

Conducting ferrocene monolayer on non-conducting surfaces.

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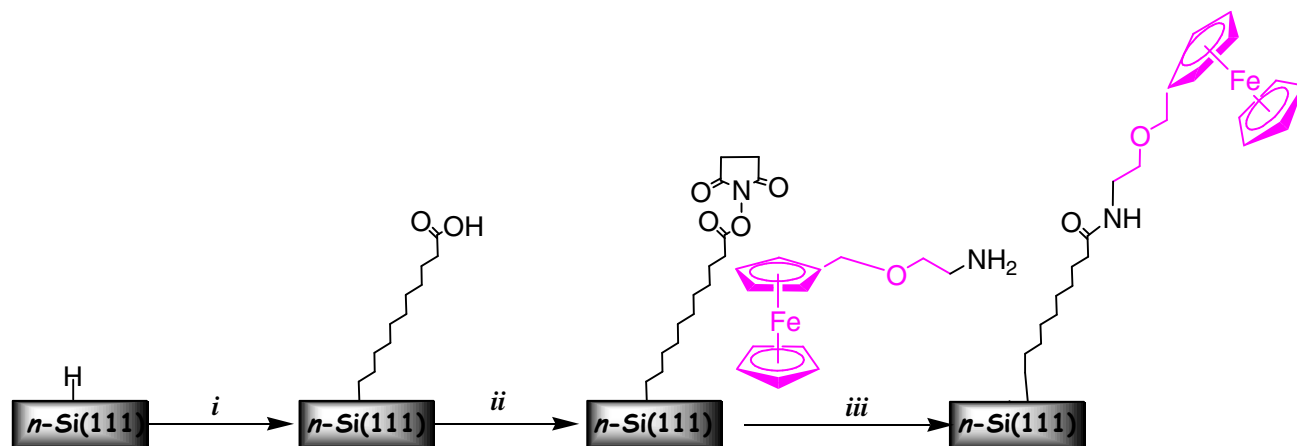
Covalent attachment of the ferrocene-terminated monolayer on *n*-type silicon surface.

The covalent derivatization of Si(111) surfaces by a ferrocene-functionalized monolayer is depicted in Scheme S1 and was adapted from a previously reported procedure for *p*-type silicon surfaces.¹

In order to limit the number of chemical steps, the direct grafting of an acid-terminated alkyl monolayer was performed using the reaction at 170°C under argon overnight of undecylenic acid² (Acros, 99%, previously passed through a neutral, activated alumina column to remove residual water and peroxides) with an hydrogen-terminated single side polished silicon(111) shard³ (1.5 x 1.5 cm², 1-5 Ω cm, *n*-type, phosphorus doped, thickness = 525 ± 25 μm, from Siltronix). The carboxylic acid-modified silicon surface was rinsed copiously with tetrahydrofuran and dichloromethane, then dipped in hot acetic acid for 2 x 20 min and dried under a nitrogen stream. It has been recently demonstrated that the rinsing in hot acetic acid leaves the functionalized surface smooth and perfectly free of physisorbed contaminants.⁴

2-Aminoethylferrocenylmethylether was synthesised in one step from commercially available (ferrocenylmethyl)trimethylammonium iodide (Strem Chemicals, 99%) following a previously reported procedure.⁵

The thickness measured by ellipsometry of the ferrocene-terminated monolayer was 26 Å, consistent with the calculations of energy minimization using the semi-empirical PM3 method giving 28 Å.



Scheme S1. Preparation of the ferrocene-terminated alkyl monolayer bound to *n*-Si(111) surfaces. *Reagents and Conditions:* (i) Undecylenic acid, 170°C, 20 hr; (ii) 0.1 M aq. NHS + 0.2 M aq. EDC, rt, 2 hr; (iii) CH₂Cl₂/0.05 M 2-aminoethylferrocenylmethylether, rt, 3 hr.

Covalent attachment of the ester-terminated monolayer on *n*-type silicon surface.

The ester-terminated monolayer was prepared using the thermal reaction at 170°C overnight under argon of hydrogen-terminated silicon with neat ethyl undecylenate (Aldrich, 97%).⁶ After cooling down to 40-50°C, the ester-modified silicon surface was rinsed copiously with toluene and dichloromethane, and dried under an argon stream.

Cyclic voltammetry.

The cyclic voltammetry measurements were performed with an Autolab electrochemical analyzer (PGSTAT 30 potentiostat/galvanostat from Eco Chemie B.V.) equipped with the GPES software in a self-designed three-electrode Teflon cell. The working electrode, modified Si(111), was pressed against an opening in the cell bottom using a FETFE (Aldrich) O-ring seal. An ohmic contact was made on the previously polished rear side of the sample by applying a drop of an In-Ga eutectic (Alfa-Aesar, 99.99%). The counter electrode

Supporting Information Section

was a platinum foil and the system 10^{-2} M $\text{Ag}^+ | \text{Ag}$ in acetonitrile was used as the reference electrode (+0.29 V vs aqueous SCE). The reported potentials are referred to SCE (uncertainty ± 0.01 V). Tetra-*n*-butylammonium perchlorate Bu_4NClO_4 was purchased from Fluka (puriss, electrochemical grade). The ($\text{CH}_3\text{CN} + 0.1$ M Bu_4NClO_4) electrolytic medium was dried over activated, neutral alumina (Aldrich) for 30 min, under stirring and under argon. About 20 mL of this solution was transferred with a syringe into the electrochemical cell prior to experiments.

All electrochemical measurements were carried out inside a home-made Faraday cage in dark, at room temperature (20 ± 2 °C) and under a constant flow of argon. Solution resistance was compensated by electronic positive feedback

Characterization by cyclic voltammetry of the ferrocene modified layer in dark.

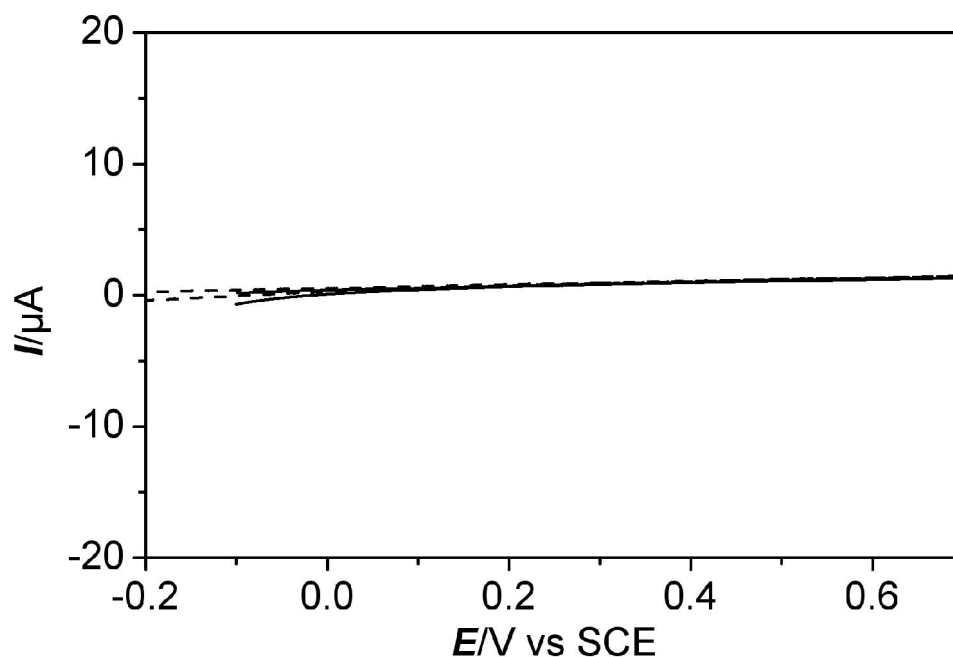


Figure S1. Cyclic voltammograms at 0.1 V s^{-1} of the ferrocene-terminated monolayer on *n*-type Si(111) in $\text{CH}_3\text{CN} + 0.1$ M Bu_4NClO_4 in dark: (---) in absence of ferrocene in solution; (—) after addition of $10^{-3} \text{ mol.L}^{-1}$ of ferrocene in solution. This CV shows the "Non-Conducting" behaviour of such modified electrode in dark

SECM measurements. SECM measurements were performed using the CHI900B instrument from CH-Instruments equipped with an adjustable stage for tilt correction. The electrochemical cell was the one furnished with the SECM and was used in a typical three-electrode configuration for unbiased experiments. The tip electrode was a 5 μm radius Pt disk ultramicroelectrode (UME, CH-Instruments) with a typical RG = 5–10 (RG is the ratio of the total electrode radius including the glass insulator over UME radius).⁷ The reference electrode was an Ag/AgCl, aqueous KCl 3 M electrode. UME was characterized by cyclic voltammetry and by typical approach curves recorded on a Pt conductive substrate.

Two redox mediators were used: the ferrocene/ferrocenium (Fluka, >98%) and decamethylferrocene/decamethylferrocenium (Aldrich, 97%) at 1mM concentration in CH_3CN (+0.1 M NBu_4ClO_4).

Approach curves were recorded under constant current mode at a tip-substrate distance expressed as $L = d/a$ around 1 (d is the distance between the tip and the substrate and a is the radius of the UME). Fittings were performed using the approximate functions following the Bard–Mirkin formalism for $\text{RG} < 10$.⁷

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