Astuti Y, Poolton NRJ, Butenko YV, Siller L. [Evaporation and alignment of 1-undecene functionalised nanodiamonds](#). *Journal of Luminescence* 2014, 156, 41-48.

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DOI link to article:

<http://dx.doi.org/10.1016/j.jlumin.2014.06.045>

Date deposited:

04/07/2014

Embargo release date:

18 July 2015

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Evaporation and alignment of 1-undecene functionalised nanodiamonds

Y. Astuti^{1,2}, N. R. J. Poolton^{1,3}, Y. V. Butenko^{1,4} and L. Šiller^{1,*}

¹ School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK

*Corresponding author: Dr. Lidija Šiller

Tel. :+44-191-222-7858

Fax:+44-191-222-7361

E-mail: lidija.siller@ncl.ac.uk

Current address:

²Chemistry Department, Diponegoro University, Tembalang, Central Java, Indonesia, 50271

³Spectral Imaging Systems, 36 Waterside House, Denton Mill, Carlisle CA2 5HF, UK

⁴European Space Agency, ESTEC, Keplerlaan 1, Noordwijk 2201 AZ, Netherlands

Abstract

The possibility to align diamond nanoparticles has a number of potential technological applications, but there are few methods by which this can be achieved, and research in this field can be considered to be in its infancy. Hitherto, two methods which have been commonly used are lithography and chemical vapour deposition (CVD), but these methods are both complex and have poor effectiveness. In this paper, we present a new technique for particle alignment, which is simpler and avoids particle structural damage. The method works by functionalising the nanodiamonds of size 5 nm by attaching 1-undecene onto the nanodiamond surfaces; the particles are then evaporated using UHV and deposited onto TEM grids and mica surfaces at 200 °C. XPS, SERS, HRTEM, luminescence spectroscopy and luminescence micro-imaging have been applied to characterise samples both before and after evaporation. Deposition of nanodiamond onto a mica surface resulted in particle alignment with length scales of 500 µm. The XPS and Raman spectra confirmed the absence of non-diamond carbon (sp^2 -hybridized carbon). Moreover, photoluminescence (emitting in the range of 2.48–1.55 eV; 500–800 nm) which is characteristic for nanodiamond with size of 5 nm was also observed, both before and after evaporation of the functionalised nanodiamonds.

Keywords: photoluminescence, particle alignment, 1-undecene, nanodiamond, evaporation

1. Introduction

Generally, well aligned nanoparticles have distinctive functionalities which cannot be found in randomly aligned particles: alignment allows them to be applied in information processing, storage and transmission systems as well as nanosensor and optical devices. Several methods have been applied to achieve the goal such as lithography [1], laser-assisted CVD [2], magnetic and electric forces [3, 4], magnetic force microscopy [5] and the generation of templates [6-8].

More specifically, nanodiamonds hold great promise for use in a variety of applications, such as electroplating, lubricating oils, polishing, magnetoresistive sensors and bio-applications due to their hardness, high thermal conductivity, electrical resistivity and biocompatibility [9]. The alignment of nanodiamond is an effective way to enhance its potential properties [10] which could advance its usage for certain applications. Several investigations on nanodiamond structuring have been reported recently [10, 11]. Nitrogen-contained diamond nanograss and nanotip have been reported recently to be a prospective candidate for electron field emitter and single photon source due to the enhancement of field emission and the high-intensity photoluminescence properties, respectively [10]. The first potential candidate is potential for vacuum electronic devices and another one is the key for production of quantum communication and quantum computation devices [10]. Moreover, the linearly aligned nanodiamonds grown on polyepoxide-based composite films exhibited increasing the composite thermal conductivity properties [11]. It was suggested that the enhancement occurred by transferring heat through the aligned nanodiamond instead of polymer itself [11]. With the intention of producing nanodiamond-based “smart” materials, new methods to organise the nanoparticles into particular order must be developed. The simplest method for producing dispersed nanodiamonds on substrates such as glass or silica is by deposition, spin-coating and drying; this produces isolated nanodiamonds, but particle

alignment cannot be achieved by this technique [12-14]. However, Sun *et al* were able to immobilise and allocate a single nanodiamond on the round metal (Au and Ti) dots on a Si substrate patterned by the electron beam lithography [8], but particles were found to agglomerate on the patterned templates, even though the standing single particles with size of 90 nm and 35 nm were observed. Several research groups have also undertaken to fabricate nanodiamond alignment in the form of nanowires [1, 15-17] which can be undertaken using atmospheric chemical vapour deposition [15], e-beam lithography (EBL) and reactive ion etch (RIE) techniques [17]. However, the major drawbacks of these methods are poor for large-scale fabrication and possibly lead to diamond degradation. Moreover, deposition of an etching mask must be carried out by pre-preparation process and the etching mask residue will still exist [17].

In the case of research into the fabrication of nanodiamond dot arrays, very little previous work has been undertaken. Generally, chemical vapour deposition (CVD) [12] and lithography [1] are commonly used methods, but these have several limitations; for instance, they need multiple-steps in their formation, during which structural damage can occur. Loh *et al* [18] employed a nanofountain probe to create dot arrays of functionalised nanodiamonds and the consistency of the dot features was assessed. Again, this investigation met a limitation, namely that the minimum size of the dot that could be created was 93 nm.

It should be born in mind that dispersed particles are most easily organised in particular order but it is hard to align particles that are constituents of agglomerates [19]. Nanodiamonds can be produced by several methods, but those fabricated by detonation have the unique advantage of being able to be produced in very small sizes, and they are therefore attractive candidates for use in technological applications. However, the problem arises since individual particles tend to agglomerate into clusters ranging from hundreds of nanometres to several micrometres in diameter owing to strong inter-particle bonding and the presence of

soot-like structures surrounding the individual crystals which hinder their potential applications [20]. Therefore, methods of removing such a graphitic layer would significantly improve the ease of alignment. Oxidising mineral acids such as HClO_4 , H_2SO_4 , HNO_3 are generally applied to purify the detonation product to obtain graphite-free nanodiamonds [9, 20]. Furthermore, Osswald and co-workers have applied a selective oxidation in air method, a simple and environmentally friendly route, to remove sp^2 -bonded carbon from nanodiamonds [21].

In this paper, we investigate the evaporation and particle alignment of undecyl-nanodiamonds produced by recently developed method of functionalisation of detonation nanodiamonds using 1-undecene accompanied by shaking, soxhletation and centrifugation which led to separation of nanodiamonds in *powder form* [22, 23]. Such functionalisation was aimed at de-agglomerating nanodiamond clusters so as to become primary particles, achieved by removing sp^2 -hybridized carbon (graphite layer) contained on the surface. In order to characterise the particles both before and after evaporation in this work [22, 23], X-ray photoemission spectroscopy (XPS), Raman spectroscopy, high resolution transmission electron microscopy (HRTEM) and Photoluminescence (PL) spectroscopy and PL micro-imaging were used.

2. Experimental methods

The nanodiamond powder used in this study was fabricated by detonation technique with a negative oxygen balance in hermetic tanks and was provided by the Federal Research and Production Centre “Altai” (Biysk, Russian Federation). The average size of the particles lies in the range 3.5–6 nm [24, 25]. First, the raw (untreated) detonation nanodiamond powder was purified with a mixture of HClO_4 and H_2SO_4 (1:1) to remove any non-diamond forms of carbon, this acid-purified nanodiamond powder was then used to produce the undecyl

nanodiamond by attachment of 1-undecene to the nanodiamond surface, followed by shaking, soxhlet extraction and centrifugation, respectively. The procedures of both acid-purified and undecyl-nanodiamonds preparation has been accounted in detail in Refs. 22, 23.

The XPS measurements were taken using a Kratos Ultra 165 spectrometer. The X-ray source was an Al K_{α} monochromated source of photon energy 1486.6 eV with an energy resolution of 0.3 eV. The pressure inside the chamber was typically of the order 10^{-9} Torr during scanning.

STEM measurements of undecyl-nanodiamond were performed with a VG HB501 series cold field emission aberration-corrected STEM (Daresbury SuperSTEM) operating at 100 keV in bright field (BF) and Z-contrast imaging modes (i.e., high angle annular dark field).

Evaporation of the sample was conducted in UHV chamber for 20 minutes onto a lacey carbon TEM grid (commonly used in other nanodiamond studies) and mica substrate; The chamber was baked to 110 °C until the pressure 2×10^{-8} Torr was achieved and the evaporation of nanocrystals was conducted at 200 °C. This temperature regards to the thermal stability of the alkyl-monolayers which has been observed on alkyl-capped silicon nanoparticles [26]. Moreover, during the evaporation, the pressure in the chamber started to rise to 4×10^{-7} Torr. The evaporation set up consists of UHV chamber with accessible ports connected to cold finger and to pump, the source (sample) holder, substrate holder and heater/temperature controller (for experimental details of the evaporation unit, see Ref. 26).

To enable surface enhanced Raman spectroscopy (SERS), silver nanoparticles were mixed with the samples. Acid-purified nanodiamond was prepared for SERS by mixing of 1 mg acid-purified nanodiamond powder and 2 mL Ag suspension (30 ppm) synthesized according to the procedure in Ref. 27 then sonicated for 15 minutes in an ultrasonic bath. Afterward two drops of the suspension were deposited onto silicon wafer and dried at room

temperature. In contrast, SERS preparation of the alkylated nanodiamond sample was conducted by drying of 4 drops of Ag suspension (30 ppm) in the vial at room temperature, subsequently adding 1 mL undecyl-nanodiamonds; this was then sonicated for 15 minutes. This second preparation method is different since the polarity between solvent of nanosilver (water) and nanodiamond suspension (pentane) is different. Finally, 2–3 drops of suspension was deposited onto silicon wafer and dried in room temperature. The SERS sample analysis was performed using LabRAM HR800 with the 514.5 nm line from an Ar ion laser. Spectra were collected with the laser beam power at ~5 mW focused to a spot of 1 μ m diameter on the sample.

The sparsely distributed particles and particle size characterisation of the evaporated nanodiamonds has been confirmed using HRTEM. Micrographs were recorded using a JEOL 2100F transmission electron microscope operating in the range 80 keV–200 keV.

Luminescence analysis in the emission range 1.48–6.2 eV (200–840 nm) was undertaken using the variable-temperature mobile luminescence end station (MoLES) as described in Ref. 28. A 30 mW semiconductor diode laser emitting at 2.79 eV (445 nm) was used as an excitation source, equipped with appropriate laser clean-up filters. A low-fluorescence 500 nm long-wave pass filter was used on the detection side to reject the scattered laser light prior to entering the monochromator. All samples were deposited onto thermally conducting carbon tape attached to a cryostat cold-finger and the measurements were made in the range 30–300K. As a result, the PL emission features do not change significantly in the temperature range and the 250K results were the most representative.

In order to map the spatial and spectral distribution of luminescence from diamond nanocrystals evaporated onto a mica surface, the CLASSIX instrument was used; this is essentially a micro-imaging version of MoLES, but deploys a CCD rather than

photomultiplier tube, and a super-array of filters, rather than diffraction grating for spectral dispersion (for experimental details, see Ref. 29). For these spatially-resolved measurements, the sample was characterized at room temperature, using the same laser and filter combination as described above.

All spectra presented have been corrected for instrumental response and monitored in the range 2.48–1.55 eV (500 nm–800 nm).

3. Results and discussion

The efficiency by which de-agglomeration of the nanodiamond clusters have been achieved can be assessed spectroscopically by the disappearance of non-diamond carbon on nanodiamond surface. Both XPS and SERS were used to determine the presence of sp^2 (non-diamond carbon) and sp^3 (diamond carbon) bonds in the sample before evaporation. Instead of using standard Raman, SERS was used with the intention of providing greatly enhanced Raman signal from nanodiamond particles adsorbed onto silver nanoparticles colloid. After evaporation, the spatial distribution of the particles can be directly determined on the nm and μm scale length using HRTEM and luminescence-micro imaging, respectively.

3.1 X-Ray photoemission spectroscopy

A rough survey of undecyl nanodiamond with scan range from 0–1100 eV was conducted to identify the presence of the elements contained in the sample. As seen in Fig 1a, the photoemission survey showed that the sample consists of Ta, Si, C, N and O atoms.

It is well reported that C1s photoemission spectra of acid-purified nanodiamonds exhibits two major peaks correlated with sp^2 and sp^3 bonds. The C1s photoemission spectrum for acid-purified nanodiamond powder (not presented here) is broad (FWHM ~ 2.8 eV) and the individual components were not resolved due presence of large amount of oxygen-

containing groups as previously noted [30]. The sp^2 and sp^3 components are were not well resolved and due to large number oxygen containing groups any fitting would not be unambiguous. Therefore, it is not possible to determine the sp^2/sp^3 ratio in this sample. On the one hand, the C1s photoemission spectrum of undecyl-nanodiamonds shown in Fig. 1b demonstrates only one peak at the binding energy of 285.8 ± 0.1 eV after fitting using Gaussian-Lorentzian line shapes (FWHM of ~ 1.7 eV) indicating the presence of C-C sp^3 bonding within the material. This binding energy was attributed to sp^3 bound carbon by Arnault *et al*[31] and Pu *et al* in their investigations[32]. Other researchers have also remarked that a binding energy of 285.8 eV is indicative as the sp^3 -hybridized state [33, 34]. Thus, it is clear that after functionalisation using 1-undecene, the sp^2 -hybridised carbon was not observed.

A small amount of nitrogen in detonation nanodiamonds is commonly found at both the surface and at the core; nitrogen, in various complexes, is responsible for the dominant PL properties in crystalline diamond and possibly in nanodiamond too (see section 3.5). Fig. 1c showed N1s photoemission spectrum analysis. The peak was fitted into 2 sub peaks with the binding energies at 401.3 ± 0.1 and 405.4 ± 0.1 eV. The binding energy at 401.3 ± 0.1 eV corresponds to $>N-N<$ and $-N=N-$ species [35]. The second peak at 405.4 ± 0.1 eV is assigned to oxidized N-species like N-O and/or N=O bonds, which might be trapped beneath the surface [35].

All the spectrometer binding energies for Fig. 1 were calibrated for each spectrum. The samples were deposited on the gold foil and energy calibration was referenced to the Au 4f. No charging was observed.

3.2 Surface enhanced Raman spectroscopy

In acid-purified nanodiamonds, treated with mixture of HClO_4 and H_2SO_4 , two SERS peaks are observed at 1331.5 and 1614 cm^{-1} as shown in Fig. 2a. These peaks correspond to the sp^3 -hybridized carbon (nanodiamond) [36] and sp^2 -hybridized carbon (graphitic G-band) structures, respectively [37]. The presence of these two peaks, of comparable intensity, indicates that the acid treatment alone does not completely remove the graphitic layer. The breadth of the 1614 cm^{-1} peak (FWHM $\sim 100\text{ cm}^{-1}$) also indicates that the graphite may become disordered within the carbon layer; this could be the extended graphitic structure generated during acid treatment.

The SERS spectrum of acid-purified nanodiamonds *after* functionalisation with 1-undecene depicted in Fig. 2b exhibited different peak positions, namely, at 1155 , 1300 , 1330 , 1360 , 1458 , 1603 and 1725 cm^{-1} . The assignments of these Raman peaks are summarised in Table 1. The sp^3 -hybridized carbon vibration mode at 1331.5 cm^{-1} is shifted to 1330 cm^{-1} . The intensity of the G-band shown at 1603 cm^{-1} decreases significantly and is barely visible.

The additional peak at 1155 cm^{-1} is in controversy having previously being assigned to either the nanocrystalline or amorphous phase of diamond [38]. We consider that the 1155 cm^{-1} signal is unlikely to arise from the presence of a sp^2 phase of the material since no sp^2 phase is observed in the XPS spectra shown in Fig. 1b. However, it is much more likely to be related to undecyl attached on nanodiamond surfaces. Polyethylene, a long-chain carbon compound without C double bonds ($\text{C}=\text{C}$), has a similar structure to undecyl; it shows the C-C stretching vibration in the range $1000\text{--}1150\text{ cm}^{-1}$ and $-\text{CH}_2$ -twisting vibrations at 1300 cm^{-1} [39]. All of those peaks are observed in our Raman spectrum.

3.3 Transmission electron microscopy

As demonstrated in HRTEM image in Fig. 3a, acid purified nanodiamond exhibits agglomerate clusters with size in the range of 2–5 nm for individual diamond particles. The lattice fringes with 2.06 Å inter-planar spacing indicated with white straight lines in the micrograph corresponds to the {111} crystallographic diamond planes [40]. The superSTEM micrograph presented in Fig. 3b suggests that undecyl-nanodiamonds can be sparsely distributed onto the TEM grid. In addition, the crystallinity of the nanodiamond can be seen in the aberration-corrected high angle annular dark field (HAADF) image shown in the inset in Fig. 3b. Most particles present in $\langle \bar{1}10 \rangle$ orientation, in which the fringe spacing is that of the {111} planes in diamond [41-43].

Fig. 4 presents HRTEM images and an associated fast fourier transform (FFT) of evaporated nanodiamond. It is seen, particularly in Fig. 4a, that diamond nanoparticles were well-separated and deposited successfully onto a lacey carbon grid by evaporation at ~200 °C. This temperature regards to the thermal stability of the alky-monolayers which has been observed on alkyl-capped silicon nanoparticles [26, 44]. Enlargement of the micrograph, Fig. 4b, shows that separated nanodiamond particles have diameters ranging from 2–4 nm. Fig. 4c shows an isolated particle with a diameter of 4 nm which was subsequently used to determine the crystalline structure of the evaporated nanodiamonds. Determination of the crystal structure was carried out by FFT analysis which can be seen in Fig. 4d. This Figure indicates that the lattice planes of isolated nanodiamond are {020}, {220}, {200} [45]. The latter two planes are in agreement with that of nanodiamond before evaporation. However, {111} crystal orientation as the standard crystalline planes of nanodiamond cannot be detected in this investigation.

3.5 Photoluminescence spectroscopy

3.5.1 Detail of emission spectra

Figure 5 depicts PL spectra of differently treated-nanodiamonds. Acid-purified nanodiamonds (Fig. 6a) show a broad structureless emission in the range 2.48–1.55 eV (500–800 nm), which can be satisfactorily fitted to two Gaussian bands with the maximum peak at 2.24 eV, HWHM 0.40 eV. Although such luminescence is typical for detonation nanodiamond with a particle size of 5 nm [46], the precise origins of the emission are uncertain. Previously, it has been variously considered to be related with: (i) structural disorder on the nanodiamond surface; (ii) presence of carbon in the threefold-coordinated state; (iii) dangling bonds on the surface of the nanoclusters [33] and; (iv) with the intrinsic defects of a single-crystal diamond [47]. Recent investigation reported that nanodiamond soot treated with a mixture of concentrated sulphuric and nitric acid by refluxing process at low temperature resulted in nanodiamonds surface decorated with 1-2 nm (smaller than graphene dots) rounded nanocarbon particles called carbon dot-decorated nanodiamond (CDD-ND) which has tiny size posses orange-red photoluminescence in its supernatant solution [48]. This PL emission was suggested mostly due to the presence of surface energy trapping sites [49, 50], defected graphitic structures of the CDD-ND and the presence of carboxylic acid groups [51]. In addition, a bump at ~1.7 eV indicated with arrow could be correlated with silicon vacancy (SiV) center [52].

As shown in Fig. 5b, functionalisation of the nanodiamond surface using 1-undecene induces a change in the photoluminescence spectra; from curve fitting, the main broad band shifts to higher energy (2.41 eV) and becomes narrower (HWHM, 0.35 eV). It can be conjectured that the shifts and the sharper peak could be as a result of removing either the amorphous carbon surrounding the crystalline nanodiamonds and interaction between undecyl and nanodiamond [53]. This finding is in agreement with Mochalin *et al* [53] and Shenderova

et al [54]. Mochalin *et al* reported that the presence of octadecylamine (ODA) onto nanodiamond surface resulted in bright blue fluorescence of its suspension observed under UV light laser excitation [53]. Moreover, Shenderova, O. A. and her group conducted several surface modification of detonation nanodiamonds by grafting small molecules on their surfaces, for instance the attachment of aminopropyltriethoxysilane (APES) onto nanodiamond surface. The results showed that the PL intensity enhancement of the surface modified nanodiamond was achieved as compared to the unmodified detonation nanodiamond. It should be noted that these small molecules do not show PL characteristics [54, 55]. It was hypothesized that, in case of the nanodiamond-APES, the defected silica domains are formed so that the PL intensity enhanced [54]. Meanwhile, the fluorescence mechanism of nanodiamond-ODA has not been established yet [53]. The same shifted broad emission band (2.33 eV peak, 0.30 HWHM) is also observed in undecyl-nanodiamonds after evaporation (Fig. 5c).

In addition to the dominant broad band emissions described above, functionalisation and evaporation resulted in very weak, but comparatively sharper, emission features in the range 2.21–2.43 eV; these become clearer if the fitted broad Gaussian bands are subtracted from the luminescence spectra (see subtracted spectra in Figs. 5b and 5c). Essentially, chemical modification caused the appearance of a sharp emission line at 2.41 eV and after evaporation the main sharp peak appears around at 2.33 eV. As these emission features have not previously been observed in either diamond or nanodiamond, we cannot yet assign them to specific defects. It should be noted that no emission was detected from the mica itself.

3.5.2 Spatial distribution of nanodiamond emission

The spatial distribution of the luminescence shown in Fig. 6a demonstrates that nanodiamonds can be evaporated and their vapour can be collected and sparsely distributed

onto substrate surface using UHV. Interestingly, the particles can be linearly ordered with the length 500 μm depicted in Fig. 6b. The structure of mica, $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, consists of aluminosilicate layers separated by the OH groups. When cleaved, the mica surface exhibits an hexagonal array corresponding to the hexagonal rings of SiO_4 tetrahedra [56] and this is almost certain to be the reason why particle alignment occurs: determination of the angle formed between the lines shows particle alignment oriented at 59° and 122° , matching the hexagonal mica structure. The angle at 18° and 22° is probably due to the different orientation of mica crystals within their layer arrangement.

In order to confirm that the evaporated particles are nanodiamonds, one single spot exhibiting particle luminescence has been selected. The spot size of this particle is close to the 1 μm spatial resolution limit of the instrument. The main broad peak at 2.25 eV (550 nm) was still detected (Fig. 6c) as observed in Figs. 5a and 5c, and a new signal at 1.80 eV (690 nm) (not observed in the previous result) is detected and potentially attributed to Cr or NE8 (nickel nitrogen complex) centres [57, 58]. The same broad-band nanodiamond emission is found to be emitted from all the linearly-aligned features, confirming that evaporation of nanoparticles using UHV has possibility to produce the ordered-nanoparticles; this could open a way for particular applications in nanoscale devices such as bio-sensing chips and single bio-molecule patterning and detection devices.

4 Conclusion

Using luminescence imaging, we have investigated the particle alignment of 1-undecene functionalised nanodiamonds by evaporation of the particles into UHV at 200 $^\circ\text{C}$. The length of the particles line order is around 500 μm . The XPS and SERS spectra applied to characterise undecyl-nanodiamond before evaporation suggests that graphitic layers which trigger agglomeration of the particles have been successfully removed. HRTEM images

showed that nanodiamond particles can be evaporated onto a TEM grid. Moreover, photoluminescence spectra proposed that undecyl-nanodiamonds and their evaporation and deposition onto mica surface using UHV still conserved their luminescence emission observed in 2.48–1.55 eV (500–800 nm) regions. These investigations could be important for their application in the future.

Acknowledgement

The authors would like to thank Physical Sciences Research Council (EPSRC) for financial support (EPSRC grant EP/F065272/1). Yayuk Astuti is grateful to Directorate General of Higher Education Republic Indonesia (DIKTI) for scholarship award. We thank School of Electrical Engineering and Computer Engineering (Newcastle University, UK) for Raman Spectroscopy instrument.

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List of table

1. Table 1. Raman peaks observed in undecyl-nanodiamonds together with their assignments

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Figure 1. The photoemission spectra of undecyl-nanodiamonds, (a) survey scan of the spectral region 0-1100 eV, (b) and (c) C1s and N1s photoemission spectra, respectively. Both C1s and N1s spectra have been curve fitted, with the spectral components displayed and with the energy peaks of the fitted components as indicated.

Figure 2. SERS of (a) acid-purified nanodiamonds and (b) undecyl-nanodiamonds.

Figure 3. (a) HRTEM image of acid-purified nanodiamonds, (b) superSTEM image of bright-field (BF) of undecyl nanodiamond with the inset showing the crystal structure of the particle.

Figure 4. HRTEM images and FFT of evaporated nanodiamond: (a) BF image of sparsely distributed nanodiamonds; (b) a magnification of a box-selected area in Fig. 4a; (c) BF image of isolated nanodiamond; (d) FFT analysis of the nanodiamond crystalline structure from Fig. 4c.

Figure 5. Photoluminescence spectra of (a) acid-purified nanodiamond, (b) undecyl-nanodiamond, and (c) evaporated-undecyl nanodiamond. The dashed line indicates the transmission filter cut-off. The measurement temperature was 250K.

Figure 6. Luminescence characteristics of undecyl-nanodiamond evaporated onto mica surface (a) Spatial image showing isolated diamond nanoparticles, (b) Spatial image showing the alignment of nanodiamonds in certain area. (c) Spectrum characteristic of the data point of the selected particle denoted by the white circle in (b). The dashed line indicated the transmission filter cut-off. The measurement temperature was 300K.

Tabel 1.

Position of Raman peak	Assignment	References
1300 cm^{-1}	A sp^2 network including sp^3 bonds	[59]
	-CH ₂ -twisting vibrations	[39]
1330 cm^{-1}	Characteristic for nanodiamond	[60]
1360 cm^{-1}	<i>D</i> peak owing to the breathing modes of sp^2 atoms in rings	[41]
	Characteristic peak for sp^3 structural diamond nanocrystals	
1458 cm^{-1}	CH ₂ bending formation	[61]
	CH ₃ asymmetrical deformation	
1603 cm^{-1}	A sp^2 -hybridized carbon (the graphitic layer (<i>G</i> -band))	[62]
1725 cm^{-1}	C=O vibration	[61]

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6