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Q1 Amino-terminated diamond surfaces: Photoelectron emission and photocatalytic properties

Q2 Di Zhu, Jason A. Bandy, Shuo Li, Robert J. Hamers*

Department of Chemistry, University of Wisconsin–Madison, 1101 University Avenue, Madison, WI, USA

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ABSTRACT

We report a new approach to making stable negative electron-affinity diamond surfaces by terminating diamond with amino groups (also known as amine groups, $-\text{NH}_2$). Previous studies have shown that negative electron affinity can be induced by terminating diamond surfaces with hydrogen, creating a surface dipole favorable toward electron emission. Here, we demonstrate that covalent tethering of positive charges in the form of protonated amino groups, $-\text{NH}_3^+$, also leads to negative electron affinity (NEA) and facile electron emission into vacuum and into water. Amino-terminated diamond was prepared using a very mild plasma discharge. Valence-band photoemission studies of the amino-terminated diamond samples show a characteristic “NEA” peak, demonstrating that the amino-terminated surface has NEA. Diamond’s ability to emit electrons into water was evaluated using photochemical conversion of N_2 to NH_3 . Time-resolved surface photovoltage studies were used to characterize charge separation at the diamond interface, and Mott–Schottky measurements were performed to characterize band-bending at the diamond–water interface. XPS studies show that the amino-terminated surfaces provide increased chemical resistance to oxidation compared with H-terminated diamond when illuminated with ultraviolet light.

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1. Introduction

Diamond is a wide-bandgap semiconductor with a bandgap of 5.5 eV. Because of its chemical stability and ability to be doped into a conductive state, diamond has been used as a high-stability substrate and electrode [1,2]. One unusual property of diamond is that its conduction band lies higher in energy than the vacuum level. This alignment of energy levels is referred to as negative electron affinity (NEA) [3–6]. NEA materials can have unusually high electron emission yields because while in conventional materials photoelectron emission is a surface-dominated process, in NEA materials, electrons that are optically excited to the conduction band in the *bulk* material can diffuse to the surface and be emitted with virtually no barrier [7]. While NEA is often considered a property of the bulk energy levels, true NEA and the accompanying facile electron emission from diamond require both downward band-bending near the surface and a surface termination whose associated surface dipole favors electron emission [8,9]. NEA of diamond has typically been achieved by terminating the surface with hydrogen; the resulting C–H surface dipole has a small positive charge on the H atom, thereby yielding a surface dipole oriented in a direction that favors electron emission [6–8].

While electron emission into vacuum has been studied for many years, electron emission into water is much less studied. Yet, it is very

important because the emission into water leads to the formation of solvated electrons, long regarded as the chemist’s perfect reducing agent [10], and because solvated electrons in water can induce many exceedingly difficult reactions of importance in chemistry and biology [7, 11–13]. However, until recently, there has not been a convenient way of producing solvated electrons in water. Most previous studies formed solvated electrons by using high-energy arcs, energetic laser pulses, or high-energy radioactive particles [10]. In recent work, we showed that diamond’s NEA and high chemical stability allows it to be used as a solid-state source of solvated electrons in water, and that these electrons can induce novel reactions such as the reduction of N_2 to NH_3 [14,15], the reduction of H^+ to neutral atomic hydrogen (H^\bullet) [16], and the one-electron reduction of CO_2 to its radical anion [17]. However, we also found that the electron-emissive properties of H-terminated diamond decreased over a duration of several hours due to oxidation of the surface [14].

While H-terminated diamond has negative electron affinity because of the C–H surface dipole, alternative strategies for forming NEA surfaces in water also exist. Chemical functional groups containing one N atom with three single bonds to any combination of H and C atoms are referred to as amino groups. Primary amino groups (one bond to the surface, C– NH_2) and secondary amino groups (two bonds to the surface, C₂–NH) are of particular interest because at circumneutral pH values in water they can be protonated to form to form positively charged quaternary cations at the diamond surface such as C– NH_3^+ (one bond to the surface) and C₂– NH_2^+ (two bonds to the surface) analogous to the

* Corresponding author.
 E-mail address: rjhamers@wisc.edu (R.J. Hamers).

aqueous ammonium ion (NH_4^+). In principle, the presence of protonated amino groups on the diamond surface could enhance electron emission because static, positive surface charge should produce downward band-bending within the adjacent diamond region and a strong electrostatic driving force for electron emission.

Here, we report investigations of the electron emission properties of amino-terminated diamond surfaces. We demonstrate that very low-power ammonia plasmas can form diamond surfaces terminated with primary amino groups. Our results show that diamond surfaces terminated with amino groups exhibit negative electron affinity in vacuum and that the emission is enhanced by intentional protonation of the surface. The amino-terminated surfaces are capable of emitting electrons into water and initiating reduction of N_2 to NH_3 in a manner similar to that of H-terminated diamond. XPS studies indicate that amino-terminated surfaces are more resistant to oxidation than the corresponding H-terminated surfaces.

2. Materials and methods

2.1. Preparation of H-terminated diamond

Electrochemical grade boron-doped diamond (Element Six) was H-terminated by exposure to a hydrogen plasma [18] in a 2.45 GHz microwave enhanced plasma CVD chamber. In the process, the sample was kept in H_2 at a pressure of 45 Torr with a microwave power of 600 W for 15 min. The microwave power was reduced to zero over a time period of several minutes, and the H-terminated diamond was left in the H_2 atmosphere for another 15 min to cool near room temperature.

2.2. Preparation of amino-terminated diamond

To form amino-terminated diamonds, we exposed H-terminated diamond samples to an ammonia plasma in a customized radio-frequency (RF) plasma chamber consisting of a 6 cm diameter quartz tube surrounded by a 3-turn RF coil, connected to an impedance-matching network and a 13.56 MHz RF source. Compared to previous studies using ammonia plasmas that have typically used RF power of 300–500 watts [19,20] or microwave excitation [21], we use much lower power to minimize fragmentation. To optimize formation of surface amino groups, we measured the concentration of surface nitrogen using XPS, and the surface density of primary amino groups (C-NH_2) using the SDTB method described below. We monitored the plasma composition via optical emission spectroscopy (OES), using an Ocean Optics spectrometer to characterize optical emission from the ($\text{A } ^3\Pi \rightarrow \text{X } ^3\Sigma^-$) emission band of NH at 337 nm and the ($\text{C } ^3\Pi_u \rightarrow \text{B } ^3\Pi_g$) emission band of N_2 at 316 nm, 337 and 358 nm [22]. At low RF powers and high pressures, the emission intensity from NH increased related to that of N_2 due to reduced fragmentation and increased collisional quenching. We found the best conditions for amino termination to be the highest pressure and lowest RF power (in our system, 1.6 Torr pressure and 25 W RF power) that would maintain a stable plasma. Amino termination was complete within 10 min under these conditions. In some cases diamond samples were intentionally protonated by immersing the samples in concentrated hydrochloric acid (36 weight%) for one minute and then drying completely in a gentle flow of pure nitrogen gas. XPS measurements of the surface chlorine yielded a N/Cl atom ratio of 2.8, with a surface Cl coverage of 6.2 atoms/ nm^2 .

2.3. Measurement of primary amino groups

We measured the density of primary amino (R-NH_2) groups via derivatization with sulfo-succinimidyl-4-O-(4,4'-dimethoxytrityl)-butyrate (sulfo-SDTB); we refer to this method of analysis as the “SDTB method” [23,24]. Samples of interest were immersed in a 0.1 mM solution of sulfo-SDTB in 50 mM NaHCO_3 at pH 8.5 for 30 min. Under these conditions, the *N*-hydroxysulfosuccinimidyl ester reacts with the surface

amino groups to form an amide bond linking the dimethoxytrityl group to the surface. After rinsing with deionized water, a 20 μL droplet of 4.1 M trifluoroacetic acid was dripped onto the sample to release the light-absorbing dimethoxytrityl (DMT) groups into solution. The concentration of released DMT groups was determined by measuring the optical absorbance at 498 nm in a semimicro cuvette, and comparing with primary amine standards of known concentration.

2.4. X-ray and ultraviolet photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) data were obtained using a custom-built ultrahigh vacuum ($P < 6 \times 10^{-10}$ Torr) Physical Electronics system equipped with an aluminum $\text{K}\alpha$ source, a quartz-crystal X-ray monochromator, and a 16-channel detector array. XPS measurements were performed using a pass energy of 58.7 eV (resolution = 0.88 eV). Quantitative measurement of nitrogen and chlorine were determined by curve-fitting and measuring the areas of the appropriate peaks. Since the N and Cl layers are monolayer or sub-monolayer coverage, there is negligible scattering within the adsorbed surface layer. In this case, the number density can be obtained using the equation [25]:

$$N_X = -\rho_C \cdot \lambda_C \cdot \left(\frac{S_C}{S_X}\right) \left(\frac{A_X}{A_C}\right) \cos(\theta).$$

where ρ_C is the number density of carbon atoms in diamond ($= 1.76 \times 10^{23}$ atoms cm^{-3}), λ_C is the inelastic mean free path of ~ 1200 eV electrons in diamond (2.0 nm [26]), S_C and S_X are the instrument-specific sensitivity factors for C and other elements of interest ($S_C = 0.296$, $S_N = 0.477$, and $S_O = 0.711$ [27]), A_X and A_C are the measured integrated peak areas corresponding to element “X” and of C in the bulk diamond, respectively, and θ is the angle of emission of the detected electrons measured with respect to the surface normal (here, 45°).

Ultraviolet photoemission spectroscopy (UPS) measurements were performed with the same apparatus, using excitation from a He(I) resonance lamp (photon energy = 21.2 eV) and an analyzer pass energy of 2.59 eV (resolution = 0.039 eV). During UPS measurements, we applied a bias of up to -9.0 V to the sample to compensate for differences in work function between sample and analyzer and to ensure that all emitted electrons would be detected by the analyzer [28]; we then subtracted the applied bias from the measured electron kinetic energies.

2.5. Transient surface photovoltage (SPV) measurements of interfacial charge separation

Transient surface photovoltage measurements [29] used a pulsed laser (NT340, EKSPLA, Inc., Vilnius, Lithuania) to produce wavelength-tunable excitation pulses (ns pulse width, 20 pulses/s, typically ~ 0.1 mJ/pulse). These pulses were directed on the face of the diamond sample. A second capacitively coupled transparent electrode (Pt mesh) was placed ~ 75 μm away. This “sense” electrode was connected directly to the input of a 2 GHz amplifier (50 Ω in put impedance, gain = 10, Model TA2000B-1, FAST ComTec GmbH, Oberhaching/München, Germany) and the output voltage was measured on a 4 GHz digital oscilloscope (Agilent Model DSO9404A).

3. Results

XPS measurements of the plasma-treated surface yielded a surface N coverage of 17.3 ± 2.0 atoms/ nm^2 . Nitrogen can form a number of different surface species that satisfy its common coordination number of 3 for neutral species. These include primary (C-NH_2) and secondary amino groups (C_2NH) with one and two bonds to the surface (where “C” represents a surface carbon atom), cyano groups, ($-\text{C}\equiv\text{N}$), and imino groups ($-\text{C}=\text{N}$ and $-\text{C}=\text{N}-\text{C}$) [21]. Of these different

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