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Letter

Boron-doped nanodiamonds as possible agents for local hyperthermia

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Abstract

In this work, the effective heating of surrounding water by heavily-boron-doped nanodiamonds (NDs) under laser irradiation of visible wavelength was found. Using Raman scattering spectroscopy of aqueous suspensions of boron-doped NDs, it was found that this abnormally high heating results in the weakening of hydrogen bonds much more so (2–5 times stronger) than for undoped NDs. The property of boron-doped NDs to heat a solvent under the influence of laser radiation (1–5 W cm^{-2}) opens broad prospects for their use to create nanoagents for medical oncology and local hyperthermia.

Keywords: nanodiamonds, boron-doped nanodiamonds, Raman spectroscopy, solvent

S Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Boron-doped diamond is an attractive material for a number of modern technological applications. A superconductivity, so unexpected property for wide bandgap semiconductors, was discovered in the boron-doped diamond [1, 2]. Diamond films obtained by the chemical vapor deposition (CVD) method and doped with boron, have the widest electrochemical window among the known materials, which is the decisive feature when creating electrodes [3, 4]. These diamond films, as well as being produced on their base electrodes, are a promising material for biomedicine. Due to their stability, chemical inertness, wide potential window, functional surface, and low background current, boron-doped diamond electrodes are the basis for various types of biosensors [5] or virus detectors [6]. The conductive properties of the diamonds doped with boron allow their use in biomedical implants, wherein their biocompatibility increases and rejection by the living tissues decreases [7]. The widespread use of the electrodes made of boron-doped diamonds has actively stimulated interest in the creation of smaller particles—boron-doped nanodiamonds (BDNDs).

The first successful attempt to create BDNDs was made in 2008, when Swain's Group produced a 100 nm ND coated with a layer of boron-doped diamond [8]. Then, in early 2014, Krueger *et al* obtained the first fully-fledged BDNDs with a size of 30 nm [9]. However, the method used in their experiments—grinding the bulk doped diamond produced by CVD and high pressure-high temperature (HPHT) techniques—is time consuming and not appropriate for obtaining ultrasmall NDs.

In 2015, the authors of the present publication developed a direct synthesis of BDND based on the HPHT treatment of a

one-component precursor containing the dopant atom(s) [10]. The diamond nanoparticles (NPs) with a variable size down to less than 10 nm, containing a high concentration of substitutional boron ($\approx$1%), were produced. The HPHT synthesis was carried out from the organoboron compound 9-borabicyclo [1, 3] nonane dimer (9BBN), $C_{16}H_{30}B_2$, at a pressure of 8–9 GPa in a temperature range of 1200–2000 K [10].

Conductive NDs, having a large specific surface area, are useful for electrode production. BDND can be used as a seed in the synthesis of a CVD film, without breaking electrical contact with the conductive substrate [11], as special inks to create conductive structures [12, 13], etc.

Besides, aqueous suspensions of BDND could be of particular interest for biomedicine. We have previously shown that boron-doped NDs and detonation nanodiamonds (DNDs) have a different effect on the hydrogen bonds in proton solvents: BDNDs being much stronger weaken hydrogen bonds in water and water-ethanol solution with 70% alcohol content [14] at 25 °C more than DNDs.

In the present study, a new property of BDNDs, namely, their ability to significantly heat up the surrounding water in the suspensions of these NPs under laser irradiation, is revealed. It is shown that the heating ability of BDNDs is more than 2–5 times (depending on the wavelength) greater than the heating ability of the DNDs under the laser radiation (1–5 W cm^{-2}). This property of the boron-doped NDs opens up broad prospects for their use as therapeutic agents for local medical and oncological hyperthermia.

2. Experimental section

2.1. Experimental setup

The absorption spectra of ND suspensions were obtained on a Perkin Elmer Lambda 35 UV–vis spectrophotometer with spectral resolution of 1 nm.

Raman scattering (RS) of ND suspensions was excited by an argon laser with a wavelength of 488 nm and power of 200–400 mW. In addition to the argon laser, the diode laser with a wavelength of 651 nm and power of 90 mW was used for heating the samples. Integral RS spectra were recorded in the 90° scheme of the experiment. The registration system consisted of the monochromator (Acton 2500i, focal length of 500 mm, grating of 900 gr mm^{-1}) and the CCD-camera (Jobin Yvon, Synapse 1024 * 128 BIUV). The width of the entrance slit was 25 μm, which provided the spectral resolution of 2 cm^{-1}. The thermal stabilization system allowed us to set the temperature of a sample in the cuvette with the accuracy of 0.2 °C.

Temperature changes of ND suspensions at laser exposure were determined with the use of the thermocouple of 1 mm size and with an accuracy of 0.1 °C. Temperature measurements were performed in a quartz cuvette at a distance of 3 mm from the focused laser beam (see figure S1, supporting information (stacks.iop.org/LPL/14/045702/mmedia)). The probing of samples was carried out by a laser beam passing through the cuvette from the bottom up, thus ensuring uniform heating over the entire height of the cuvette.

2.2. Objects of research

Water suspensions of BDNDs and DNDs have been studied in this work.

The BDNDs were produced by direct HTPT synthesis ($T = 1310$ °C, $P = 9$ GPa), as described in [10]. The produced BDND powder was purified by boiling it in a mixture of nitric/sulfuric (1:3) acid for 3 h. Then, the acid was washed out with distilled water in seven 20 min washing/centrifugation cycles (Centrifuge LMC-3000, BioSan, 1700 g).

The DND were synthesized by detonation of a mixture of trinitrotoluene (TNT) and 1,3,5-trinitrotoluene-1,3,5-x-triazine (RDX) in a media with water cooling ('New Technologies', Chelyabinsk, Russia). The soot purification and DND treatment procedures were described in detail in [15].

The aqueous suspension of the BDND with a concentration of 3 g l^{-1} and an aqueous suspension of the DND with a concentration of 28 g l^{-1} were prepared. For the preparation of these suspensions, the deionized bidistilled water with electrical conductivity of 0.1 μSm cm^{-1} was used. The measurements by dynamic light scattering have shown that more than 90% of the ND dispersed in the suspension had a size of 10 nm (DND) and 9 nm (BDND). The RS spectra of BDND and DND evaporated from the aqueous suspensions (figures S2 and S3, supporting information) have demonstrated the high degree of their purification. The boron content in the studied BDND was about 1%.

Afterwards, initial ND suspensions were diluted with distilled water up to the studied concentrations of 0.5, 1, or 2 g l^{-1}.

3. Results and discussion

3.1. Raman spectroscopy of ND suspensions

RS spectroscopy is one of the most effective methods for the study of molecular interactions in suspensions. In order to investigate the effect of the ND dispersed in water on the hydrogen bonding surroundings, the RS spectra of water and aqueous suspensions of BDND and DND with concentrations of 0.5 g l^{-1} and 2 g l^{-1}, respectively, were obtained in the temperature range from 0°C–80°C. As known, the band of stretching vibrations of OH groups in the range of 3000–3700 cm^{-1} is the most sensitive to the changes of strength and dynamics of hydrogen bonds in water [16–19]. With the increasing temperature, the intensity of the high-frequency component of the stretching band of OH groups increases, and of the low-frequency component decreases, while the maximum of the band shifts to higher frequencies, and the half-width decreases (figure 1). This behavior is explained by the fact that with the increasing temperature the hydrogen bonds between water molecules weaken, and the frequency of the OH stretching vibrations increases. Therefore, the intensity of the high-frequency region of the valence band I_2 increases, and the band maximum shifts to higher frequencies (figure 1) [16–19].

Similar changes of the stretching band of OH groups were also found in the temperature dependence of the RS spectra of aqueous suspensions of BDND and DND. Moreover, in
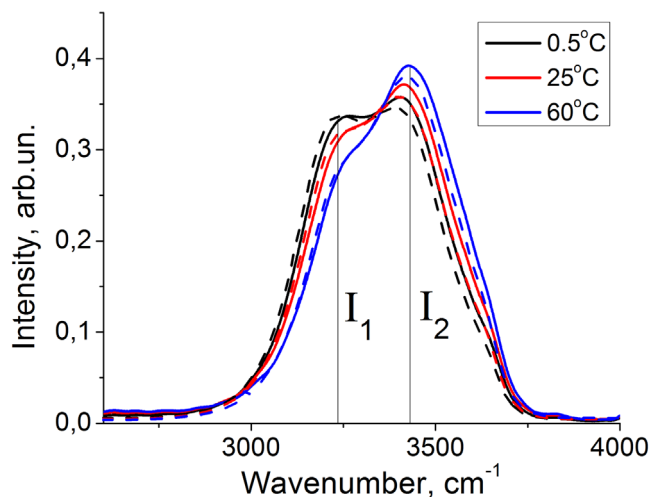
Figure 1. Temperature dependences of the stretching band of OH groups in water (dashed lines) and in aqueous suspension of BDND with a concentration of $0.5\,\mathrm{g\,l^{-1}}$ (solid lines). Excitation wavelength 488 nm, laser power 400 mW.

Figure 2. Temperature dependences of the χ_{21} parameter of the stretching band of OH groups in pure water and in aqueous suspensions of BDND and DND. The concentration of BDND was $0.5\,\mathrm{g\,l^{-1}}$, and that of DND was $2\,\mathrm{g\,l^{-1}}$. Excitation wavelength 488 nm, laser power 400 mW.

the same temperature interval the changes of the stretching band of OH groups in aqueous suspensions of NDs proved to be stronger than in pure water. These results once again demonstrate the significant influence of NDs on the strength of hydrogen bonds previously observed by us in BDND and DND, dispersed in different solvents [14, 20–22] at 25 °C.

For a quantitative analysis of the changes in the strengths of hydrogen bonds in aqueous solutions, the parameter $\chi_{21} = I_2/I_1$, equal to the ratio of the intensities of high-frequency and low-frequency components of the stretching band is used (figure 1) [18–22]. It is assumed that the high-frequency component of the stretching band (I_2) is caused by vibrations of hydroxyl groups with weak hydrogen bonds, and that of the low-frequency (I_1) by vibrations of the groups with strong hydrogen bonds. Therefore, the χ_{21} parameter characterizes the ratio of weakly bounded OH groups in the solution to the strongly-bonded OH groups. Thus, the value of this parameter allows us to determine the relative strength of hydrogen bonds in the suspension.

The temperature dependences of the χ_{21} parameter of the stretching band were calculated and plotted for both suspensions and for pure water (figure 2).

As can be seen from figure 2, for the whole temperature interval, the hydrogen bonds in aqueous suspension of DND are slightly weaker than that in pure water, and in aqueous suspension of BDND they are essentially weaker than that in the suspension of DND and in pure water. Moreover, such a significant weakening of hydrogen bonds in the BDND suspension is observed at the concentration of BDND, which is four times lower than the concentration of DND. To explain the observed particular behavior of BDND in water, we assumed the presence of special 'heating' abilities of BDND.

3.2. Heating of the ND suspensions by laser

An experiment on measuring the temperature in the aqueous suspensions of NDs was held under laser radiation with a wavelength of 488 nm and power of 400 mW.
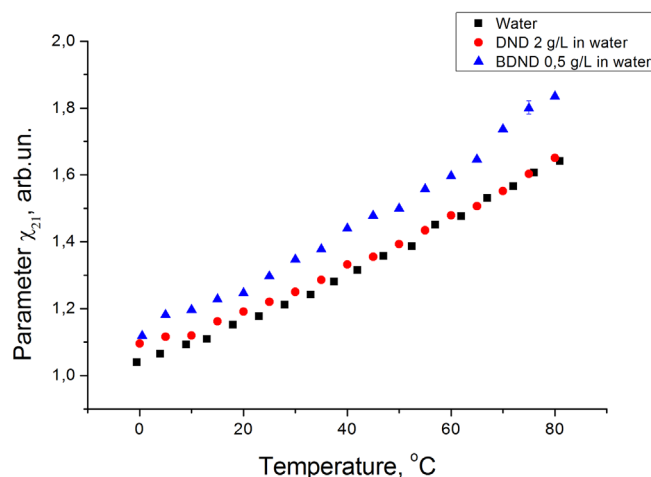
The aqueous suspensions of BDND ($0.5\,\mathrm{g\,l^{-1}}$) and DND ($2\,\mathrm{g\,l^{-1}}$) were irradiated with the laser under identical conditions. The temperature measurement scheme is described in section 2.1 and is shown in figure S1 (supporting information). It was found that under laser irradiation, BDND heats surrounding water more effectively compared to DND even at the concentration four times lower than the concentration of DND.

For a correct comparison of the 'heating' abilities of BDND and DND, the same experiment with aqueous suspensions of BDND and DND with two identical concentrations of $0.5\,\mathrm{g\,l^{-1}}$ and $1\,\mathrm{g\,l^{-1}}$ was performed. Figure 3 shows the dependences of the measured temperature of BDND and DND suspensions with concentrations of 0.5 and $1\,\mathrm{g\,l^{-1}}$ on the time of the laser exposure.

As can be seen from the results shown in figure 3 and table 1, under the same conditions, after 5 min of laser irradiation at the wavelength of 488 nm and a power density of $5.6\,\mathrm{W\,cm^{-2}}$ at the same point of the cuvette, the temperature increment in the BDND suspension is 2–2.5 times higher than that in the DND suspension, and 10 times higher than that in pure water.

Thus, we have found that under laser irradiation of NDs aqueous suspensions, the BDND with size 9 nm has the ability to effectively heat the surrounding water.

3.3. Dependence of the 'heating' ability of ND on the laser irradiation wavelength

Experimentally obtained absorption spectra of aqueous suspensions of BDND and DND with the concentration of $1\,\mathrm{g\,l^{-1}}$ have shown that BDND better absorbs light in the infrared region, and DND in the UV region (figure 4).

In this regard, we have investigated the dependence of the heating ability of BDND and DND suspensions on the irradiation wavelength. The experiments on heating of both aqueous suspensions were conducted under radiation with the
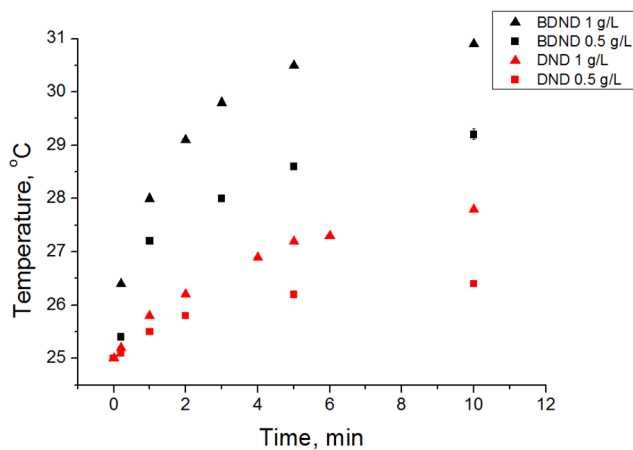
Figure 3. The dependences of the temperature of aqueous suspensions of BDND and DND on the time of laser exposure (488 nm, 400 mW). The concentrations of BDND and DND were 1 g l^{-1} (triangles) and 0.5 g l^{-1} (squares).

Table 1. Changes of the temperature of water and aqueous suspensions of DND and BDND under laser exposure.

	Changes of the temperature of suspensions under laser exposure (°C)					
	488 nm, 2.8 W cm^{-2}		488 nm, 5.6 W cm^{-2}		651 nm, 1.3 W cm^{-2}	
Samples	5 min	10 min	5 min	10 min	5 min	10 min
Water	0.2	0.3	0.3	0.4	0.2	0.3
DND, 0.5 g l^{-1}	1.0	1.2	1.2	1.4	0.2	0.2
BDND, 0.5 g l^{-1}	2.5	2.8	3.2	3.8	1.7	1.9
DND, 1 g l^{-1}	1.2	1.3	2.0	2.6	0.4	0.5
BDND, 1 g $^{-1}$	3.5	3.7	4.1	4.5	1.8	2.3

wavelengths of 488 nm and 651 nm. The results of the measurements of the heating of the aqueous suspensions are presented in table 1.

The results show that under the radiation with any of the used wavelengths, the aqueous suspensions of BDND are heated more efficiently than suspensions of DND and pure water. The larger the wavelength, the greater the heating ability of BDND compared to that of DND at both concentrations. Thus, under laser irradiation for 10 min with a wavelength of 651 nm and with a power density of 1.3 W cm^{-2} the temperature increment for the aqueous suspension of BDND with the concentration of 0.5 g l^{-1} is nine times higher than for the aqueous suspension of DND with the same concentration.

The higher heating ability of BDND compared to DND under radiation with different wavelengths means that the higher absorption of BDND in the red spectral region only amplifies the heating mechanism. The absorption of BDND against DND increased due to the dopant metal or metalloid atoms changing the band gap of the NDs. However, in order to fully understand the heating mechanism of BDNDs further research is needed.
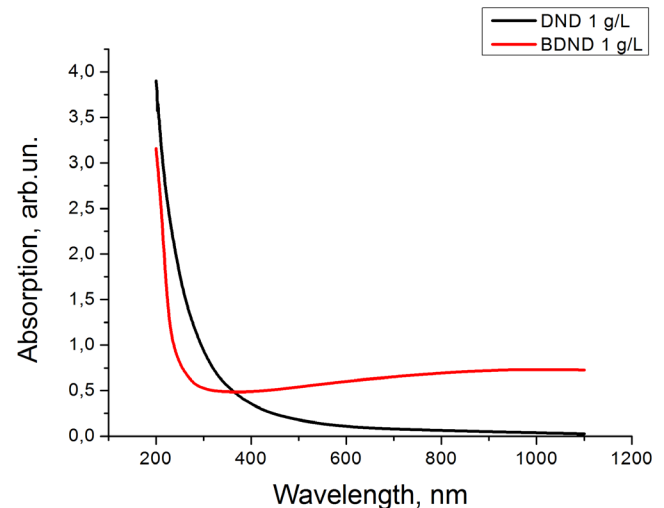

Figure 4. Absorption spectra of aqueous suspensions of DND and BDND after the subtraction of the absorption spectrum of water.

3.4. BDND as a potential agent for therapeutic local hyperthermia

The established heating properties of the BDNDs open new application possibilities of these NPs in medicine, particularly in local laser hyperthermia (therapeutical and oncological). It is known that even a small increase of temperature of the tumor makes cancerous cells more sensitive to radiation and chemotherapy [23]. Under temperatures of 40°C–42 °C tumor vasculature is increased, leading to a more active delivery of chemotherapeutic agents. Besides, in the temperature range 40.5°C–43 °C the cellular toxicity of many chemotherapeutic agents is enhanced [24]. Moreover, at temperatures of 42°C–43 °C the mechanisms of activity of cancer cells get violated and the cells die [23].

At present, it is proposed to use a variety of NPs for oncological treatment by hyperthermia [23, 25–33]. Basically, there are about three classes of NPs: gold or silver NPs [23, 25–28], NPs with soft ferromagnetic properties [23, 30, 31], carbon nanotubes [23], as well as nanocomplexes as their basis [34, 35].

The NPs made from precious metals absorb the incident radiation and convert it into heat due to surface plasmon resonance [23]. The treatment of a mouse cancer tumor by IR laser with the wavelength of 808 nm and power of 800 mW (4 W cm^{-2}) for 3 min showed a significant difference between the treated and untreated tissue [27]. The advantage of the gold/silver NPs is in their inertness for biological tissues and non-toxicity that has been shown by the use of gold particles with a size of tens of microns for the treatment of rheumatoid arthritis. However, a disadvantage of gold NPs is that their use in high concentrations increases the immunity of cancer cells [29].

A hysteresis dependence is observed in the change of magnetization of ferromagnetic particles under the influence of an external alternating magnetic field. These hysteresis losses are converted into heat. Therefore, the biological tissues with introduced ferromagnetic NPs are heated in an alternating

magnetic field [23, 30, 31]. The main disadvantage of the ferromagnetic NPs is their toxicity for normal cells [31].

Carbon nanotubes are also capable of absorbing electromagnetic waves and converting the absorbed energy into heat [23, 32, 33]. As a result of light absorption by the carbon nanotubes, electronic transitions are excited and vibrational modes within the carbon lattice are amplified. Unlike gold, nanotubes absorb in a wider frequency range, including visible light, near-IR and even RF. Burke *et al* [33] has demonstrated the successful use of carbon nanotubes in hyperthermia of the tumor under irradiation with IR laser with the power density of 3 W cm^{-2} for 30 s. The main obstacle for wider introduction of nanotubes in cancer therapy is their toxicity due to the high tendency to aggregate [36].

Nanocomplexes—NPs of different nature covered either by gold or ferromagnetic are synthesized for oncological hyperthermia. Later on, in order to improve their biocompatibility, these nanocomplexes are coated by folic acid, copolymers, etc. There are several works in which detonation [35, 37–39] or fluorescent [34, 40] NDs were used as a basis for these nanocomplexes. For example, fluorescent conjugates of NDs with a size of 100 nm and of gold nanorods (10 × 41 nm) were synthesized by Hsiao *et al* [40]. Local heating by 10 °C was reached as a result of irradiation of HeLa cells with the introduced conjugates by IR laser (808 nm) with a power of 10 mW.

According to the comparative analysis of heating capacities of different NPs, presented by Shrand in the book [41], under the influence of the laser with a wavelength of 1064 nm and a power of 2.2 W for 5 min, the aqueous suspensions of carbon powder, single-walled carbon nanotubes, gold NPs, copper NPs, and pure water were heated by 15 °C, 5 °C, 4 °C, 3.5 °C, and 3 °C, respectively.

Unfortunately, in all given literature sources there is no information either about the concentration, or about the irradiated area, or about the quantitative temperature change. Therefore, it is impossible to correctly compare the data obtained by the authors of this article with results of the other groups. Nevertheless, even the available information in the literature (see above) and the results of this work (see table 1) show that the BDNDs are capable of heating the surroundings as well as most of the NPs and nanocomplexes proposed in the literature. In the present paper, it is shown that the efficiency of heating the surrounding water by BDNDs depends on their concentration as well as on the wavelength and power of irradiation. It should be noted that in our study the used suspensions had a low concentration of BDNDs, and the irradiation was performed by visible light. Furthermore, the temperature was measured in the point spaced by approximately 3 mm from the probe beam (see figure S1). Thus, by varying all the parameters, the optimal BDND suspensions and modes of tissue irradiation for heating to 41 °C (indirect cellular damage) and to 41°C–45 °C (direct cellular damage) can be chosen.

It should be noted that as agents for local hyperthermia, the BDNDs have undoubted advantages in comparison with the used NPs, namely they: (1) do not require coating by gold or ferromagnetic; (2) have high biocompatibility [7]; (3) have a high dispersibility [14]; (4) are non-toxic [5, 7, 42, 43]; (5) can be easily modified and be reliable drug carriers [44].

4. Conclusion

In this work, the abnormally high ability of BDNDs to heat up the surrounding water under laser radiation was found. With the use of RS spectra of aqueous suspensions of NDs it was shown that the heating ability of BDNDs results in stronger weakening of the net of the hydrogen bonds in the surrounding water compared to DNDs. It was found that under laser exposure (488 nm wavelength, 2.8 W cm^{-2} power density) for 5 min the aqueous suspension of BDND with the concentration of 1 g l^{-1} is heated by 3.5 °C at the distance 3 mm from the laser beam. Based on the obtained results, it can be argued that the newly synthesized BDND with the size 9 nm is a novel nanomaterial platform for the development of nanoagents for therapeutic and oncological local hyperthermia.

Acknowledgments

References

[1] Ekimov E A, Sidorov V A, Bauer E D, Mel'nik N N, Curro N J, Thompson J D and Stishov S M 2004 *Nature* **428** 542–5

[2] Zhang G *et al* 2014 *Adv. Mater.* **26** 2034–40

[3] Kim D Y, Yang J C, Kim H W and Swain G M 2013 *Electrochim. Acta* **94** 49–56

[4] Kato H, Hees J, Hoffmann R, Wolfer M, Yang N, Yamasaki S and Nebel C E 2013 *Electrochem. Commun.* **33** 88–91

[5] Fierro S, Seishima R, Nagano O, Saya H and Einaga Y 2013 *Sci. Rep.* **3** 3257

[6] Matsubara T, Ujie M, Yamamoto T, Akahori M, Einaga Y and Sato T 2016 *Proc. Natl Acad. Sci.* **113** 8981–4

[7] Garrett D J, Saunders A L, McGowan C, Specks J, Ganesan K, Meffin H, Williams R A and Nayagam D A 2016 *J. Biomed. Mater. Res.* B **104** 19–26

[8] Ay A, Swope V M and Swain G M 2008 *J. Electrochem. Soc.* **155** B1013–22

[9] Heyer S, Janssen W, Turner S, Lu Y G, Yeap W S, Verbeeck J, Haenen K and Krueger A 2014 *ACS Nano* **8** 5757–64

[10] Ekimov E A, Kudryavtsev O S, Khomich A A, Lebedev O I, Dolenko T A and Vlasov I I 2015 *Adv. Mater.* **27** 5518–22

[11] Tsigkourakos M, Hantschel T, Simon D K, Nuytten T, Verhulst A S, Douhard B and Vandervorst W 2014 *Carbon* **79** 103–12

[12] Kondo T, Sakamoto H, Kato T, Horitani M, Shitanda I, Itagaki M and Yuasa M 2011 *Electrochem. Commun.* **13** 1546–9

[13] Kondo T, Horitani M, Sakamoto H, Shitanda I, Hoshi Y, Itagaki M and Yuasa M 2013 *Chem. Lett.* **42** 352–4

[14] Vervald A M, Ekimov E A, Kudryavtsev O S, Vlasov I I and Dolenko T A 2016 *Proc. SPIE* **9917** 99172O

[15] Shenderova O, Koscheev A, Zaripov N, Petrov I, Skryabin Y, Detkov P, Turner S and Van Tendeloo G 2011 *J. Phys. Chem.* C **115** 9827–37

[16] Chaplin M 2016 Water Structure and science www1.lsbu.ac.uk/water/water_sitemap.html (Updated on 16 February 2016)

[17] Walrafen G E, Fisher M R, Hokmabadi M S and Yang W-H 1986 *J. Chem. Phys.* **85** 6970–82

[18] Dolenko T A, Churina I V, Fadeev V V and Glushkov S M 2000 *J. Raman Spectrosc.* **31** 863–70

[19] Burikov S A, Dolenko T A, Velikotnyi P A, Sugonyaev A V and Fadeev V V 2005 *Opt. Spectrosc.* **98** 235–9

[20] Dolenko T A, Burikov S A, Rosenholm J M, Shenderova O A and Vlasov I I 2012 *J. Phys. Chem.* C **116** 24314–9

[21] Dolenko T A, Burikov S A, Laptinskiy K A, Rosenholm J M, Shenderova O A and Vlasov I I 2015 *Phys. Status Solidi* **212** 2512–8

[22] Vervald A M, Burikov S A, Shenderova O A, Nunn N, Podkopaev D O, Vlasov I I and Dolenko T A 2016 *J. Phys. Chem.* C **120** 19375–83

[23] Chatterjee D K, Diagaradjane P and Krishnan S 2011 *Ther. Deliv.* **2** 1001–14

[24] Urano M, Kuroda M and Nishimura Y 1999 *Int. J. Hyperth.* **15** 79–107

[25] Mirkin C, Meade T J, Petrosko S H and Stegh A H 2015 *Nanotechnology-Based Precision Tools for the Detection and Treatment of Cancer* (Berlin: Springer) p 321

[26] Cherukuri P, Glazer E S and Curley S A 2010 *Adv. Drug. Deliv. Rev.* **62** 339–45

[27] O'Neal D P, Hirsch L R, Halas N J, Payne J D and West J L 2004 *Cancer Lett.* **209** 171–6

[28] Diagaradjane P *et al* 2008 *Nano Lett.* **8** 1492–500

[29] Hulander M, Hong J, Andersson M, Gervén F, Ohrlander M, Tengvall P and Elwing H 2009 *ACS Appl. Mater. Interfaces* **1** 1053–62

[30] Elsherbini A A, Saber M, Aggag M, El-Shahawy A and Shokier H A 2011 *Magn. Reson. Imaging* **29** 272–80

[31] Wu X, Tan Y, Mao H and Zhang M 2010 *Int. J. Nanomed.* **5** 385–99

[32] Huang N, Wang H, Zhao J, Lui H, Korbelik M and Zeng H 2010 *Lasers Surg. Med.* **42** 638–48

[33] Burke A *et al* 2009 *Proc. Natl Acad. Sci. USA* **106** 12897–902

[34] Cheng L-C, Chen H M, Lai T-C, Chan Y C, Liu R S, Sung J C, Hsiao M, Chen C H, Her L J and Tsai D P 2013 *Nanoscale* **5** 3931–40

[35] Orel V E *et al* 2012 *J. Superhard Mater.* **34** 179

[36] Poland C A *et al* 2008 *Nat. Nanotechnol.* **3** 423–8

[37] Epperla C P, Chen O Y and Chang H-C 2016 *Nanomedicine* **11** 443–5

[38] Douvalis A P, Bourlinos A B, Tucek J, Čépe K, Bakas T and Zboril R 2016 *J. Nanopart. Res.* **18** 115

[39] Rehor I *et al* 2015 *Adv. Healthcare Mater.* **4** 460–8

[40] Hsiao W-W, Hui Y Y, Tsai P-C and Chang H-C 2016 *Acc. Chem. Res.* **49** 400–7

[41] Zhang M, Naik R R and Dai L (ed) 2016 *Carbon Nanomaterials for Biomedical Applications* (Switzerland: Springer) p 16

[42] Mochalin V N, Shenderova O, Ho D and Gogotsi Y 2012 *Nat. Nanotech.* **7** 11–23

[43] Krueger A 2008 *Chem. Eur. J.* **14** 1382–90

[44] Rosenholm J M, Vlasov I I, Burikov S A, Dolenko T A and Shenderova O A 2015 *J. Nanosci. Nanotechnol.* **15** 959–71