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The Ion Sensitivity of Surface Conductive Single Crystalline Diamond

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Abstract: Charge build-up at the solid/aqueous interface is a ubiquitous phenomenon that determines the properties of interfacial electrical double layers. Due to its unique properties, the surface of diamond offers an attractive platform to investigate charging mechanisms in aqueous solutions. We investigate the surface charge by studying the ion sensitivity of H-terminated single crystalline diamond surface conductive layers. The effect of monovalent and divalent salts has been probed at different pH values. For a pH above 3.5, increasing the ionic strength results in a decrease of the surface conductivity, in contrast to the results obtained for pH below 3.5. Electrokinetic experiments are in good agreement with the surface conductivity measurements, showing an isoelectric point at pH 3.5 for the H-terminated diamond surface. We discuss the results in terms of the Coulombic screening by electrolyte ions of the surface potential, which is induced by a pH-dependent surface charge. The origin of this surface charge is discussed in terms of charge regulation by amphoteric hydroxyl surface groups and unsymmetrical adsorption of hydroxide and hydronium ions induced by the hydrophobic nature of the H-terminated diamond surface. This surface charge can have important consequences for processes governed by the diamond/aqueous interface, such as electron transfer to charged redox molecules, adsorption of charged molecules and proteins, and ion sensitivity.

Introduction

The importance of the solid/aqueous interface is evident for a broad spectrum of physical and chemical phenomena, as for example electron-transfer processes,[1] transport and separation processes in microchannels,[2] the interaction of molecules, biomolecules and living cells with solid surfaces,[3,4] etc. In addition, the electrical double layer induced at a metal or semiconductor interface with an aqueous solution determines the ultimate performance of electrodes in electrochemical applications, as well as of ion sensitive field effect transistors.[5] The properties of electrical double layers strongly depend on charge build-up processes occurring at the solid/aqueous interface, which are influenced by specific and nonspecific adsorption of ions, charge regulation by surface groups, water/solid interactions, etc.[6] Due to its very unique properties, such as chemical stability and excellent performance in electrochemical applications,[7] the surface of diamond offers an ideal platform to investigate interfacial charging mechanisms in aqueous solutions. In addition, both hydrophobic (H-terminated) and hydrophilic (O-terminated) surfaces are very stable in aqueous solution, which is an important advantage compared to other semiconductors and metals. Finally, the surface conductivity of H-terminated diamond surfaces provides a unique tool to investigate the process of charge formation on diamond surfaces in situ.[8]

In this paper, we report on our investigation of the charge formation adsorption at the diamond/aqueous interface by studying the ion sensitivity of diamond surfaces. Since the first report in 1970,[5] the ion-sensitive field effect transistor (ISFET) has become an important and versatile sensing tool. Useful modifications like the EnzymeFET (ENFET) or the ImmunoFET have expanded the number of possible applications to the broad area of biosensors, medical, and health care.[9] The use of diamond for ISFET applications has been limited so far,[10−14] although this material could be very advantageous in this field.

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The large potential window and the chemical inertness provide a useful platform for electrochemistry, the excellent biocompatibility and the possibility of a stable surface functionalization are ideal for biosensor applications.[15−16] Diamond ISFETs make use of the pronounced surface conductivity observed for hydrogen-terminated diamond.[17] The best established model to explain this surface conductivity, the transfer doping model,[8] relies on the presence of atmospheric surface adsorbates acting as acceptors for electrons from the diamond valence band. However, the question remains what happens exactly at the diamond/aqueous electrolyte interface. In this context, the role of electrolyte ions is of particular relevance.

In earlier reports on the ion-sensitivity of ISFETs based on hydrogenated polycrystalline diamond, a shift of the threshold voltage, leading to an increase of the drain-source current with salt concentration, was reported.[12−14] To explain this behavior, it was suggested that negatively charged halogen anions could adsorb specifically on the diamond surface as a result of the $C^{-}-H^{+}$ surface dipole. However, in the light of the new experiments reported in this paper, we propose a rather different explanation. We found that the influence of ionic strength, increasing or decreasing the surface conductivity, depends on the pH of the solution. Even more, within our experimental conditions, we can conclude that the main effect of ionic strength is the screening of a pH-dependent surface potential and, therefore, the effect of specific adsorption of dissolved salt ions is not dominant. We discuss two possible mechanisms of charge build-up at the diamond/aqueous solution interface: (i) charge regulation by amphoteric hydroxyl groups, which are present due to the incomplete H-termination of the surface, and (ii) unsymmetrical adsorption of hydroxide (OH^{-}) and hydronium (H_3O^{+}) ions at the H-terminated diamond surface. From the electrokinetic experiments reported in this paper, there is evidence for the unsymmetrical adsorption of OH^{-} and H_3O^{+} ions. Recently, the adsorption of hydroxide ions on hydrophobic surfaces, as is the case of the H-terminated diamond surface, has been investigated by different methods.[18−21] It has been suggested that interfacial water ordering can induce the adsorption of hydroxide ions.[21,22] We have conducted molecular dynamic simulations to investigate the microscopic structure of the water phase at the surface of the hydrophobic H-terminated diamond, showing that the interfacial water layers are strongly oriented and thus promoting OH^{-} adsorption.

Materials and Methods

Diamond Surfaces Preparation. Natural type-IIa single-crystal diamond (scd) samples were used (both 100 and 111 oriented, from Element Six BV, The Netherlands). The samples had a size of 3 × 3 mm^2 and exhibited an average surface roughness below 0.5 nm, as determined by AFM measurements.

Before any process, the samples were cleaned in aqua regia (HCl/HNO_3 3:1) at 120 °C for 1 h to remove metal contaminations from the surface. Next, the samples were chemically oxidized via the following steps: first, concentrated H_2SO_4 containing the scd samples was heated to 225 °C, and then some mm^3 of KNO_3 salt were added. The samples were kept in this solution for 1 h and afterward thoroughly rinsed with DI−water. Besides the surface oxygen termination, this chemical treatment is known to remove non-diamond carbon from the surface. The oxidation was confirmed using contact angle experiments. Finally, the samples were hydrogen-terminated using a hot-filament setup. The samples were heated in a vacuum chamber (base pressure $5\ 10^{-7}$ mbar) to a temperature of 700 °C. H_2 (flux of 150 sccm) was introduced and activated with two 2000 °C hot tungsten wires. The hot sample was exposed to hydrogen radicals for 30 min at a constant chamber pressure of 1.5 mbar. After cooling down in hydrogen atmosphere, the samples were kept for 1 day in ambient atmosphere to induce the surface conductivity.[8] Contact angles between 80 and 90° revealed highly hydrophobic surfaces. The surface conductivity with typical values of $10^{-4}\ \Omega^{-1}\ cm^{-1}$ was confirmed by Hall-effect-experiments. The corresponding hole densities were of the order of $10^{13}\ cm^{-2}$, and the mobilities were around 50−100 $cm^2\ V^{-1}\ s^{-1}$.

Ion Sensitivity Field Effect Transistor Fabrication. ISFET devices were fabricated by standard photolithography: First, Ti/Au (20/200 nm) contacts were deposited by electron-beam evaporation, acting as drain and source contacts. The 1 × 1 mm^2 active area between these contacts was defined by oxidizing the sample area outside in an oxygen plasma, leaving just the active area hydrogen-terminated and conductive. The processed diamond samples were mounted onto a ceramic holder, and the drain and source metal contacts were wire-bonded to Au contact pads on the holder. Chemically resistant silicone glue was used to prevent direct contact between any metal and the electrolyte. Only the active diamond area was exposed to the electrolyte solution.

Ion Sensitivity Measurements. The devices were operated as working electrodes in a three-electrode electrochemical cell, consisting of a double junction Ag/AgCl (1.5/3 M saturated KCl) reference electrode and a Pt wire counter electrode. A commercial potentiostat (BANK LB81M) was employed to control the electrode potentials. The experimental setup is designed for simultaneous recording of the drain−source current and voltage as well as the gate (electrolyte)−source voltage. All the potential values quoted here are referred to the Ag/AgCl electrode. The standard electrolyte is a 10 mM phosphate buffer solution; however, when using divalent salts, we had to use a HEPES buffer because of solubility problems. The electrolyte solution is stirred, and the pH value and the temperature are monitored continuously. Typical transistor characteristic curves of the diamond ISFETs are shown in the Supporting Information (Figure S2). The drain−source current (I_{DS}) was recorded while the salt concentration of the electrolyte was changed by addition of defined salt quantities dissolved in buffer solution, in the range from 10 μM to 100 mM. The measurement parameters were a constant drain-source voltage (U_{DS}) of −100 mV, and a constant gate-source voltage (U_{GS}) of −500 or −400 mV.

Electrokinetic Measurements. Streaming current experiments were conducted using the Microslit Electrokinetic Setup.[23] The device permits the determination of the zeta potential by streaming potential and streaming current measurements at a rectangular streaming channel formed by two parallel sample surfaces (20 × 10 mm^2). Streaming current experiments were conducted at different salt concentrations and different pH values using undoped polished (rms < 1 nm) polycrystalline diamond plates. The calculation of the Zeta potential was done as described in detail in the work of Werner and co-workers.[23]

Molecular Dynamic Simulations. For the molecular dynamics (MD) simulation, we have created a model of an interface between a 100-

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oriented hydrogen terminated diamond surface and water. A 3 nm × 3 nm × 2 nm big block of diamond was placed in a rectangular simulation box of 3 nm × 3 nm × 9 nm. The remaining space in the box was filled with water. The force field parameters for the carbon and hydrogen atoms of the diamond were taken from the Gromos96 force field.[24] The diamond atoms were assumed to be uncharged. The water model chosen was Simple Point Charge−Extended (SPC/E).[25] The total system consisted of ∼2500 diamond atoms and ∼7000 atoms for the water. The GROMACS program was used for all simulations.[26,27] Periodic boundary conditions were applied, and the long-range electrostatic energy was calculated by the Particle mesh Ewald method (PME). After minimization and equilibration, 2 ns long simulations were performed in the NPT ensemble (number of particles, pressure normal to the surface, and temperature constant). All further analysis was based on the resulting trajectories. We calculated the thickness of the depletion layer at the interface along with the profiles of the average dipole moment and the electrostatic potential along the interface. The potential of mean force (PMF) for the adsorption of OH^- and Na^+ was calculated by umbrella sampling. More details of the MD simulations can be found in the Supporting Information section.

Results and Discussion

Effect of Monovalent and Divalent Ions. We investigate the ion sensitivity of diamond surfaces by evaluating the effect of ion concentration on the drain source current (I_{DS}) of diamond ISFETs (see Materials and Methods, and Supporting Information sections for further information). In contrast to our experimental method, the ion sensitivity was estimated in earlier reports from the change in threshold voltage in solutions of different salt concentrations.[12−14] With increasing concentration of salts containing halogen anions, a threshold voltage shift to lower values and higher transistor currents have been reported for ISFETs based on hydrogenated polycrystalline diamond. This was explained by an adsorption of the negative anions due to the polarization of the C−H bond.[12−14]

However, in our measurements performed at pH 7, the drain−source current decreases upon an increase of the concentration of different monovalent and divalent salts, as shown in Figure 1a. This I_{DS} decrease suggests a dominant influence of the positively charged cations: an increased amount of positive charge at the interface is expected to lead to a depletion of the hole accumulation layer close to the diamond surface and, as a consequence, to a I_{DS} decrease. This is in clear contradiction to the adsorption of negative ions proposed in earlier reports.[12−14]

At pH 7, the dominant role of the positive cations for the ion sensitivity of diamond ISFETs has been corroborated by comparing the effect of different salts such as KCl, $CaCl_2$, and $MgCl_2$ (see Supporting Information, Figure S1). These salts have the same anion (Cl^-) but differ in the cation, monovalent K^+ and divalent Ca^{2+} or Mg^{2+}. Due to its 2-fold positive charge, a larger influence on the conductivity is expected for divalent cations, in accordance with the results shown in Figure 1a.

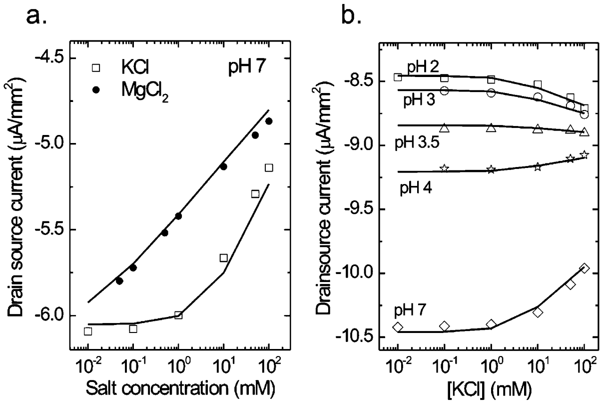

Figure 1. (a) Comparison of the effect of a monovalent (KCl) and a divalent salt ($MgCl_2$) on the surface conductivity at pH 7. Symbols represent the experimental results, measured in 10 mM HEPES buffer and with $U_{GS} = -400$mV. Lines are the results of the fits using the model described in the text. (b) Effect of pH of the solution on the ion sensitivity. Symbols correspond to the experimental results measured with $U_{GS} = -500$mV. The surface conductivity decreases with increasing salt concentration for pH values above 3.5. In contrast, the opposite effect is observed for pH values below 3.5. Solid lines are fits using the model described in the text, assuming a surface charge of −1 μC/cm² for pH 7, −0.2 μC/cm² for pH 4, +0.1 μC/cm² for pH 3.5, +0.35 μC/cm² for pH 3, and +0.45 μC/cm² for pH 2.

Screening versus Adsorption. The observed interaction of the positive ions with the diamond surface can be explained by two main effects, screening and specific adsorption. In the diamond film, a hole accumulation layer with a charge density close to 10^{13} holes/cm² is formed very close to the surface. In the case of the diamond/air interface, it has been suggested that the positive charge is compensated by the negative charge of atmospheric adsorbates.[8] However, at the diamond/aqueous electrolyte interface, ions from the electrolyte solution are expected to play an important role in maintaining the overall charge neutrality. One possibility to explain the effect of the electrolyte ionic strength, as shown in Figure 1a, is the specific adsorption of positive ions at the surface. Possible binding sites are amphoteric oxygen groups, always present at the H-terminated surface due to imperfections of the hydrogenation. Cations and anions have been reported to form complexes with negatively and positively charged surface functionalities, respectively.[28,29] Additionally, specific adsorption can also occur directly on the hydrogenated regions. The shift toward a more positive surface charge on the solution side (and in consequence a more positive surface potential) should decrease the number of positive holes in the conductive channel under the neighboring hydrogenated areas and in turn lead to a reduction of the drain-source current. However, it is well-known that specific adsorption of ions strongly depends on different ion properties.[30] Although a clear microscopic description of the ionic specificity is not yet available,[31] different mechanisms have been suggested, such as solvent structure effects, ion−solvent interaction, as well as interactions between ions and specific sites on the surface. Our experimental results show a very weak dependence on the ion type, in contrast to a larger dependence on the ion valency (Supporting Information, Figure S1), which can be better

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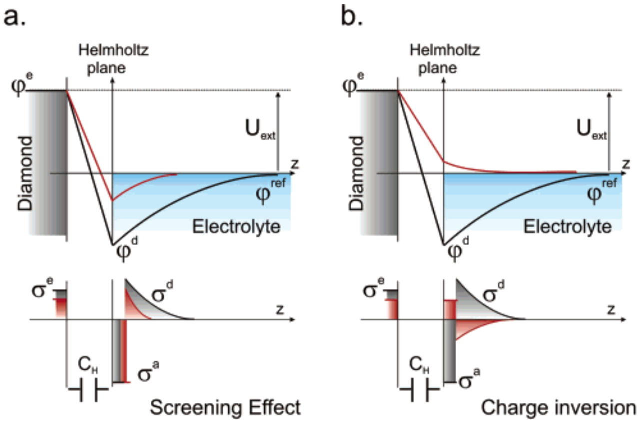

Figure 2. Schematic of the diamond/aqueous electrolyte interface. The inner and the outer Helmholtz planes have been merged together. The adsorbed charge (σ^a) is considered to be at the Helmholtz plane. This charge is compensated by the induced charge at the diamond side of the interface (σ^e) and the diffuse charge (σ^d). The bottom diagrams represent the charge distribution and the upper diagrams correspond to the potential distribution at the interface, assuming a constant Helmholtz capacitance (C_H). U_{ext} is the externally applied gate potential. (a) Screening effect: A negative surface charge ($\sigma^a < 0$), gray area in the bottom diagram, induces a negative surface potential (black line in the upper diagram). Increasing the ionic strength results in a lowering of the negative surface potential (red lines), which leads to a decrease of the surface conductivity (due to the decrease of $\varphi^e - \varphi^a$). (b**)** Charge inversion: for pH below 3.5 the surface charge is positive (red area in the bottom diagram). In this situation the decrease of the positive surface potential (red line in the upper figure) as a result of the increase of the ionic strength leads to an increase of the surface conductivity (due to the increase of $\varphi^e - \varphi^a$).

described by screening effects. Thus, for the discussion hereafter, we will assume that salt ions are not specifically adsorbed at the diamond surface.

The Diamond/Aqueous Interface. To quantify the influence of the ionic strength on the surface conductivity in terms of screening, we use the simple model based on the Gouy−Chapman−Stern theory, which is schematically shown in Figure 2. The classical description of the solid/liquid interface based on the Gouy−Chapman−Stern model assumes that the charge is distributed in different regions.[32] First, a layer of specifically bound (nonhydrated) ions from the electrolyte can be formed right at the surface (at the inner Helmholtz plane). Second, a layer of nonspecifically bound (hydrated) ions from the solution forms the outer Helmholtz plane. Finally, there is the extended, smeared-out region of diffuse charges. The schematics in Figure 2 shows a simplified version of the diamond/liquid interface in which, as a first approximation, the two planes of the Helmholtz layer have been merged together.

Let us first assume that the surface of diamond is negatively charged in contact with the electrolyte, with a surface charge per unit area σ^a. This negative charge, whose origin will be discussed later, induces a negative surface potential φ^a. The potential profile across the interface, as depicted in upper schematic of Figure 2a (black line), starts from a positive value (hole accumulation layer, applied positive potential), then strongly drops to negative values (countercharge layer), and finally slowly rises exponentially to zero (diffuse layer). The corresponding charge distribution is shown in the bottom diagram of Figure 2a (black curves and gray shadowed regions). In the diffuse region of the electrolyte, the charge per unit area (σ^d) and the potential (φ^d) are related by the Poisson−Boltzmann equation. With the help of the Gauss law, it is possible to derive the relation between φ^d and σ^d using the simplifying assumptions of the Gouy−Chapman theory: namely, ions are considered as point-like charges that interact via their mean field in a solvent treated as a continuum. This leads to the Grahame equation:

$$\sigma^d = \sqrt{2\epsilon_r\epsilon RT}\,[\sum_i c_i\cdot(\exp\{-z_i\cdot F\cdot\varphi^d/R\cdot T\})]^{1/2} \qquad (1)$$

in which the index i refers to the different ions in the electrolyte, with concentration c_i and valency z_i, F is the Faraday constant, R the general gas constant, and T the absolute temperature.

The mobile charge (σ^e) induced at the diamond side of the interface is related to the potential drop at the interface through the interfacial capacitance (C_H) by the equation

$$\sigma^e = C_H(\varphi^e - \varphi^a) \qquad (2)$$

Since the inner and outer Helmholtz planes are merged together (see Figure 2a), in eq 2 the potential φ^a at the Helmholtz plane can be substituted by φ^d.

Finally, the drain source current (I_{DS}) can be calculated using the charge induced at the diamond surface (σ^e) and the mobility (μ) of the carriers,

$$I_{DS} = \mu\sigma^e U_{DS} = \mu C_H(\varphi^e - \varphi^a)\, U_{DS} = \mu C_H(U_{ext} - \varphi^d)\, U_{DS} \qquad (3)$$

where U_{DS} is the applied drain source voltage. As discussed above, φ^a can be substituted by φ^d; in addition, as the potentials are referred to a reference electrode (see Figure 2), the potential at the diamond surface φ^e corresponds to the externally applied potential or gate potential, U_{ext}. Finally, the charge neutrality condition, $\sigma^a + \sigma^d + \sigma^e = 0$, completes the set of equations. Figure 1a compares the experimental results (symbols) with the predictions of this simple model; solid lines correspond to the results obtained from eq 3 using a negative surface charge of $-9\ \mu C/cm^2$, which approximately corresponds to 6×10^{13} negative charges per cm^2. In the calculations, we have used an interfacial capacitance $C_H = 2\mu F/cm^2$ and a carrier mobility $\mu = 55\ cm^2/Vs$,[33] which are typical values (see Supporting Information for further discussion). Other parameters used in the calculation are external gate voltage $U_{ext} = +0.4V$, drain source voltage $U_{DS} = -0.1V$, and relative dielectric constant of bulk water $\epsilon_r = 80$. As in the experiment, a 10 mM monovalent (1:1) background electrolyte is used.

As can be seen in Figure 1a, the prediction based on the model discussed above follows quite reasonably the experimentally observed effect of both monovalent and divalent salts on the surface conductivity. At a given constant negative surface charge, an increase of the ionic strength results in a decrease of the negative surface potential φ^d (i.e., it becomes less negative), which then produces a decrease of the accumulated holes at the diamond surface and therefore of the drain source current, see eq 3. This effect is schematically shown in Figure 2a. For the surface charge of $-9\ \mu C/cm^2$ (as used in the calculation shown in Figure 1), the increase of the ionic strength from 1 to 100 mM leads to a decrease of the induced hole density at the

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diamond surface from 7×10^{12} to 6×10^{12} cm^{-2}. The different behavior of divalent and monovalent cations is simply the result of their different screening effect on the negative surface potential, which is determined by their different valency z in eq 1.

The ion sensitivity has been investigated as a function of the pH of the aqueous solution, and the results are summarized in Figure 1b. In this experiment, the background buffer was 10 mM, the drain source voltage $U_{DS} = -0.1$ V, and the applied external potential (gate voltage) was +0.5V vs Ag/AgCl. At low ionic strength, a decrease of the pH (obtained by adding HCl to the solution) results in a decrease of the drain source current, a dependence which we have previously attributed to the presence of amphoteric oxygen functionalities on the diamond surface.[10] Due to the amphoteric behavior of hydroxyl groups (C−OH), variations in the pH modify the surface charge (σ^a) and therefore the surface potential. We referred to this process as surface charge regulation. At low pH, OH-groups become protonated, reducing the negative charge of the surface. Interestingly, the variation of the drain source current with the ionic strength is reversed for pH below 3.5. At low pH values an increase of the ion concentration leads to an increase of the drain source current, in contrast to the opposite behavior observed for pH values above 3.5. This can be understood using the same model described above: for pH below 3.5 the surface charge becomes positive, and so does the surface potential (φ^d), as shown by the red curve in Figure 2b. In this situation, the positively charged surface is mainly compensated by a negative charge in the diffuse region. Therefore, an increase of the ionic strength results in a lowering of the surface potential, which becomes less positive and increases the term $U_{ext} - \varphi^d$ in eq 3; as a result, I_{DS} increases. The experiments (symbols) in Figure 1b have been simulated (solid lines) using different values of the surface charge: -1 μC/cm^2 for pH 7, -0.2 μC/cm^2 for pH 4, $+0.1$ μC/cm^2 for pH 3.5, $+0.35$ μC/cm^2 for pH 3, and $+0.45$ μC/cm^2 for pH 2. Our results suggest that hydroxide (OH^-) and hydronium ions (H_3O^+) are the main potential determining ions (i.e., ions that are able to modulate the surface charge). The concentration ratio of the two potential determining ions varies the value and the sign of the charge at the diamond/aqueous electrolyte interface. Thus, we can conclude that the point of zero charge of the diamond surface is close to pH 3.5.

In the discussion above, the surface charge at the diamond/aqueous electrolyte interface has been assumed to be induced by amphoteric C−OH groups at the diamond surface. These surface groups can become protonated ($C-OH_2^+$) or deprotonated ($C-O^-$) depending on the pH of the solution. From the calculations presented above, a charge density as high as 6×10^{13} cm^{-2} can be expected at pH above 7. If this charge is related to hydroxyl groups, it would imply that more than 5% of the carbon atoms at the diamond surface are saturated with −OH functionalities. XPS experiments reveal that in our samples the contribution of oxygen on the surface is of the order of 10% of surface coverage. However, of this high amount of oxygen functionalities only a small fraction is expected to be OH-groups, typically less than 50% for the 100-oriented diamond surface and less than 10% for the 111-oriented surface.[34] These numbers have to be taken with caution due to the difficulty in obtaining an accurate value for the density of hydroxyl groups, even using high-resolution XPS. In addition, physisorbed oxygen-containing species cannot be completely ruled out.

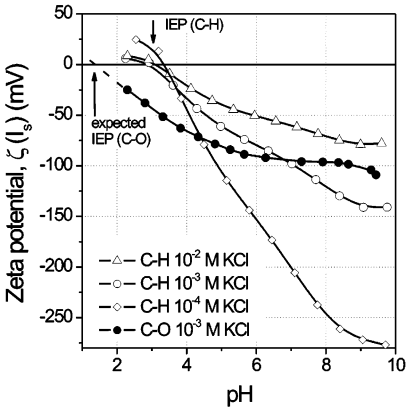

Figure 3. Zeta potential calculated from streaming current measurements for H-terminated and O-terminated diamond surfaces. The experiments were conducted with different ionic strengths of the solution as a function of the pH. In the case of the H-terminated diamond surfaces, negative Zeta potentials are obtained above pH 3−3.5, which is considered as the isoelectric point (IEP). A very small variation of the IEP is observed for different salt concentrations. In the case of the O-terminated diamond surface, the IEP occurs at lower pH (below pH 1.5) and a plateau of the Zeta potential is observed for pH above 6.

Unsymmetrical Adsorption of OH^- and H_3O^+. However, even if the density of C−OH groups at the diamond surface is not high enough, OH^- and H_3O^+ are still able to modulate the surface charge if they are adsorbed on the H-terminated surface. The adsorption of hydroxide at a water/hydrophobic interface, as is the case for the water/H-terminated diamond, has been recently investigated both theoretically and experimentally.[18−21] To further investigate the charge build-up process at the diamond/aqueous electrolyte interface, we have employed streaming current experiments (the experiment is described in the Methods Section) to derive the Zeta potential at the diamond surface.

The results of the streaming current experiments performed using H-terminated and O-terminated diamond surfaces are shown in Figure 3. In the case of the H-terminated surface, the pH dependence was measured for 10^{-4}, 10^{-3}, and 10^{-2} M KCl. The derived Zeta potential has a negative value and decreases as the pH is lowered. For all investigated salt concentrations, the Zeta potential becomes positive for pH below 3.5. Therefore, pH 3.5 is the isoelectric point (IEP) of the H-terminated diamond surface, in very good agreement with the results of the ion sensitivity experiments (see Figure S3 in the Supporting Information). The fact that the salt concentration has an almost negligible influence on the IEP supports our previous assumption about the specific adsorption of ions: the specific adsorption of K+ or Cl^- is negligible, at least for salt concentrations in the range of $10^{-2}-10^{-4}$ M. The absence of any clear plateaus of the Zeta potential in the investigated pH range (from pH 2 to 10) indicates that the surface charge is not only caused by the dissociation of hydroxyl groups (C−OH) but by the preferential adsorption of hydroxide and hydronium ions from the electrolyte.

These results are in very good agreement with the previous work of Werner and co-workers, in which the unsymmetrical adsorption of OH^- and H_3O^+ to unpolar polymer films was reported.[18] Interestingly, the derived Zeta potential for the

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(34) Ferro, S.; Colle, M. D.; De Battisti, A. *Carbon* **2005**, *43*, 1191−1203.

unpolar polymer films revealed a point of zero charge at pH 4,[18] close to the value we find for the H-terminated diamond surfaces. We have additionally conducted streaming current experiments with the same samples after oxygen plasma treatment (see Figure 3). After surface oxidation, the low contact angle of the diamond surface indicates the presence of C−OH, which has been confirmed by HREELS experiments.[35] In the case of the oxidized diamond surface a negative Zeta potential is also obtained. However, the IEP of the O-terminated diamond surface is close to pH 1.5, well below the IEP for the H-terminated diamond surface. In addition, a clear plateau of the Zeta potential (of about −100mV for a salt concentration of 1 mM) is observed for pH values above 6. These two results indicate that, in the case of the oxygen terminated diamond surface, the interfacial charge is strongly influenced by the dissociation of C−OH surface groups (charge regulation process), in contrast to the H-terminated diamond surface where unsymmetrical adsorption of OH^- and H_3O^+ dominates. The slightly difference between the IEP measured for the hydrophobic diamond surface (at pH 3.5) and for the hydrophobic unpolar films (at pH 4)[18] can be attributed to the presence of residual hydroxyl groups at the diamond surface.

Water Ordering and OH^- Adsorption. The driving force originating the unsymmetrical adsorption of OH^- and H_3O^+ is still not well understood. It has been suggested that in the case of hydrophobic surfaces, the presence of a highly oriented interfacial water layer acts as a template for hydroxide ion adsorption.[18] To understand the microscopic structure of the water/H-terminated diamond interface, we have performed molecular dynamic (MD) simulations (see Materials and Methods section for a detailed description of the MD simulations). In principle, charge-transfer reactions can take place between the solution and the solid, and only quantum chemical methods (such as density functional theory, DFT) are able to account for them. However, it is reasonable to assume that the completely hydrogen-terminated diamond surface is inert under the studied conditions and acts neither as a donor or acceptor for electrons or protons at the neutral conditions of the simulation. Therefore, a classical description without much chemical detail of the diamond side is possible (see Supporting Information for a detailed discussion about the validity of the molecular dynamic simulations). Figure 4 shows a snapshot of the simulation, and the profile of the dipole moment (μ_Z) of the water phase normal to the interface. Our MD simulations show that the interfacial water layers are indeed strongly oriented. The driving force for this ordering is the tendency of the water to keep a high number of hydrogen bonds.[36] Zangi and Engberts have suggested that water ordering induces an electrical potential gradient which favorably interacts with the dipole moment of hydroxide ions, which are then preferentially physisorbed at the interface.[21] To investigate the adsorption of OH^- ions we have performed MD simulations in which different concentrations of NaOH were added to the water. Indeed, the potentials of mean force (PMF) obtained from MD for Na^+ and OH^- ions have minima in the interfacial region (see Figure 4), indicating that OH^- ions are indeed adsorbed in the second interfacial water layer, where the first solvation sphere of the ions is in contact with the interface (See Materials and Methods and Supporting Information sections for further discussion of the MD results).

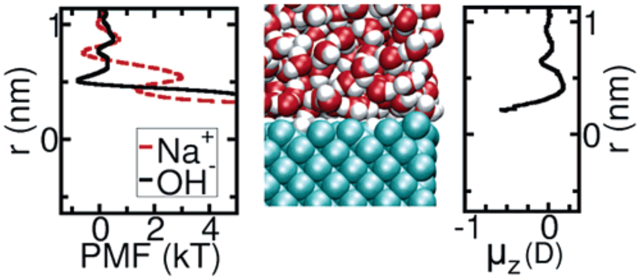

Figure 4. Molecular dynamics simulations of the hydrogenated diamond/water interface. A snapshot of the simulation of the diamond/water interface is shown in the middle, where the water occupies the upper part, and the diamond the lower part. Oxygen atoms are represented in red, hydrogen atoms in white, and carbon atoms in blue. Left: potential of mean force (PMF) for the adsorption of Na^+ and OH^- at the diamond/water interface. Right: profile of the average dipole moment normal to the interface of pure water. A negative dipole moment indicates that the hydrogen atoms point toward the diamond. The orientation of water molecules is caused by the presence of the hydrophobic diamond interface, and decays with increasing distance (r) from the surface. Above 1 nm, the dipole moment is very low. In this region, the potentials of mean force for ion adsorption also reach the values in bulk water.

Conclusion

In this paper, we have demonstrated that diamond surfaces are suitable platforms to investigate charging processes at the solid/aqueous solution interface. From two complementary methods we have found that the point of zero charge of H-terminated diamond surfaces is about pH 3.5. The ion sensitivity of H-terminated single crystalline diamond surfaces was explained in terms of Coulombic screening of the surface charge by electrolyte ions. The origin of the pH-dependent surface charge has been discussed in terms of (i) amphoteric hydroxyl (C−OH) surface groups, and (ii) unsymmetrical adsorption of hydroxide and hydronium ions from the aqueous solution. Electrokinetic experiments indicate that, in the case of the H-terminated surfaces, the surface charge is mainly induced by the unsymmetrical adsorption of OH^- and H_3O^+. We suggest that the hydrophobic nature of the H-terminated diamond surface induces the adsorption of OH^- and H_3O^+ ions from the aqueous solution, resulting in a large interfacial charge. These are relevant results with important implications in different fields such as electrochemistry, bio-sensors, colloidal and interfacial science, as well as in any field in which hydrophobic interactions and "double-layer" formation are of concern.

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Supporting Information Available: Ion sensitivity curves for different monovalent and divalent salts, transistor curves of diamond ISFETs, point of zero charge curves, and detailed discussion of molecular dynamic simulations and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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