Redox Potentials of Surface-bonded Viologen (2+/+) at Gold Electrode Surfaces

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Recently it has been reported that noticeable shifts in redox potential for redox-active molecule immobilized at gold electrode surfaces *via* sulfur bridge were observed by varying the nature of coadsorbate alkanthiols[1] and aggergates[2] of long-chain alcohols. The rationalization of the results was then made by a physical model whereby the shift in redox potential can be interpreted in the context of a classical solvent effects[3]. The redox component used was ferrocene, a widely used reagent in redox reaction, with one alkyl chain. The other versatile redox component of interest would be viologen. Viologens were often the choice of redox reagent but the change in the redox potential of viologen component has been neglected as the microenvionment surrounding viologen is varied[4]. In this work we describe preliminary results of another example that change in the redox potential of the redox site, viologen (2+/+), immobilized at gold electrode surfaces *via* sulfur bridge could be observed by varying the alkyl chain length of coadsorbate thiols.

The viologen probe used in this first investigation was N-(n-undecyl)-N′-(10-mercaptodecyl)-4,4′-bipyridinium(C_{11}-$VC_{10}SH$). The synthetic precedures were similar to those of Buttry for N-(n-decyl)-N′-(10-mercaptodecyl)-4,4′-bipyridinium[5]. Due to the handling procedures followed, the product may contain a mixture of thiols and disulfides. Both of these are, however, known to chemisorb epitaxially on the gold substrate[6]. All the electrochemical instrumentations were conventional[4]. Solutions were prepared from laboratory distilled water that was passed through a purification train (Millipore Milli-Q water system). All of the electrochemical experiments were performed under a purified nitrogen atmosphere. Polycrystalline gold electrodes were polished successively with 3 μm and 0.05 μm alumina-water slurries, washed with copious amounts of water and sonicated before being activated with isopropanol. Surface-bonded monolayers were formed by soaking for two days the activated gold electrodes in a coating solution containing the viologen thiol and a nonsubstituted *n*-alkanethiol (mole fraction of viologen<0.5) in ethanol. The coated electrodes were removed from the sample solutions, washed with ethanol and water, and transfered to an electrochemical cell for voltammetric experiments. The surface coverage of the viologen was maintained at 2×10^{11} mole/cm^2 (0.04 monolayer) or less to ensure that the voltammogram in each case represents the reactivity of isolated viologen sites[1].

Figure 1 represents typical cyclic voltammograms with viologen-containing surface-bonded monolayers of *n*-nonanethiol and *n*-hexadecanethiol at gold electrode surfaces. The electrode potential was scanned to investgate the first (2+/+) redox process only. No change in voltammogram was observed upon repeated cycling, demonstrating that the monolayers were stable to electrochemical cycling. The shape of each voltammogram did not change with scan rate and the peak current scaled with scan rate as expected for surface-confined redox species[7]. The redox potential of viologen is shifted to positive direction with the longer alkyl chain of the monolayer. The shift is thermodynamic in nature because both anodic and cathodic peak potentials shift together. The shift in redox potential may be interpreted, as was the case with the ferrocene/ferricenium system[1-3], to be due to a more alkane-like environment around the redox site; this environment would destabilize viologen dication to a greater extent than it would viologen monocation radical. Further experiments were performed with the chemisorbed monolayers of *n*-pentanethiol, *n*-dodecanethiol and *n*-octadecanethiol to closely see the variation in the redox potential of viologen with local environment changes. The results are summarized in Table 1. The change in redox potential observed was in the range of 100 mV. The observed shifts in redox potential for immobilized viologen(2+/+) can be understood by using the Born's equation for ion solvation in a dielectric medium[3,8]. Because the dielectric constant of alkane environment (<10) is smaller than that of water (78)[9], it can be readily rationalized that the redox potential would shift to positive direction in going from water to alkane environment. Quantitative calculation of the shift in redox potential should, however,

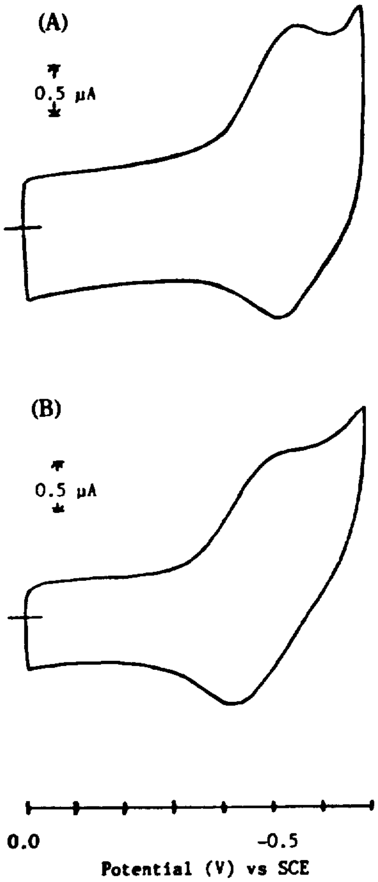
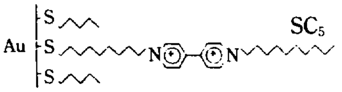
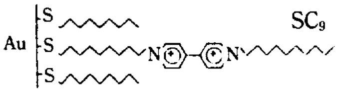
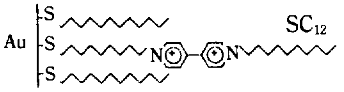
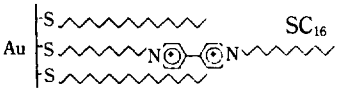
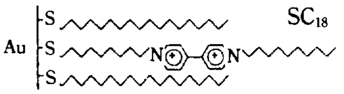


Figure 1. Cyclic voltammograms of gold electrodes coated with viologen thiol and n-nonanethiol (A) and *n*-hexadecanethiol (B) in aqueous solution of 50 mM NaCl. Electrode Area: 0.21 cm^2, Scan rate: 500 mV/S.

Table 1. Voltammetric Data of Gold Electrode (Area: 0.21 cm^2) Coated with Viologen Thiol and *n*-alkane Thiods[a]

Monolayer structure	Cathoodic peak potential(V)	Anodic peak potential(V)	Redox potential (V)
	−0.57	−0.53	−0.55
	−0.55	−0.52	−0.53
	−0.52	−0.48	−0.50
	−0.50	−0.42	−0.46
	−0.48	−0.42	−0.45

[a] All potential were measured in aqueous solution of 50 mM NaCl against SCE at 25(± 2)℃. Scan rate: 500 mV/S

include the effects of solvation counterions in the local microenvironment, double layer structure[10,11] and ion pairing between counterions and viologens. Further experimental measurements together with the theoretical considerations in this line are in progress in this laboratory.

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