Layer-by-Layer Oxidation for Decreasing the Size of Detonation Nanodiamond

Bastian J. M. Etzold†,*, Ioannis Neitzel‡, Manfred Kett†, Florian Strobl†, Vadym N. Mochalin‡, and Yury Gogotsi‡

†Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), 91058 Erlangen, Germany
‡Department of Materials Science & Engineering and A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania 19104, United States

Supporting Information

ABSTRACT: Diamond nanoparticles attract much attention as they combine outstanding mechanical properties with bio-compatibility and are available in large quantities. Control and tunability of the particle size is very important for any nanomaterial. Although oxidation can burn carbon and lead to a particle size decrease, this technique could not be successfully employed for nanodiamond size reduction on the nanoscale. In this work, two commercial nanodiamond powders are used to demonstrate separation of the oxidation reaction into two steps (i) the oxygen chemisorption and (ii) the CO and/or CO₂ desorption. This allows for an effective control of the oxidation process. In situ thermogravimetric analysis suggests that the oxidation is thermodynamically rather than kinetically controlled, and that the carbon burn off can be adjusted by repeating chemisorption/desorption steps to remove carbon layer after layer. Small-angle X-ray scattering (SAXS) characterization of the diamond nanoparticles showed a continuous size decrease from 5.2 to 4.8 nm during 15 layer-by-layer (LbL) oxidation cycles, in contrast to average particle size increase observed in the case of continuous oxidation in air. In accordance with the size decrease after LbL oxidation, the specific surface area (SSA) of the nanopowders increased.

1. INTRODUCTION

Nanodiamonds combine the extraordinary bulk properties of diamond with a high surface to volume ratio.¹,² This, in combination with the tunable carbon surface chemistry and good biocompatibility,³−⁵ make nanodiamond (ND) an attractive candidate for applications such as drug delivery and biomarkers,⁶−⁹ polymer reinforcement,¹⁰−¹⁴ catalysis,¹⁵,¹⁶ and lubricants or polishing compositions.¹⁷−¹⁹ In contrast to many other nanomaterials, the availability and cost of ND do not pose significant problems in large scale applications because of its well-established and inexpensive commercial production by detonation synthesis.²⁰−²²

As for all nanomaterials, tuning the size is of major importance and can be used to vary the surface to volume ratio. However, the detonation synthesis allows only for a limited control of the ND size during the production. Interestingly, man-made ND shows an average particle size around 5 nm,⁴ whereas extraterrestrial NDs extracted from meteorites or found in proto-planetary nebulae are smaller in size (around 1.5 to 2.5 nm).²³−²⁷ It was unclear whether similar NDs of 1.5−2.5 nm diameter can be produced on Earth until a recent publication reported on synthesis of small 2−5 nm NDs in ethanol microplasma at near ambient temperature and pressure.²⁸ This technique, although interesting, can hardly be scaled up for industrial production or compete in terms of cost with detonation synthesis, which remains the most viable industrial method for ND particles production. Theoretical calculations have proven that the size of interstellar and man-made NDs is controlled by changing from a hydrogenated surface for smaller NDs to a reconstructed sp² carbon surface, which occurs at certain size and stops the growth.²⁹,³⁰ Although small NDs are stable at ambient conditions, no technique is currently available to reduce the size of ~5 nm NDs produced by detonation synthesis. Oxidation is commonly used for post synthesis modification of carbon nanomaterials.³¹ Air oxidation of ND is already employed for removing amorphous carbon during purification of the diamond soot.³² Altering the ND size with air oxidation was attempted and, surprisingly, resulted in an increase of the average particle size due to burn off of the smallest particles.³³ It is assumed that the exothermic reaction is difficult to control locally and it leads to an uncontrolled burn off of very small ND particles.³⁴ Thus, air oxidation can be used for enrichment of a ND sample with larger particles, although there is no post-treatment known resulting in smaller ND particles.

To avoid a runaway oxidation reaction, especially for the small particles, a self-limiting mechanism is necessary. Splitting the oxidation in two independent steps was demonstrated to be...
a way for controlling the pore size of activated carbons.\textsuperscript{35−37} This is achieved by separating the oxidation process into a low temperature chemisorption step, in which oxygen is covalently bonded to the NDs surface, and a high temperature desorption step that is carried out in a nonoxidizing environment. Importantly, both steps are self-limiting. During the chemisorption, only a monolayer of oxygen-containing surface groups can be formed, and during desorption this monolayer is removed along with the attached carbon atoms in the form of carbon monoxide or dioxide. Hence, the thermodynamic control of the chemisorption is the key of this process. Repetition of both steps results in a LbL oxidation (see Figure 1). Despite the principle was demonstrated for activated carbons, the LbL-oxidation has never been applied to carbon nanoparticles. The goal of this work is to demonstrate the applicability of the LbL-oxidation to tune (reduce) ND particle size.

2. RESULTS AND DISCUSSION

To carry out the LbL oxidation, temperatures for the chemisorption and desorption steps need to be chosen. A minimum oxidation temperature of 350 °C was reported for ND by Kulakova\textsuperscript{38} and Osswald et al.\textsuperscript{32} To avoid oxidation of the nanocarbon, we set the temperature during the chemisorption in this work to 300 °C. Temperature-programmed desorption (TPD) data on oxidized ND in literature shows that the desorption can roughly be parted in three temperature regions.\textsuperscript{14} Below 400 °C, only desorption of physisorbed water occurs. A majority of surface groups desorb from 400 to 800 °C (e.g., anhydrides). And even at higher temperatures desorption still continues (e.g., of carbonyl and quinone groups). TPD of ND from by Adámas Nano-technologies Inc. (NDAD) used in this study shows a similar behavior and is discussed later in detail along with the characterization of surface functionalization during LbL-oxidation (Figure 2a). Thus, temperatures above 400 °C are necessary for desorption. A higher temperature results in a more complete removal of surface oxygen groups, but leads to sp\textsuperscript{3} to sp\textsuperscript{2} carbon transformation.\textsuperscript{7} To determine the upper temperature limit, ND was annealed at 600, 700, and 800 °C. Raman analysis of the annealed samples (see Figure 3) shows that starting at 700 °C the D and G bands, characteristic of sp\textsuperscript{2} carbon, become more visible and are pronounced at 800 °C. This is in agreement with recently published NMR\textsuperscript{39} and in situ Raman spectroscopy\textsuperscript{40} results addressing the onset temperature for ND graphitization. Thus, 600 °C was chosen for the desorption step, to avoid graphitization, even though not all surface groups will desorb at this temperature. Additionally, desorption was carried out in a hydrogen atmosphere, which is known to suppress ND graphitization.\textsuperscript{41} For a homogeneous modification of the nanoparticles, the time for chemisorption and desorption must be long enough to come close to equilibrium. To study the kinetics of both steps, the LbL oxidation was monitored by in situ thermogravimetric analysis (TGA) for two commercial ND powders supplied by
Adámas Nanotechnologies Inc. (NDAD) and by Heyuan Zhonglian Nanotechnology Co. Ltd. (NDZH). Figure 4a shows the mass increase and decrease for several LbL cycles of NDAD, a single cycle being magnified in the insertion. A mass increase due to the formation of oxygen containing surface functionalities is observed during the chemisorption step. Regarding the kinetics, the initially fast mass increase slows down after 10 min. The desorption kinetics show a similar trend the mass loss leveling off after 15 min. In the desorption step, more mass is lost (due to the loss of carbon), when compared to the mass gain during the prior chemisorption of oxygen, leading in total to a decrease in mass in a single LbL cycle. The average mass loss per cycle is 0.99 wt % (StDev = 0.07 wt %) and, together with an initial mass loss of 4.8 wt % due to physisorbed water and organics, the total mass loss was 38.5 wt % after 34 cycles. Analyzing the mass gain per cycle from the first to the last chemisorption step, a drop of the gain by 30% per step is observed. Assuming ideal spheres having the same size, the surface area is reduced by 28% and a mass or volume reduction of 38.5%, explains this trend.

Additionally, the LbL oxidation was carried out on a larger scale using a tube reactor. The diffusion length in the fixed bed was kept constant. LbL oxidations for 5, 10, 15, 20, and 30 cycles were carried out. The recorded mass loss for NDAD and NDZH for a number of cycles are given in Figure 4b. A trend line following the mass loss for an ideal sphere calculated using a shrinking core model (SCM) was added as guidance for the eyes. A higher initial mass loss compared to the TGA results can be explained by the initial desorption of physisorbed species, e.g. water, below 300 °C, which cannot be decoupled in this ex situ experiment. This and the external weight measurements (laboratory microbalance) are assumed to cause the observed scattering. The average weight loss per cycle deduced from the SCM is found to be 1.12 wt % and therefore lies within the observed mass loss measured in the TGA runs.

The change of NDAD’s surface chemistry occurring during the two step LbL-oxidation—(i) oxygen chemisorption and (ii) desorption—was characterized by TPD. Figure 2a compares the differential mass losses. Desorption of surface groups from NDAD treated in air at 300 °C starts at 400 °C and has a maximum around 600 °C. This is in agreement with literature data on oxidized ND. After treatment of this material in hydrogen at 600 °C, the desorption onset temperature increases to approximately 550 °C. First, physisorbed water and organics are removed below 200 °C. Comparison of both desorption curves shows that the groups desorbing at T < 600 °C have been almost completely removed after hydrogen treatment of the oxidized ND, being accompanied by some amounts of groups desorbing at T ≥ 600 °C. In total, a significant number of carbon-containing surface groups are removed by oxidation followed by desorption in hydrogen, providing the basis for carbon removal during LbL oxidation.

The surface chemistry of the samples after 5, 15, and 30 LbL cycles (always ending with the desorption in H 2) was characterized by FTIR. The spectra of the modified and as-received NDAD are compared in Figure 2b. A similar trend is observed for NDZH. As-received NDAD shows an absorption maximum for ether (C–O–C) and carbonyl groups (C=O) most probably resulting from the oxidative purification of the detonation soot. After 5 chemisorption/desorption cycles, the C=O is fully removed and the C–O–C peak is diminished. This can partly be attributed to the desorption of surface groups as well as to the hydrogenation of C=O. Furthermore, bands characteristic for CH x species (both stretching and deformation vibrations) are observed in the FTIR spectra after 5 cycles and onward. Those could stem from hydrogenation of dangling bonds formed upon desorption of CO and CO2. The spectra after 15 and 30 cycles are similar to the 5-cycle spectra, a further proof that the LbL process is controlled thermodynamically, not kinetically.

The size of the as-received and modified ND particles was characterized by SAXS measurements, assuming a fractal aggregate morphology. Reproducibility tests proved the high accuracy of this approach (see the Supporting Information). The obtained size distributions are all bimodal with the first peak around 5 nm and the second broader peak in the range from 18 to 40 nm. The first peak is believed to represent the majority of ND primary particles. The second peak accounts for a minority of larger primary particles that are also observed in TEM studies, as well as twinned and sintered particles formed during the detonation synthesis. The total fraction of these larger ND particles calculated from the second SAXS peak is 2.4 wt % in NDAD and 2.9 wt % in NDZH. The resulting particle size distributions for as-received and LbL oxidized NDAD are shown in Figure 5a. The nonmodified sample has a primary median value of 5.2 nm (dotted line). The

Figure 4. (a) Mass loss during LbL oxidation of NDAD, recorded in situ by TGA; (b) ex situ determined mass loss dependency with LbL cycles for NDAD and NDZH observed in the lab scale reactor. As guidance for the eyes, the loss for ideal spheres of a single size following a shrinking core model (SCM) is given by a dashed line for NDAD.

Figure 5. (a) Particle size distributions of as-received and LbL oxidized NDAD obtained from SAXS measurements. The dotted and full vertical lines show the first median of the as-received and final sample. The second peaks are magnified by a factor of 20. (b) Dependency of SAXS determined median particle diameter of smaller particles in a bimodal distribution for NDAD and NDZH on the mass loss.
LbL oxidation lowers the median of both modes in the bimodal distribution. The smallest median size found was 4.77 nm for 15 and 30 cycles. With the exception of the 20-cycle experiment, the determined median values decrease steadily.

Calculations of ND particle sizes by Scherrer analysis of XRD diffractograms and testing for phonon confinement in UV-Raman spectra could not resolve the particle size change, due to limited accuracy, especially for small particles. Those methods also result only in average crystal sizes and do not allow extracting the particle size distributions. Furthermore, due to the high sensitivity of both of these techniques to the scattering domain size, a small fraction of bigger particles present in the sample can affect the measured value of the average particle size. In addition, both methods are strongly influenced by defects in the particles and thus cannot, for example, distinguish between small particles and large but twinned particles.

NDZH shows a similar trend during LbL oxidation. Figure 5b shows the resulting median size of the first peak for both materials over the recorded mass loss. The particle size decreases for both nanomaterials linearly before a threshold is reached at approximately 25% mass loss. In this regime, the decrease in size is similar to the size reduction of an ideal single sphere. At higher mass losses, a constant size is observed with the SAXS, and could be explained by vanishing of very small particles that become unstable under the treatment conditions. NDAD shows a size increase at a mass loss of 32%, which is not in accordance with the observed general trend. However, the following step at a 42% mass loss again follows the general trend of size decrease. The reason for the deviation is unclear.

N₂ adsorption was used to determine the specific surface area (SSA), which is an indirect indicator of the particle size. Furthermore, this is one of the few characterization techniques giving a higher accuracy for smaller particle sizes (larger SSA). In Figure 6, the SSAs for NDAD are compared with the SAXS determined median sizes for different numbers of LbL oxidation cycles. As expected, SSA increases with a decrease in average particle size until cycle 15. The primary particle size determined by SAXS decreases constantly by 8.3% in this region and the SSA increases by 5.7%, while the surface area of an ideal sphere would increase by 9.1%. Interestingly, the SSA continues to increase up to 15.2% after 30 cycles, even when the SAXS determined size stays constant. This indicates that a further size reduction could take place, which is probably hard to detect by SAXS, or that the surface roughness increases because of nonuniform surface oxidation.

A continuous oxidation for 4 h at 425 °C in air, similar to the conditions used for purification of ND, was carried out for comparison. The resulting particle size distribution determined by SAXS is shown in comparison to the as-received material in Figure 7. The primary particles increased in size from 5.2 to 6.5 nm as reported for other ND powders for continuous oxidation. The median of the bigger sized particles decreases from 30.5 to 21.8 nm, and their content increases from 2.5 to 5.2 wt %. These findings are in agreement with the assumption of a thermal runaway, which takes place for very small particles (<5 nm) during the continuous oxidation. Thus, only the first peak shifts toward larger particle sizes while their total content decreases, whereas for larger particles (>10 nm) a decrease in particle size due to surface oxidation can be observed. This is further corroborated by an observed SSA decrease of 4.8%.

3. CONCLUSIONS
The LbL oxidation has been demonstrated to enable a fine control over the size of diamond nanoparticles. Splitting the oxidation of carbon in two steps, the chemisorption of oxygen and desorption of oxygen-containing surface groups, prevents thermal runaway and allows for a thermodynamic control of the oxidation process. The advantages arising when changing from a kinetically controlled to a thermodynamic and surface limited process are comparable to those known for chemical vapor deposition (CVD) compared to atomic layer deposition (ALD). In some sense, the LbL oxidation, allowing for removal of carbon layer by layer, is the reverse of an ALD process. A size decrease in the Ångström range controlled by the cycle number was demonstrated for two different commercial ND powders. The LbL oxidation is the first process allowing for size reduction of commercial detonation ND powders. Using the LbL oxidation process, the ND diameter was reduced from ∼5.2 to ∼4.8 nm (mass loss of approximately 25%) and reached a threshold. Further studies are necessary to investigate if this threshold arises from vanishing of smaller particles, lower accuracy of most characterization techniques for very small nanoparticles or from other phenomena.

4. METHODS
The detonation nanodiamond powders were supplied by Adámás Nanotechnologies Inc. (NDAD) and by Heyuan Zhonglian Nanotechnology Co. Ltd. (NDZH). They feature high-purity (>95% sp³) carbon. NDZH characterization was reported earlier.
The Lbl. oxidation was carried out in a tube reactor operated at slightly excessive pressure of approximately 40 mbar to avoid oxygen leaking into the reactor. The chemisorptions step was performed at 300 °C in air ($1 \times 10^{-5}$ m$_{\text{STP}}$/min) for 150 min and the desorption step at 600 °C in a H$_2$/Ar atmosphere ($6.5 \times 10^{-6}$ m$_{\text{STP}}$/min/$8.1 \times 10^{-8}$ m$_{\text{STP}}$/min) for 30 min. The heating ramp for the initial heating as well as the change from chemisorption to desorption temperature was set to 10 K/min and carried out in inert atmosphere. The reactor was cooled from desorption to chemisorption temperature for 160 min. Additionally, the Lbl. oxidation was performed using a thermogravimetric balance (SETSYS-1750 CS Evolution, SETARAM Instruments) at the same flow rates, concentrations and temperatures. In TGA, the time for oxidation was 60 min, for desorption 30 min, and for flushing 30 min.

SAXS measurements were performed using a Rigaku S-MAX 3000 setup with a 3 pinhole collimation, a MicroMax 002+ CuK$_\alpha$ ($\lambda = 1.54$ Å) radiation source and a Gabriel 2D Multiwire X-ray detector. For q vector and center calibration, a silver behenate standard sample was used. The setup with a 3 pinhole collimation, a MicroMax 002+ CuK$_\alpha$ radiation source and a Gabriel 2D Multiwire X-ray detector. For q vector and center calibration, a silver behenate standard sample was used. The detector was cooled from desorption to chemisorption temperature for 160 min. Additionally, the Lbl. oxidation was performed using a thermogravimetric balance (SETSYS-1750 CS Evolution, SETARAM Instruments) at the same flow rates, concentrations and temperatures. In TGA, the time for oxidation was 60 min, for desorption 30 min, and for flushing 30 min.

SAXS measurements were performed using a Rigaku S-MAX 3000 setup with a 3 pinhole collimation, a MicroMax 002+ CuK$_\alpha$ ($\lambda = 1.54$ Å) radiation source and a Gabriel 2D Multiwire X-ray detector. For q vector and center calibration, a silver behenate standard sample was recorded before each measurement. A glassy carbon standard was used for q vector and center calibration, a silver behenate standard sample was recorded before each measurement. A glassy carbon standard was used.

FTIR spectra were recorded with a Varian Excalibur FTS-3000 spectrometer using a DTGS detector in transmission mode. For sample preparation, 1 mg of ND was mixed with 199 mg of KBr powder and then pelleted at 10,000 ponds load. The FTIR spectra were recorded in the range 400–4000 cm$^{-1}$ with 5 kHz oscillation and a 1.2 UDR filter.

TPD was performed with Netzsch STA 409 PC thermogravimetric balance under helium, heating from room temperature to 1000 °C with a temperature ramp of 5 °C/min. Correction curves using the same conditions were accounted. The TGA data was processed using Netzsch "Proteus Analysis" software.

Gas adsorption was done using a Quadrasorb unit from Quantachrome in the p/p$_0$ range of 0.00075 to 0.995 in nitrogen atmosphere at 77 K. Before the measurement, the samples were outgassed for 12h at 200 °C. The BET fit was applied in the 0.05 to 0.30 p/p$_0$ range.

Samples were analyzed by micro-Raman spectroscopy (Renishaw 1000) using an Ar ion laser ($514.5$ nm) and 20 × optical magnification (spot size $\leq 5 \mu$m) at $<2$ mW laser power on the samples.

- **Supporting Information**

Reproducibility of SAXS particle size determination. This material is available free of charge via the Internet at http://pubs.acs.org.

---

**AUTHOR INFORMATION**

**Corresponding Author**

E-mail: bastian.etzold@fau.de.

**Author Contributions**

B.J.M.E., I.N., M.K. and F.S. performed experiments. B.J.M.E., V.N.M., and Y.G. planned the study. All authors contributed to writing the manuscript and approved the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

B.E. and F.S. gratefully acknowledge the funding of the German Research Council (DFG), which within the framework of its "Excellence Initiative" supports the Cluster of Excellence "Engineering of Advanced Materials" (www.eam.uni-erlangen.de) at the University of Erlangen-Nuremberg. J.M. acknowledges the financial support from the Alexander von Humboldt Foundation and M.K. of the DAAD. The authors thank Dr. James Giammarco for his comments on the manuscript. FTIR, SAXS, and Raman measurements were performed at Drexel University’s college of Engineering Core Facilities.

**ABBREVIATIONS**

DTA, differential thermogravimetric analysis; Lbl., layer-by-layer; ND, nanodiamond; PSD, particle size distribution; SAXS, small-angle X-ray scattering; SSA, specific surface area; STP, standard temperature and pressure; TGA, thermogravimetric analysis; TPD, temperature-programmed desorption.