Water interaction with hydrogenated and oxidized detonation nanodiamonds - microscopic and spectroscopic analysis

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Abstract

Water interaction with surface modified nanodiamonds (NDs) is critical for many possible applications of NDs e.g. in biomedicine. Here we report on investigation of water interaction with hydrogenated and oxidized detonation nanodiamonds (H-DNDs, O-DNDs) by means of Fourier transform infrared spectroscopy (FTIR), thermal analysis, and Kelvin probe force microscopy (KPFM). Higher water content (4.4%) as well as weaker interaction of water with H-DNDs is identified by thermal analysis. It is explained by hydrophobicity of the H-DNDs surface, as revealed by analysis of bending and stretching vibrations of surface water in FTIR spectra. On the other hand, hydrophilic nature of O-DNDs leads to lower water content (3.1%) but stronger interaction with the O-DNDs surface. This is evidenced by as high as 300°C desorption temperature of the surface water from O-DNDs. KPFM analysis shows that the surface-bound water can have significant screening effect on contact potential difference (CPD) of nanodiamonds (up to 510 mV) as well as on the CPD difference between H-DNDs and O-DNDs (from 50 mV to 210 mV). Nevertheless, H-DNDs exhibit always lower work function.

Keywords: detonation nanodiamond, surface termination, water, FTIR, KPFM, thermal analysis, contact potential difference, work function

Introduction

Detonation nanodiamonds (DNDs) represent a fascinating nanomaterial which is made by a detonation of oxygen-deficient explosives such as trinitrotoluene (TNT) and hexogen (RDX). Their size is typically 4-5 nm, however, by using nano-textured explosives one can even further reduce their typical size below 3 nm as recently shown^{1,2}. Once the DNDs are extracted from detonation soot by various wet-chemical purification treatments they can serve in many diverse applications such as polishing, electroplating, lubrication, catalysis, drug delivery, etc.^{3,4} The

surface properties of DNDs often play an important role due to the high surface-to-volume ratio and the possibility of adjusting the surface chemistry⁵. The most common, well-defined surface chemistry of DNDs is obtained by oxidation or hydrogenation of raw DND powders. Hydrogen termination of DNDs is typically achieved by a hydrogen plasma treatment^{6,7} or by annealing in hydrogen gas at elevated temperature^{8,9}. Both processes lead to the formation of carbon-hydrogen bonds on the DND surface and the formation of positive zeta potential in colloidal solution of hydrogenated H-DNDs^{9, 10}. Oxygen termination of DNDs is typically achieved by annealing in air at temperatures between 400-500°C^{11,12}. In contrast to H-DNDs the formation of functional groups containing oxygen on the surface of DNDs leads to a negative zeta potential of oxidized O-DNDs in colloidal solution^{10,13}. It is known that hydrogenated or oxidized surface of bulk diamond (mono or polycrystalline) exhibits very different physicochemical properties such as contact angle, surface conductivity or work function. Whether hydrogenated and oxidized DNDs exhibit also such differences is still an open question¹⁴ though some recent reports indicate a surface conductivity of H-DNDs¹⁵ or difference in work function between H-DNDs and O-DNDs¹⁰.

Geometric constraints of a solid surface as well as the presence of specific functional groups generally leads to structural changes of a surface-bound water layer compared to bulk water properties. In this respect, the water interaction with DNDs is fundamental for both the technology and applications. However it is still not fully understood and explanations of various phenomena are debated. For instance, formation of nanophase water on DNDs was reported, however, no attention was paid to the surface chemistry of the studied DNDs¹⁶. Recent study showed that orientation of water molecules in the first solvation shell depends on the zeta potential of NDs¹⁷. Giant dielectric permittivity of DNDs was also attributed to adsorbed water (1%-4%) but actual mechanism required further investigation, being tentatively related to proton-releasing functional groups on DNDs¹⁸.

In this paper we provide experimental evidence of different water interaction with H-DNDs and O-DNDs by using Fourier transform infrared (FTIR) and thermal analysis (TA) techniques. We observe different water adsorption ability and different water binding on H-DNDs and O-DNDs surfaces and we deduce a corresponding structural model. By using Kelvin probe force microscopy (KPFM) we also show how the adsorbed water significantly and differently affects the contact potential difference (CPD) of H-DNDs and O-DNDs that are deposited on highly ordered pyrolytic graphite (HOPG).

Experimental

Detonation nanodiamonds were synthesized from TNT and RDX precursors in a detonation chamber. The DNDs were purified in HCl/HNO₃ (1:3) and then rinsed with deionised water to pH 5¹². Oxidized O-DNDs were obtained by air annealing at 385°C for 14 hours. A part of already oxidized O-DNDs was subsequently hydrogenated by annealing under hydrogen atmosphere at 700°C for 3 hours. By this approach hydrogenated H-DNDs were obtained.

The specific surface area (SSA) of H-DNDs and O-DNDs were measured by using an ASAP 2020 system. Thermal desorption at 225°C during 12 h were applied to the samples before measurements. SSA values of 368 m²/g and 355 m²/g were measured for H-DNDs and O-DNDs respectively.

FTIR was measured on a Bruker Tensor 27 apparatus equipped with a single attenuated total reflectance (ATR) accessory (PIKE MIRacle). The detector was a Digitec RT-DLATGS and the resolution was 4 cm⁻¹. The ATR crystal was a diamond (with a Zn/Se lens). The measurement was performed at the temperature of 20°C. The H-DNDs and O-DNDs were measured in form of powders.

TGA was performed on a SII Seiko Instruments Exstar 6000 (TG/DTA 6200) and Differential Scanning Analyses (DSC) was performed using a TA instruments Q1000 apparatus. The experiments were carried out in alumina cups and gold crucibles for TGA and DSC respectively. Both analyses were conducted under a nitrogen flow (100mL/min). An isothermal step at 25°C during 2 hours was maintained before heating, and then a ramp of 5°C/min was applied to reach 500°C.

For the KPFM experiments colloidal suspensions from H-DNDs and O-DNDs powders were prepared at first by ultrasonication (ultrasonic bath 100W) and ultracentrifugation (350000g, 30 min), and then used for electrophoretic deposition on highly ordered pyrolytic graphite (HOPG)¹⁹ using positive zeta potential of the H-DNDs and negative zeta potential of the O-DNDs. The prepared samples were then left few days at ambient conditions to reach equilibrium with air humidity (typical RH ~ 50 %). The samples were then introduced into a glovebox filled with dry nitrogen, ensuring inert and humidity-free atmosphere (O₂ and H₂O were kept below 0.1 ppm level) and analyzed by in-situ KPFM immediately. These KPFM data are denoted as “not annealed”. In order to check the effect of adsorbed water on the CPD of H-DNDs and O-DNDs an annealing sequence in the glovebox was performed by following steps: 50°C, 100°C, 150°C, 200°C, 250°C, 300°C for 30 min, each step followed by immediate KPFM measurement. A FlexAFM with a C3000 controller (Nanosurf) was used for topography acquisition and a UHFLI lock-in amplifier (Zurich Instruments) served as an external Kelvin controller. The KPFM measurement was carried out in a single pass regime with amplitude (AM) modulation, i.e. both topography and CPD were acquired simultaneously using the first and second resonance of AFM cantilever²⁰. For all reported data we used a single Pt/Ir5-coated PPP-EFM cantilever (Nanosensors) with a resonance frequency of $f_1 = 76950$ Hz. This fundamental resonance frequency was used for topography acquisition. The second resonance frequency of the cantilever ($f_2 = 481498$ Hz) was used for KPFM. The free oscillation amplitude was 10 nm, setpoint 65%, scan size 2×2 μm, scan speed 0.5 Hz, and AC oscillation voltage 1 V. The cantilever was grounded and both AC oscillation and DC compensation voltage were applied to the sample. Using this arrangement, lower CPD value corresponds to lower work function value however work function of cantilever would need to be determined to get absolute values. We used a compensation of the capacitive crosstalk to obtain accurate KPFM results²¹.

Results

Figure 1a shows full range FTIR spectra of DNDs after oxidation in air (O-DNDs, red spectrum) and subsequent hydrogenation (H-DNDs, blue spectrum). The FTIR spectra of both H-DNDs and O-DNDs were acquired several weeks after the respective treatments, stored at ambient conditions meanwhile. Thus we suppose that equilibrium with respect to ambient humidity was reached. The common features in the spectra are related to O–H stretching ($2500\text{--}3500\text{ cm}^{-1}$) and bending (1625 cm^{-1}) vibrations from the adsorbed water^{8,22}.

In addition, the spectrum of O-DNDs exhibits a carbonyl peak (C=O stretching at 1800 cm^{-1}) indicating the formation of anhydrides and lactones by air-annealing which shifts the peak to higher wavenumbers than in carboxylic acid groups²³. A broad absorption feature at $1000\text{--}1500\text{ cm}^{-1}$ is related to a combination of many overlapping peaks, which besides C–O–C stretching may include also the O–H deformation and other groups²³. The FTIR spectrum of H-DNDs shows the successful hydrogenation by the formation of C–H bonds ($2800\text{--}3000\text{ cm}^{-1}$) accompanied by complete disappearance of the carbonyl peak and suppression of the carbon-oxygen related features in the $1000\text{--}1500\text{ cm}^{-1}$ region. The features in $2200\text{--}2400\text{ cm}^{-1}$ region are not related to DNDs but arise from software subtraction of atmospheric CO₂ absorption.

Figure 1b shows a magnified range of $1500\text{--}1800\text{ cm}^{-1}$ where the bending vibrations originating from OH bonds of both H-DNDs and O-DNDs are visualized in detail. We identified a clear difference between the shape of the –OH related peak of H-DNDs and O-DNDs. While O-DNDs exhibit a single peak with maximum at 1630 cm^{-1} , the H-DNDs exhibit a broader peak with the maximum at 1640 cm^{-1} and an apparent shoulder at lower wavenumber. This may indicate different bonding states of the –OH groups on H-DNDs and O-DNDs surfaces which typically come from the adsorbed water. The spectra of both H-DNDs and O-DNDs also exhibit a shoulder around 1590 cm^{-1} related to sp² carbon²⁴.

Figure 1. Full range FTIR spectra of H-DNDs (blue curve) and O-DNDs (red curve) equilibrated (eq.) in ambient air (a). Magnified region of 1500-1800 cm^{-1} shows in detail the different shape of the -OH bending peak of H-DNDs and O-DNDs (b).

Figure 2a shows the full range FTIR spectra of H-DNDs measured immediately after hydrogenation treatment (black), after several weeks of ambient storage (blue), and after putting them to water and dried again (green). First of all, preservation of the C-H bonds shows good long-term stability of such hydrogenated DNDs under various conditions. However, we evidenced the gradual evolution of a 3000-3750 cm^{-1} broad band coming from the stretching vibrations of -OH groups which indicates a gradual adsorption of water on the H-DNDs surface. Moreover, a distinct sharp peak at 3690 cm^{-1} appears with the evolution of the 3000-3750 cm^{-1} band. There is also an increasing band around 1100 cm^{-1} in the blue and green spectra in comparison to the freshly hydrogenated DNDs (black). Figure 2b shows the 1000-2000 cm^{-1}

range in detail. The -OH related (bending vibrations) peak of freshly hydrogenated H-DNDs (black) clearly exhibits two maxima at 1642 cm^{-1} and 1616 cm^{-1} . After longer exposure to water from humid air (blue) and liquid water (green) the peak at 1616 cm^{-1} becomes a shoulder and the peak at 1642 cm^{-1} becomes dominant.

Figure 2. Full range FTIR spectra of H-DNDs measured immediately after hydrogenation treatment (black), after several weeks of ambient storage (blue), and after putting in water and dried (green) (a). Magnified region of $1000\text{-}2000\text{ cm}^{-1}$ shows in detail mainly the evolution of the -OH bending peak of H-DNDs in dependence on history of the particular sample (b).

TGA and DSC curves of H-DNDs and O-DNDs are shown in the Figure 3. Thermal behavior of both H-DNDs and O-DNDs can be roughly divided into three regions. In the first region (I; $25\text{-}100^\circ\text{C}$) the evaporation of bulk water occurs. In the second region (II; $100\text{-}300^\circ\text{C}$)

mainly desorption of surface bound water happens. In the third region (III; above 300°C) other exothermic processes like oxidation take place. From the presented data it is obvious that the thermal behavior depends on the particular surface chemistry of the DNDs.

The TGA curve of H-DNDs (Figure 3a) indicates that the total water content in H-DNDs powder is 4.4% and the surface water desorbs up to 250°C. This is well documented also by the DSC curve of H-DNDs (Figure 3b). An endothermic peak with a minimum around 65°C corresponds to the evaporation of bulk water. In consensus with the related TGA curve desorption of surface bound water continues up to 250°C. Beyond this temperature a mild increase of the mass occurs as a result of the oxidation of C-H bonds by residual oxygen. This oxidation is clearly visible on the DSC curve as two exothermic peaks above 300°C.

The TGA curve of O-DNDs (Figure 3a) shows that the total water content in O-DNDs in powder form is 3.1% and the surface water desorbs up to 300°C as evidenced by broad endothermic peak on the DSC curve between 100-300°C. The more rapid mass loss above 400°C is most probably related to oxidative etching of the O-DNDs which exhibit itself as an exothermic rise on the DSC curve. H-DNDs are noticeably more resistant to the mass loss, most likely because C-H bonds must be oxidized prior to diamond etching.

Figure 3. TGA (a) and DSC (b) curves of H-DNDs (blue) and O-DNDs (red).

KPFM images and related CPD histograms in dependence on the annealing temperature are shown in the Figure 4 for both H-DNDs and O-DNDs. The annealing sequence from room temperature up to 300°C has significant effect on the CPD of both H-DNDs and O-DNDs while the CPD of HOPG substrate remains almost unchanged. It can thus serve as good reference of CPD and it indicates no significant tip change during the KPFM experiment at the same time providing ΔCPD values of the DNDs versus HOPG ($\Delta\text{CPD} = \text{CPD}_{\text{DNDs}} - \text{CPD}_{\text{HOPG}}$). In the case of H-DNDs there is large shift from positive ΔCPD values prior annealing ($\sim +110$ mV) down to strongly negative ΔCPD values (~ -400 mV) after the annealing at 300°C. Although the O-DNDs exhibit a similar trend they have a higher ΔCPD ($\sim +160$ mV) prior to annealing and a lower ΔCPD (~ -190 mV) after the annealing at 300°C at variance with the H-DNDs data. KPFM data

thus show only slight (~ 50 mV) CPD difference between H-DNDs and O-DNDs before annealing, in agreement with similar prior experiments on gold and silicon¹⁰ and pronounced CPD difference (~ 210 mV) after annealing. The KPFM data also show that the annealing in the glovebox has more pronounced effect on H-DNDs than on O-DNDs. This is clearly evidenced by the ratio of H-DND and O-DND Δ CPD values prior and after annealing: $(160/110 = 1.45) < (400/190 = 2.11)$.

Figure 4. Histograms of the CPD values (H-DNDs (a), O-DNDs (b)) extracted from KPFM images ($2 \times 2 \mu\text{m}^2$) before and after 30 min at particular temperature up to 300°C. Initial and final KPFM images before and after annealing at 300°C are shown for both H-DNDs and O-DNDs, and marked by arrows for easy assignment.

Discussion

Our FTIR data show significant differences in the stretching and bending vibrations of OH bonds between H-DNDs and O-DNDs. Particularly, we identified a distinct sharp peak in the stretching region at 3690 cm^{-1} which appears only in the spectra of H-DNDs that are saturated with water (Fig.2a eq. and sol.). As all the vibrational bands in liquid water originate from contributions of water molecules in different hydrogen bonded environments, the molecular stretch vibrations shift to higher frequency as hydrogen bonding weakens²⁵, whereas the molecular bending vibration peak shifts to lower frequencies and becomes both narrower and stronger²⁶. Scatena et al.²⁷ showed that the hydrogen bonding between adjacent water molecules at the hydrophobic-water interfaces is weak. This weakening was also theoretically calculated for water on H-terminated bulk diamond surfaces²⁸. The weak hydrogen bonding then leads to a strengthening of the OH oscillator resulting in a blue shift in energy and sharpening of spectral peaks²⁹. Moreover, interactions between these water molecules and a hydrophobic surface result in substantial orientation of these weakly hydrogen-bonded water molecules in the interfacial region. The stretching peak at 3690 cm^{-1} thus corresponds to the “free” OH bond of water molecules that straddle the interface between the water and hydrophobic surface of H-DNDs. The wavenumber of the “free” OH bond depends on specific condition at the interface. For instance, 3660 cm^{-1} for water/propan-1-ol interface³⁰ and 3669 cm^{-1} for water/tetrachloromethane interface²⁷. Relatively higher wavenumber found on H-DNDs (3690 cm^{-1}) may be due to rigidity of solid H-DNDs surface where the “free” OH bond stretching is less damped in contrast to the liquid–liquid interfaces.

The analysis of the bending vibration region of the H-DNDs FTIR spectra (Figure 2b) revealed two distinct peaks at 1616 cm^{-1} and at 1642 cm^{-1} . The value of bending vibration corresponding to liquid bulk water at 25°C is 1643.5 cm^{-1} . We propose that the peak located at 1616 cm^{-1} originates from initial water interaction with the hydrophobic surface of the H-DNDs and its shift compared to the value of bulk liquid water is a result of the weak hydrogen bond on the H-DNDs-water interface as mentioned above. The second peak at 1642 cm^{-1} corresponds well with the value of bending vibration for bulk liquid water. This peak as well as the broad -OH stretching $3000\text{--}3750\text{ cm}^{-1}$ feature increase its intensity due to gradual adsorption of “bulk” water. Note, that the strong -OH bending feature (Figure 2a, maxima at 1616 and 1642 cm^{-1}) is already present in the FTIR spectrum of “fresh” H-DNDs (low hydration level) although the -OH stretching feature ($2750\text{--}3750\text{ cm}^{-1}$) is negligible and increases only with more pronounced hydration. This may be due to higher absorption cross sections of bending -OH vibrations in comparison with stretching -OH vibrations on the surface of H-DNDs.

The bending vibration peak of the O-DNDs has the maximum at 1630 cm^{-1} (Figure 1b) which suggests generally a weaker hydrogen bond between the water and the O-DNDs surface than in bulk water. The absence of a distinct bulk water peak at 1643.5 cm^{-1} indicates that most of the water on the O-DNDs is surface-bound water. Mochalin et al.³¹ reported a considerable shift of the bending vibration peak to lower wavenumbers as well as a decrease of its intensity upon

annealing of acid oxidized DNDs up to 300°C. Such shift is probably a temperature effect since the higher the temperature the lower is the hydrogen bond strength resulting in a shift to lower frequencies²⁶. It is important to mention that according to Mochalin et al.³¹, the bending vibration peak of water disappeared only after 15 min annealing at 425°C suggesting rather strong, hydrophilic interaction of water with the surface of oxidized DNDs. Thermal analysis (TGA, DSC) provides complementary information to FTIR about specific the water interaction with H-DNDs and O-DNDs. We showed that H-DNDs can adsorb generally more water than the O-DNDs. This could be explained by the difference in SSA of the H-DNDs compared to O-DNDs but we found almost identical SSA of H-DNDs and O-DNDs ($\sim 360 \text{ m}^2/\text{g}$). Thus we expect that both H-DNDs and O-DNDs have a similar, fractal structure with numerous pores and cavities which is typical for DND powders^{32,33}.

The higher water content in the H-DNDs compared to O-DNDs can be thus explained by the formation of a thick water layer on the H-DNDs surface and probably also the formation of water nanodroplets in the porous structure of the powder. Such behavior has been described by the so-called water bridging-cluster model based on thermodynamics that assigns the interaction to organized elongated water clusters between close hydrophobic surfaces³⁴. Specific interaction of H-terminated diamond with water has been also indicated by theoretical calculations²⁸. Thus it is the different surface chemistry of H-DNDs and O-DNDs and more specifically the hydrophobicity of H-DNDs (similarly to hydrogenated bulk diamond) which causes the higher water content in the H-DNDs. On the other hand, one can expect the formation of a thin water layer on O-DNDs since the oxygen-terminated bulk diamond surface is hydrophilic³⁵. It was suggested that an ordered water monolayers may exist on other hydrophilic surfaces like mica³⁶ as well as on the oxygen terminated diamond surface³⁷. According to the DSC data (Figure 3b) the DSC curve of O-DNDs in the 120-300°C region shows a broad endothermic peak which we relate to the desorption of tightly bound surface water.

Based on the FTIR and thermal analysis data and above arguments we suggest the formation of a thick water layer and water nanodroplets in the H-DNDs powder due to hydrophobic interaction of H-DNDs and water. On the other hand, we suggest the predominant formation of a thin water layer which is tightly bound to the hydrophilic surface of O-DNDs. This model is schematically visualized in Figure 5.

Figure 5. Simplified scheme of H-DND and O-DND interaction with water. The image (a) shows hydrophobic interaction resulting in formation of a thick, weakly bound water layer and possible water nanodroplet in the structure of H-DNDs. The image (b) shows hydrophilic interaction resulting in formation of a thin, strongly bound surface water layer on O-DNDs.

KPFM images (Figure 4) show that DNDs were deposited on HOPG in similar chain-like deposits using electrophoretic deposition¹⁹ without any obvious morphology dependence on the DNDs surface chemistry or water adsorption differences. The deposition of both H-DNDs and O-DNDs on HOPG from the related colloids took place preferentially at the step edges of otherwise atomically flat HOPG. This is most likely due to rather common effect of step edges that behave like low-energy sites and enable preferential deposition. Due to the equal morphology of the DND deposits a possible averaging effect, which may influence KPFM data when studied objects have close size to the tip apex^{38,39}, is thus expected to be similar on both H-DNDs and O-DNDs and the KPFM data are directly comparable.

The KPFM data show that the adsorbed water has a pronounced impact on electronic properties of DNDs, namely the CPD. The observed dependence of the CPD on the annealing temperature as well as differences related to the specific surface chemistry of DNDs can be explained by using the FTIR, TGA, DSC data and the corresponding model in Fig.5. The change of DNDs CPD is directly correlated with the removal of water adsorbed on DNDs as evidenced by the TGA and DSC data. In general, adsorbed water layers and ions may decrease the overall CPD contrast in KPFM under ambient conditions which is known as screening effect⁴⁰. Our KPFM data indeed show a large shift of the CPD to more negative values during the annealing sequence for both H-DNDs and O-DNDs indicating strong screening effect at the room temperature. The screening effect is about 50% stronger on H-DNDs than on O-DNDs. This may be readily explained by a thicker water layer as well as a different water structure on H-DNDs as suggested by FTIR and thermal analysis. However, we have to consider also a change of the electronic properties of diamond itself due to the removal of surface water.

As the Fermi level is pinned at the surface states of oxidized diamond⁴¹ we do not suppose other than water screening effects on the CPD of O-DNDs in the employed temperature

range. In other words, the shift of the CPD to more negative values during the annealing sequence by as much as 350 mV is caused only by gradual desorption of water. However, in the case of H-DNDs also the effect of transfer doping may influence the surface electronic properties including the work function⁴². The specific interaction of hydrogen terminated diamond with adsorbed ambient moisture leads to an electron transfer from diamond to the surface water layer resulting in a positive charge (holes) in the diamond and the formation of compensating counter anions in the water layer^{42,43}. Based on thermal analysis it is reasonable to assume that the annealing up to 300°C leads to the complete desorption of water from both H-DNDs and O-DNDs but whether the counter anions also desorb is unclear.

It was suggested by Ristein et al. that the desorption temperature of the counter anions from hydrogenated diamond in ultrahigh vacuum (UHV) is higher than 400°C⁴². In accordance with the energetic band diagrams⁴², the removal of the counter anions should be accompanied by an abrupt decrease in the work function. In our case we did not observe any abrupt change of the H-DNDs work function but rather gradual change with increasing temperature as in the case of O-DNDs. In that respect note also that KPFM showed always a lower work function of H-DNDs compared to O-DNDs at both ambient and annealed condition, similarly to previous ambient KPFM studies¹⁰ and in agreement with the KPFM measurements on hydrogen and oxygen terminated bulk diamond⁴⁴. Based on these arguments we assume that also in the case of H-DNDs the effect of annealing on the KPFM data corresponds only to reduced screening via a gradual desorption of water from the H-DNDs. Nevertheless, this still needs to be corroborated by other techniques such as photoelectron spectroscopy⁴⁵.

Conclusion

Thermal analysis (TGA/DSC), vibrational spectroscopy (FTIR) and Kelvin probe force microscopy were used to study the water interaction with the surface of hydrogenated and oxidized detonation nanodiamonds. By FTIR analysis of stretching and bending vibrations of adsorbed water molecules we identified a hydrophobic interaction of water with H-DNDs, in analogy with H-terminated bulk diamond. This leads to a higher amount of water on H-DNDs (4.4%) compared to hydrophilic O-DNDs (3.1%). At the same time, water binds more weakly to the H-DNDs surface and thus desorbs at lower temperatures (~250°C on H-DNDs, ~300°C or higher on O-DNDs). This all indicated a different structure of water on hydrogenated and oxidized DNDs as schematically shown by the presented model. By correlating FTIR, TGA/DSC and KPFM data we showed that the adsorbed water caused a significant screening effect (up to 0.5 V) on the CPD of nanodiamonds which evolved gradually with the annealing temperature up to 300°C. Change of the surface Fermi level (transfer doping, surface state pinning) can be neglected in this annealing range. The screening effect is more pronounced on H-DNDs, which can be attributed to the different water amount and structure as provided by the FTIR and thermal analysis.

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