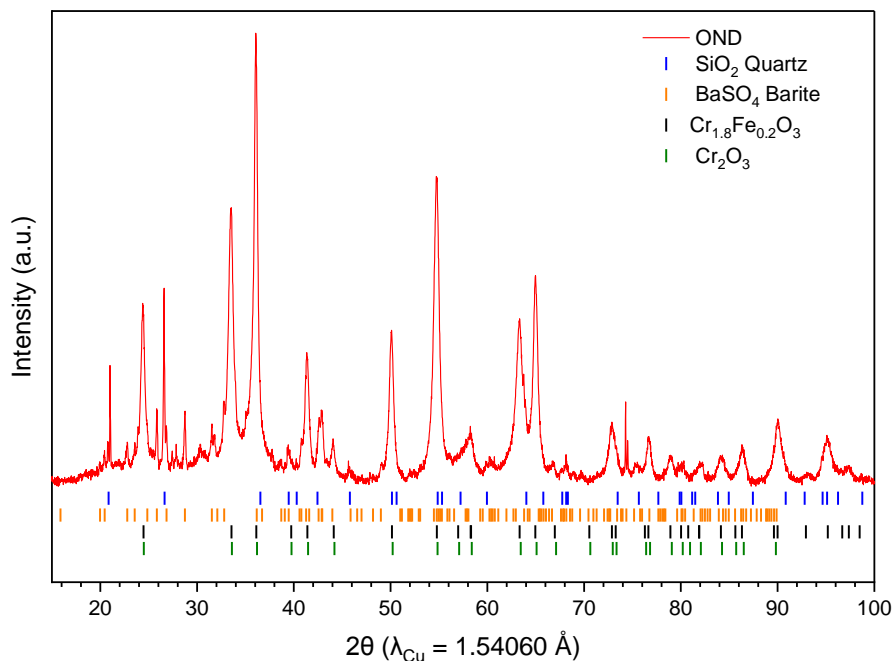
283 **Table 1** Content of the elements found in DND and ODND from ICP-MS and their relative
 284 content with respect with Cr, the most concentrated heteroatom impurity.

Element	DND		ODND	
	wt.%	Factor of dilution with respect to Cr	wt.%	Factor of dilution with respect to Cr
Cr	0.641	--	23.965	--
Si	0.128	6	6.745	3.5
Fe	0.101	6	6.582	3.6
Cu	0.024	30	1.212	20
Al	0.025	20	1.033	24
Na	0.020	30	0.880	27
Pb	0.034	20	0.776	30
Ba	0.022	60	0.388	60
Ti	<0.01	60	0.235	120
Ca	0.007	60	0.138	240
Zn	0.002	300	0.074	240

285

286 3.3 DND impurity detection and determination of their nature and origin

287 Identification of the compounds in DND after being treated under air and determination of
 288 the corresponding impurity nature in DND were first based on PXRD investigation. A typical
 289 diffractogram of ODND is displayed in Figure 7 where numerous peaks are observable. For
 290 their assignment, the elements already known to be present from XPS and EDX analyses and
 291 the reported chemical treatments undergone by the used as-produced DNDs have been
 292 considered. In the following, the main compounds determined in ODND are described one by
 293 one along with the results from different characterization methods complementary to PXRD
 294 in order to ascertain their presence.



295

296 **Figure 7** PXR D pattern of ODND, performed with a Cu source ($\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$). Five
 297 possible phases were indexed, and shown as colored stick: quartz SiO₂ (PDF 46-1045) in
 298 blue, barite BaSO₄ (PDF 83-2053) in orange, Cr_{1.8}Fe_{0.2}O₃ (PDF 04-006-8202) in black and
 299 chromium oxide Cr₂O₃ (PDF 85-0730) in green.

300

301 3.3.1 Silicon – SiO₂

302 Silicon is one of the main elements detected in both DND and ODND by EDX spectroscopy
 303 and XPS. From EDX mapping, silicon was most often observed in the same area than that of
 304 oxygen, which seems to make clear that silicon oxide (SiO₂) is present in both samples
 305 (Figure 4, Figures S3, S5 and S6, Supporting Information). The α -quartz phase could be
 306 identified in ODND by PXR D (Figure 7), and further confirmed by Raman (Figure S7,
 307 Supporting Information) and FTIR spectroscopies (Figure S8, Supporting Information),
 308 where all Raman- and IR-actives bands of SiO₂ were observed.

309 3.3.2 Chromium and iron – Cr_2O_3 , Fe_2O_3 and $\text{Cr}_{2-x}\text{Fe}_x\text{O}_3$

310 Figure S6 clearly indicates there are areas where chromium oxides are not surrounded by iron,
311 being the sign of presence of pure chromium oxides, possibly Cr_2O_3 , since it is the most
312 stable oxide form of chromium at 600°C [39]. Also, chromium oxides are commonly found
313 in literature as residual impurities of DNDs. BaCrO_4 is used as detonator/initiator for DND
314 synthesis and a mixture of H_2SO_4 and CrO_3 or $\text{K}_2\text{Cr}_2\text{O}_7$ (Jones oxidation) have been reported
315 to be used as oxidant for post-synthesis purification by the supplier [23]. Thus, all chromium
316 residuals could have been altered during the combustion of the DND, leading to chromium
317 oxides.

318 Raman spectroscopy on DNDs thermally treated under air (Figures S9 and S10) have
319 revealed the presence of Cr_2O_3 , which is in agreement with the TEM observation (Figure S6,
320 Supporting Information), but also the presence of the solid solution $\text{Cr}_{2-x}\text{Fe}_x\text{O}_3$ characterized
321 in the spectrum by the addition of three magnon peaks. This could explain the systematic
322 presence of Fe alongside Cr and O during our TEM observation in the last section. This is not
323 surprising since the detonation chamber is composed of steel alloys that might contain Cr, as
324 well as other metals.

325 On the other side, FTIR spectroscopy (Figure S8) shows all the typical vibration modes of
326 Cr_2O_3 . Also, since the spectrum is composed of multiple overlapping contributions, some
327 peaks might correspond to the vibration modes of Fe_2O_3 . However, it is not possible to
328 confirm if they belong to pristine material (α - or γ - Fe_2O_3), the most probable origin of these
329 peaks is due to the presence of iron in the $\text{Cr}_{2-x}\text{Fe}_x\text{O}_3$ solid-solution.

330 Therefore, the diffractogram of ODND in Figure 7 can be indexed by both Cr_2O_3 and
331 $\text{Cr}_{2-x}\text{Fe}_x\text{O}_3$. However, it is impossible to know the exact level of iron substitution inside the
332 compound, thus the $\text{Cr}_{1.8}\text{Fe}_{0.2}\text{O}_3$ phase was chosen since it matches perfectly with the
333 diffraction peaks observed.

334 **3.3.3 Barium – Barite BaSO₄**

335 Barite (BaSO₄), *Pnma* (62), can be well identified by PXRD (Figure 7). It has already been
 336 reported as residual impurity after acidic-purification treatment [23,25]. As mentioned early,
 337 BaCrO₄ being a detonator/initiator during the detonation process certainly remains in DND.
 338 Its reaction with sulfuric acid by the post-synthesis purification treatment could explain the
 339 detection of BaSO₄ by PXRD [23,25].

340

341 **3.4 Investigation of DNDs by standard and non-standard techniques**

342 Table 2 summarizes the results found from the conducted in-depth analysis of DND and
 343 ODND by means of standard and non-standard methods as defined below. Characterization
 344 of the thermally DND treated under air by non-standard techniques leads to similar results
 345 than those found for as-produced DND and its characterization by standard techniques allows
 346 to determine the heteroatoms present in DND in a simple manner.

347 **Table 2** Classification of the material characterization techniques depending on their
 348 specificity of use and on their ability to detect and identify the impurities in DND and
 349 ODND.

Non-standard characterization techniques*	Technique	Elements/Phase detected	
		DND	ODND
Non-standard characterization techniques*	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	Cr, Si, Fe, Cu, Al, Na, Pb, Ba, Ca, Ti, Zn	Cr, Si, Fe, Cu, Al, Na, Pb, Ba, Ca, Ti, Zn
	Transmission Electron microscopy (TEM) / EDX-mapping	C, N, O, S, Si, Cr, Fe, Ba	C, N, O, Al, Si, Ti, Cr, Fe, Ba
Standard characterization techniques**	X-ray diffraction (XRD)	C _{diamond}	SiO ₂ , BaSO ₄ , Cr ₂ O ₃ , Fe _x Cr _{2-x} O ₃
	Fourier Transform Infrared spectroscopy (FTIR) – ATR mode	C _{diamond}	SiO ₂ , Cr ₂ O ₃
	Raman spectroscopy	C _{diamond}	SiO ₂ , Cr ₂ O ₃ , Fe _x Cr _{2-x} O ₃
	X-ray photoelectron spectrometry (XPS)	C, N, O, S	C, N, O, Cr, Fe, Al, Si, Na

350 *A characterization technique is considered as non-standard if its accessibility is restrained because of, for
 351 example, proposal submission process for very large instruments or a specific sample preparation required or
 352 very long exposure time and a high which-how is required to run the experiments so that the material science
 353 scholars cannot run the analysis themselves.

354 ** A standard characterization technique requires an available equipment in common material laboratories.
355 Such technique is easy to use without with simple sample preparation and fast result delivery with reasonable
356 data treatment and fitting.

357 **4 Conclusion**

358 In this work, we have developed an alternative approach which provides a useful tool to
359 overcome the long-standing issues of hidden metallic impurities in DNDs. The noncarbon
360 impurities could be concentrated by simply applied a combustion treatment to DND in air.
361 Both as-received and thermally treated under air DND samples were analyzed by means of
362 commonly available local and bulk characterization methods. The developed approach has
363 been proven to be reliable and allows to follow in a simple manner the inorganic element
364 content and their nature in DND samples. This process can be applied after any chemical
365 treatment or modifications of DND. The proposed approach could hence help scholars in
366 developing further applications of DNDs and it could become a universal process to
367 concentrate the metallic impurities contained of any kind of carbonaceous nanomaterial to
368 overcome the limit of detection of standard characterization techniques.

369

370 **Acknowledgments**

371 B.V. and K.H. would like to thank Lionel Aranda for his valuable help in TGA experiments.
372 The authors are grateful to ANR for the funding of this work with the project NERF (ANR-
373 20-CE08-0034).

374 **References**

- 375 [1] V.Y. Dolmatov, A.N. Ozerin, I.I. Kulakova, O.O. Bochechka, N.M. Lapchuk, V. Myllymäki, A.
376 Vehanen, Detonation nanodiamonds: new aspects in the theory and practice of synthesis,
377 properties and applications, *Russ. Chem. Rev.* 89 (2020) 1428.
378 <https://doi.org/10.1070/RCR4924>.
379 [2] I.I. Kulakova, Surface chemistry of nanodiamonds, *Phys. Solid State.* 46 (2004) 636–643.
380 <https://doi.org/10.1134/1.1711440>.
381 [3] V.N. Mochalin, O. Shenderova, D. Ho, Y. Gogotsi, The properties and applications of
382 nanodiamonds, *Nature Nanotech.* 7 (2012) 11–23. <https://doi.org/10.1038/nnano.2011.209>.

- 383 [4] G. Reina, L. Zhao, A. Bianco, N. Komatsu, Chemical Functionalization of Nanodiamonds:
384 Opportunities and Challenges Ahead, *Angewandte Chemie International Edition*. 58 (2019)
385 17918–17929. <https://doi.org/10.1002/anie.201905997>.
- 386 [5] M.L. Terranova, S. Orlanducci, M. Rossi, E. Tamburri, Nanodiamonds for field emission: state of
387 the art, *Nanoscale*. 7 (2015) 5094–5114. <https://doi.org/10.1039/C4NR07171A>.
- 388 [6] E. Janitz, K. Herb, L.A. Völker, W.S. Huxter, C.L. Degen, J.M. Abendroth, Diamond surface
389 engineering for molecular sensing with nitrogen—vacancy centers, *J. Mater. Chem. C*. 10
390 (2022) 13533–13569. <https://doi.org/10.1039/D2TC01258H>.
- 391 [7] A.V. Shvidchenko, E.D. Eidelman, A.Ya. Vul', N.M. Kuznetsov, D.Yu. Stolyarova, S.I. Belousov,
392 S.N. Chvalun, Colloids of detonation nanodiamond particles for advanced applications,
393 *Advances in Colloid and Interface Science*. 268 (2019) 64–81.
394 <https://doi.org/10.1016/j.cis.2019.03.008>.
- 395 [8] N. Nunn, M. Torelli, G. McGuire, O. Shenderova, Nanodiamond: A high impact nanomaterial,
396 *Current Opinion in Solid State and Materials Science*. 21 (2017) 1–9.
397 <https://doi.org/10.1016/j.cossms.2016.06.008>.
- 398 [9] S. Navalón, A. Dhakshinamoorthy, M. Álvaro, H. García, Diamond Nanoparticles in
399 Heterogeneous Catalysis, *Chem. Mater.* 32 (2020) 4116–4143.
400 <https://doi.org/10.1021/acs.chemmater.0c00204>.
- 401 [10] A.S. Barnard, Predicting the impact of structural diversity on the performance of nanodiamond
402 drug carriers, *Nanoscale*. 10 (2018) 8893–8910. <https://doi.org/10.1039/C8NR01688G>.
- 403 [11] N. Bondon, L. Raehm, C. Charnay, R. Boukherroub, J.-O. Durand, Nanodiamonds for
404 bioapplications, recent developments, *J. Mater. Chem. B*. 8 (2020) 10878–10896.
405 <https://doi.org/10.1039/D0TB02221G>.
- 406 [12] M. Bilal, H. Cheng, R.B. González-González, R. Parra-Saldívar, H.M.N. Iqbal, Bio-applications and
407 biotechnological applications of nanodiamonds, *Journal of Materials Research and Technology*.
408 15 (2021) 6175–6189. <https://doi.org/10.1016/j.jmrt.2021.11.037>.
- 409 [13] S. Chauhan, N. Jain, U. Nagaich, Nanodiamonds with powerful ability for drug delivery and
410 biomedical applications: Recent updates on in vivo study and patents, *Journal of*
411 *Pharmaceutical Analysis*. 10 (2020) 1–12. <https://doi.org/10.1016/j.jpha.2019.09.003>.
- 412 [14] N. Prabhakar, J.M. Rosenholm, Nanodiamonds for advanced optical bioimaging and beyond,
413 *Current Opinion in Colloid & Interface Science*. 39 (2019) 220–231.
414 <https://doi.org/10.1016/j.cocis.2019.02.014>.
- 415 [15] R. Namdar, S. Nafisi, Nanodiamond applications in skin preparations, *Drug Discovery Today*. 23
416 (2018) 1152–1158. <https://doi.org/10.1016/j.drudis.2018.04.006>.
- 417 [16] M. Barzegar Amiri Olia, P.S. Donnelly, L.C.L. Hollenberg, P. Mulvaney, D.A. Simpson, Advances
418 in the Surface Functionalization of Nanodiamonds for Biological Applications: A Review, *ACS*
419 *Appl. Nano Mater.* 4 (2021) 9985–10005. <https://doi.org/10.1021/acsanm.1c02698>.
- 420 [17] A.M. Schrand, S.A.C. Hens, O.A. Shenderova, Nanodiamond Particles: Properties and
421 Perspectives for Bioapplications, *Critical Reviews in Solid State and Materials Sciences*. 34
422 (2009) 18–74. <https://doi.org/10.1080/10408430902831987>.
- 423 [18] J.-X. Qin, X.-G. Yang, C.-F. Lv, Y.-Z. Li, K.-K. Liu, J.-H. Zang, X. Yang, L. Dong, C.-X. Shan,
424 Nanodiamonds: Synthesis, properties, and applications in nanomedicine, *Materials & Design*.
425 210 (2021) 110091. <https://doi.org/10.1016/j.matdes.2021.110091>.
- 426 [19] V. Nesvizhevsky, R. Cubitt, E. Lychagin, A. Muzychka, G. Nekhaev, G. Pignol, K. Protasov, A.
427 Strelkov, Application of Diamond Nanoparticles in Low-Energy Neutron Physics, *Materials*. 3
428 (2010) 1768–1781. <https://doi.org/10.3390/ma3031768>.
- 429 [20] V. Nesvizhevsky, U. Köster, M. Dubois, N. Batisse, L. Frezet, A. Bosak, L. Gines, O. Williams,
430 Fluorinated nanodiamonds as unique neutron reflector, *Carbon*. 130 (2018) 799–805.
431 <https://doi.org/10.1016/j.carbon.2018.01.086>.
- 432 [21] R.Yu. Yakovlev, N.N. Dogadkin, I.I. Kulakova, G.V. Lisichkin, N.B. Leonidov, V.P. Kolotov,
433 Determination of impurities in detonation nanodiamonds by gamma activation analysis

- 434 method, *Diamond and Related Materials*. 55 (2015) 77–86.
435 <https://doi.org/10.1016/j.diamond.2015.03.010>.
- 436 [22] D.P. Mitev, A.T. Townsend, B. Paull, P.N. Nesterenko, Direct sector field ICP-MS determination
437 of metal impurities in detonation nanodiamond, *Carbon*. 60 (2013) 326–334.
438 <https://doi.org/10.1016/j.carbon.2013.04.045>.
- 439 [23] D.P. Mitev, A.T. Townsend, B. Paull, P.N. Nesterenko, Screening of elemental impurities in
440 commercial detonation nanodiamond using sector field inductively coupled plasma-mass
441 spectrometry, *J Mater Sci*. 49 (2014) 3573–3591. <https://doi.org/10.1007/s10853-014-8036-3>.
- 442 [24] P.N. Nesterenko, D. Mitev, B. Paull, Chapter 5 - Elemental analysis of nanodiamonds by
443 inductively coupled plasma hyphenated methods, in: J.-C. Arnault (Ed.), *Nanodiamonds*,
444 Elsevier, 2017: pp. 109–130. <https://doi.org/10.1016/B978-0-32-343029-6.00005-2>.
- 445 [25] D.P. Mitev, A.T. Townsend, B. Paull, P.N. Nesterenko, Microwave-assisted purification of
446 detonation nanodiamond, *Diamond and Related Materials*. 48 (2014) 37–46.
447 <https://doi.org/10.1016/j.diamond.2014.06.007>.
- 448 [26] V.Yu. Dolmatov, A. Vehanen, V. Myllymäki, K.A. Rudometkin, A.N. Panova, K.M. Korolev, T.A.
449 Shpadkovskaya, Deep purification of detonation nanodiamond material, *J. Superhard Mater*.
450 35 (2013) 408–414. <https://doi.org/10.3103/S1063457613060099>.
- 451 [27] S.P. Hong, T.H. Kim, S.W. Lee, Plasma-assisted purification of nanodiamonds and their
452 application for direct writing of a high purity nanodiamond pattern, *Carbon*. 116 (2017) 640–
453 647. <https://doi.org/10.1016/j.carbon.2017.02.040>.
- 454 [28] Trace and Ultratrace Elemental Analysis, in: ACS Reagent Chemicals, American Chemical
455 Society, Washington, DC, 2017. <https://doi.org/10.1021/acsreagents.2006.20200501>.
- 456 [29] V.N. Mochalin, O. Shenderova, D. Ho, Y. Gogotsi, The properties and applications of
457 nanodiamonds, *Nature Nanotech*. 7 (2012) 11–23. <https://doi.org/10.1038/nnano.2011.209>.
- 458 [30] V.Yu. Dolmatov, T. Fujimura, Physical and Chemical Problems of Modification of Detonation
459 Nanodiamond Surface Properties, in: D.M. Gruen, O.A. Shenderova, A.Ya. Vul' (Eds.), *Synthesis,*
460 *Properties and Applications of Ultrananocrystalline Diamond*, Springer Netherlands, Dordrecht,
461 2005: pp. 217–230. https://doi.org/10.1007/1-4020-3322-2_16.
- 462 [31] V. Danilenko, O.A. Shenderova, Chapter 5 - Advances in Synthesis of Nanodiamond Particles,
463 in: O.A. Shenderova, D.M. Gruen (Eds.), *Ultrananocrystalline Diamond (Second Edition)*, William
464 Andrew Publishing, Oxford, 2012: pp. 133–164. <https://doi.org/10.1016/B978-1-4377-3465-2.00005-0>.
- 466 [32] P.M.V. Baidakova, *Methods of Characterization and Models of Nanodiamond Particles*, in:
467 *Detonation Nanodiamonds*, Jenny Stanford Publishing, 2013.
- 468 [33] A. Krueger, The structure and reactivity of nanoscale diamond, *J. Mater. Chem*. 18 (2008) 1485.
469 <https://doi.org/10.1039/b716673g>.
- 470 [34] M. Baidakova, A. Vul', New prospects and frontiers of nanodiamond clusters, *J. Phys. D: Appl.*
471 *Phys*. 40 (2007) 6300–6311. <https://doi.org/10.1088/0022-3727/40/20/S14>.
- 472 [35] J. Chen, S.Z. Deng, J. Chen, Z.X. Yu, N.S. Xu, Graphitization of nanodiamond powder annealed in
473 argon ambient, *Appl. Phys. Lett*. 74 (1999) 3651–3653. <https://doi.org/10.1063/1.123211>.
- 474 [36] A.P. Puzyr, V.S. Bondar, A.A. Bukayemsky, G.E. Selyutin, V.F. Kargin, Physical and Chemical
475 Properties of Modified Nanodiamonds, in: D.M. Gruen, O.A. Shenderova, A.Ya. Vul' (Eds.),
476 *Synthesis, Properties and Applications of Ultrananocrystalline Diamond*, Springer Netherlands,
477 Dordrecht, 2005: pp. 261–270. https://doi.org/10.1007/1-4020-3322-2_20.
- 478 [37] V.Yu. Osipov, F.M. Shakhov, K.V. Bogdanov, K. Takai, T. Hayashi, F. Treussart, A. Baldycheva,
479 B.T. Hogan, C. Jentgens, High-Quality Green-Emitting Nanodiamonds Fabricated by HPHT
480 Sintering of Polycrystalline Shockwave Diamonds, *Nanoscale Res Lett*. 15 (2020) 209.
481 <https://doi.org/10.1186/s11671-020-03433-7>.
- 482 [38] V.Yu. Dolmatov, 11 - Synthesis and Post-Synthesis Treatment of Detonation Nanodiamonds, in:
483 O.A. Shenderova, D.M. Gruen (Eds.), *Ultrananocrystalline Diamond*, William Andrew

484 Publishing, Norwich, NY, 2006: pp. 347–377. [https://doi.org/10.1016/B978-081551524-](https://doi.org/10.1016/B978-081551524-1.50013-5)
485 [1.50013-5](https://doi.org/10.1016/B978-081551524-1.50013-5).
486 [39] B.L. Chamberland, The chemical and physical properties of CrO₂ and tetravalent chromium
487 oxide derivatives, *Critical Reviews in Solid State and Materials Sciences*. 7 (1977) 1–31.
488 <https://doi.org/10.1080/10408437708243431>.
489