Efficient chlorine atom functionalization at nanodiamond surfaces by electron beam irradiation

Jieying Zhou[a,1], Christian Laube[a,1], Wolfgang Knolle[a,*], Sergej Naumov[a], Andrea Prager[a], Frank-Dieter Kopinke[b], Bernd Abel[a,*]

[a] Leibniz-Institut für Oberflächenmodifizierung (IOM), Permoserstrasse 15, D-04303 Leipzig, Germany
[b] Department of Environmental Engineering, Helmholtz Centre for Environmental Research - UFZ, Permoserstrasse 15, D-04318 Leipzig, Germany

ARTICLE INFO

ABSTRACT

Surface functionality of nanodiamonds is of crucial importance for their desired chemical, optical and electromagnetic properties. Chlorinated surfaces are expected to enable an easy further modification of diamond surfaces via various substitution reactions for targeted molecule grafting, particularly interesting for biochemical applications. Previously reported chlorination approaches of diamonds required troublesome handling of hazardous chemicals, such as chlorine gas, and long chlorination time or high temperature. Here, we describe a radiation chemistry approach using electron beam irradiation for efficient surface chlorination of nanodiamonds (with averaged diameter of ca. 30 nm) at ambient temperature. Nanodiamonds with hydrogenated and graphitized surfaces were used for chlorination in CCl_4, $CHCl_3$ and CH_2Cl_2 at increasing radiation doses. A comprehensive set of measurements, including XPS, ATR-FTIR and in-source thermal desorption mass spectrometry (IS-TD-MS) was applied to characterize the chlorinated products. Density functional theory (DFT) calculations were performed to assist the discussion of reaction mechanisms. It is confirmed that remarkable covalently chlorine-covered surfaces bearing adequate stability against air and water were achieved for hydrogenated nanodiamonds in CCl_4 by applying doses ≥ 500 kGy.

1. Introduction

Recently, nanoscale diamonds (briefly nanodiamonds, NDs) have attracted increasing attention due to their unique properties. This relatively inexpensive alternative carbon nanomaterial consists of sp^3-hybridized carbon core, chemically tunable surface [1, 2] along with modifiable colour centres [3, 4] and has been explored for a wide spectrum of applications in fields such as wear-resistance additives [5, 6], drug delivery [7, 8], biolabeling [9, 10], sensing [3, 9] and quantum computing [11].

One of the most exciting promises of NDs lies in their application in biochemistry. ND-mediated drug delivery was reported to suppress chemoresistance of cancer cells in a similar manner as for nanopharmaceutical systems based on gold or silver nanoparticles [12–14]. Being mechanically robust and chemically inert resembling their metal nanoparticle competitors, however, NDs stand out through their excellent biocompatibility [8, 15] and flexible carbon surface to be readily modified. On the other hand, NDs containing nitrogen vacancies (NV centres) could be a superior biomarker over organic dyes thanks to the

higher stability of their photoluminescence and their lower toxicity [3, 16]. Therefore, it is highly interesting to design ND based theranostics with self-labeling property. To form fluorescent NDs, NDs produced through a High Pressure High Temperature process (HPHT NDs) with 100–200 ppm [17] nitrogen impurity are promising starting materials. NV centres can be generated and activated from these nitrogen impurity through electron beam irradiation, followed by an annealing step to obtain desired photoluminescence [18]. Through certain post treatments, such as a simple, controlled annealing and centrifugation process reported by Stehlik et al. [19], HPHT NDs with smaller size < 10 nm and narrowed size distribution are achievable, ideal for use in the intracellular domain. Although most of the surface modification of ND was reported so far for detonation NDs [20–22], the present work shows that it is worth to investigate the surface modification of HPHT NDs for the long-term purpose of designing robust, bifunctional, fluorescent drug delivers.

The surface chemistry of NDs is a key factor in tuning its optical and biochemical properties [23–25]. Understanding the surface chemistry of NDs and furthermore, tailoring NDs with well-defined surface

---

* Corresponding authors.
  E-mail addresses: wolfgang.knolle@iom-leipzig.de (W. Knolle), bernd.abel@iom-leipzig.de (B. Abel).
[1] Contributed equally to this work.

functionalization is, therefore, of great interest [1, 17]. Commercially available HPHT NDs are mostly purified with strong, oxidative acids before entering the market, in order to remove the majority of surface amorphous carbon and metal traces introduced from catalyst, reaction chamber and/or storage. Such purification leaves NDs with a highly inhomogeneous surface, containing a variety of oxygen-containing functional groups, graphitic carbon, etc. [19, 26]. Different approaches were employed to prepare NDs with a more defined surface a step further for targeted properties or for particular subsequent chemical reactions. Various oxidative treatments, for instance, in air [18, 27] or in ozone [28] atmosphere, lead to a narrowed spectrum of surface oxygen functionalities and a reduction of surface sp^2 carbon species. Through a controlled subsequent step of hydrogenation [29, 30] or re-graphitization [31], ND surfaces, covered with H terminations or sp^2 shells, respectively, become suitable platforms for diverse radical grafting reactions, such as fluorination [32], polymerization [31] and others [33–36].

Amidst the common primary functionalities on the ND surfaces, Cl is one candidate performing versatile functions. Well-known as a good leaving group in organic chemistry, surface chlorine enables an easier alteration of ND's surfaces via substitution reactions, such as amination [37], cyanation [38] and alkylation [38]. In particular, alkyl linkers carrying desired terminal functional groups can be introduced to NDs in such a way for targeted molecule loading [8]. Moreover, through surface chlorination, it is possible to regulate the electronic properties and the surface charge of NDs in various media [39, 40], interesting for electromagnetic application and molecule immobilization and release. Previously, several approaches for surface chlorination of nano- to submicron diamonds were published. Spitsyn et al. [41] and Ando et al. [42] reported the chlorination of oxidized detonation NDs in CCl_4 vapor and of hydrogenated submicron diamond in Cl_2 gas, respectively, via thermal annealing at elevated temperatures. UV induced chlorination of hydrogenated diamond in Cl_2 gas and in chlorine-saturated CCl_4 were reported by Sotowa et al. [37] and Lisichkin et al. [38]. Nevertheless, all these synthetic routes required long chlorination times $\geq 1\,h$ and troublesome handling of hazardous chemicals, asking for alternative approaches for efficient surface chlorination of NDs.

Electron accelerators were being used as a powerful tool for functionalization of various materials [43–45], including carbon nanomaterials such as graphene oxides [46]. In a suspension, where the material to be functionalized acts as the dispersed phase, the high-energy electron beam interacts with the solvent to efficiently generate abundant reactive species, i.e. ions, free radicals and excited molecules, which then react with the dispersed material. Such EB-induced modification of materials offers high flexibility. By wisely choosing the solvent, and therefore the reactive species formed, and the scavengers, which selectively quench undesired transients, certain reaction channels can be selected for targeted modification. Also, multi-functionalization of a material is feasible by choice of additives to trigger desired subsequent reactions. Further, by variating the applied doses, it is possible to control the functionalization of materials to the extent requested. In addition, the EB-induced approach obviously favors efficient functionalization of materials under ambient conditions and within short treatment time.

Nevertheless, to the best of our knowledge, no surface modification of NDs by means of electron beam irradiation has yet been reported. Herein, we present the first time an EB-induced surface chlorination of nanodiamonds. We employed a 10 MeV linear electron accelerator for modifying HPHT NDs in nitrogen-saturated carbon tetrachloride, chloroform and dichloromethane, where chlorine-containing radicals with long lifetime (> hundreds of ns [47, 48]) are generated for reaction. The impact of solvent and applied dose as well as the influence of the type of ND precursors (with hydrogenated (HND) or graphitized (BND) surfaces) on the surface chlorination performance was investigated. The present work aimed at an optimized surface chlorination of HPHT NDs, and meanwhile, a deeper understanding of the

reaction mechanisms, i.e. radical substitution and radical addition on surfaces of HNDs and BNDs, respectively, with Cl-containing radicals. X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), Raman spectroscopy, X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and in-source thermal desorption (pyrolysis) mass spectrometry (IS-TD-MS) were applied for the characterization of the precursors and the chlorinated products. Density functional theory (DFT) calculations were performed to elucidate the underlying reaction mechanisms.

2. Experimental

2.1. Materials

HPHT NDs (0–0.05 μm) were purchased from Micro Diamond AG MSY, Switzerland. Carbon tetrachloride (> 99.8%, Merck), diethyl ether (> 99.0%, Fluka), chloroform (with 0.6% ethanol, 99.0%, VWR PROLABO® Chemicals; and with ca. 50 ppm amylene, > 99.0%, Alfa Aesar), dichloromethane (dried, > 99.8%, AppliChem), sulfuric acid (96%, Carl Roth), sodium hydrogen carbonate (> 99%, Carl Roth), sodium sulfate (anhydrous, $\geq 99.0\%$, Merck) and molecular sieve (4A, Merck or Carl Roth) were used without further purification, except when specially mentioned. Chloroform with 0.6% ethanol was destabilized by being washed once with conc. H_2SO_4, then Millipore water, aq. $NaHCO_3$ and once again with Millipore water. After drying over Na_2SO_4 and distillation, the as-purified chloroform was confirmed with ^1H NMR to be ethanol- and water-free (≤ 3 ppm), kept over molecular sieve 4A and used within three days.

2.2. Syntheses

2.2.1. Precursors

Oxidized nanodiamonds (ONDs) were prepared by annealing as-received HPHT ND in air (600 °C, 17–24 h) according to the previously optimized protocol [18]. A tube furnace as described elsewhere [18] was employed for preparing the precursors from ONDs. Before each surface modification (hydrogenation or graphitization), Ar (50 mL/min) was used to purge the system (20 min). Hydrogenated nanodiamonds (HNDs) were prepared by heating ONDs in H_2 (flow rate: 40 mL/min, heating rate: 15 K/min, treatment temperature: 700 °C, treatment time: 5 h, spontaneously cooling down to 150 °C within 3 h in H_2 atmosphere, then within 2 h to r.t. in Ar atmosphere). Bucky nanodiamonds (BNDs) were prepared by annealing ONDs in Ar (flow rate: 50 mL/min, heating rate: 15 K/min, treatment temperature: 1050 °C, treatment time: 5 h, spontaneously cooling down to 150 °C within 5 h, then within 2 h to r.t.).

2.2.2. Chlorinated nanodiamonds (ND-Cls)

HNDs or BNDs (20–30 mg) were suspended in either liquid CCl_4, $CHCl_3$ (as-received or destabilized) or CH_2Cl_2 (ca. 3 mL) in a 5-mL glass flask covered with a plastic cap containing a septum in the middle. The suspension was bubbled with N_2 for 10 min shortly before the electron beam (EB) irradiation to remove oxygen, which would otherwise quench the chlorine-containing radicals. A 10 MeV linear electron accelerator (Mevex Corp, Stittsville, Canada, pulse width: 8 μs, repetition rate: 450 Hz, pulse current: 250 mA, 25 kGy/path, Fig. S1) was employed for irradiation. The dosimetry was done by using a graphite-calorimeter. The glass flask containing the sample was kept under ice in a beaker and shaken along its axis during the irradiation. Ice was changed before complete melting once every 100–150 kGy of applied dose. After irradiation, NDs were transferred to centrifuge tube and precipitated by centrifugation (SIGMA 3-18K, Sigma, 4700 min^{-1} or T10, Heinz Janetzki, 3000–4000 min^{-1} for ca. 30 min). After removal of the supernatant, the NDs were washed once with Millipore water and thrice with diethyl ether. For each washing step, centrifugation (for ca.