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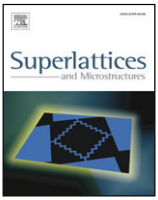

Chemical routes to molecular SAMs on H-Si(100) with distinct and well-defined redox potentials

A.G. Marrani [a,*], F. Cattaruzza [a], F. Decker [a], P. Galloni [b], R. Zanoni [a]

[a] *Dipartimento di Chimica, Università di Roma "La Sapienza", I-00185 Roma, Italy*
[b] *Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", I-00133 Roma, Italy*

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ABSTRACT

New or rarely reported synthetic routes have been applied to produce electroactive hybrid materials from ferrocene (Fc) derivatives with a known and pre-established variation in the tethering arm bound to Si. The series is characterized for having the shortest molecular link for a direct covalent attachment to H-terminated Si(100). Grignard derivatization, Lewis acid catalysis and nucleophilic substitution by an acetilyde anion have been applied for the first time in order to obtain the full series of possible unsaturations in the C–C lateral chain bound to Si: ethyl (**EtFC**/Si), vinyl (**VFC**/Si) and ethynyl group (**EFC**/Si). The redox potentials of these three molecule/surface hybrids, measured by cyclic voltammetry, are respectively 0.059, 0.136 and 0.251 V *vs.* Ag/Ag$^+$, and increase with the extent of unsaturation in the tethering arm. XPS and electrochemical measurements have been used to assess the chemical nature and electronic properties of the hybrids.

1. Introduction

Ferrocenes are known to display fast e-transfer rates and relatively accessible low redox potentials, appealing properties which place them among the best candidates for the formation of self-assembled, redox-active organic monolayers on Si electrodes for the implementation of molecule-based hybrid devices into FLASH and DRAM memories [1] and chemical/biological sensors [2]. In a previous paper, we reported a theoretical and experimental study of self-organization properties of Fc derivatives on Si(100) as a function of the nature of the tethering group attached to Si [3]. Such results were obtained

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[*] Corresponding author. Tel.: +39 335 8011699; fax: +39 06 490324.
E-mail address: andrea.marrani@uniroma1.it (A.G. Marrani).

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by making use of a mild photochemical anchoring procedure. A possible drawback of such route is that light-promoted attachment of unsaturated C–C bonds to Si might result in a mixture of species, which cannot be sufficiently separated and assigned on the basis of their electrochemical response. In the light of such findings, we propose here novel or rarely explored reaction routes allowing one to establish, in a controlled fashion, the whole series of possible unsaturations in the C–C linking arm between H-Si(100) and the Fc heads. These routes are: (a) reaction with a Grignard derivative of EtFC, to produce an ethyl–Fc termination on Si, **EtFC**/Si; (b) reaction with EFC in the presence of a Lewis-acid catalyst, to produce a vinyl–Fc termination on Si, **VFC**/Si; (c) reaction with a Li-organic derivative of EFC, to produce an ethynyl-Fc termination on Si, **EFC**/Si. Grignard reaction has been widely used to anchor molecules on Si(111) [4–6] but its application to EtFC on Si(100) is unprecedented. Lewis acid-catalyzed hydrosilylation of alkynes has been applied to porous Si [7,8] to obtain alkenyl-bound molecular layers, while on crystalline Si it has only been studied for alkenes on H-Si(111) [5,9]. As to the alkynyl-bound molecular monolayers on crystalline Si, just one example has been so far reported in the literature [10].

The hybrids here reported have been characterized by means of X-ray Photoelectron Spectroscopy (XPS), in order to assess the nature and composition of the surface species, while their redox behavior has been studied by electrochemical methods.

2. Experimental

The functionalization experiments on the surface-activated samples were carried out in a N_2(g)-purged standard preparative Schlenk-line. All solvents used were freshly distilled. Single-side polished Si(100) wafers were purchased by Si-Mat, ~350 μm thick and p-doped (0.02 Ω cm resistivity). Before use, Si(100) wafers (1 × 1 cm) were first cleaned, oxidized and etched according to the procedure reported in Ref. [11]. 2-bromoethylferrocene was prepared from Fc acylation with 2-bromoacetyl chloride (Aldrich) followed by reduction with $NaBH_4$/trifluoroacetic acid (Fluka) [12]. The **EtFC**/Si hybrid was obtained by adding a freshly prepared H-terminated Si(100) surface into a flask containing 2-bromoethylferrocene with Mg turnings (Carlo Erba Reagents) suspended in dry diethyl ether (Fluka) and I_2 (Fluka). The reaction was stirred overnight at r.t. after which the excess of Grignard reagent was quenched with water. The sample was then rinsed in ultrasonic bath at r.t. with 1% TFA solution in tetrahydrofuran (THF, Aldrich), de-ionized water, and trichloroethane.

The **VFC**/Si hybrid was obtained from reaction of ethynylferrocene (EFC) with a freshly prepared H-Si(100) surface in the presence of diethylaluminum chloride, $(C_2H_5)_2AlCl$ (Aldrich), 3 ml 0.1 M in hexane. After overnight reaction at r.t. the hybrid was sonicated with a series of solvents: petroleum ether (Carlo Erba Reagents), THF, ethanol, water.

The **EFC**/Si hybrid was prepared by adding the freshly etched Si sample to a solution of lithium ferrocenylethynylide in dry diethyl ether and allowing them to react for 15 h at room temperature, according to the procedure reported in Ref. [13].

Electrochemical measurements consisted of cyclic voltammetry at different scan rate and prolonged redox cycling to simulate ageing in 0.1 M tetrabutylammonium perchlorate (TBAP, Fluka) in dry CH_3CN (Fluka). Details of the experimental set-up for XPS and electrochemical measurements have been reported in Ref. [11].

3. Results and discussion

XPS results (shown in Fig. 1 for the Si 2p and Fe 2p regions from the **VFC**/Si hybrid) confirm the presence of the anchored molecules on the silicon surface. The Si 2p regions for the three hybrids show a positively shifted surface component associated with the Si–C bond (shadowed in Fig. 1) near the predominant bulk component located at a binding energy (BE) of 99.7 eV. The energy region in the range typical for silica (103–104 eV) is nearly flat, suggesting the preservation of Si(100) from oxidation during functionalization. In all the investigated samples, Fe species in the oxidation state (II) have been found, the Fe(III) contribution being almost *nihil*. Fe(II) and Fe(III) data sets have been separated by curve fitting, which allows to assign the ionization region to ferrocene (a sharp line at