ELECTRON TRANSFER KINETICS OF SOLUBLE REDOX PROBES ON ELECTRODES MODIFIED WITH GOLD NANOCLUSTER MONOLAYERS

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INTRODUCTION

Gold nanocluster systems have shown potential as components of electrochemical sensors and devices. To further understand these systems, the kinetics of electron transfer mediated by gold nanoclusters has been explored. Gold nanoclusters (diameter 1.8 nm) encapsulated with hydrophilic (triethylene oxide thiol, EO_3) protective layers ($AuEO_3$ clusters) were confined to gold electrodes, previously modified with mixed 1-octane thiol/1,9-nonane dithiol monolayers [1,2] by an exchange reaction, according to the Scheme 1:

$$Au\text{-}S\text{-}C_9H_{18}\text{-}SH + (EO_3)Au \rightarrow$$
$$\rightarrow EO_3\text{-}SH + Au\text{-}S\text{-}C_9H_{18}\text{-}SAuEO_3 \qquad (1)$$

With these electrodes the electron transfer (ET) of a redox couple dissolved in the bulk phase of an aqueous supporting electrolyte was examined by cyclic voltammetry (CV) and AC voltammetry (ACV). Hexafluorophosphate anions induced quantized capacitance charging. In ACV the Faradic current, associated with redox couples (ferricyanide, ferrocenecarboxylic acid, Fc-COOH, or $Ru(NH_3)_4(1,10\text{-phenanthroline})^{3+/2+}$, R4AP) was superimposed onto the quantized capacitance charging, characteristic to tethered cluster systems.

EXPERIMENTAL

Working electrodes (WE) were coiled gold wires (1.0 ± 0.2 cm^2). Mixed monolayers were self-assembled on the WE as described previously [1]. Gold clusters, AuEO3, were prepared according to reported methods [2] and were attached to modified Au electrodes, from aqueous solution (2 h, under vacuum). Three-electrode mode electrochemical measurements were performed with a chemically modified Au wire WE, a Pt counter, and Ag/AgCl, 3 M KCl reference, Ag(RE). Supporting electrolyte was 0.1 M NH_4PF_6 in de-ionized water, buffered to pH 7 with 10 mM ammonium phosphates.

CV was recorded from -0.30 to 0.50 V vs. Ag(RE), at 0.100 V s^{-1}. ACV was acquired in the stepped mode, with 10 mV rms amplitude. Data points were recorded every 10 mV at fixed frequency values (1 Hz to 1 kHz). CV and ACV were performed with a Model 660a Electrochemical Workstation (CH Instruments, Austin, TX) equipped with a Faraday cage.

RESULTS

Fig. 1 displays the schematic of the described system interacting with bulk phase redox couple.

The ACV in Fig. 2 shows small peaks related to the presence of the hydrophobic PF_6^- anion in the supporting electrolyte [3]. No such peaks have been observed in media based exclusively on phosphates [1]. When a redox couple is added to the bulk of the supporting electrolyte, a Faradaic peak associated with its electron exchange is superimposed onto the quantized capacitance charging pattern.

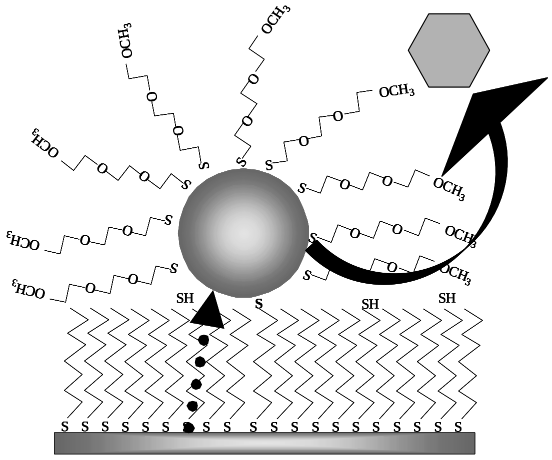

Fig. 1: AuEO3 clusters tethered to a SAM-coated Au electrode with bulk phase redox couple (hexagon). Dotted arrow: tunneling from electrode to AuEO3, curved arrow: ET from AuEO3 to redox couple.

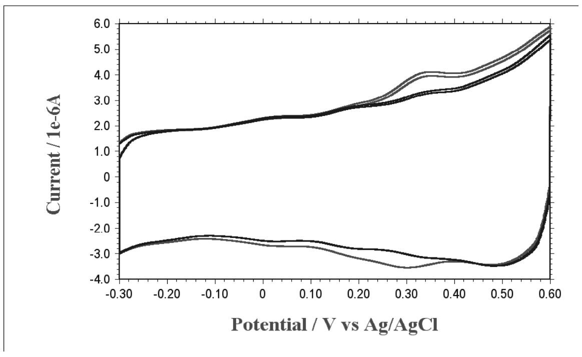

Fig. 2: CV of 12 µM Fc-COOH in PF_6^-/phosphate buffer (outer) and CV in the absence of redox couple (inner).

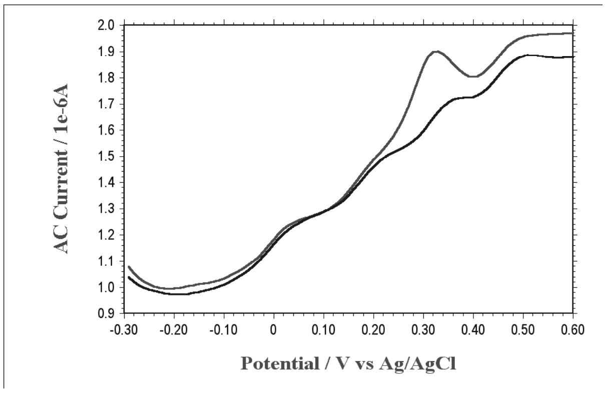

Fig. 3: ACV (1 Hz) of 20 µM R4AP in PF_6^-/phosphate buffer (upper) relative to clean buffer (lower).

Ongoing kinetic studies attempt to elucidate the ET rate of the redox couple at the $AuEO_3$/supporting electrolyte interface, which may open avenues for the use of our hydrophilic cluster systems in electrochemical detection.

REFERENCES

1. S. D. Jhaveri, D. A Lowy, E. E. Foos, A. W. Snow, M. G. Ancona, and L. M. Tender, *Chem. Comm.*, *(14)*, 1544 (2002).
2. E. E. Foos, A. W. Snow, M. E. Twigg and M. G. Ancona, *Chem. Mater.*, *14*, 2401 (2002).
3. Sh. Chen and R. Pei, *J. Am. Chem. Soc.*, *123*, 10607 (2001).