Deagglomeration and functionalisation of detonation nanodiamond with long alkyl chains

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Abstract

We have achieved the covalent functionalisation of detonation nanodiamond by an esterification reaction of carboxylic acid chlorides on hydroxylated nanodiamond. The resulting "nanodiamond esters" with a surface loading of 0.3–0.4 mmol g^{-1} of alkyl groups have been characterized by FTIR spectroscopy, thermogravimetry and elemental analysis. They exhibit a significantly improved dispersibility in organic solvents such as tetrahydrofurane and dichloromethane.
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1. Introduction

Diamond nanoparticles have found considerable interest recently due to their potential applications in biological systems, composites and electronic applications [1]. Their apparent biocompatibility [2] and chemical inertness make them an ideal candidate for all kinds of biomedical devices. On the other hand, their surface can be functionalised with a variety of groups in order to incorporate them into polymer matrices, surface coatings and the like [3]. An essential prerequisite for these applications is the control of surface structure and particle size and agglomeration.

So far, different approaches for the surface functionalisation and deagglomeration have been taken. Chiganova produced diamond hydrosols from oxidized detonation diamond [4], whereas Xu and coworkers used surface active compounds for the dispersion of nanodiamond particles [5]. Khabashesku et al. obtained small agglomerates of ~160 nm in size by the fluorination of detonation diamond [6]. These particles formed stable suspensions in THF. Another approach is the mechanical deagglomeration in suspension by stirred media milling [7] or beads assisted sonic disintegration [8]. Covalent surface modification of nanodiamond has been reported by several authors. Reactions with fluorine [6], chlorine

[9], ammonia [10] and hydrogen [10,11] lead to homogenized, surface modified nanodiamond materials with increased reactivity and the option for further functionalisation. Oxidation of the surface can be achieved by air oxidation [12] or treatment with oxidizing mineral acids [13]. We have recently reported on a wet-chemical method for the hydroxylation of the nanodiamond surface [14]. This allowed for the subsequent grafting of different trialkoxysilanes and the further functionalisation by covalent bonding [15]. On the other hand, Nakamura and coworkers as well as Tsubota and coworkers have reported on the covalent grafting of alkyl and aryl moieties by radical reactions [16,17].

Here we report on the grafting of alkyl chains by an esterification reaction on hydroxylated detonation diamond. This simple and efficient method yields "nanodiamond esters" with alkyl chains with different lengths. The latter should have an impact on the dispersibility of the functionalised nanodiamond in organic solvents.

2. Experimental

2.1. Chemicals

Detonation nanodiamond was purchased from Gansu Lingyun Corp., Lanzhou, China. All other chemicals have been purchased from Fluka and Sigma Aldrich and used without further purification if not stated otherwise. Solvents were dried according to

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Table 1
Solvent dependence of sedimentation of alkylated nanodiamond

| Sample | Time of beginning sedimentation | | | |
	Pentane (min)	Toluene (min)	THF	CH_2Cl_2
ND, pristine	0	1	22 h	0 min
ND–OH (**1**)	0	1	22 h	0 min
ND–OOC–C_3H_7 (**2**)	4	3	_a)	_a)
ND–OOC–C_5H_{11} (**3**)	4	3	_a)	_a)
ND–OOC–$C_{11}H_{23}$ (**4**)	4	4	10 days	_a)
ND–OOC–$C_{17}H_{37}$ (**5**)	1	6[b)	15 days	_a)

[a) No sedimentation occurred during the observation period; [b) no complete sedimentation after prolonged time.

literature procedures. The acid chlorides were synthesized from the respective carboxylic acids using oxalyl chloride [18].

2.2. Instrumentation

The FTIR spectra were measured on a Perkin Elmer Paragon 1000 spectrometer with KBr pellets. Thermogravimetry was carried out on a Netzsch ST2010. Elemental compositions were measured on a Euro EA 3000 Series elemental analyzer. Measurements of the particle size were executed on a Photal Otsuka FPAR1000 fiber-optics particle analyzer.

The synthesis of hydroxylated nanodiamond (**1**) was carried out according to a literature procedure [14]. Prior to the borane treatment the samples were sonicated in a conventional bath-type sonicator for 45 min. IR (KBr): 3437 (O–H), 1628 (O–H) cm^{-1}; elemental analysis: C: 90.11, H: 0.757 N: 2.16.

2.3. General procedure for the synthesis of alkylated detonation nanodiamond

0.350 g of hydroxylated nanodiamond were dispersed in 20 ml abs. toluene and sonicated for 30 min. Under argon atmosphere 7.0 mmol acid chloride in 10 ml abs. toluene were added dropwise and the mixture was heated for 70 h under reflux. After cooling the mixture was sonicated for 30 min and centrifuged. After washing with acetone (altogether 60 ml, used in portions) under sonication the mixture was centrifuged. After drying *in vacuo*, a light grey powder was obtained.

2.4. ND–OOC–C_3H_7 (2)

According to the general procedure 0.423 g of ND–OH were reacted with 0.955 g (9.0 mmol) butyric acid chloride. 0.428 g of a light grey powder was obtained. IR (KBr): 3420 (O–H), 2958, 2923 (CH aliph.), 1719 (C=O), 1628 (O–H), 1100 (C–O–C)

cm^{-1}; elemental analysis: C: 88.73, H: 0.881, N: 2.11; thermogravimetry (N_2, 4 K min^1): −2.72%; surface loading: 0.401 mmol g^{-1}.

2.5. ND–OOC–C_5H_{11} (3)

According to the general procedure 0.353 g of ND–OH were reacted with 0.906 g (7.0 mmol) caproic acid chloride. 0.344 g of a light grey powder was obtained. IR (KBr): 3422 (O–H), 2958, 2931 (CH aliph.), 1720 (C=O), 1627 (O–H), 1460 (CH-deform.), 1160 (C=O), 1102 (C–O–C) cm^{-1}; elemental analysis: C: 89.97, H: 1.139, N: 1.90; thermogravimetry (N_2, 4 K min^1): −3.25%; surface loading: 0.352 mmol g^{-1}.

2.6. ND–OOC–$C_{11}H_{23}$ (4)

According to the general procedure 0.350 g of ND–OH were reacted with 1.444 g (7.0 mmol) lauric acid chloride. 0.310 g of a light grey powder was obtained. IR (KBr): 3422 (O–H), 2923, 2852 (CH aliph.), 1720 (C=O), 1627 (O–H), 1460 (CH-deform.), 1149 (C=O), 1111 (C–O–C) cm^{-1}; elemental analysis: C: 90.02, H: 1.449, N: 2.01; thermogravimetry (N_2, 4 K min^1): −5.35%; surface loading: 0.313 mmol g^{-1}.

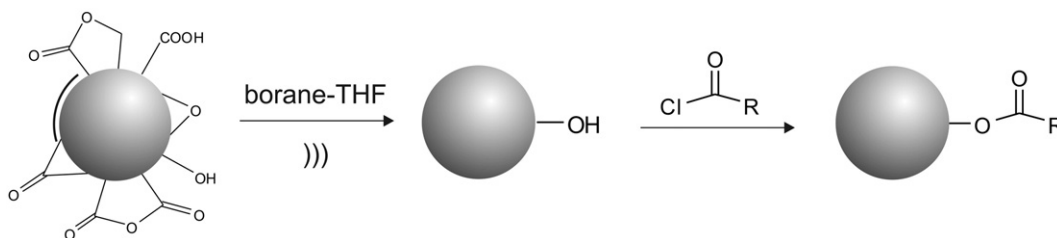## 2.7. ND–OOC–$C_{17}H_{37}$ (5)

According to the general procedure 0.359 g of ND–OH were reacted with 2.352 g (8.0 mmol) stearic acid chloride. 0.315 g of a light grey powder was obtained. IR (KBr): 3422 (O–H), 2922, 2842 (CH aliph.), 1720 (C=O), 1627 (O–H), 1460 (CH-deform.), 1151 (C=O), 1107 (C–O–C) cm^{-1}; elemental analysis: C: 90.67, H: 1.923, N: 1.80; thermogravimetry (N_2, 4 K min^1): −8.89%; surface loading: 0.375 mmol g^{-1}.

2.8. Dispersion stability experiments

The solvents were dried according to literature procedures. For each test 5 mg of alkylated diamond was suspended in 15 ml of the solvent and sonicated for 30 min in a conventional bath-type sonicator. The resulting suspensions were let to stand and checked in time intervals. The time of the first observation of flocculation was recorded (see Table 1).

3. Results and discussion

Nanodiamond has been hydroxylated according to a literature procedure. This procedure homogenizes the diamond surface by

Scheme 1. Esterification of surface hydroxyl groups on detonation diamond can be done by reaction with the respective acid chlorides (R = alkyl).

reducing keto groups to hydroxyl groups [14,15]. The resulting hydrophilic material with an agglomerate size of several hundred nanometers up to several microns was reacted with carboxylic acid chlorides in a toluene suspension (Scheme 1). It has to be mentioned that the synthesis of acid chlorides with oxalyl chloride ($(COCl)_2$) rather than thionyl chloride ($SOCl_2$) is to be favored. The removal of excess reagent and complete removal of side products proved more difficult in the latter case.

Better dispersion during the reaction was achieved by sonication. The acid chlorides readily reacted with the surface hydroxyl groups. No change to the diamond structure was inflicted as proven by powder XRD measurements (not shown). The IR spectra show a significant increase in the C–H signal for the alkylated samples, and its intensity corresponds to the chain length of the alkyl group (Fig. 1). Additionally, the existence of an ester bond is indicated by the C=O signal at 1720 cm^{-1}, which was not present in the hydroxylated nanodiamond.

Thermogravimetric measurements were carried out in order to further support the covalent nature of the grafting and to determine the surface loading. Fig. 2 shows the thermograms of pristine and the three higher alkyl ester diamond materials.

The removal of the surface functional groups begins only beyond 300 °C (independently of the boiling point of the potentially adsorbed carboxylic acids), indicating a covalent bonding via the same structural moiety, i.e. an ester bond, for all alkylated species. The graph for pristine material shows the desorption of adsorbed water (up to 120 °C) and a weight increase above 450 °C. The latter is due to the reaction with the surrounding atmosphere (nitrogen) and is typical for this type of nanodiamond. The further weight loss is due to sublimation of carbon clusters as proven by mass spectrometric investigation of the exhaust gas. Table 2 summarizes the elemental composition, thermogravimetric data and the resulting surface loading with alkyl ester groups.

For all diamond alkyl esters the surface loading was found to be in the range of 0.3–0.4 mmol g^{-1}. Compared to silanization of the hydroxylated diamond (up to 1.5 mmol g^{-1}) this surface coverage is comparatively low. One of the reasons for this difference might be that only the most reactive hydroxyl groups,
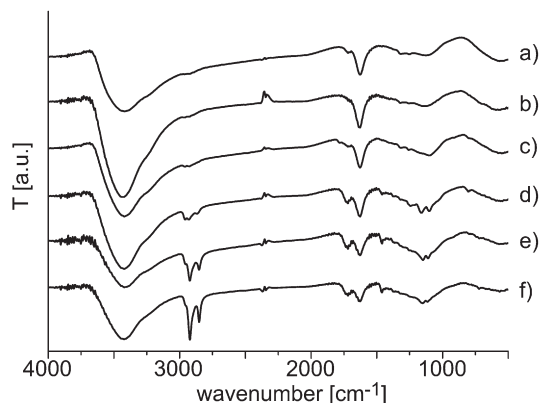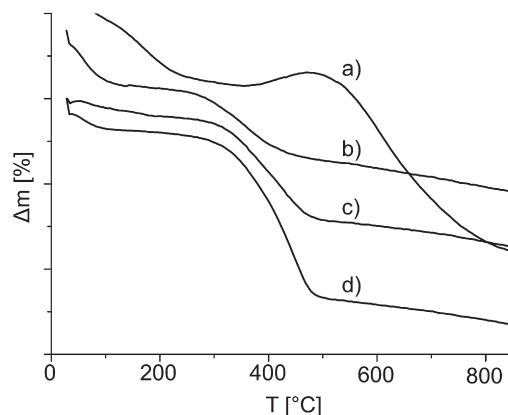

Fig. 2. Thermogravimetric analysis of different nanodiamond samples: a) pristine detonation diamond, b) ND–OOC–C$_5$H$_{11}$, c) ND–OOC–C$_{11}$H$_{23}$, d) ND–OOC–C$_{17}$H$_{35}$.

i.e. neopentyl or *tert*-butyl alcohols, do react with the acid chlorides. Additionally, the long alkyl chains are able to wrap around the diamond surface, hindering the reaction of further existing surface groups. This is supported by the fact that the highest loading is obtained for the shortest chain. Another indication for the preferred reaction of neopentyl or *tert*-butyl hydroxyl groups is the fact, that the resulting diamond esters are not stable in water, methanol and to a lesser extent ethanol. Most likely, steric reasons are responsible for the preferred hydrolysis of these branched ester moieties as steric strain is reduced upon cleavage of the ester bond. It is highly likely, that the diamond surface bears a large number of neopentyl and *tert*-butyl hydroxyl groups as the diamond lattice is directly connected with the surface.

The stability of these diamond esters in non-protic organic solvents is not affected by this structural peculiarity, though. No cleavage was observed even after prolonged sonication in large amounts of the respective organic solvents. Instead, we observed that the grafting of long alkyl chains considerably increases the dispersion stability of these functionalised diamond materials and reduced the size of the existing agglomerates. Pentane, toluene, tetrahydrofurane (THF) and dichloromethane (CH_2Cl_2) were tested for dispersibility of the different diamond materials. Pristine and hydroxylated nanodiamond did not form

Fig. 1. FTIR spectra of nanodiamond samples: a) pristine detonation diamond, b) ND–OH, c) ND–OOC–C$_3$H$_7$, d) ND–OOC–C$_5$H$_{11}$, e) ND–OOC–C$_{11}$H$_{23}$, f) ND–OOC–C$_{17}$H$_{35}$.

Table 2
Elemental analysis, TGA data and surface loading of alkylated nanodiamond samples

Sample	C (%)	H (%)	N (%)	TGA, Δm (%)	Surface loading (mmol g^{-1})
ND, pristine	88.46	0.490	2.24	–[a]	n.d.
ND–OH (**1**)	90.11	0.757	2.16	8.6[a]	n.d.
ND–OOC–C$_3$H$_7$ (**2**)	88.73	0.881	2.11	2.72	0.40
ND–OOC–C$_5$H$_{11}$ (**3**)	89.97	1.139	1.90	3.25	0.35
ND–OOC–C$_{11}$H$_{23}$ (**4**)	90.02	1.449	2.01	5.35	0.31
ND–OOC–C$_{17}$H$_{37}$ (**5**)	90.67	1.923	1.80	8.89	0.38

n.d.: not determined.
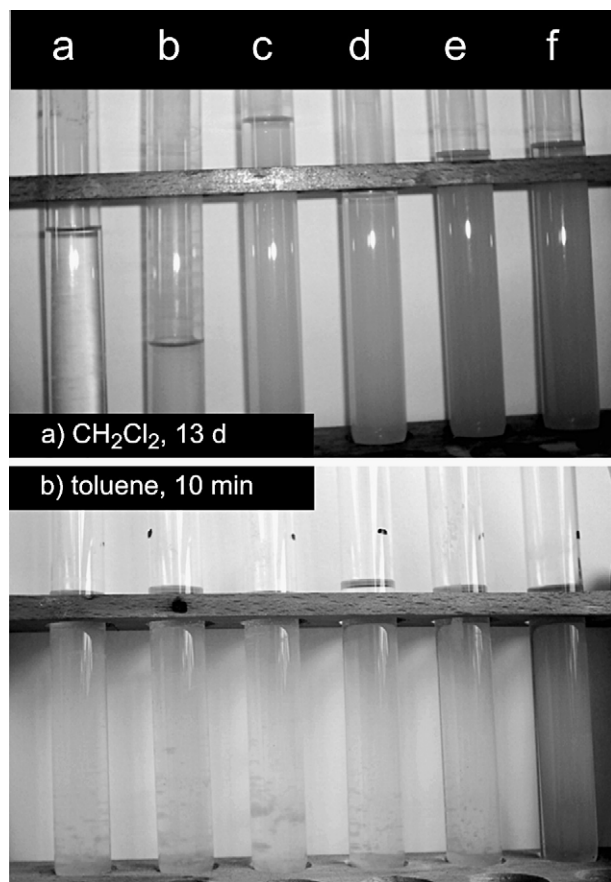[a] Weight loss due to water desorption, no detectable step for functional group desorption.

Fig. 3. Sedimentation of functionalised nanodiamond in dichloromethane after 13 days (top) and in toluene after 1 h (bottom). The alkylated samples c–f did not show any precipitation, whereas the pristine detonation diamond flocculated completely and the hydroxylated ND formed a significant precipitate in CH_2Cl_2. In toluene, all samples flocculated after several minutes, only sample f formed a stable supernatant suspension (a: pristine ND, b: ND–OH (**1**), c: ND–OOC–C_3H_7 (**2**), d: ND–OOC–C_5H_{11} (**3**), e: ND–OOC–$C_{11}H_{23}$ (**4**), f: ND–OOC–$C_{17}H_{35}$ (**5**)).

4. Conclusion

In summary we have modified the surface of hydroxylated detonation nanodiamond with alkyl chains of different length by an esterification reaction of carboxylic acid chlorides with the surface hydroxyl groups. The resulting materials had a surface loading of 0.3–0.4 mmol g^{-1} and showed a much better dispersibility in several organic solvents along with a smaller particle size of the remaining agglomerates. This enables the homogeneous incorporation of such materials in non-hydrophilic matrices and further modification in stable suspension. In the future, it will be important to further reduce the agglomerate size by such chemical deagglomeration and stabilization techniques down to the primary particles.

Acknowledgements

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stable suspensions in any of the tested solvents, only slightly slower sedimentation in THF was observed. This could be the result of hydrogen bonding between surface hydroxyl groups and the ether moiety of THF. The diamond esters formed stable suspension in THF and even more in dichloromethane. In the latter solvent no sedimentation was observed for a period of one month. The particle size of the agglomerates in the suspensions was reduced from several micron (pristine ND: $\sim$ 15 μm, ND–OH: $\sim$ 6 μm) to 300–450 nm in the case of ND–OOC–C_3H_7 (**2**), 150–260 nm for ND–OOC–C_5H_{11} (**3**), $\sim$ 170 nm for ND–OOC–$C_{12}H_{23}$ (**4**), and 170–300 nm for ND–OOC–$C_{18}H_{37}$ (**5**). Fig. 3 shows the development of suspensions of pristine detonation diamond and compounds **1**–**5** in dichloromethane.

The stable dispersion of functionalised nanodiamond in organic solvents opens the way to further surface modification in more homogeneous systems leading to better accessibility of the surface groups as well as a more homogeneous distribution of the diamond particles in the medium. Carboxylic groups with terminal surface groups have to be reacted with the diamond surface if further reactions are to be carried out. This work is under way and will be reported elsewhere.