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Title	Patterning of Alkylamine Molecules on Highly Oriented Pyrolytic Graphite Surfaces via Deep UV Light Irradiation
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Patterning of alkylamine molecules on HOPG surfaces via deep UV light irradiation

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A method for the removal of alkylamine groups and patterning of alkylamine monolayer on carbon surfaces is proposed. Deep UV light irradiation (172 nm) was used to remove alkylamine monolayers on carbon surfaces. When a photo mask was employed, patterned alkylamine monolayers were obtained. Labeling of COOH- and NH_2-terminated alkylamine monolayers on carbon surfaces with redox probes and fluorescent-dyes respectively via amide coupling clearly indicated that deep UV light patterning was successfully achieved.

Methods for the self-assembled monolayer's patterning on various substrates, such as metals, metal oxides, and silicon that rely on lithography, scanning probe-based lithography, biological reactions, energetic beams, and ozone oxidation,[1-12] have been proposed. These methods have significantly contributed to the advancement of nanotechnology. For example, Zschieschang et al. demonstrated the preparation of integrated circuits via stamping methods using tetradecylphosphonic acid and pentadecylfluoro-octadecylphosphonic acid.[13]

In a previous study, the construction method of the condensed alkylamine monolayer on carbon surface was reported. Here, we propose the removal method of the alkylamine monolayer from carbon surface via deep UV light irradiation. We think that the research of surface modification needs not only coating technique but also the removal.

First, NH_2- (1,11-diaminoundecane) and COOH- (11-aminoundecanoic acid) terminated alkylamine monolayers were prepared via electrochemical oxidation in a three-electrode cell. A highly oriented pyrolytic graphite (HOPG) electrode, platinized platinum, and Ag/AgCl (saturated KCl) were used as the working electrode, auxiliary electrode, and reference electrode, respectively, for each reaction. During the electrochemical immobilization process, the potential was swept from +1.0 to +1.6 V at a rate of 0.01 V s^{-1} and held at +1.6 V for 60 min. As a result, two types of HOPG electrodes with different alkylamine monolayers on the HOPG surfaces were obtained. Next to remove the alkylamine monolayers, deep UV irradiation (172 nm, 20 mW·cm^{-2}) was applied to the surface for 120 min. The distance from the light source to the electrodes was approximately 3 mm. It is thought that C-N covalently bonds were cleaved upon exposure to the deep UV irradiation.

Figure 1 shows the cyclic voltammograms of alkylamine monolayer modified HOPG electrode before and after the deep UV light irradiation in 200 μM $K_4[Fe(CN)_6]$ + 0.1 M KCl solution. The alkylamine monolayer-modified HOPG samples did not exhibit ferrocyanide redox behavior. However, the deep UV light irradiated HOPG electrodes exhibited the same redox behavior as the untreated HOPG. Modification of the HOPG with an alkylamine monolayer followed by removal of the monolayer via deep UV irradiation was then repeated more than 10 times. The averaged capacitance of the irradiated HOPG electrode was 253.0 ± 40.6 μC·cm^{-2}. Thus, the deep UV light irradiation completely removed CH_3-, OH-, NH_2-, and COOH-terminated alkylamine monolayer from the HOPG electrode, and the surface was returned to its initial condition.

Based on this result, it was thought that patterned alkylamine monolayer-modified HOPG electrodes could be prepared via deep-UV light irradiation using photo masks. To characterize the patterned alkylamine monolayers on the HOPG surfaces, the functional groups of the monolayers were labeled with a fluorescent dye (pyrene butyric acid for the NH_2-terminated monolayer) or an electrochemical redox probe (aminoferrocene for the COOH-terminated monolayer). Both labels were covalently immobilized via amide coupling, as shown in Scheme 1.

Figure 2-inset shows a photograph of the pyrene-labeled, NH_2-terminated alkylamine and OH-terminated alkylamine monolayer-modified HOPG electrode under ultraviolet (UV) light (254 nm). In the pyrene-labeled NH_2-terminated alkylamine (pyrene-terminated alkylamine masking) area, the fluorescent emission of pyrene butyric acid was observed; however, in the OH-terminated alkylamine (irradiated, star-shaped) area no fluorescent emission was observed. This result clearly indicated that the pyrene butyric acid was selectively immobilized on the NH_2-terminated alkylamine monolayer on the HOPG surface, while the OH-terminated alkylamine monolayer did not react with the pyrene, although it was susceptible to agglomeration. Hence it was concluded that the patterning of alkylamine monolayers on HOPG electrodes could be achieved via deep UV light irradiation.

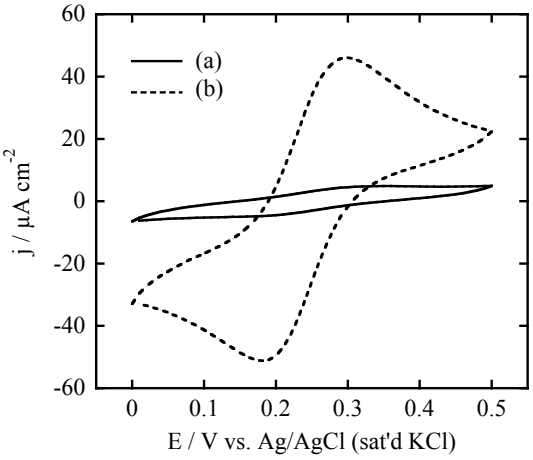
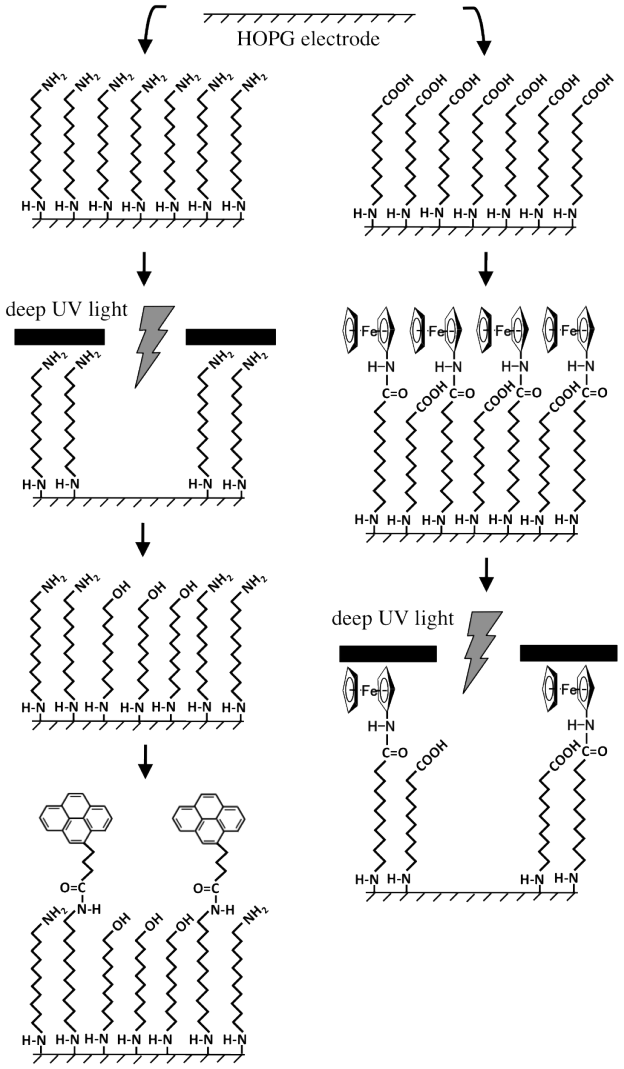


Figure 1. Cyclic voltammograms of COOH-terminated alkylamine modified HOPG electrode (a) before and (b) after the deep UV light irradiation in 200 μM $K_4[Fe(CN)_6]$ + 0.1 M KCl solution at the sweep rate of 0.02 V s^{-1}.



Scheme 1. Procedure for the preparation of hybrid functional group-terminated alkylamine-modified HOPG electrodes. Left side: pyrene-labeled NH_2-terminated alkylamine monolayer and OH-terminated alkylamine monolayer; right side: ferrocene-labeled COOH-terminated alkylamine monolayer and unmodified.

Figure 2 shows the reflected UV–Vis absorption spectra of the pyrene-labeled, NH_2-terminated alkylamine monolayer and OH-terminated alkylamine monolayer. The reflected UV–Vis absorption spectra were obtained via optical waveguide spectroscopy (SSPR-6000, System Instruments Co., Japan). The difference spectrum for these two monolayers was the same as that for pyrene, and includes peak near 511 nm. The peak in the fluorescent emission spectrum of pyrene has been previously reported to appear at 490 nm. However, this peak position is affected by the solvent, temperature, side structures, functional groups, and molecular interactions such as van der Walls forces and hydrogen bonds.[15-17] Therefore, the shift in the peak for pyrene suggested that the pyrene molecules on the HOPG surface formed a stacked structure, because pyrene is known to agglomerate via intermolecular forces, such as van der Walls forces and π–π stacking. The maximum fluorescent emission wavelength reported for pyrene monomer is 375 nm, and this value was shifted to 475 nm upon the formation of pyrene dimer.[18-19] Therefore, it is reasonable to consider that a stacked pyrene structure was formed on the HOPG surface. Hence, the fluorescent emission peak was observed at a long wavelength, and the fluorescent emission of pyrene was easily visible to the naked eye. Moreover, the OH groups of the monolayer served to prevent nonspecific adsorption, which was thus effectively avoided.

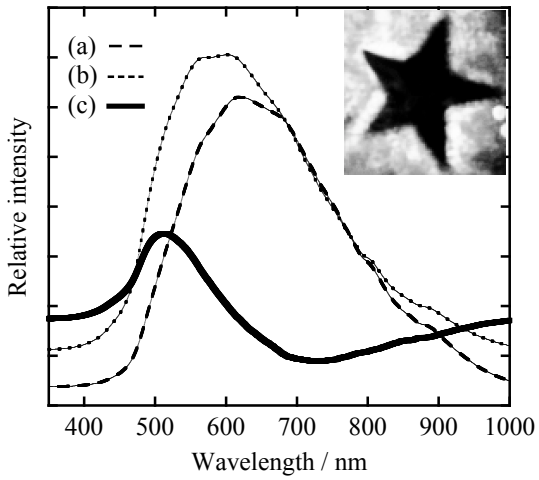


Figure 2. Reflected UV–Vis absorption spectra of the (a) OH-terminated alkylamine monolayer and (b) pyrene-labeled, NH_2-terminated alkylamine monolayer on a HOPG surface. (c) Reflected UV–Vis absorption difference spectrum of (a) and (b). An adapted incandescent light was used as the irradiation source. Inset is the photograph of the pyrene-labeled, NH_2-terminated alkylamine monolayer (bright areas) and OH-terminated alkylamine monolayer (dark areas) on a HOPG surface. The image was taken under ultraviolet light at a wavelength of 254 nm.

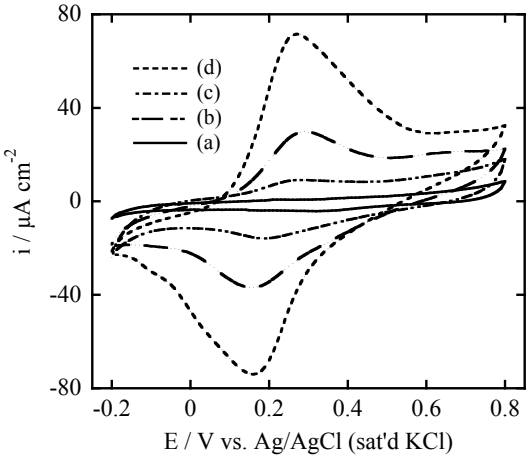


Figure 3. Cyclic voltammograms of the ferrocene- labeled, COOH-terminated alkylamine monolayer on the HOPG surface in 0.1 M $HClO_4$ at the sweep rate of 0.1 V s^{-1}. The coverages of ferrocene were (a) 0 %, (b) 33 %, (c) 67 %, and (d) 100 %, respectively.

Figure 3 shows the cyclic voltammograms of the ferrocene-labeled, COOH-terminated alkylamine monolayer on HOPG electrode in 0.1 M $HClO_4$ solution. The ferrocene coverage was controlled by the area of deep UV light exposure. The oxidation charge density of ferrocene was decreased with decreasing of ferrocene coverage. However, the charge density was not linearly related to the surface coverage, because the double layer charging current significantly affected on the estimation of the charge density. But, it was noticed that the total capacitance was linearly proportioned to the ferrocene coverage. Thus, it can be concluded that the electric double layer capacitance of a carbon electrode can be adjusted via patterning of an alkylamine monolayer using deep UV light irradiation.

These results for the NH_2- and COOH-terminated alkylamine monolayer-modified HOPG electrodes led to the conclusion that alkylamine monolayers on HOPG electrodes can be selectively removed using deep UV light irradiation. Furthermore the fluorescent dye pyrene and redox label ferrocene were shown to react with the appropriate type of alkylamine monolayer on a carbon surface. Therefore, as with self-assembled monolayers on gold and silicon, these methods for the patterning of monolayers on carbon should be very useful. Specifically, unlike gold and silicon, carbon has low reflectivity and does not undergo quenching. Thus, it is expected that alkylamine monolayer-modified carbon surfaces can be used in highly sensitive fluorescence applications, such as DNA and enzyme probes.

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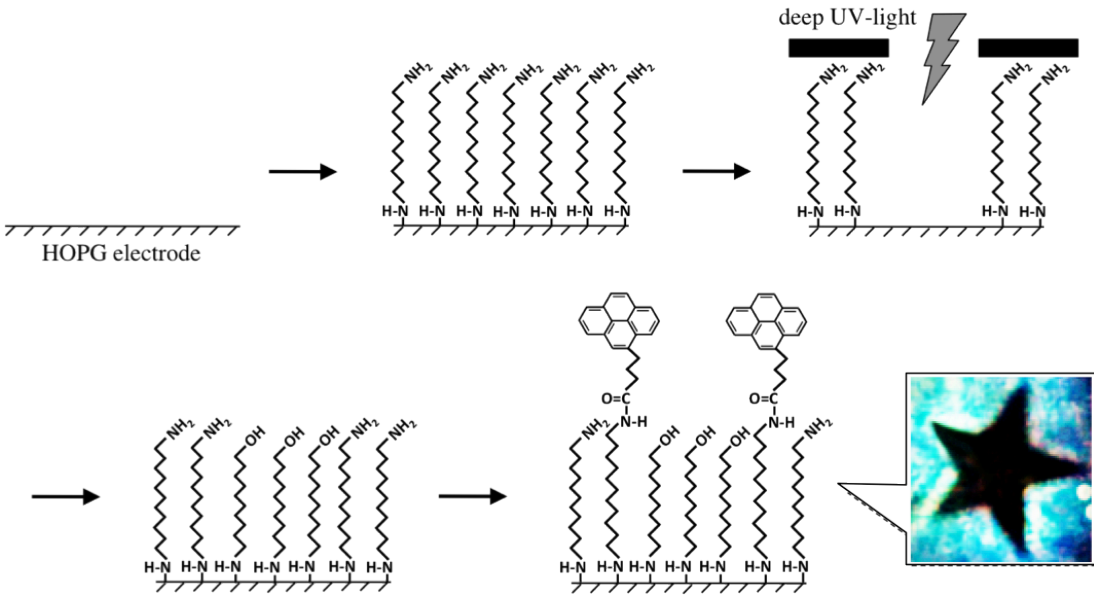
Graphical Abstract

Textual Information

A brief abstract (required)	Deep UV light irradiation (172 nm) removed alkylamine molecules covalently immobilized on carbon surfaces. In addition, deep UV-patterned monolayers with NH_2- and COOH-terminated alkylamine groups were fabricated. Fluorescence and electrochemical redox probe labeling of the respective patterned monolayers was also demonstrated, confriming that deep UV patterning was successfully achieved.
Title(required)	Pattering of alkylamine molecules on HOPG surfaces via deep UV light irradiation
Authors' Names(required)	Yusuke Sato, Toshikazu Kawaguchi

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