

Tuning the redox potential in molecular monolayers covalently bound to H-Si(100) electrodes via distinct C-C tethering arms

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Redox-active organic monolayers on Si electrodes constitute a promising step toward molecule-based hybrid devices compatible with the crystalline silicon platforms. Due to the attractive electrochemical properties of ferrocenes (fast e-transfer rates and favorable redox potentials), their introduction in organic monolayers bound to gold has been widely described in the literature.

We report here a combined experimental/theoretical approach on ferrocene (Fc)-silicon hybrids redox potential.[1,2] The systems were modeled with a slab of H-terminated Si(100) 1x1 and 2x1 surfaces: geometries were optimized using the ONIOM method, and solute-solvent interactions were included through the polarizable continuum model (PCM) method.

Two new routes for Si functionalization with ethyl- (EtFC) and ethynyl-Fc (EFC) differing only for the unsaturation degree of the anchoring arm have been successfully explored, and the redox potential of the resulting hybrids has been measured by cyclic voltammetry: 0.675 and 0.851 V vs. NHE for the EtFC and EFC derivatives, respectively. These values, along with the previously measured potential (0.700 V) for the mono-unsaturated derivative, vinyl-Fc (VFC), allow to study the relation between the unsaturation degree and the adduct redox potential.

The comparison among the measured and computed potentials allows to discriminate between different adduct isomers for the saturated species, and more importantly provides strong indications that the carbon-carbon unsaturation initially present in the molecular arm used for anchoring to the surface is preserved upon addition, in contrast with the commonly accepted reaction mechanism. A full characterization is reported by AFM and XPS of the resulting hybrids.

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References

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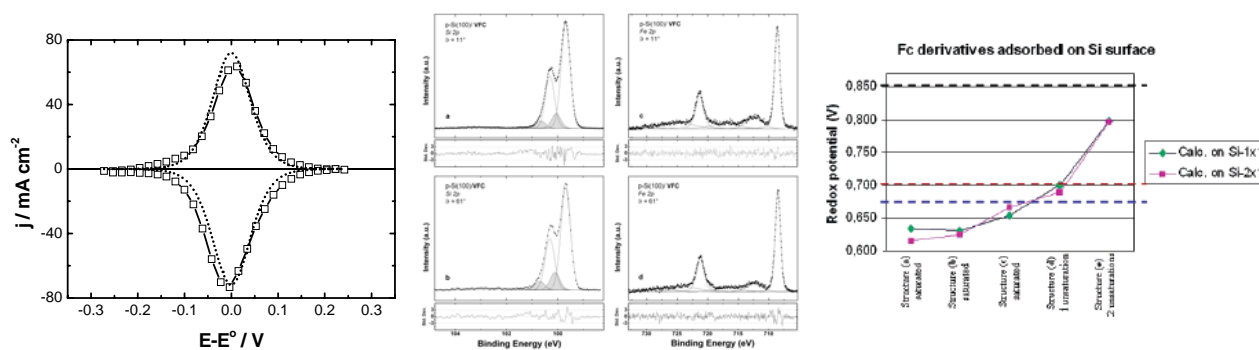


Figure 1. (Left) Experimental CV of a VFC/p-Si(100) electrode in 0.1 M TEAP/CH₃CN compared with the theoretical calculated response for an ideal Nernstian curve. E^0 is the formal potential (73 mV). Scan rate: 1 Vs⁻¹; (Middle) XPS spectra from the same system, taken on Si2p and Fe2p ionization regions at 11° (top) and 61° (bottom) photoemission directions from the surface normal. (Right) Computed redox potential (volts, referred to NHE) for different Fc derivative adducts on mono- and di-hydrogenated silicon surfaces. The experimental values for the adducts obtained with EfFC (top dashed line), VFC (middle), and EFC (bottom) are also reported for comparison.