

## Electrochemical Behavior of Hydrogen-Bonded Bilayers of Azobenzene Langmuir-Blodgett Film and Self-Assembled Monolayer on Gold

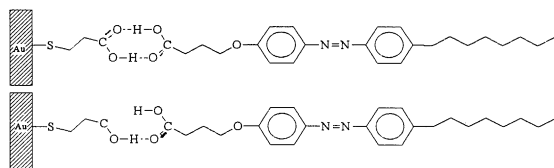
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Langmuir-Blodgett (LB) monolayer of  $C_8H_{17}-C_6H_4-N=N-C_6H_4-O-(CH_2)_3-COOH$  (referred as ABD) was deposited on  $X-(CH_2)_2-SH$  self-assembled monolayer (SAM) modified gold electrode ( $X=COOH, OH$ ), and hydrogen bond was created at the SAM-LB interface as evidenced by FTIR results. Electrochemical studies demonstrated that, different hydrogen bonding structures give different stabilities and redox behaviors.

Molecular assembling technique has attracted much attention recently as an effective method to design electrode surfaces with well-defined composition, structure and thickness for interfacial electrochemical studies.<sup>1-7</sup> We have paid particular and continuous interests on the electrochemistry of azobenzene functional group in highly-organized monolayer assemblies involving self-assembled monolayers (SAMs) and Langmuir-Blodgett (LB) films.<sup>3-7</sup> In our previous paper,<sup>4</sup> we designed a coulombic barrier,  $-NH_3^+OOC-$ , between the underlying electrode and the azobenzene redox centers by combining the SAM and LB techniques together: modifying the gold electrode first by the SAM of  $NH_2-(CH_2)_2-SH$  and then depositing the LB monolayer of  $C_8H_{17}-C_6H_4-N=N-C_6H_4-O-(CH_2)_3-COOH$  (ABD) on it, and investigated the electrochemical behavior of azobenzene groups in such SAM-LB composite films. It shows that, the  $-NH_3^+OOC-$  coulombic interaction at the SAM-LB interface has effectively stabilized the ordered film structure, which exhibited stable and repetitive electrochemical behavior analogous to that of pure ABD LB films.<sup>6</sup> In this work, we use the same strategy to design two different hydrogen bonding SAM-LB interfaces by using  $X-(CH_2)_2-SH$  self-assembled monolayers ( $X=COOH, OH$ ), and examine how they affect the electrochemical reactions of the attached azobenzene group. For convenience of description, thus fabricated interfaces are shortly represented as  $Au/COOH-HOOC$  and  $Au/OH-HOOC$  in the following.



Scheme 1.

The SAM and LB films were deposited on gold electrode using the same procedure as described in our previous paper.<sup>4</sup> Electrochemical experiments were carried out in a three-electrode cell, and  $Ag/AgCl$  and  $Pt$  wire were used as the reference and counter electrodes, respectively. The cis isomer of ABD was produced by 1-2 min UV irradiation of the electrochemically inactive trans-form ABD film.<sup>4,6</sup> The electrolyte solution was 0.1 mol/L  $KClO_4$  buffered by Britton-

Robinson method, with the ionic strength being kept constant.

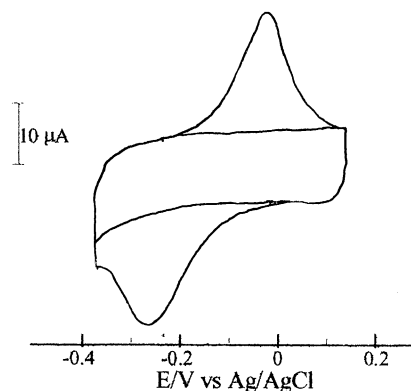


Figure 1. Cyclic voltammogram of  $Au/COOH-COOH$  electrode, obtained after 1 min UV irradiation and in Britton-Robinson Buffer solution, pH 6.0, scan rate 200 mV/sec.

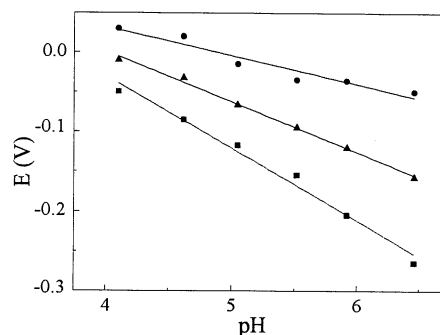
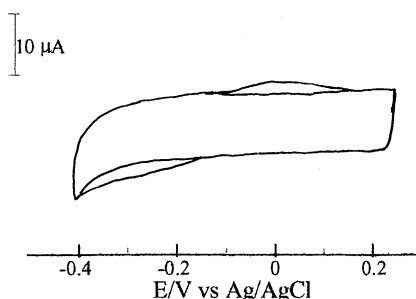


Figure 2. Linear dependences of anodic peak potential  $E_{p,a}$  (●), cathodic peak potential  $E_{p,c}$  (■), and midpoint potential  $E_{a,c}$  ( $E_{a,c} = (E_{p,a} + E_{p,c})/2$ ) (▲) on the solution pH value.

RA-FTIR studies have confirmed that hydrogen bonding is created at the SAM-LB interface for both of composite films.<sup>5</sup> For  $Au/COOH-HOOC$  system, the hydrogen-bonded  $-COOH$  band is clearly observed at  $1713cm^{-1}$ , while no spectral evidence was obtained for the presence of free  $-COOH$  and of  $-COO^-$ , suggesting that the hydrogen bonding dimer is the predominating structure at this SAM/LB interface. In the case of  $Au/OH-HOOC$  system, two peaks at  $1707cm^{-1}$  and  $1729cm^{-1}$  were clearly observed, which can be attributed to a *face to face* hydrogen bonding between the surface  $-OH$  and the  $HOOC-$  of ABD LB film and a lateral hydrogen bonding created between adjacent ABD molecules, respectively. Scheme 1 exhibits the schematic of the hydrogen bonding structures formed at two different SAM-LB interfaces. Figure 1 shows the cyclic voltammogram (CV) of  $Au/COOH-COOH$  system, obtained

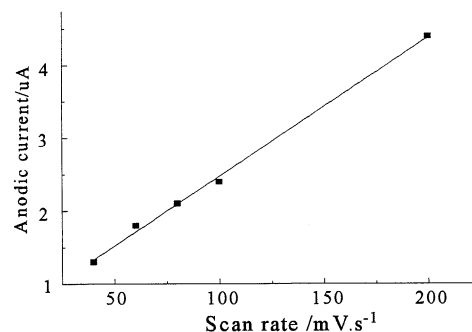
after 1 min UV irradiation. Two coupled redox peaks were clearly observed, which had considerably large peak-to-peak separation and were very stable and excellently reproducible within several tens repetition of potential scans. The observed electrochemical responses were, respectively, attributed to the reduction and re-oxidation of the immobilized cis-form azobenzene group.<sup>3-7</sup> These observations indicate that the hydrogen bonding formed at the SAM-LB interface has greatly stabilized the ABD LB film, and also allowed the electron transport across it, very similar to the case of Au/NH<sub>3</sub><sup>+</sup>OOC system.<sup>4</sup> Within the pH range of 4.1 to 6.5, linear relationships between anodic peak potential  $E_{p,a}$ , cathodic peak potential  $E_{p,c}$ , midpoint potential  $E_{a,c}$  ( $E_{a,c} = (E_{p,a} + E_{p,c}) / 2$ ) and the solution pH value were observed as shown in Figure 2, suggesting that at least the interfacial hydrogen bond is stable in this pH region. The slope  $dE_{a,c}/dpH$  was calculated as -63mV, close to the theoretical value, -60 mV/pH unit for a 2e-, 2H+ process.<sup>8,9</sup> At higher pH, the CV behavior became instable and less reproducible. This can be attributed to the cleavage of hydrogen bond at the SAM-LB interface due to the deprotonation of -COOH to -COO<sup>-</sup>.



**Figure 3.** Cyclic voltammogram of Au/OH-COOH electrode, obtained after 1 min UV irradiation and in Britton-Robinson Buffer solution, pH 6.0, scan rate 200 mV/sec.

Figure 3 demonstrates the cyclic voltammogram of Au/OH-HOOC system, measured after 1 min UV illumination. Still, two clear redox peaks were observed but they were very small compared with the Au/COOH-COOH and also Au/NH<sub>3</sub><sup>+</sup>OOC<sup>4</sup> cases. The peak current ( $I_{p,a}$  or  $I_{p,c}$ ) was found to be proportional to the scan rate of potential as expected for a surface reaction<sup>8</sup> (see, Figure 4). These observations suggest that similar reduction and re-oxidation reactions of the electroactive azobenzene groups have occurred in the Au/OH-HOOC composite film. Since the transfer ratio of ABD LB monolayer from air/water interface to the SAM-modified Au substrate was 0.9-1.1, being the same as the Au/COOH-HOOC and Au/NH<sub>3</sub><sup>+</sup>OOC<sup>4</sup> cases, we believe that the distinctly small peak, which is equivalent to the electrochemically reacted ABD molecules, was a result of desorption of ABD monolayer from the electrode surface, occurred after the electrode was immersed in aqueous electrolyte solution. This instability is obviously coming from the SAM-LB interfacial bonding feature (see, Scheme 1). Although one hydrogen bond is created between OH and HOOC at SAM-LB interface, the inter-molecular matching

between SAM and LB layers was not as well as the cases of Au/COOH-HOOC and Au/NH<sub>3</sub><sup>+</sup>OOC<sup>4</sup>. FTIR data suggests that some ABD molecules at the LB monolayer also formed *shoulder-by-shoulder* hydrogen bond with each other in Au/OH-HOOC system.<sup>5</sup> Actually the instability of Au/OH-COOH system was even observed in air as indicated by our previous atomic force microscopy (AFM) data, in which aggregation of ABD molecules on OH terminated gold surface was clearly seen.<sup>5</sup>



**Figure 4.** Variation of the anodic peak current in Au/OH-HOOC system as a function of potential scan rate (pH 6.0).

In summary, we have designed two types of SAM-LB composite films in which hydrogen bonded structures have been created at the SAM-LB interface. Both films exhibited clear electrochemical reactivity attributable to the red-oxidation of the attached azobenzene groups. Our studies demonstrate that, a suitable molecular level design of the electrode surface can effectively improve the stability of LB films on it, making various electrochemical investigation possible.

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