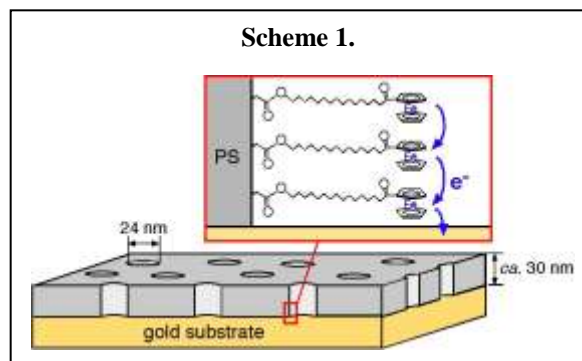


Electrochemical Sensing Based on Redox-Involved Electron Propagation through Ferrocenes Anchored to Electrode-Supported Cylindrical Nanopores

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This presentation will report a new approach to electrochemical sensing with redox moieties anchored to an insulator-based surface. The approach is based on the measurements of a Faradaic current originating from electron hopping through anchored redox moieties, which is known as bounded diffusion [1]. Since electrons cannot conduct through the insulator-based support, they propagate through the surface-anchored redox moieties as a result of electron self-exchange reaction between adjacent moieties. In our current experimental system, redox moieties have been covalently anchored on insulator-based cylindrical nanopores aligned vertical to an underlying electrode (**Scheme 1**; Taken from the TOC of [2]), and thus electron propagation through the redox moieties can be measured as a Faradaic current at the electrode. If complexation of surface-anchored redox moieties with analytes alters the efficiency of the electron propagation, it can be recognized as a change in Faradaic current. This mechanism will provide a new and versatile electroanalytical method for detection of redox-inactive species.



This approach has been built upon our recent experimental results on electron propagation through ferrocene moieties covalently anchored onto insulator-based nanopores (**Scheme 1**; [2]). In the research, thin insulator films comprising vertically-aligned cylindrical nanopores (24 nm in diameter, 30 nm long) were prepared on planar gold electrodes from cylinder-forming polystyrene-poly(methylmethacrylate) diblock copolymers (CF-PS-*b*-PMMA). The surface of the nanopores was covalently modified with ferrocene moieties via esterification of -COOH groups on the nanopore surface [3] with OH-terminated ferrocene derivatives having different alkyl linkers. The average spacing between adjacent ferrocene moieties (ca. 1.2 nm) was larger than the size of the ferrocene moiety (ca. 0.66 nm in diameter), and thus adjacent surface-anchored ferrocene moieties needed to approach closely enough for electron self-exchange reaction. Cyclic voltammograms (CVs) were measured for ferrocene-functionalized nanoporous films in aqueous 0.1 M NaBF₄. We have found that the redox peaks of the anchored ferrocenes were observed at nanoporous films decorated with ferrocenes anchored through sufficiently long linkers. The apparent diffusion coefficient (D_{ap}) was much smaller

($10^{-12} \sim 10^{-13} \text{ cm}^2/\text{s}$) than the diffusion coefficient of a ferrocene molecule dissolved in an aqueous solution (ca. $6 \times 10^{-6} \text{ cm}^2/\text{s}$), and maximum electron hopping length (h) was less than 10 nm, reflecting inefficient electron propagation through the insulator-anchored ferrocenes. More importantly, D_{ap} and h values were larger for longer linkers, reflecting the facilitation of the approach of the adjacent ferrocene moieties within a distance required for electron self-exchange reaction due to the larger physical displacement range of anchored ferrocene moieties.

Here, we have newly found that such a Faradaic current through nanopore-anchored ferrocene moieties decreased as the concentration of β -cyclodextrin (β -CD) was increased in aqueous solution. The current could be recovered upon addition of redox-inactive guest molecules (1-adamantanol) to the solution. This decrease and recovery of the Faradaic current was reversible. These results indicate that electrode-supported vertical nanopores functionalized with redox moieties provide unique platforms for electroanalytical sensing based on redox-involved electron hopping and host-guest chemistry.

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