Self-Assembled Silica Gel Networks

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The sol−gel process offers a low-temperature approach for the production of ceramic and glass materials[1,2] and for the encapsulation of a variety of molecules.[3,4] The ability to anchor silica gel networks to different surfaces is thus of extreme technological significance. Unfortunately, there is no general procedure for assembling silica gels onto metal surfaces. Here we describe an attractive approach for the formation of silica gel confined interfaces based on the coupling of sol−gel and self-assembled monolayers (SAM)[5,6] technologies. Since most sol−gel techniques rely on the hydrolysis and condensation of alkoxysilane precursors[1,2] and as alkanethiol monolayers on gold electrodes represent the most popular form of SAM systems,[5,6] it is logical to employ thiolated silicon alkoxides for creating three-dimensional sol−gel surface networks. Two such preparation routes have been developed in our laboratory. The first avenue relies on the initial chemisorption of a thiolated precursor, while the second avenue involves one-step self-assembly of thiol-containing gels. We anticipate that such novel coupling of sol−gel and SAM processes will lead to a wide range of technological applications, including chemical sensing, bioactive and chemically reactive surfaces, self-assembled nanostructures, or molecular electronics and optoelectronics.

To our knowledge, no previous attempts have been made to use thiolated silicon alkoxides for designing three-dimensional silica gel interfacial structures via the direct coupling of sol−gel and SAM technologies. Organosilane reagents were tethered to hydroxylated platinum[7] or silicon[8] electrodes, but not in connection to sol−gel chemistry. Titanium precursors have been coupled recently to pre-modified gold surfaces through a mercaptoethanol cross linker.[9] The electrochemical preparation of two-dimensional monolayers of (3-mercaptopropyl)trimethoxysilane, possessing different defect sizes, was reported recently in connection to molecular recognition.[10]

The formation of the silicon−alkoxide monolayers and the one-step assembly of three-dimensional thiol-containing gels (Figure 1) were probed with a variety of characterization techniques. Cyclic voltammetric blocking experiments,[5,11] using the ferrocyanide redox marker, offered useful insights into the electron-transfer barrier properties of the silica gel surface layers. Figure 2 displays the voltammetric response of gold electrodes that were immersed in solutions of various silicon alkoxides and alkanethiols. Well-defined cyclic voltammograms, characteristic of a diffusion-limited redox process, are observed at the bare gold electrode (A) and at a gold disk immersed in the propyltrimethoxysilane precursor (B). Apparently, in the absence of the thiol moiety, the silicon alkoxide cannot assemble on the gold surface. A markedly different voltammogram, with a greatly diminished ferrocyanide response, is observed following a similar immersion in a solution of the thiolated precursor (3-mercaptopropyl)-trimethoxysilane (C). The electron-transfer barrier properties of the resulting thiolated alkoxide monolayer are similar to those of the self-assembled 1-propanethiol (C_3) film (D), with ca. 50% reduction of the anodic peak and nearly disappearance of the cathodic one. Such behavior is characteristic of short-chain monolayers and is indicative of low packing density and coverage. A complete blockage of the ferrocyanide transport is observed at the 1-decanethiol (C_{10}) coated electrode (E). The formation of precursor monolayers (Figure 2C) can be utilized for subsequent solid-phase growth of surface-confined silica gel networks (through dipping of the modified electrode in a sol−gel solution of the nonthiolated precursor). For example, a 12 h immersion of the monolayer-coated electrode into a tetraethoxysilane (TEOS) based gel resulted in a further (60%) decrease of the ferrocyanide marker peak. Apparently, such a two-step preparation route is relatively slow. The fact that the gel formation is confined to the metal/liquid interface indicates that the hydrolysis and condensation of the thiolated precursor are accelerated at the gold surface.

A faster, simpler (one-step), and more effective route for the creation of gel surface layers involves the immersion of the bare gold electrode in a sol−gel containing the thiolated precursor (along with the acid catalyst and ethanol; Figure 1). Figure 3 compares cyclic voltammograms for the ferrocyanide marker, recorded after dipping the gold electrode in sol−gels containing propyl trimethoxysilane (A) and (3-mercaptopropyl)trimethoxysilane (B) for different periods (a−c). The exposure to the nonthiolated precursor solution has no effect upon the voltammetric response. In contrast, greatly diminished ferrocyanide signals are observed in connection to the (mercaptopropyl)-trimethoxysilane based sol, reflecting the spontaneous adsorption of the thiol-containing gel. Stronger barrier properties are observed for longer chemisorption times. Note the complete blockage of the ferrocyanide response following the 16 h exposure (as compared to the 50% diminution observed over the same period with use of the catalyst-free precursor solution; Figure 2C). Such substantial barrier to electron transfer reflects the increased thickness and packing density of the self-assembled silica gel (in comparison to the short-chain precursor monolayer). Extensive washing and sonication had negligible effect on the ferrocyanide response, reflecting the very strong adhesion features of the anchored gel network.

The ability to entrap redox agents in sol−gels was reported earlier.[12] Such encapsulation can provide more evidence for the formation of a strongly attached silica gel surface structure. A 6 h encapsulation of ferrocene (5 mg per 1 mL of the sol−gel of the thiolated precursor) was followed by immersion of the gold disk electrode for 24 h into the resulting sol. The modified electrode was subsequently rinsed with ethanol, sonicated in deionized water, and placed in a phosphate buffer blank solution to yield a well-defined cyclic voltammetric anodic peak ($E_{p,a} = +0.35$ V), corresponding to the oxidation of the surface-anchored silica gel encapsulated ferrocene species.

Double-layer capacitance measurements provided another means for examining the new gel-confined interfaces. Cyclic voltammograms recorded at different scan rates (5−400 mV/s) with the supporting electrolyte solution were employed for estimating the differential capacitance. Plots of the charging current (at +0.3 V) vs the scan rate were linear (correlation

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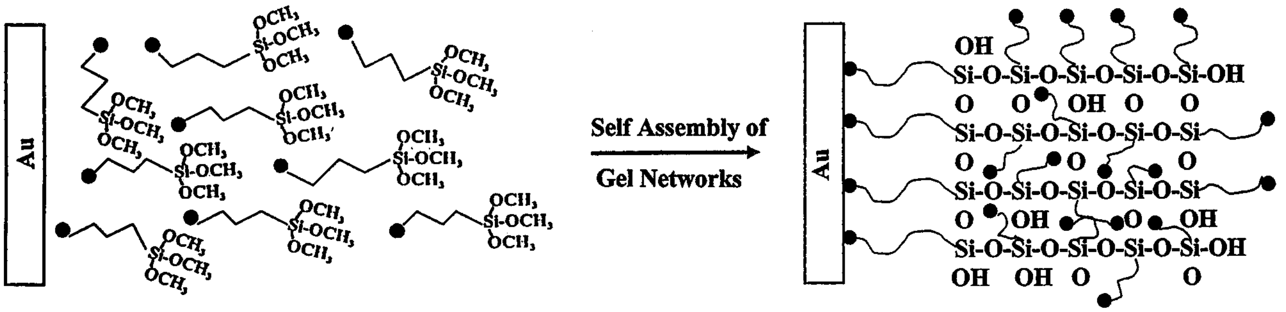

Figure 1. Schematic drawing showing the formation of sol−gel surface layers based on the self-assembly of thiol-containing gels.

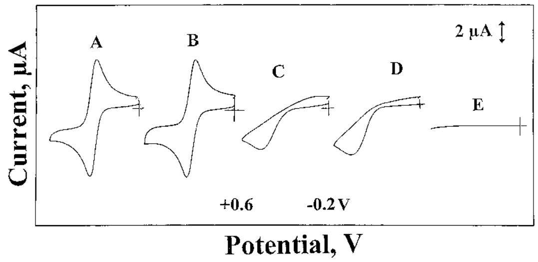

Figure 2. Cyclic voltammograms for 2 × 10^{-3} M ferrocyanide at the bare (A) and propyltrimethoxysilane (B), (3-mercaptopropyl)trimethoxysilane (C), 1-propanethiol (D), and 1-decanethiol (E) coated gold electrodes. Scan rate, 50 mV/s; electrolyte, phosphate buffer (0.05M, pH 7.4) prepared from a 1/4 mixture of KH_2PO_4 and K_2HPO_4. The gold disk electrode (1.6 mm diameter, BAS) was modified by soaking for 16 h in a quiescent ethanolic solution containing 0.3 M alkoxide precursor (B, C) or 0.3 M alkanethiol (D, E). Before its modification, the gold electrode was polished with a 2000 grit polishing paper and a 15 μm diamond slurry, sonicated in deionized water for 10 s, dipped in a 1:1 HCl−H_2O_2 mixture for 10 s, rinsed with distilled water, and dried. Voltammetric measurements were performed with the BAS CV-27 voltammetric analyzer and a 10 mL cell, containing the gold electrode, a Ag/AgCl reference electrode (BAS), and a platinum wire counter electrode. The thiolated precursors were obtained from Gelest Inc., while the various alkanethiols and potassium ferrocyanide were received from Aldrich.

coefficients greater than 0.99), and yielded differential capacitance values of 17.2, 15.3, and 4.1 μF/cm^2 for the propanethiol, thiolated-alkoxide, and silica gel modified electrodes, respectively (16 h preparation). Similar values were obtained after an 8 h immersion. Differences in the thickness of the two films (supported below by ellipsometric measurements) account for these markedly different values.[5,13] The capacitance of the bare substrate electrode was 33.5 μF/cm^2.

Ellipsometric and FTIR reflectance absorbance spectroscopic measurements[14] provided further evidence for the formation of the self-assembled silica gel networks. Ellipsometric measurements (at 632.8 nm and 70° angle incidence) yielded an average film thickness of 20 and 140 Å following a 6 h assembly of the thiolated alkoxide monolayer and thiol-containing gel, respectively. The former is larger than the theoretical thickness of the monolayer (8 Å), indicating a multilayer formation (due to possible dimerization related to traces of water in the ethanol). Roughness of the gold substrate may also account for the higher than expected thickness of the alkoxide layer. Yet, this layer is substantially (7-fold) thinner than the gel film. A 24 h immersion in the sol−gel solution of the thiolated precursor resulted in the appearance of a well-defined FTIR band at 1120 cm^{-1}, corresponding to the Si−O−Si asymmetric vibrational stretching associated with the siloxane network (see Supporting Information). No such band was observed in analogous experiments involving a sol−gel solution of the nonthiolated (propyltrimethoxysilane) precursor.

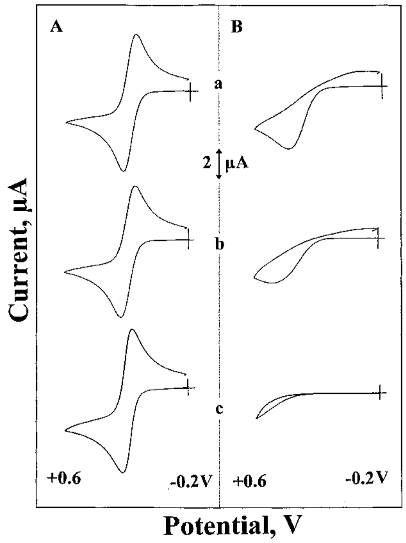

Figure 3. Cyclic voltammograms for 2 × 10^{-3} M ferrocyanide obtained at the gold after 3 (a), 8 (b), and 16 (c) h of dipping in sol−gel solutions of propyltrimethoxysilane (A) and (3-mercaptopropyl)trimethoxysilane (B). Sol−gels made of 0.5 mL of the precursor, 0.5 mL of ethanol, and 20 μL of 0.1 M HCl. Other conditions were as given in the caption for Figure 2.

In conclusion, we have described a simple and attractive route for the design of three-dimensional silica gel surface networks based on the coupling of SAM and sol−gel processes. Such a one-step avenue results in interfaces combining the strong adhesion features of thiolated layers along with the reagent encapsulation, controlled porosity, and optical transparency advantages of sol−gel microstructures. The protocol is general and versatile, and can lead to the deliberate design of three-dimensional silica gel structures on metal surfaces and to a layer-by-layer creation of multifunctional surface networks (through the judicious encapsulation of reactive species). We anticipate that the new procedure will lead to a wide range of technological applications, including chemical sensing, thin-film optics, bioactive interfaces, adhesion, or catalysis, and we are currently investigating these possibilities.

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Supporting Information Available: FTIR Spectra of related surfaces (1 page, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[14] FTIR measurements were performed with the Biorad FTS-40 instrument, while film thickness measurements were carried out with a variable angle ellipsometer (Model L104-B, Gaertner Scientific). Gold film electrodes (2000 Å gold thickness; International Crystal Manufacturing Inc.) were used in the FTIR and ellipsometric measurements. With the exception of polishing, these gold slides were pretreated in a manner similar to that described for the gold disks.