Photochemical functionalization of diamond films using a short carbon chain acid

Chun Wang a, Nan Huang a, Hao Zhuang b, Bing Yang b, Zhaofeng Zhai a, Xin Jiang a,b,*

a Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Wenhua Road 72, 110016 Shenyang, China
b Institute of Materials Engineering, University of Siegen, Paul-Bonatz-Str. 9-11, 57076 Siegen, Germany

Abstract

Diamond is recognized as a promising semiconductor material for biological applications, because of its high chemical stability and biocompatibility. Here, we report an acid with only three carbon chain, acrylic acid (AA), for the functionalization of H-terminated diamond film via photochemical method. The successfully modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy and contact angle analyzer. Our functionalization approach was proven to be simple and facile, which shows a new potential opportunity for the photochemical modification of diamond surface with short carbon chain acid.

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1. Introduction

Diamond is a semiconductor material with outstanding electrical, thermal, optical, and mechanical properties [1]. Specifically, on the basis of its high physical and chemical stability and good biocompatibility, diamond film has become an attractive platform for biological applications [2]. However, the chemical inactivity of diamond also implies that it is difficult to directly link biomolecules onto its surface. Therefore, many efforts have been devoted to the chemical modification of diamond surface, and thus appropriate organic linker molecules for the formation of covalent bonding have been introduced on the diamond surface to immobilize the biological species. The approaches such as thermochemical [3,4], electrochemical [5,6] and photochemical [7–9] surface functionalization have been applied to successfully introduce various organic functional groups onto the diamond surface. As a mild and facile procedure, photochemical functionalization of diamond films receives intensive attention. Furthermore, it is feasible for all kinds of diamond films regardless of their conductivity. In this respect, Yang et al. [8] were the first to photochemically modify diamond films by using 10-aminodec-1-ene protected with trifluoroacetamide (TFAAD). DNA probes were subsequently attached to diamond via the linkage of the amino (–NH2) functional group.

However, –NH2 linkers are sensitive to ultraviolet (UV) light, those trifluoroacetic anhydride protection and de-protection steps would add the complexity and hazard [10]. Except for the –NH2 linker, –COOH group is another widely used chemical group for the immobilization of biomolecules in biological applications [11–13]. Generally, the incorporation of different aliphatic carboxylic acids is a requisite during the photochemical modification process [12,13]. It has been already reported that both 10-undecenoic acid (10UA) [12] and 4-pentenoic acid (4PA) [13] have been introduced onto diamond films for linking biomolecules. However, the electrical signal of DNA hybridization process obtained from the 10-UA modified diamond electrode is much weaker than that from the 4-PA functionalized one, due to the surface insulation caused by the organic layer with the long carbon chain [13], which in turn suppresses the detection sensitivity of diamond DNA biosensor. Furthermore, based on the theoretical calculation, the organic linker molecule should be as short as possible on the diamond film to achieve the highest sensor sensitivity [14]. As a result, it is important to achieve a diamond surface with short carbon chain modification for the linking the biomolecules. In our previous work [15], we have proven the feasibility of diamond DNA biosensor fabrication by functionalizing diamond surface with a short carbon molecule with –NH2 groups. Even though direct carboxylation of the diamond surface has been achieved by using UV/ozone oxidation [16], a significant damage in the diamond surface has been observed. This defect induced feature is related to a disruption of the diamond lattice, which leads to a deteriorated surface quality [17]. Acetic acid using benzoyl peroxide has also been reported for the modification of diamond surface via a radical reaction 75 °C [11].
Nevertheless, very limited reports have been reported about the mild photochemical functionalization of diamond film by the short carbon chain acid. With this purpose in mind, in this context, we primary study the photochemical modification using acrylic acid for the functionalization of H-terminated diamond. This approach has been evaluated by XPS, FTIR and contact angle measurement to confirm a successful functionalization of diamond surface.

2. Material and methods

Polycrystalline diamond films were deposited on (1 0 0) silicon at 6 kW power for 3 h with a pressure of 60 mbar by using a microwave plasma enhanced chemical vapour deposition (MPCVD, Iplas Cyranus) system. Methane (CH₄) and hydrogen (H₂) were introduced as gas sources. The gas flow rate of hydrogen was remained at 400 sccm and the flow rate of methane was 12 sccm. Scanning electron microscope (SEM) and atomic force microscope (AFM) images of the grown diamond films are shown in Fig. S1. The sizes of as deposited diamond crystals are about 1–1.5 μm and the roughness (Ra) of the film is 54.7 nm. A sharp sp² carbon peak locating on 1332 cm⁻¹ was observable on the Raman spectra also shown in Fig. S1, indicating a high quality of diamond film. Before modification, diamond films were firstly dipped into aqua regia solution (HNO₃:HCl = 1:3) to remove the impurities. The films were then oxidized in piranha solution for 30 min to remove organic contaminations. Afterwards, diamond films were washed in deionized water produced by a Millipore Milli-Q system and dried with nitrogen gas. The samples were then treated in hydrogen plasma to get hydrogen-terminated diamond surfaces. During functionalization process, a drop of acrylic acid was placed on the hydrogenated diamond film at room temperature to form a liquid layer on the surface. The sample was then placed into an eraser box with a UV lamp (λ = 254 nm, Philips). The whole modification procedure was carried out in a glove box (Unilab, Braun) in N₂ atmosphere. After modification, carboxyl-terminated diamond films were rinsed several times with 10% sodium dodecyl sulfate (SDS) and de-ionized water to remove the adsorbed acids. Acrylic acid and SDS were purchased from Sinopharm chemical reagent Co. Ltd. They were of analytical grade and used as received without further purification.

XPS (ESCALAB250, Thermo VG) was employed to analysis the surface chemical bonds using a monochromated Al Kα beam as an X-ray source. FTIR spectrum was recorded by the Bruker’s Vertex 70v analyser using attenuated total reflection (ATR) mode. H-terminated diamond film was used as reference and the baseline was calibrated to improve the clarity of the spectrum. The static contact angles of modified surfaces were characterized by a contact angle analyser (OCA15pro, Dataphysics).

3. Results and discussion

The C(1s) XPS spectra of H-terminated diamond films before and after photochemical modification are shown in Figure 1. The bulk C(1s) peak is positioned at 284.6 eV for all samples as shown in Figure 1a. The peaks with shifts about 0.7 eV (~285.3 eV) assigned to the CH₄ (x ≥ 2) groups from the carbon–hydrogen bonds on the hydrogenated diamond surface [18]. No extra carbon peaks appear on diamond films as shown in Figure 1b, indicating the chemical surface status is nearly unchanged after 20 h UV illumination. While an increase of CH₄ (x ≥ 2) peak is due to the increase of the C–H bond length after UV illumination and indicates more defects forming on the hydrogenated diamond surface [19]. Figure 1c reveals that peak with shifts around +1.9 eV (~286.5 eV) emerge after reacting with AA solution in a dark box, which are assigned to C–OH groups [13]. While two weak peaks with shifts around +3.4 eV (~288.0 eV) and around +4.6 eV (~289.2 eV) also appear on the XPS spectrum,
which are related to C=O and −COOH groups, respectively [20]. Their existence can be attributed to the weak adsorption of AA on to the diamond surface. As shown in the inset of Figure 1c, the intensities of those groups are very low. It should be noticed that after UV illumination for 20 h with AA on the diamond surface, the intensity of the C=O and −COOH peaks drastically increases, which indicates the successful attachment of C=O and −COOH functional groups on the diamond surface by AA.

Accordingly, the O(1s) XPS spectra of samples with different modification strategies are shown in Figure 2. A weak peak locating at 532.8 eV shown in Figure 2a may be attributed to little physical adsorbed oxygen when the freshly deposited diamond film exposed to air. After UV illumination shown in Figure 2b, no more other peaks appear. The intensity of the adsorbed oxygen peak increases which is possible due to the oxygen-related defective components have been formed by UV illumination [16]. After reacting with AA solution in a dark box, the intensity of oxygen slightly increases. Moreover, an additional peak locating at 531.3 eV presents, which is related to C=O groups due to the adsorption of AA [21]. Noted, the intensity of this peak drastically increases after UV illumination with AA for 20 h, as shown in Figure 2d, which confirms the presence of a large amount of C=O group. Those results are in good accordance with the variation trends of the ratio of O(1s)/C(1s) shown in Table S1. For the H-terminated diamond, the ratio is 0.009. After UV illumination with AA, the ratio obviously increases to 0.246.

The FTIR spectrum of photochemical modified diamond film after UV illumination after 20 h with AA is shown in Figure 3. The absorbance peak at 1713 cm\(^{-1}\) is related to stretching vibration of C=O, showing the presence of carboxylic acids [22]. The peaks at 2852 cm\(^{-1}\) and 2921 cm\(^{-1}\) are ascribable to symmetric and asymmetric stretching vibrations of −CH\(_2\) [22]. Peaks in the region of 1000–1500 cm\(^{-1}\) are related to −CH or −CH\(_2\) groups [23]. The existence of hydrocarbon bonds proves the absence of unreacted AA molecules on the hydrogen terminated diamond surface after modification.

The contact angles of samples after different treatments are shown in Figure 4. The contact angle of H-terminated diamond is 97.5 ± 0.6°, showing the surface is hydrophobic, which is similar to the previous work [24]. After UV illumination, the contact angle slightly decreases and the surface is still hydrophobic. Noted, after exposed to AA solution without UV illumination, the contact angle of diamond film decreases to 72.1 ± 2.3° and the surface became slightly hydrophilic. After UV illumination with AA solution, the contact angle of the film continues to quickly decrease to 25.6 ± 2.6°. The increase in the hydrophilicity is due to the higher density of hydrophilic −COOH related groups on the diamond surface, which is revealed by XPS and FTIR spectra on the surface. Such a value is even similar to the result of that with direct carboxylation ~23° [16], confirming the successful functionalization of the

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**Figure 2.** O(1s) XPS spectra of diamond surfaces: (a) with H-terminated; (b) after UV illumination for 20 h; (c) after treated with AA in the darkness for 20 h; (d) after UV illumination with AA for 20 h.

**Figure 3.** FTIR absorbance spectra of diamond surfaces after UV illumination with AA for 20 h.

**Figure 4.** (a) The contact angle of diamond surfaces: with H-terminated (H – D); after UV illumination without AA for 20 h (H – D + UV); after treated with AA in the darkness for 20 h (H – D + AA); after UV illumination with AA for 20 h (H – D + UV/AA). (b) The contact angle of diamond surface after different UV illumination time with AA.
diamond surface with the —COOH group by short carbon acrylic acid.

The contact angles of diamond films with different UV illumination time were also recorded. As shown in Figure 4b, the contact angle initially continuously decreases with increasing UV illumination time, indicating the increased coverage of AA on the surface. After 5 h UV illumination, the decrease of contact angle slowed down and the minimum contact angle $\sim 25.6 \pm 2.6^\circ$ is obtained after 20 h indicating the full coverage of AA on the surface. In the biological systems, the adsorption of specific biomolecules can be promoted by tuning the wettability of surface [24] and thus the improved hydrophilicity of the functionalized diamond in this work could be beneficial for the biological application.

4. Conclusions

In summary, we successfully modified the polycrystalline diamond film with a short carbon chain molecule-acrylic acid via photochemical method. The appearance of C=O and —COOH groups in C(1s) and O(1s) XPS spectra shows the successful carboxylation. This is also proven by the FTIR measurement. The diamond film became hydrophilic after photochemical modification. On the basis of our results, photochemical route with acrylic acid provides a promising opportunity to subsequently fabricate diamond DNA biosensors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2016.01.024.

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