

# The structure and reactivity of nanoscale diamond†

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Diamond nanoparticles are another form of carbon nanomaterials with unique properties and applications. This article discusses the progress made in the production, characterisation and functionalisation of this material. The surface structure of nanodiamond allows for the investigation of chemical modifications of the particle surface leading to new materials for composite, biomedical or electronic applications.

## Introduction

Not only did nanoscale  $sp^2$  carbon, like fullerenes, carbon nanotubes and carbon onions, come into focus in the last decades, but also nanoscopic versions of  $sp^3$  carbon, namely nanodiamond (Fig. 1a).<sup>1,2</sup> Due to its unique properties originating from the lattice structure and the large and sometimes functionalised surface, this material is not only interesting for the basic understanding of the universe of carbon modifications, but it has a multitude of potential applications in the macroscopic world. In this article, we will discuss important points of the structure and surface reactivity of nanoscale diamond particles.

Historically speaking, nanodiamond is not really a “new” carbon modification. It was already produced back in the 60s by Russian and American scientists.<sup>1,4</sup> The research intensified in the 1980s and 1990s when bigger amounts of the material became available and the unique properties had been discovered.<sup>5</sup> Although there is no natural terrestrial source for nanodiamond, nanoscopic diamond particles have been discussed as the potential source for a characteristic light absorption feature of interstellar dust.<sup>3,6</sup> In some chondrites (a class of meteorites), nanoscopic diamond structures have been found (Fig. 1b). These nanodiamonds are much older than our solar system and can give valuable information on the formation of stars and the reactions taking place in them. The structure of these interstellar diamonds has been the focus of discussion for the formation mechanism.

Recently, another class of subnanoscale diamond related compounds came into focus: the so-called diamondoids, isolated from petroleum.<sup>7</sup> These compounds, consisting of several adamantane cages possess very interesting properties and can serve as molecular models for diamond (Fig. 1c). In this article, the diamondoids will not be discussed, as they are defined molecular compounds and have been discussed in detail elsewhere.<sup>8</sup> Additionally, nanocrystalline diamond can also be produced in the form of films by chemical vapour deposition. This so-called *ultrananocrystalline diamond (UNCD)* has been studied in detail

and a variety of applications, including electrochemical and biological ones, are currently under investigation.<sup>1a</sup>

## Production of nanoscale diamond

There are several methods to produce nanoscale diamond particles. The simplest one is the milling of larger synthetic or natural microdiamonds and sorting the smaller fraction out by sieving and fractionated centrifugation. Another procedure that is used in large scale, is the transformation of graphitic material (usually graphite dust) into diamond crystallites by the application of circular shockwaves.<sup>9</sup> The carbon material is placed in an inner tube covered with a driving tube. The whole system is then placed in the outer tube and the free space is filled with an explosive. The ignition of this explosive at one end of the apparatus leads to the propagation of a circular shock wave that compresses the driving tube and as a consequence, transforms the  $sp^2$  carbon material into sintered nanodiamond particles. The resulting powder is mainly used for polishing applications.<sup>2</sup> Shockwave diamond can also be produced by mechanical shock generated, for example, with an accelerated cantilever or with shooting bullets onto the carbon materials.<sup>10</sup> These latter techniques in general give only small amounts of diamond material.

Another technique for the bulk-scale production of nanometric diamond particles is the so-called detonation synthesis.<sup>3,5</sup> It had been already described by Russian scientists in the 60s and

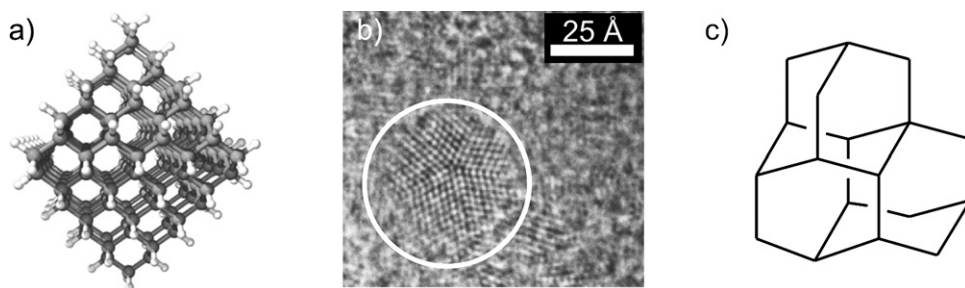


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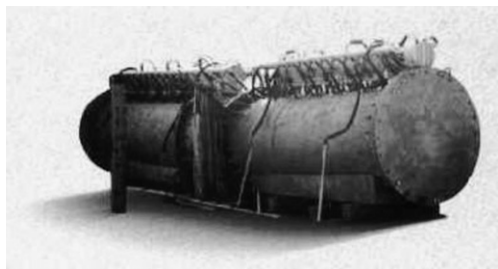
on the properties and functionalisation of nanoscale carbon materials.

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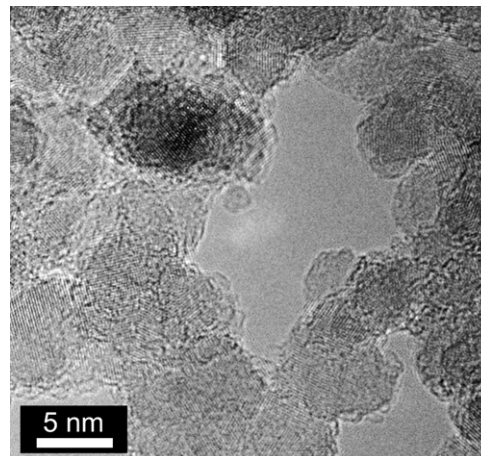
**Fig. 1** (a) Octahedral nanodiamond model, (b) meteoritic diamond with multiple twinning (with permission from Elsevier),<sup>3</sup> (c) triamantane, a diamondoid molecule.



**Fig. 2** Industrial scale reactor for nanodiamond detonation synthesis (courtesy of Alit Corp., Ukraine).<sup>11</sup>

nowadays several large industrial reactors are in operation (Fig. 2).<sup>4,12</sup> The process consists of placing an explosive charge into a detonation chamber and igniting it either by another accelerator charge or electrically.<sup>1,2,4,5,10</sup> In this process, no additional carbon material is needed for the formation of diamond soot. The explosive itself delivers the carbon. In an oxygen-deficient atmosphere the incomplete combustion of organic explosives, such as TNT, and hexogen leads to the formation of elemental carbon, in addition to the combustion products CO<sub>2</sub>, CO, water and nitrogen. Many experiments have been carried out to find the optimal mixture of explosives for a maximum production of diamond. It turned out that a 3 : 2 mixture of TNT and hexogen, known as hexolite, delivers the best results.<sup>13</sup> But in principle, the process can be carried out with other explosives like HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and TATB (2,4,6-trinitro-1,3,5-benzenetriamine) too, provided that the overall oxygen balance is negative.<sup>2,13</sup>

Under optimal conditions, the detonation soot contains up to 80% diamond nanoparticles (Fig. 3). The yield with reference to the carbon in the employed explosive goes up to 4–10%.<sup>2,10</sup> The diamond soot contains a variety of impurities, including metal and concrete debris from the reaction chamber and a significant amount of non-diamond carbon.<sup>1,2,10</sup> First purification steps include the mechanical separation from larger debris by sieving, and the removal of magnetic impurities (e.g. iron particles) by magnetic separation. Afterwards, the raw soot is collected and purified by acid treatment.<sup>1,2,10</sup> The goal of this treatment is not only to further reduce the metal content of the material but to oxidise the non-diamond carbon in the soot. It is well-known that the reactivity of sp<sup>2</sup> carbon, especially disordered graphitic material, towards oxidation is much higher than that of diamond carbon. It is therefore possible to selectively remove the sp<sup>2</sup> and

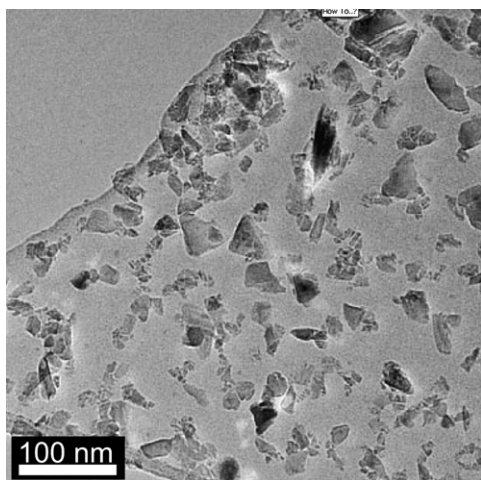


**Fig. 3** HRTEM images of raw detonation diamond (courtesy of A. Thorel).

enrich the material in diamond content. Samples of good quality contain over 95% carbon, with the rest being nitrogen (~2%), hydrogen and oxygen (and traces of iron and other metals).<sup>2,10</sup> Recently, it has been found that the complete removal of iron from the detonation diamond is a more challenging task than thought before. Only after air oxidation can those iron particles carrying a carbon shell react with the oxidising acid.<sup>14</sup>

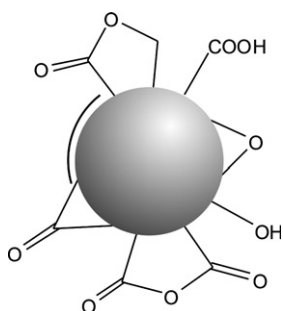
### The structure of nanodiamond

Depending on the production method, nanodiamond particles come in different size ranges. Samples that have been isolated from milled synthetic microdiamond particles possess a rather large size distribution of the resulting nanodiamond crystallites of ~0–50 nm.<sup>15</sup> On the other hand, the size and size distribution of shockwave nanodiamond depends on the granulometry of the original graphite material that is being compressed.<sup>9,10</sup> In this case, the particles are sintered together and do not form isolated crystallites. A polycrystalline material similar to the naturally occurring *carbonados* (black polycrystalline diamond) is obtained. Detonation diamond consists usually of particles with a size of ~5 nm and a very narrow size distribution.<sup>2,10,16</sup> This uniformity is due to several experimental and thermodynamic factors: the upper size limit of the growing diamond particles is set by the duration of the detonation shock wave that is propagating in the reaction chamber (see above). Only during this



**Fig. 4** SEM image of nanocrystalline diamond produced by milling microdiamond (courtesy of A. Thorel).

period is the pressure sufficient for the formation of diamond soot.<sup>1,2,10</sup> After the pressure drops and with a still elevated temperature, graphitic soot is formed. Therefore, the rapid cooling of the reactor after the detonation is of great importance. The shape of the diamond crystallites also depends on the production methods. Those particles made by milling exhibit pronounced



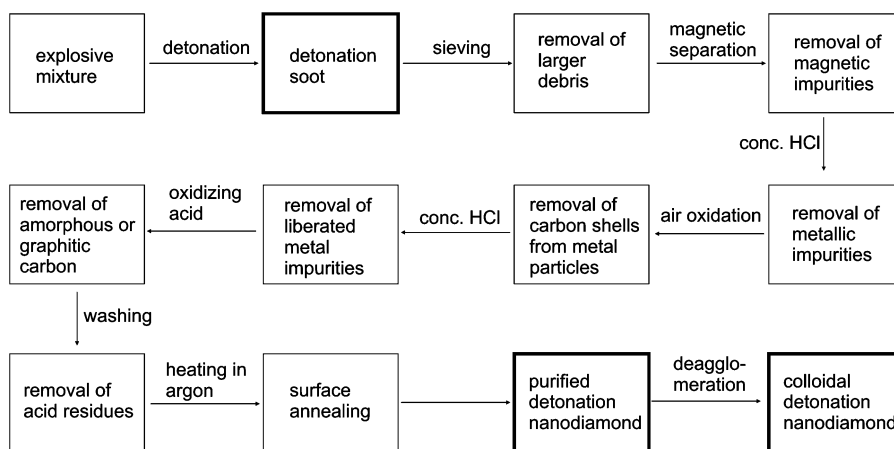
**Fig. 5** The diamond surface is covered with a variety of functional groups as determined by IR spectroscopy and TPD-MS (temperature programmed desorption-mass spectrometry).

facets, as they originate from splitting larger crystals along their lattice planes (Fig. 4). Shockwave and detonation diamond usually possess rather rounded shapes without pronounced facets. This results from the isotropic growth or transformation of the particles and an increased reactivity at tips and steps.<sup>2</sup>

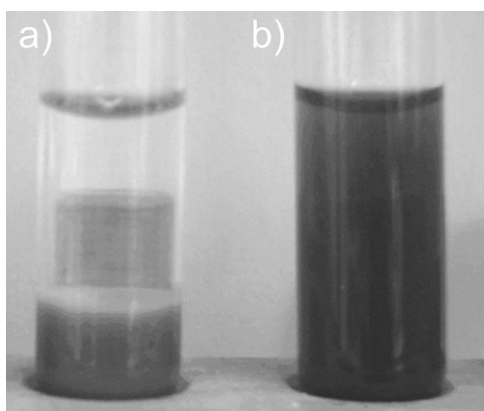
The surface of pristine nanodiamond particles shows distinctive features depending on the production method. Shockwave diamond has a graphitised surface (see below). In the case of detonation diamond, oxygen-containing groups are usually present on the particle surface.<sup>16,17,18</sup> These stem from the reaction of newly formed diamond crystallites with the cooling medium in the detonation reactor (see above) or from the purification process using concentrated mineral acids. That is why most of the functional groups are carboxylic, hydroxyl, lactones, ketones and ethers (Fig. 5). Hydrogen-terminated nanodiamond cannot be synthesised by the detonation or shock wave methods. But it is the product of substrate-free CVD (chemical vapour deposition) of acetylene in a microwave-enhanced plasma oven.<sup>19</sup>

In addition to functional groups, the surface of nanodiamond particles carries usually a certain amount of graphitic material.<sup>2,10,14,16</sup> In the case of detonation diamond, the content lies in the range of ~5% after thorough oxidative purification. For shock wave diamond, the material consists of polycrystalline, sintered agglomerates with a much larger fraction of  $sp^2$  carbon in the conglomerates.<sup>2,9,10</sup> But the surface of detonation diamond shows at least partial coverage with graphitic structures (Fig. 3), which coalesce to form larger structures when heated or electron-irradiated.<sup>20,21</sup> The  $sp^2$  content is massively dependent on the production and purification of a certain diamond sample. Therefore, a standardised purification procedure is absolutely necessary to ensure reproducible results in functionalisation experiments. An example for such a procedure is shown in Scheme 1.

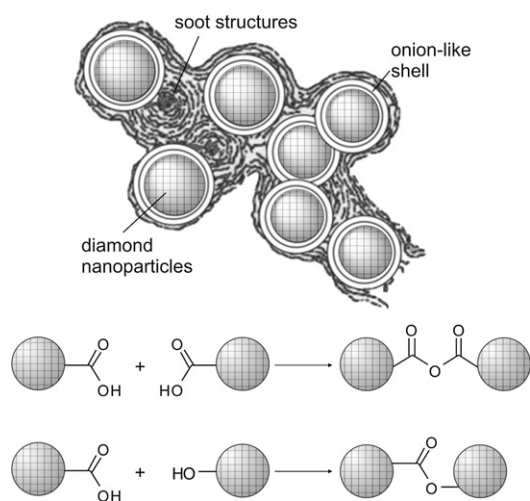
The resulting detonation diamond is a fine powder that cannot be easily dispersed in organic solvents or water due to very strong agglomeration of the primary particles (Fig. 6a).<sup>16</sup> Loose aggregation, due to electrostatic interactions, can be easily overcome by ultrasonic treatment. In the case of diamond agglomerates this is not sufficient. But the core agglomerates are not affected by this treatment. These structures are much more strongly bound by graphitic soot-like structures.<sup>16,17,22</sup> They cover the surface of agglomerates consisting of several nanodiamond



**Scheme 1** Example for the purification process of detonation soot for the production of detonation nanodiamond.



**Fig. 6** Precipitation behaviour in water. (a) Agglomerated samples precipitate immediately, (b) deagglomerated samples form stable colloidal solutions.



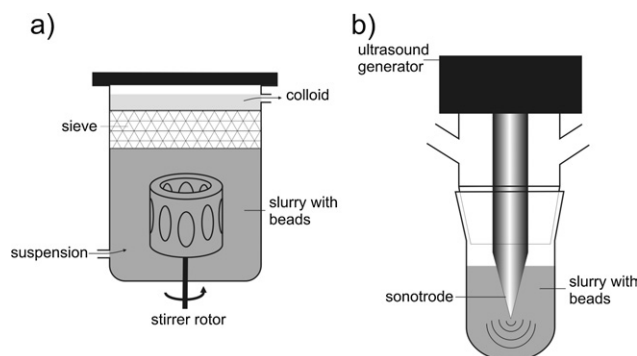
**Fig. 7** A possible structure model for diamond agglomerates in detonation diamond.

particles, which leads to a much larger agglomerate size than expected for a nanoscale material (Fig. 7).

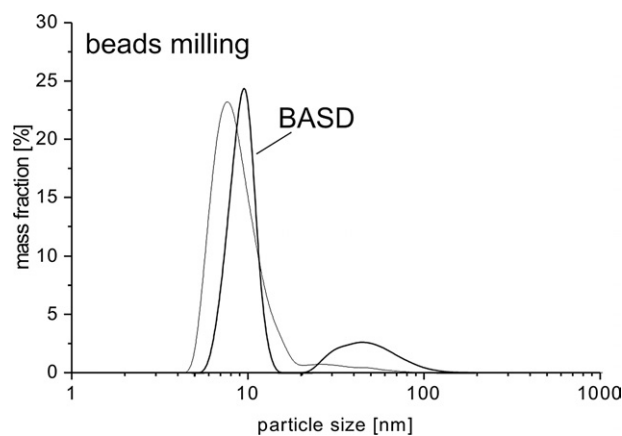
Additionally, the functional surface groups play an important role in the strong agglomeration of detonation diamond. Interparticular bonding results in the covalent attachment of nanodiamond particles with each other and consequently, formation of large agglomerates in the range of several hundred nanometres up to microns.<sup>23,24</sup>

In cooperation with the group of E. Osawa, we have reported on a technique where these agglomerates can be destroyed mechanically using shear force inflicted by small zirconia milling beads. They can be accelerated either in a fast stirring mill<sup>16</sup> or in the cavitations of strong ultrasound (Fig. 8).<sup>25,26</sup> The resulting nanodiamond primary particles form stable colloids (Fig. 6b, 9) in a variety of polar solvents, including water and DMSO (dimethylsulfoxide). In non-polar organic solvents the colloidal solution is not stable and rapid precipitation occurs. This is due to the hydrophilic functional groups on the surface of the primary particles, resulting in a zeta potential of +30 mV.<sup>26</sup>

Other authors reported on the use of surface active compounds for the production of smaller diamond particles.<sup>27</sup>



**Fig. 8** Schematic setup of (a) a stirred media mill and (b) a BASD (beads assisted sonic disintegration) apparatus for the mechanical deagglomeration of detonation nanodiamond.

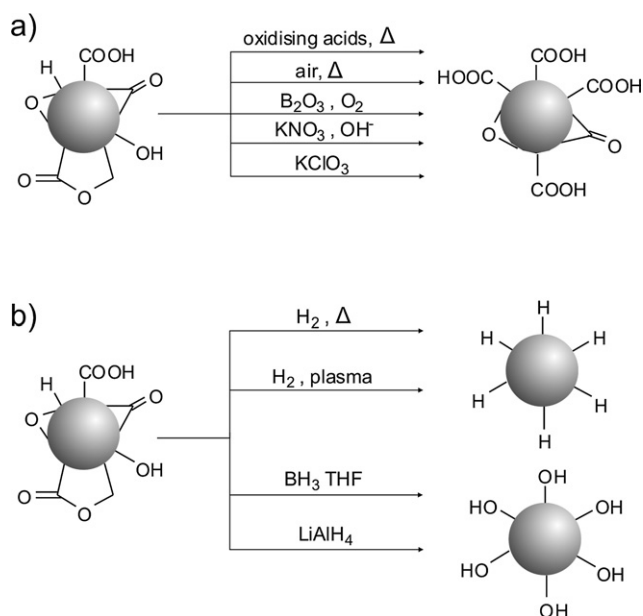


**Fig. 9** Particle size distribution of deagglomerated detonation nanodiamond. Beads milling and beads assisted sonication give comparable results.

Xu *et al.* used graphitisation and subsequent surface oxidation for the production of particles with significantly reduced agglomerate size in the range of 50 nm.<sup>28</sup> The chemical deagglomeration was also achieved by fluorination of detonation diamond (see below).<sup>29</sup> In this case, agglomerate size was reduced to ~160 nm. Gogotsi and coworkers reported on the air oxidation of detonation diamond and the resulting removal of graphitic and amorphous carbon, leading to the breaking of the large agglomerates.<sup>14</sup> Chiganova also reported on the production of detonation diamond hydrosols by surface oxidation.<sup>30</sup>

## Reactivity and surface modification of nanodiamond

One of the first chemical treatments of detonation nanodiamond was already carried out during the purification: the heating with concentrated oxidising acids or other compounds (like  $\text{KNO}_3$ ) leads to the selective oxidation of existing graphitic and amorphous  $\text{sp}^2$  carbon material, the removal of metallic impurities (such as iron from the reaction chamber).<sup>2,10</sup> Additionally, functional groups are installed on the surface of primary particles but also on the outer side of larger agglomerates. Loktev *et al.* have described the reaction with oxidising mineral acids leading to carboxylic groups on the surface of detonation diamond agglomerates.<sup>31</sup> It remained unclear though, whether



**Fig. 10** The surface of nanodiamond can be homogenised using (a) oxidative or (b) reductive methods.

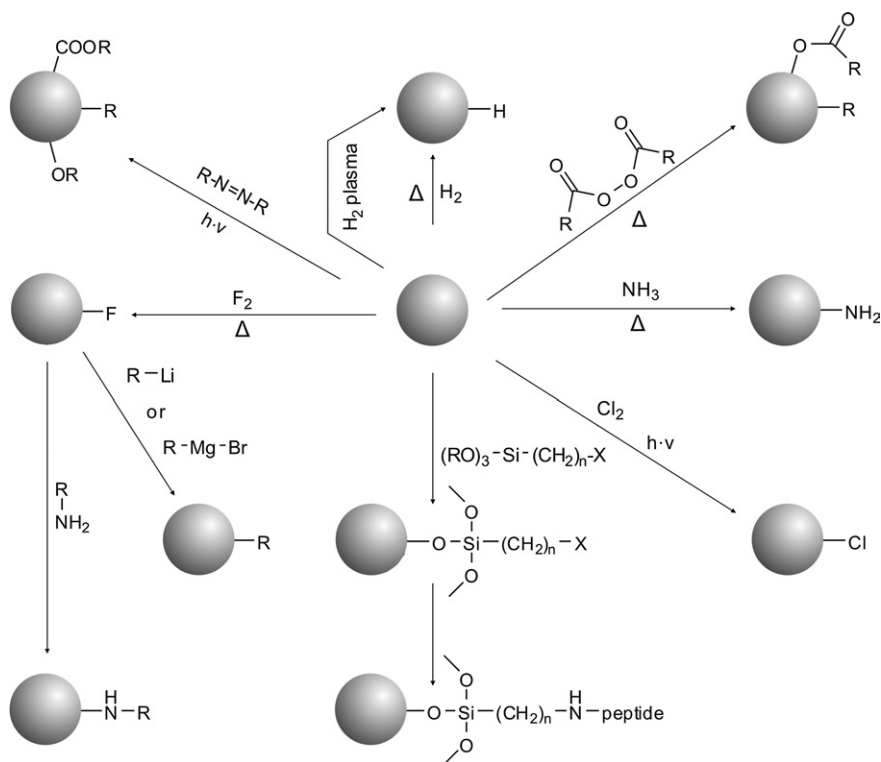
a complete oxidation of other oxygen-containing groups was achieved. As already mentioned, Gogotsi and coworkers established a procedure for the air oxidation of detonation diamond.<sup>14</sup> The products not only show a much lighter colour than the pristine material but are covered with different oxygen-containing groups, mainly carboxylic and keto groups. Another approach

for the oxidation was taken by Chiganov *et al.* They used boric oxide for the oxidation of the diamond surface and the subsequent production of diamond hydrosols (Fig. 10).<sup>30,32</sup>

On the other hand, it is possible to use reductive treatment as well for the homogenisation of the surface functionality of detonation diamond. In addition to the reported treatment with hydrogen leading to hydrogenated diamond,<sup>33</sup> we have used the reaction of oxygen-containing surface groups with borane to establish hydroxyl functions on the diamond surface (Fig. 10).<sup>24</sup>

Other reactions for the primary functionalisation of nanodiamond include the reaction with gaseous fluorine at elevated temperatures,<sup>29</sup> the reaction with ammonia<sup>33</sup> and chlorine<sup>34</sup> yielding the respectively functionalised diamond material. These materials can then be modified in a secondary step with more complex moieties (Fig 11).

For example, we have shown the reaction of hydroxylated nanodiamond with functional silanes leading to a surface coverage of about 1.4 mmol g<sup>-1</sup>.<sup>24</sup> These compounds can be used for the covalent grafting of bioactive structures, such as peptides<sup>24</sup> or biotin<sup>35</sup> or the immobilisation of maleimide linkers,<sup>36</sup> as well as for the immobilisation of other structures (initiators, monomers for polymerisation *etc.*). Fluorinated and chlorinated diamond can be reacted with lithium organic or Grignard reagents to yield the C–C-coupled derivatives (Fig. 11).<sup>29,34</sup> Aminated nanodiamond can be obtained by reaction of fluorinated nanodiamond with diamines.<sup>29</sup> Additionally, the diamond surface can be functionalised with radical reagents. Nakamura *et al.* reported on the grafting of perfluoroalkyl chains,<sup>37</sup> whereas Tsubota *et al.* used aroyl and acyl peroxides for the covalent grafting of the respective moieties onto submicron diamond particles.<sup>38</sup> One challenging



**Fig. 11** Surface functionalisation of nanodiamond yields various covalently modified derivatives with different terminal groups for further surface modification.

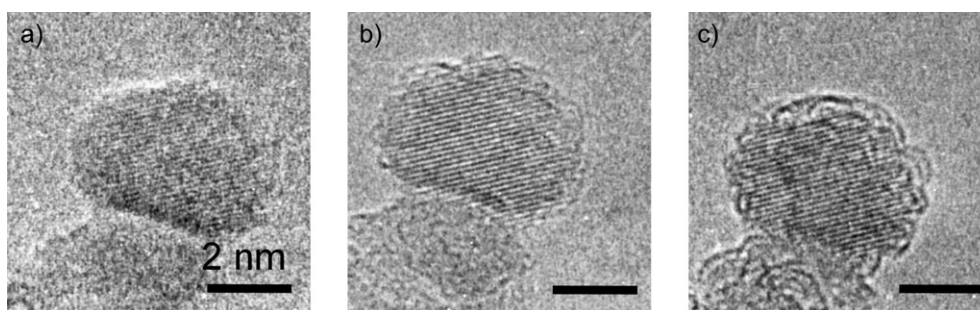
issue in the covalent surface functionalisation of nanodiamond remains unsolved though. The production of adducts with defined stoichiometry has not been successfully achieved yet.

The same is valid for non-covalent, hence adsorptive functionalisation of nanodiamond materials. In the last years, there has been considerable progress in the non-covalent coating of nanodiamond particles, though. The surface of detonation diamond easily adsorbs various kinds of small and larger polar molecules. For example, water forms a difficult to remove layer on the diamond surface.<sup>39</sup>

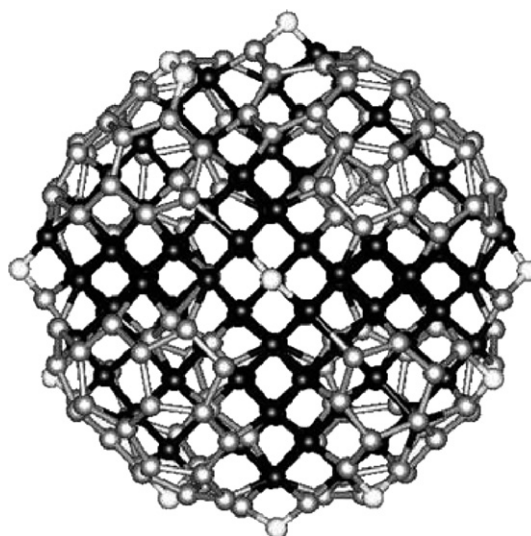
But also, larger organic molecules and biological structures, such as proteins, can be immobilised on the diamond surface. In this, the surface termination of the respective nanodiamond has a big influence on the binding strength. Diamond with hydrophilic oxygen-containing surface groups is very prone to adsorb polar molecules by hydrogen bonding and other polar interactions.<sup>40</sup> Hydrogen-terminated surfaces are much less likely to adsorb proteins and other biological compounds due to the lack of possible polar interactions, *e.g.* hydrogen bonding.<sup>41</sup>

Examples for the adsorptive functionalisation of nanodiamond include the coating with poly-L-lysine,<sup>42</sup> protein lysozyme,<sup>43</sup> cytochrome *c*<sup>44</sup> and apoobelin.<sup>45</sup> The resulting adducts were tested for their usability in a variety of sensing and biomedical application. It turned out that the adsorbed species retain their biological activity and can be used for sensing or labelling applications (see below).

Another kind of reactivity is concerned when nanodiamond particles are treated at elevated temperatures in vacuum. It is known that a transformation into onion-like graphitic material takes place. Kuznetsov *et al.* and Hayashi *et al.* have studied this process in detail and reported on the temperature dependency of the transformation process.<sup>46,47</sup> At temperatures between 1100 °C and 1500 °C, spherical onion-shaped particles are formed.<sup>20,48</sup> Heating the samples to more than 1800 °C leads to faceted graphitic nanoparticles with hollow cores.<sup>49</sup> Not only heating induces the transformation of nanodiamond into graphitic particles: the same effect can be obtained by electron irradiation, *e.g.* in a transmission electron microscope.<sup>21</sup> The carbon atoms are displaced by knock-on effects of the accelerated electrons. Fig. 12 shows the stepwise transformation beginning at the particle surface.<sup>50</sup> The easy transformation of nanodiamond particles shows the fragile equilibrium between different types of nanoscale carbon modifications that have also been predicted by several computational investigations.<sup>51–53</sup>



**Fig. 12** Surface graphitisation of detonation nanodiamond by electron irradiation. (a) Before irradiation, (b) after 5 min, (c) after 15 min (all scale bars 2 nm).

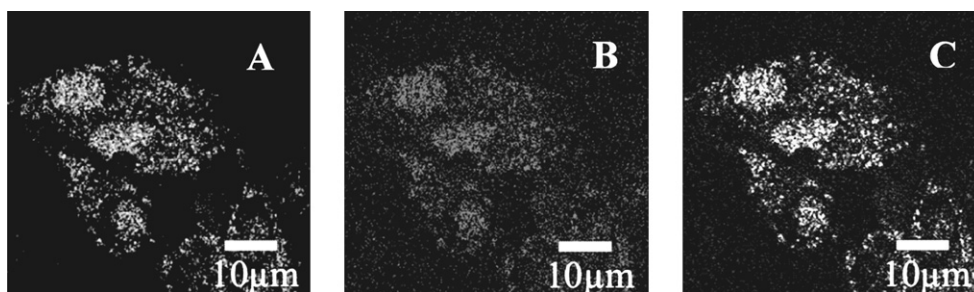


**Fig. 13** Geometry optimized structure of a bucky diamond with graphitic surface structures (with permission from Elsevier).<sup>53</sup>

It has been shown in calculations that so-called *bucky diamond* (a nanoscale diamond core with a fullerene shell, see Fig. 13) provides the smooth link between stable fullerenes (below ~900 atoms) and stable nanodiamond crystals (above ~1500 atoms) and is coexisting with fullerenes (500–900 atoms), onions (900–1350 atoms) and nanodiamond (1350–1850 atoms).<sup>51,52</sup> Above ~1120 carbon atoms a  $sp^3$  core seems to be more stable than a  $sp^2$  core irrespective of the surface structure.<sup>51</sup>

## Applications and perspectives for nanodiamond

In the future it will be important to bundle all these efforts for truly deagglomerated and functionalised diamond nanoparticles. Only if it will be possible to produce defined materials with tunable properties, will technological applications become viable. Nevertheless, the material offers a multitude of potential applications. This includes the production of nanodiamond composites, especially with polymer matrices but also with other materials, such as metals. For the optimal property transfer, a tight and stable bonding between the matrix and the diamond is necessary. A first example for a polymer composite has been reported by Lukehart *et al.*<sup>54</sup> But even with non-covalently integrated diamond particles, significant improvement of the mechanical properties takes place.<sup>2,5</sup>



**Fig. 14** Confocal images of nanodiamonds inside a HeLa cell. A: reflected light, B: fluorescence, C: overlay of A and B (with permission from ACS).<sup>61</sup>

Tsubota *et al.* have described composites of small diamond particles with nickel. However, the particle size still remains in the upper hundred nanometres.<sup>55</sup> The application of nanodiamond in galvanic platings has been studied in detail.<sup>2,56</sup> A small additive (~0.5%) of nanodiamond increases the mechanical resistance of these coatings and improves the adhesion with the substrate.

On the other hand, there is a big potential for doped diamond particles as biolabels. Not only the Raman signal,<sup>57</sup> but also the fluorescence of certain lattice defects in diamond can be observed in living cells, too.<sup>58</sup> This has been demonstrated for the so-called N-V centre, a defect consisting of a substitutional nitrogen atom with a neighbouring vacancy in the diamond lattice.<sup>59</sup> The red fluorescence is excited by irradiation in the green region of the spectrum (1–530 nm). Depending on the surface structure, the diamond particles enter the cells usually by endocytosis.<sup>58</sup> Chang and Fu *et al.* showed the feasibility of *in vivo* observation of the diamond particles in the cytosol.<sup>58</sup> But many questions remain to be answered: it is not truly understood where the diamond nanoparticles locate after cellular uptake, neither their excretion nor metabolism have been studied. For the time being, there are studies on the biocompatibility of the material that are very promising for future biomedical applications. So far, no adverse effects of diamond nanoparticles have been observed, neither in cells nor in living organisms (*i.e.* rats).<sup>60</sup> But long-term studies and information on human tissue are still lacking. Nevertheless, the first experiments on fluorescence labelling in human cell lines were successful. Human kidney 293T cells<sup>42</sup> and HeLa cells (Fig. 14)<sup>58,61</sup> have been incubated with diamond nanoparticles and the red fluorescence of nitrogen defects detected in the confocal fluorescence microscope. This offers the opportunity to develop a biocompatible, non-bleaching and possibly non-blinking<sup>58</sup> labelling system on the basis of nanodiamond particles.

The electrochemical properties of diamond make it an interesting material for sensing applications. Sensor arrays and “lab on a chip” come into reach with suitably and stably functionalised diamond nanoparticles that can be immobilised on the respective substrate. Puzyr’ *et al.* have presented a prototype for a Ca<sup>2+</sup> sensor, where the light-emitting protein obelin was immobilised on detonation nanodiamond.<sup>62</sup> Other reports include the coating of electrodes with nanodiamond.<sup>63</sup> Zhao *et al.* reported on the use of surface modified nanodiamond on gold electrodes for the sensing of glucose.<sup>63a</sup>

Another application of detonation diamond as a material for chromatography has been demonstrated recently.<sup>64</sup> They can be used either as the stationary phase in HPLC columns but ion

exchanging properties have been observed as well.<sup>65</sup> Well-dispersed nanodiamond is also a good candidate for substrate structuring in diamond CVD. First experiments showed the feasibility of seeding with nanodiamond colloids for the production of nanocrystalline diamond films.<sup>66</sup>

## Conclusions

In summary, nanodiamond is an attractive material for the investigation of relations in the world of carbon nanomaterials and a candidate for valuable technological applications. It can be produced in bulk quantities, can be functionalised non-covalently and covalently and so far did not show any biohazardous effects. This makes it a prospective material for a variety of biomedical applications, such as labelling or targeted drug delivery. On the other hand, its mechanical and electronic properties are attractive for the production of various composite materials, either with polymer or metallic matrices. But further research is necessary to achieve complete control over the surface properties and the agglomeration of the primary particles. Especially, the production of adducts with defined stoichiometry (compared to statistic approaches) remains a challenging task. Only with control over the materials composition can further progress in advanced technological applications be envisaged.

## Acknowledgements

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