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Carbamate-Based Surface Reactions for Release of Amine Molecules from Electroactive Self-Assembled Monolayers

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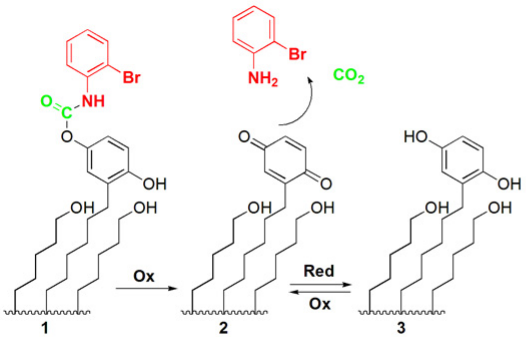
In this work, we developed self-assembled monolayers (SAMs) of alkanethiols on gold that can release amine groups, when an electrical potential was applied to the gold. The strategy was based on the introduction of the electroactive carbamate group, which underwent the two-electron oxidation with simultaneous release of the amine molecules, to alkanethiols. The synthesis of the designed thiol compounds was achieved by coupling isocyanate-containing compound with hydroquinone. The electroactive thiols were mixed with hydroxyl-containing alkanethiol [$HS(CH_2)_{11}OH$] to form mixed monolayers, and cyclic votammetry was used for the characterization of the release. The mixed SAMs showed a first oxidation peak at +540 mV (versus Ag/AgCl reference electrode), demonstrating irreversible conversion from carbamate to hydroqinone with simultaneous release of the amine groups. The second and third cycles showed typical reversible redox reaction of hydroquinone and quione: the oxidation and reduction occurred at +290 mV and -110 mV, respectively. The measurement of ToF-SIMS further indicates that electrochemical-assisted chemical reaction successfully released amine groups. This new SAM-based electrochemistry would be applicable for direct release of biologically active molecules that contain amine groups.

Keywords: Electroactive Self-Assembled Monolayers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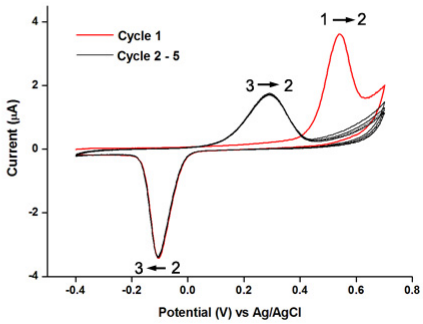
Cycle 1
Cycle 2 - 5
1 → 2
3 → 2
3 ← 2
Current (μA)
Potential (V) vs Ag/AgCl
4
2
0
-2
-4
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8