

Electrografting of Stimuli-Responsive, Redox Active Organometallic Polymers to Gold from Ionic Liquids

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S Supporting Information

ABSTRACT: Robust, dense, redox active organometallic poly(ferrocenylsilane) (PFS) grafted films were formed within 5 min by cathodic reduction of Au substrates, immersed in a solution of imidazolium–functionalized PFS chains in the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate. The electrografted polymer films were employed as an electrochemical sensor, exhibiting high sensitivity, stability, and reproducibility.

Surface modifications of electrodes have played a pivotal role in the building of novel interfaces for potential applications in ion recognition,¹ anticorrosion coatings,² electronic devices,³ sensors,⁴ biofuel cells,⁵ and other fields.⁶ Various strategies have been proposed to form mono- or multilayered structures aiming at controlling physicochemical properties of interfaces. The modification of electrodes with redox-active materials is an area of intense activity, featuring wide-ranging strategies that include electropolymerization,⁷ self-assembly through tethered functional groups,⁸ thermolysis, click chemistry, and electrografting.⁹ Among these approaches, the electrografting method has been proposed as a convenient approach to produce modified and functionalized surfaces and obtain molecularly altered electrodes and other metal surfaces.⁹ Here we report on the grafting of redox stimulus responsive poly(ferrocenylsilane) (PFS) films to Au electrode surfaces by employing cathodic electrografting from an ionic liquid solution of the polymer.

Electrografting encompasses electrochemical reactions for the attachment of organic layers to conducting, solid substrates.⁹ Various small molecules have been attached with success to electrodes by the electrografting method. For example, the electrochemical reduction of diazonium groups has been investigated in organic, aqueous, and ionic liquid media.¹⁰ Covalent attachment of ferrocenyl derivatives and porphyrin through ethynyl linkages to electrode surfaces and the direct anodic oxidation of the vinyl group through a radical-based electrografting procedure were also studied.¹¹ Ghilane et al. reported the inclusion of ferrocene into the electrode material by cathodic treatment.¹² It has been also shown that, under cathodic polarization of noble metals, the metal could be electrochemically modified. Gold is unique among the transition metals in its ability to form isolable nonmetallic compounds that contain a monatomic anion. The auride ion (Au⁻) is the first monatomic metal anion proposed to exist in liquid ammonia.¹³ Bard reported on the electrochemical formation of the auride ion in liquid NH₃ containing KI as

supporting electrolyte.¹⁴ The formation of tetramethylammonium auride in which gold carries a negative charge¹⁵ was also reported. The auride ion displays similar behavior as halogen ions.¹⁶ In the above-mentioned studies the possibility to prepare grafts electrochemically has been demonstrated.

PFSs are a fascinating class of redox-active materials which are composed of alternating ferrocene and silane units in the main chain and combine a high density of redox centers with excellent processability and redox characteristics.¹⁷ The post-functionalization of polymers is an appealing approach to obtain new materials with tailor-made properties.¹⁸ For example, functionalization of PFSs with imidazole side groups yielded novel poly(ionic liquid)s¹⁹ which offer novel properties.²⁰

The synthetic route employed to obtain methylimidazolium functionalized PFS-MID-Cl is shown in Figure 1a. Interestingly,

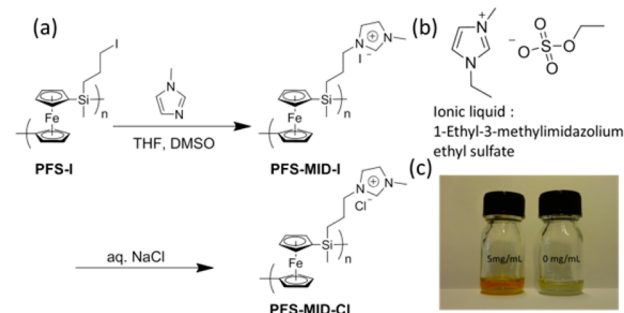


Figure 1. (a) Synthesis of PFS-methylimidazole (PFS-MID-Cl), (b) the ionic liquid used in this study, and (c) pure ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate (right vial) and PFS-MID-Cl dissolved in this ionic liquid (5 mg/mL, left vial).

we found that the PFS-MID-Cl is well soluble (up to 20 mg/mL) in the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate (Figure 1b) with the help of heating (Figure 1c left vial). With the increasing concentration of PFS-MID-Cl, the color of the solution changed from light yellow to dark orange (Figure S1). To the best of our knowledge, this is the first example of a redox-active organometallic poly(ionic liquid) that is soluble in ionic liquids. The ionic liquid here fulfills a dual role as a solvent and electrolyte; it is a nonvolatile liquid and has intrinsic ionic conductivity and a wide potential window suitable for electrochemical applications.²¹

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Cathodic electrografting of the PFS (Figure 2a) was achieved using the PFS/ionic liquid solution (5 mg/mL). It was shown

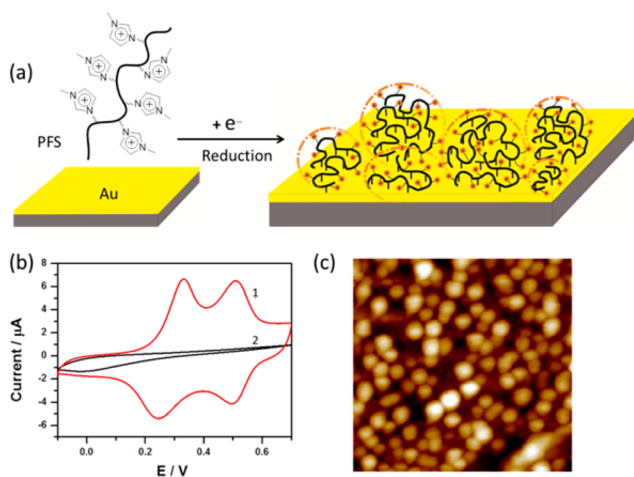


Figure 2. (a) Schematic illustrating the electrografting of PFS-MID-Cl in ionic liquid. (b) Cyclic voltammogram of a PFS modified Au electrode (1) with deposition potential at -2.2 V and (2) with deposition potential at -0.8 V in 0.1 M NaClO_4 , using an Ag/AgCl reference electrode and Pt counter electrode. Scan rate: 50 mV/s, (c) AFM height image of PFS grafts on Au, tapping mode in air; Scan size: $1 \mu\text{m} \times 1 \mu\text{m}$, z-scale: 30 nm.

earlier that the electrochemical reduction of Au in the PFS ionic liquid solution takes place at -2.0 V (Figure S2). Following a cyclic voltammetry (CV) scan from -2.55 to -0.55 V, the surface modification was performed by cathodic polarization at -2.2 V during 200 s. After electrografting, the modified electrodes were removed from the grafting solution and were sonicated in acetonitrile for 5 min and thoroughly rinsed with acetonitrile and water to remove any weakly adsorbed molecules. Then the electrodes were transferred to 0.1 M NaClO_4 aqueous solution for the electrochemistry studies.

Figure 2b shows the electrochemical response of the decorated Au electrode in 0.1 M NaClO_4 aqueous solution. A double-wave voltammogram, displaying the characteristic peaks of PFS, is very visible.²² The presence of these signals confirms the existence of the organometallic polymer at the Au electrode surface. A differential pulse voltammogram (DPV) also displayed the double waves. The best fit of the area under the DPV curve (Figure S3) was obtained with a peak area ratio of $1.1:1:1$, which reflects the influence of intra- and interchain interactions, and the distance of the redox centers to the electrode surface, on oxidation potentials. When the Au electrode was kept at -0.8 V in the presence of PFS in the ionic liquid, the characteristic I - V response of the polymer was not observed, indicating that at this potential no grafting takes place. The cathodic polarization at -2.2 V which exceeds the Au reduction potential is essential for the electrografting of the polymer onto the Au surface.

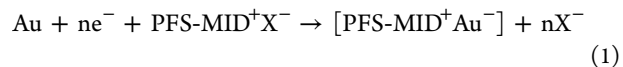
The electrochemical stability of the PFS grafts was examined by successive potential cycling in electrolyte solution with a potential sweep rate of 50 mV/s. The current variation in the CVs was negligible, about 3% , after 30 potential cycles (Figure S4), showing that no PFS chains desorbed from the substrate surface. After a fixed oxidizing potential of 0.6 V (vs Ag/AgCl) was maintained for 2 h, which is a rather severe test for gauging film stability,²³ only 15% material loss occurred (Figure S5). The voltammetric performance of the grafts remained

unchanged following storage of the modified Au substrate for several weeks under ambient conditions. Integration of the anodic peak current gave an apparent surface coverage of ferrocene sites (Γ) of 1.85×10^{-9} mol cm^{-2} . Peak currents plotted against the scan rate showed a linear dependence, and the ratio of anodic and cathodic current was close to unity (Figure S6). These characteristics indicated that the redox process on these electrodes was controlled by charge-transfer kinetics²⁴ and confirmed that PFS grafts were immobilized on the gold surface.

XPS was used to accurately analyze the surface chemical composition of the electrografted electrode (Figure S7). Following cathodic electrochemical grafting, the gold signal (the doublets at 84.4 and 88.0 eV for $\text{Au } 4f_{7/2}$ and $\text{Au } 4f_{5/2}$) is strongly attenuated. Conversely, the relative intensity of carbon increases considerably. The presence of carbon on the gold surface before the electrochemical treatment is due to surface contamination. The marked increase of the carbon signal after electrografting suggests the presence of an organic layer at the gold surface, and the observation of substrate signals indicates that the organic layer is thinner than the XPS escape depth (on the order of 10 nm). In addition, after electrografting, new XPS peaks appeared at 152.1 , 708.2 , and 721.3 eV corresponding to Si ($2s$), Fe($2p_{3/2}$), and Fe($2p_{1/2}$), which originate from the PFS main chain;²⁵ the peak found at 401.2 eV is assigned to nitrogen N($1s$) from the imidazole ring.²⁶ The ratio of Fe/Si is approximately 1 , and N/Fe almost equals to 2 , which agrees well with the theoretical composition of the polymer. These results confirm the presence of PFS which is strongly attached to the gold surface after the electrochemical reduction.

The morphology of poly(ionic liquid) grafts was investigated by AFM (Figure S8). The AFM images shown in Figure 2c exhibited a globular surface structure, superimposed on the Au surface with an average roughness of 4.56 nm.

Electrochemistry, XPS, and AFM results indicate that the PFS is intercalated in the Au surface after the electrografting. The reaction can be described as follows:



By analogy with a previous study with small molecules,¹² the electrografting of the organometallic polymer followed eq 1, where X^- is the anion in the solution. The imidazolium side group of the PFS forms a complex with the auride ion generated during the cathodic reduction of the Au substrate leading to the formation of new phases with the general formula $[\text{PFS-MID}^+\text{Au}^-]$.

The decorated electrode also displayed an XPS peak for S($2p_{3/2}$) at 168.7 eV, which is attributed to sulfate groups,²⁷ while the peak for Cl($2p_{3/2}$) (200.6 eV)²⁷ is almost invisible in the noise. In control experiments, a substrate was exposed to the same electrografting process in pure ionic liquid without PFS. In this case, sulfur (S) was not detected by XPS, indicating the absence of an ionic liquid anion (ethyl sulfate) at the electrode surface. These two facts demonstrate the following: (1) in our case, X^- in eq 1 represents the anion ethyl sulfate; (2) the anchored PFS chains possess unreacted imidazolium ethyl sulfate side groups.

We further studied the performance of the Au electrode electrografted with PFS as a potential sensor for the detection of ascorbic acid.

Ascorbic acid, one form of Vitamin C, is well-known for its radical-scavenging capacity, presented naturally in fruits and

vegetables. It is an important preservative and antioxidant agent used in the food and drinks industry, pharmaceutical formulations, animal feed, and cosmetic applications.²⁸ It also plays a vital role in biological metabolism. The accurate determination of its concentration is of considerable importance. Thus, the development of a simple, rapid, and reliable method to detect ascorbic acid has attracted great attention and is desirable for diagnostic and food-safe applications.²⁹ Hence we chose this molecule to demonstrate the redox sensing ability of the Au electrodes electrografted with PFS.

Figure 3a illustrates the cyclic voltammograms of the PFS decorated Au substrate in the absence and presence of ascorbic acid

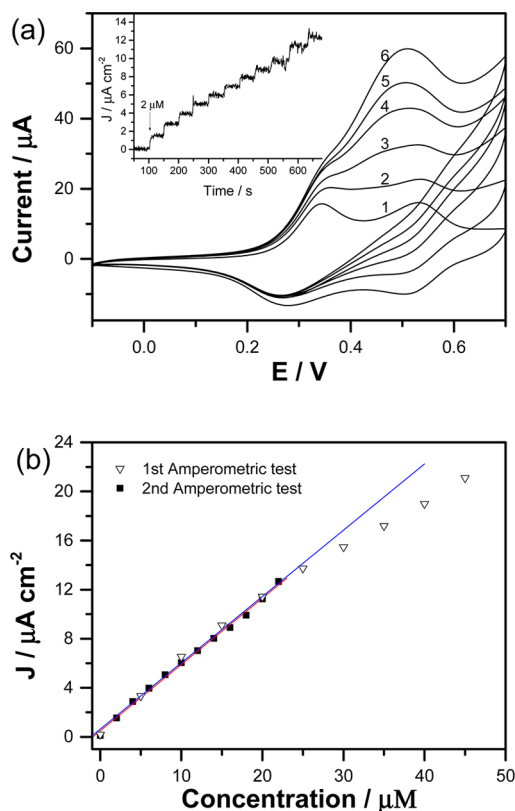


Figure 3. (a) Cyclic voltammograms of Au electrografted with PFS (1) in the absence of the analyte; and in the presence of (2) 0.1 mM, (3) 0.2 mM, (4) 0.3 mM, (5) 0.4 mM, and (6) 0.5 mM ascorbic acid in 0.1 M NaClO₄ aqueous solution. Scan rate was 50 mV/s; Ag/AgCl and Pt were used as the reference and counter electrodes. Inset: Amperometric response of the sensor to successive additions of ascorbic acid into stirred aqueous 0.1 M NaClO₄ at room temperature. Each addition represented 2 μM ascorbic acid added. Applied potential = 0.52 V. (b) The calibration curve of the sensor.

acid, showing the electrocatalytic responses of the electrode. The peak potentials do not change, and the oxidation peak currents increase with the addition of ascorbic acid, indicating that the electrografted PFS on Au effectively catalyzes the oxidation of ascorbic acid. This amperometric response forms the basis for the application of these PFS decorated Au electrodes in electrochemical sensing. The amperometric response (Figure 3a inset, Figure S9) of the modified electrode to successive additions of ascorbic acid was evaluated by applying a fixed potential of 0.52 V (Ag/AgCl) at room

temperature. The current–time curve indicates that the PFS grafts show a rapid response and a high sensitivity.

After the first amperometric response test (Figure S9a), the PFS-modified electrode was washed thoroughly with distilled water. The second amperometric measurement was conducted on the same electrode to study its sensing reproducibility (Figure S9b). The working plot of the oxidation peak current of oxidation current density vs ascorbic acid concentration is shown in Figure 3b. A linear relationship between oxidation current and ascorbic acid concentration was obtained up to 25 μM. The sensitivity of the modified electrode remained unchanged. The limit of detection was estimated to be 0.9 μM at a signal-to-noise ratio of 3. Overall, the electrodes electrografted with PFS exhibit a high sensitivity, stable responses, and a low detection limit. The sensing ability compares favorably to other reported ascorbic acid sensors based on ferrocene derivatives.^{4,30}

In summary, a simple and fast electrografting method to chemically modify Au electrodes with a redox-active organometallic polymer is described based on the direct cathodic reduction from a polymer/ionic liquid solution. This technique allows the generation of a robust redox-active graft on the electrode. Construction and performance tests of an ascorbic acid sensor based on the grafts has been demonstrated. These findings constitute a significant step in the development of a new class of modified electrodes for sensors, fuel cells, and energy conversion.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures for the polymer synthesis, and electrode modifications. Figures giving experimental details and additional characterization data for the modified electrode. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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