

New Advances in Electrochemical Surface-Enhanced Raman Spectroscopy

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The stability and reproducibility of most SERS-active electrode surfaces are far from ideal. We have focused on this problem by developing and characterizing a metal film over nanosphere (MFON) electrode which solves these shortcomings. Atomic force microscopy (AFM), cyclic voltammetry, and surface-enhanced Raman spectroscopy (SERS) of representative molecules were used to characterize and evaluate the electrochemical and SERS performance of MFON electrodes. Tremendous stability to extremely negative potential excursions is observed for MFON electrodes as compared to standard metal oxidation reduction cycle (MORC) roughened electrodes. Consequently, irreversible loss of SERS intensity at negative potentials is not observed on these MFON electrodes. We conclude that MFON electrodes present a significant advantage over MORC electrodes because SERS enhancement is not lost upon excursion to extremely negative potentials. This work demonstrates that the MFON substrate, while easily prepared and temporally stable, offers unprecedented stability and reproducibility for electrochemical SERS experiments. Furthermore, one can conclude that irreversible loss is not a distinguishing characteristic of electrochemical SERS and consequently cannot be used as evidence to support the chemical enhancement mechanism.

As an additional example of the application of MFON electrodes, we will discuss the SERS detected electrochemistry of surface-confined ferrocyanide (Fe²⁺/C₆H₄COO⁻). The distance and orientation dependence of the heterogeneous electron-transfer reaction between Fe²⁺/C₆H₄COO⁻ and a silver film over nanosphere (AgFON) electrode is examined in detail using electrochemical surface-enhanced resonance Raman spectroscopy (SERRS) as a molecularly specific and structurally sensitive probe. The distance between the Fe²⁺ redox center and the electrode surface is controlled by varying the chain length *x* of an intervening carboxylic acid terminated alkanethiol, HS(CH₂)_{*x*}COOH, self-assembled monolayer (SAM). The orientation of the heme in Fe²⁺/C₆H₄COO⁻ with respect to the AgFON/S(CH₂)_{*x*}COOH electrode surface is controlled by its binding motif. Electrostatic binding of Fe²⁺/C₆H₄COO⁻ to AgFON/S(CH₂)_{*x*}COOH yields a highly oriented redox system with the heme edge directed toward the electrode surface. The binding constants were determined to be $K = 5.0 \times 10^6 \text{ M}^{-1}$ and $1.1 \times 10^6 \text{ M}^{-1}$, respectively, for the *x* = 5 and *x* = 10 SAMs. In contrast, covalent binding of Fe²⁺/C₆H₄COO⁻ yields a randomly oriented redox system with no preferred direction between the heme edge and the electrode surface. SERRS detected electrochemistry demonstrates that Fe²⁺/C₆H₄COO⁻ electrostatically bound to the *x* = 5 AgFON/S(CH₂)_{*x*}COOH surface exhibits reversible oxidation to ferricyanide, whereas Fe²⁺/C₆H₄COO⁻ electrostatically bound to the *x* = 10 surface exhibits irreversible oxidation. In comparison, Fe²⁺/C₆H₄COO⁻ covalently

bound to the *x* = 5 and *x* = 10 surfaces both exhibit oxidation with an intermediate degree of reversibility. In addition to these primary results, the work presented here shows that AgFON/S(CH₂)_{*x*}COOH surfaces (1) are biocompatible - Fe²⁺/C₆H₄COO⁻ is observed in its native state and (2) are stable to supporting electrolyte changes spanning a wide range of ionic strength and pH thus enabling, for the first time, SERRS studies of these variables in a manner not accessible with either the widely used colloid or electrochemically roughened SERS-active surfaces.