Effect of Hydrogen Bonding on the Stability of Thiol Self-Assembled Monolayers (SAMs) on Gold

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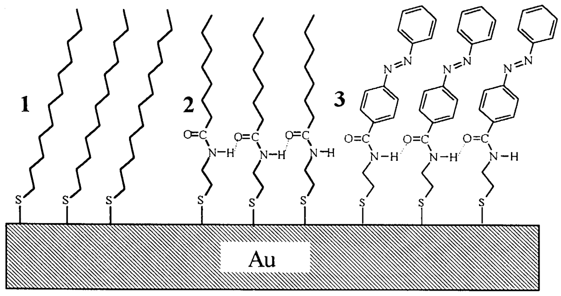
The electrochemical stability of SAMs prepared from dodecanethiol (**1**), (N-2'-mercaptoethyl)-amino)octaneamide (**2**) and ((N-(2'-mercaptoethyl)-amino)carbonyl)azobenzene (**3**) in ethanol was studied. The results reveal that introducing hydrogen bonds into SAMs could effectively increase their stability in electrical environment. The presence of large rigid aromatic group in the film may, however, cause a decrease of stability.

Researches on ordered, tightly packed and well-defined self-assembled thiol monolayers (SAMs) adsorbed on gold surfaces have gained much attention in the recent years,[1,2] and systematic understanding of the relationship between the structure and stability would provide a general guideline for designing new SAMs that are stable enough for various applications.

In order to reveal the relationship between molecular structure and stability, we have selected compound **1**, **2** and **3** as probe molecules in this work. The compound **1** was used as a reference. The other two molecules were designed and synthesized in our laboratory. The three molecules, although having similar length, are quite different in structure, so investigation and comparison among the SAMs from them could help us to understand the influence of structure on stability.



Scheme1. The hypothetical model of the three SAMs studied in this work. Interchain hydrogen bonds formed among the amide groups in film of **2** and **3** are shown as dash line.

The compound **1** was purchased from Qingpu Reagent Company (P. R. China.). The other two compounds **2** and **3** were synthesized as reported method[3]. The gold-coated glass slide was prepared, cleaned and modified by SAM as our earlier work[3].

Electrochemical experiments were performed on a Bioanalytical Analyzer, BAS100B (U.S.A). The working electrode was a thiol modified slide, the counter and the reference electrode were a Pt wire and an Ag / AgCl (3 M KCl, BAS.), respectively. N_2 was purged into solution for 20 min to remove dissolved O_2 before measurement.

In order to eliminate the influence of the solvent, no organic solvent besides fresh absolute ethanol was used in this work. In experiments, the modified electrode was conditioned in 0.1 M $(C_4H_9)_4NClO_4$ / ethanol solution for bulk electrolysis at various potentials for different times, rinsed with ethanol and then analyzed for the remaining monolayer coverage. The coverage (Γ) of **1** and **2** monolayers was determined from the reductive desorption peak of thiols observed by scanning at 0.5 V s^{-1} from 0 to -1.5 V in 0.5 M KOH aqueous solution. The slides modified with **3** were potentially scanned from -0.6 V to 0.6 V in 0.1 M KCl(pH 5.7, phosphate buffered). Then the coverage was directly obtained from the electrochemical redox peak of azobenzene moiety, assuming a two-electron and two-proton reaction mechanism.[3] The average surface concentration before electrolysis (Γ^0) of the compounds **1**, **2** and **3** were found to be 8.9×10^{-10} mol cm^{-2}, 9.1×10^{-10} mol cm^{-2} and 4.2×10^{-10} mol cm^{-2} respectively. In order to make a comparison among the three SAMs, the surface molecular coverage Γ obtained from our measurements were converted to θ, as $\theta = \Gamma / \Gamma^0$. Therefore, the θ corresponds to the fraction of the SAMs remaining on the gold surface.

Figure 1 shows that the plots of θ of SAMs from 1, 2 and 3 vs. potential have similar shape and the curve of 2 is highest. Figure 2 shows that **2** lost much slowly from the surface, comparing with the others at 800 mV. Similar result was obtained at -1800 mV. All of the above mentioned

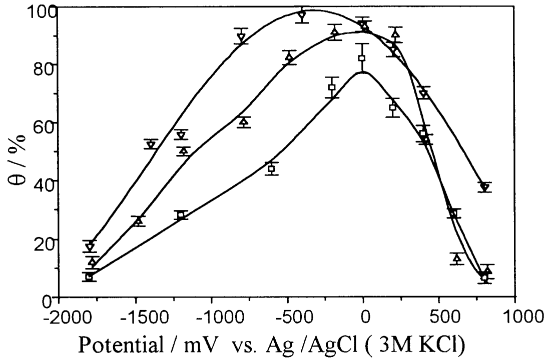


Figure 1. The potential-dependent stability of three SAMs. □, SAM from **1** after electrolysis for 10 min; ∇, SAM from **2** after electrolysis for 20 min; Δ, SAM from **3** after electrolysis for 10 min.

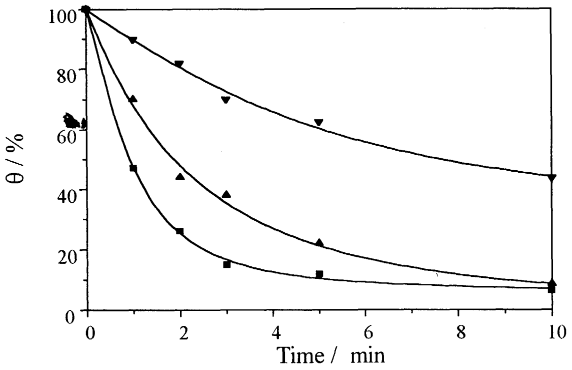


Figure 2. Time-dependent stability of SAMs from **1**(■), **2**(▼) and **3**(▲) at +800 mV.

results suggest that SAM of **2** is of the highest stability and the SAM of **1** is of the lest.

Electrochemical stability is a complicated issue to be fully understood. Until now, the mechanism of the potential-dependent stability of SAMs is not clear. We believe that the differences in stability among the three SAMs in this work can mostly be attributed to the different intermolecular interactions in monolayers. In the monolayer of **1**, only van der Waals attraction between the hydrocarbon chains exists. Comparing with **1**, **2** provide an additional hydrogen bonding effect among the amide moiety. In the SAM of **3**, both hydrogen bonding among amide groups and aromatic interaction among azobenzene chromorphoes could occur, but very little van der Waals attraction among alkyl chain exists. Whitesides[4] found that the internal hydrogen bonding could stabilize SAMs in vacuum. The behavior of SAMs from **2** observed in our experiment gives similar results that, with presence of the intermolecular hydrogen bond, the stability of SAMs against electrolysis in organic solvent is efficiently increased. The network of hydrogen bond forming in monolayers also cause effectively cross linking of molecules in the film. We believe the reason of intermolecular hydrogen bonding stabilizing the SAMs is similar to that of polymerization.

The behavior of SAM from **3** is somehow complicated to be realized. Some previous works[5,6] have indicated that molecules with large rigid group, due to their large cross sectional area, usually cause highly tilt and may introduce some disorder and the quality of the monolayers was dependent on the length of the aliphatic chain. So it is reasonable to propose that the film from **3** is not as highly ordered as the other two because of lacking enough length of aliphatic chain. Furthermore, both the high tilt angle and less order of molecules in the SAM would obviously disturb the hydrogen bond network in monolayer. We believe this is the reason why SAM from **3** is not as stable as we expected.

In summary, we provide the evidence that the intermolecular hydrogen bonding will improve the electrochemical stability of SAMs in organic solvent for the first time. Furthermore, instead the alkyl chain with a large rigid group, such as azobenzene group, was found to cause a decrease in stability. These results should be important in designing a new SAM.

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