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Preparation of Hydrogel-Silica Composite Films by Electrochemically Triggered Deposition

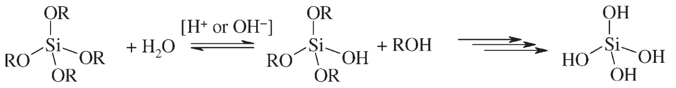
*Johanna Bünsow, Judith Petri, Diethelm Johannsmann**

Summary: The electrochemical formation of hybrid films containing both a polymer and porous silica was performed in two different ways. In both cases, the deposition of the inorganic oxide was triggered by an electrochemical pH modulation in front of an electrode. Hydrolysis and condensation of the alkoxysilane precursors in the pH gradient yielded silica structures on the electrode surface. In the first route, an electrode was employed which had been previously coated with a polymer hydrogel. In this case, the silica readily precipitated into the hydrogel, forming rigid structures with thicknesses in the range of 100 nm. A second approach makes use of the deposition of an alkoxyvinylsilane precursor. Subsequent electrochemically induced polymerization of a polymer hydrogel inside these films is possible, but yields lower thicknesses than route I. This is explained by a blocking of the electrode by the vinyl-functionalized silica film.

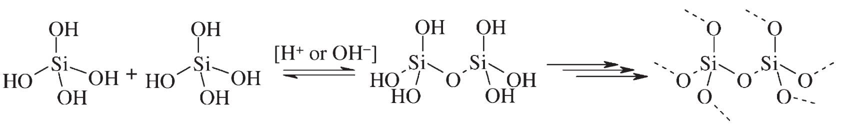
Keywords: composites; electrodeposition; hydrogels; organic-inorganic hybrids; sol-gel process

Introduction

Hybrid materials consisting of an organic and an inorganic part are attractive for a myriad of reasons including mechanical strength,[1] corrosion protection,[2] and biofunctionality.[3] The organic material often is a polymer such as polystyrene[4] or the thermoresponsive poly(*N*-isopropylacrylamide) (pNIPAm)[2,5,6] which has a lower critical solution temperature (LCST) at 32 °C.[7] In most cases, the inorganic component consists of silica, but it can be formed from titanium oxide[8] or zirconia oxide,[9] as well. Silica coatings can be easily prepared by dip-coating. Usually, the solution contains an alkoxysilane precursor dissolved in a water-alcohol mixture and an acid or base catalyst. Hydrolysis and condensation according to Equation 1 and 2 yield a silica layer:



$$\mathrm{Si(OR)_4} + \mathrm{H_2O} \xrightleftharpoons{[\mathrm{H^+}\text{ or }\mathrm{OH^-}]} \mathrm{Si(OR)_3OH} + \mathrm{ROH} \longrightarrow \mathrm{Si(OH)_4} \quad (1)$$



$$\mathrm{Si(OH)_4} + \mathrm{Si(OH)_4} \xrightleftharpoons{[\mathrm{H^+}\text{ or }\mathrm{OH^-}]} \mathrm{(HO)_3Si{-}O{-}Si(OH)_3} \longrightarrow \cdots\mathrm{O_3Si{-}O{-}SiO_3}\cdots \quad (2)$$

Dip-coating is an easy, low-cost technique to produce silica coatings. However, it is only applicable to substrates with a simple architecture. If conducting substrates are to be coated, electrophoretic deposition (EPD) is an alternative.[10,11] EPD is based on the migration of charged silica particles in an electric field, followed by deposition. Another elegant way of

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Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Strasse 4, 38678 Clausthal-Zellerfeld, Germany
Fax: + 49-5323-72 4835;
E-mail: johannsmann@pc.tu-clausthal.de

coating conducting substrates uses an electrochemical pH modulation in front of an electrode surface.[8,9,12,13] In this case, the deposition of the precursor is induced by the electrochemical reduction of water, which produces a pH gradient in front of the electrode (Equation 3).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)$$

Here, we report on the extension of this technique to the formation of organic-inorganic hybrids.

Polymer-silica hybrids can be prepared in either a two-step or a one-step approach. A typical two-step approach includes the preparation of the polymer matrix first followed by the condensation of the silane precursor in the matrix.[2,5,14] Alternatively, the formation of the organic and the inorganic part can be carried out simultaneously. In this case, the sol-gel process occurs in parallel to the polymerization of the monomer.[6,15,16] The inorganic and organic parts can be covalently attached to each other if the inorganic part contains a non-hydrolysable group which is amenable to free-radical polymerization.[17]

We report on two approaches that allow for the electrochemical production of hybrid films consisting of silica and the thermoresponsive hydrogel pNIPAm. A cartoon depiction of the two methods is given in Figure 1.

Approach A uses a hydrogel film produced by electrochemically induced polymerization.[18–20] This hydrogel film is swollen in a tetraethoxysilane (TEOS) solution. Application of a negative voltage shifts the pH to higher values, which induces the deposition of silica into the hydrogel film. In approach B, a vinyltrimethoxysilane (VTMOS) precursor is deposited in the pH gradient. Subsequent free-radical polymerization gives rise to a hydrogel which is covalently attached to the pre-formed silica film.

Experimental Part

Materials

Tetraethoxysilane (TEOS, Riedel-de-Haen), vinyltrimethoxysilane (VTMOS, Sigma Aldrich), ammonium perchlorate (Alfa Aesar), ammonium sulphate (Fluka), ethanol and methanol (Acros Organics), ammonium persulphate (Sigma Aldrich), *N,N′*-methylenebisacrylamide (Merck), and potassium ferricyanide were used as received. *N*-isopropylacrylamide (Acros Organics) was purified by triple recrystallization from hexane and dried under vacuum prior to use. All solutions were prepared with ultrapure water (arium 611VF, Sartorius, Germany). The structures of TEOS, VTMOS, and NIPAm are sketched in Figure 2.

Electrochemical Deposition of TEOS into pNIPAm Hydrogel Films

TEOS was deposited into hydrogel films which were produced by electrochemically induced polymerization. A detailed description of the preparation of the hydrogel films is given in reference 18. The hydrogel coated gold electrode was the front electrode of a 5 MHz quartz crystal resonator (Maxtek, Santa Fe Springs, C.A.). The

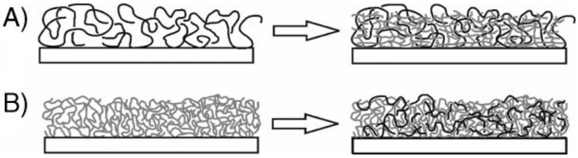

Figure 1.
Scheme of the two approaches used for the electrochemical formation of hydrogel-SiO_2 hybrid films. Black lines and grey lines represent the polymer and the SiO_2, respectively. A: An electrochemically produced hydrogel is swollen in the precursor solution and the sol-gel process is induced electrochemically. B: The hydrogel is polymerized in an electrochemically produced SiO_2-film that contains vinyl groups.

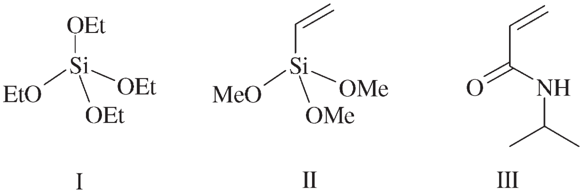

Figure 2.
Chemical structures of TEOS (I), VTMOS (II), and NIPAm (III).

quartz crystal was used as the working electrode in a three-electrode setup with a platinum plate as the counter electrode and a saturated calomel reference electrode (SCE, Sensortechnik Meinsberg, Germany). The potential was applied by a potentiostat (PGU 10V-1A IMP, Jaissle, Germany). The frequency and the bandwidth shifts were determined by impedance analysis with a network analyzer (HP4396A, Hewlett Packard). The frequency shifts were converted to a film thickness using the Sauerbrey equation

$$\Delta f = -\frac{2nf_{\mathrm{f}}^2}{Z_{\mathrm{q}}} m_{\mathrm{S}} = -\frac{2nf_{\mathrm{f}}^2}{Z_q} \rho_{\mathrm{f}} d_{\mathrm{S}} \qquad (4)$$

where n is the overtone order, f_{f} is the frequency of the fundamental, $Z_{\mathrm{q}} = 8.8 \times 10^6$ kg m^{-2} s^{-1} is the acoustic impedance of AT-cut quartz, m_{S} is the mass per unit area, $\rho_{\mathrm{f}} = 1$ g cm^{-3} is the density of the film, and d_{S} is the film thickness in the Sauerbrey sense (called "Sauerbrey thickness"). The reference states were the crystals coated with pNIPAm either in air or in the reactant solution. Note that the Sauerbrey equation often does not yield the geometric thickness when operated in a liquid environment due to roughness effects, trapped solvent, and viscoelastic contributions.

The reactant solution contained 0.5 mol/L ammonium perchlorate and 0.3 mol/L TEOS dissolved in a 70 vol-% water-ethanol mixture. The solution was filtered (0.2 μm PVDF filter, Titan, U.S.A.) and bubbled with nitrogen for 10 min prior to injection into the electrochemical cell. A pre-pulse of −1.2 V was applied for 15 min before the deposition of TEOS was induced by switching the potential to −1.3 V for 10 min. After the deposition, the samples were extensively rinsed and stored in ultrapure water.

Electrochemical Deposition of VTMOS

VTMOS was produced on the gold front electrode of a quartz crystal resonator by a similar procedure as TEOS. The reactant solution contained 0.3 mol/L VTMOS and 0.5 mol/L ammonium perchlorate dissolved in a 70 vol-% water-methanol mixture. The deposition was induced by applying a potential of −1 V for 10 min.

Electrochemical Modification of Vinylsilica Films with NIPAm

Vinylsilica films were modified with a pNIPAm hydrogel by electrochemically induced polymerization (see reference 18). Briefly, a reactant solution containing 0.3 mol/L NIPAm, 12.5 mmol/L ammonium persulphate as the electro-active initiator, 3 mmol/L *N,N′*-methylenebisacrylamide, and 0.25 mol/L ammonium sulphate was filtered and bubbled with nitrogen for 10 min. The vinylsilica modified electrode was immersed in the reactant solution and the polymerization of NIPAm was induced at −0.8 V for 15 min.

Cyclic Voltammetry with Potassium Ferricyanide

To test for the barrier properties of vinylsilica films, cyclovoltammograms on bare and on coated gold electrodes were acquired in an aqueous solution of 0.25 mol/L ammonium sulphate and 5 mmol/L potassium ferricyanide in a potential range from +0.6 to −0.6 V with a ramp rate of 100 mV/s.

Results

Electrochemical Deposition of Tetraethoxysilane into Hydrogel Films

Tetraethoxysilane (TEOS) was deposited into a pre-formed pNIPAm hydrogel film by an electrochemically induced pH gradient. The pre-formed pNIPAm film used here had a wet and a dry thickness of 58 and 38 nm, respectively. The film was swollen in the TEOS solution and a negative voltage was applied to the electrode. Figure 3 shows a typical data set. When −1.2 V were applied to the pNIPAm coated electrode (first arrow in panel C), no deposition occurred. Shifting the potential to −1.3 V (second arrow in panel C) induced the deposition of the silica film, as indicated by a strong shift in frequency (panel A). The decrease of frequency is enhanced in the course of the deposition. We attribute this enhancement to the ongoing reduction of water which increases the pH gradient. The wet (panel D) and the dry film thickness (data not shown) as calculated from the frequency shifts (Equation 4) were 100 nm both. The silica seems to be deposited as a rigid, only slightly hydrated structure. This hypothesis is supported by the low bandwidth shifts (panel B). An additional hint for the formation of a rigid silica structure is that the film thickness scales with the overtone order, indicating that the deposition proceeds in the Sauerbrey regime which is valid for rigid films. The results give no information on whether the silica is deposited as a network or as particles. In all cases studied, pre-application of a negative potential was necessary to induce the deposition. For instance, when a potential of −1 V was applied first, the deposition started when it was shifted to −1.2 V in a second step. The current density in panel C shows a decrease during the first potential pulse but it is constant during the second one. The pre-pulse seems to induce a blocking of the electrode surface. The decrease of current density during the pre-pulse is accompanied by a decrease of bandwidth (panel B), indicative of a collapse of the hydrogel. We are not aware of a process where the hydrogel collapses and blocks the surface first and enhances the deposition when the potential decreases afterwards. However, the results clearly prove that the formation of silica-pNIPAm hybrid films is possible by this electrochemical approach.

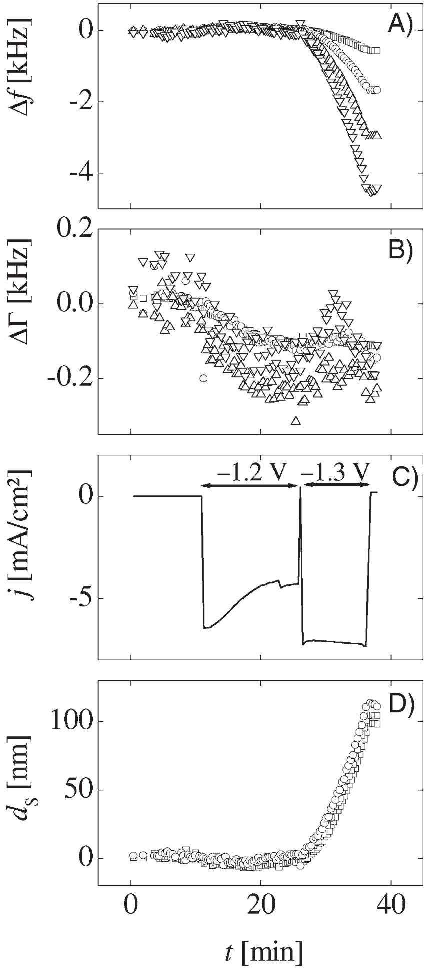

Figure 3.
Shifts of frequency (Δf, A) and bandwidth ($\Delta\Gamma$, B), both measured on the 5 (squares), 15 (circles), 25 (triangles), and 35 MHz (inverted triangles) overtone, current density (j, C), and film thickness calculated from Δf (d_S, D) acquired during the electrochemically triggered deposition of silica from a TEOS solution into a pre-formed pNIPAm hydrogel film.

Electrochemical Deposition of Vinyltrimethoxysilane

A typical data set obtained during the electrochemically triggered deposition of vinyltrimethoxysilane (VTMOS) from a 70 vol-% water-methanol mixture is shown in Figure 4. As a result of the deposition of VTMOS, the frequency shift in panel A decreases strongly when a voltage of −1 V is applied to the working electrode. No deposition was observed when the quartz crystal was immersed in the reactant solution without application of a voltage (data not shown). The frequency shifts were converted to a film thickness, d_S, by using the Sauerbrey equation (Equation 4). The film thicknesses were 270 nm and 240 nm in the reactant solution and after drying in air (data not shown), respectively. The difference between the wet and the dry thickness can be explained by the loss of water from the vinylsilica upon drying. The bandwidth shifts in panel B are large, indicative of the formation of either a very soft, strongly hydrated or of a rough film. The current

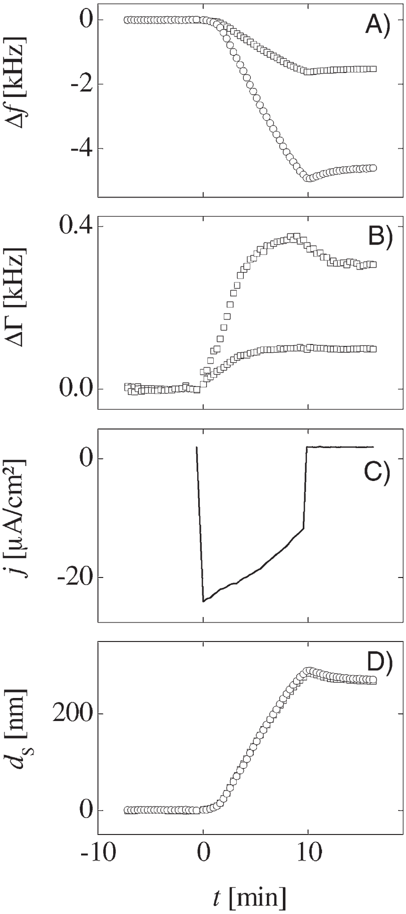

Figure 4.
Shifts of frequency (Δf, A), and bandwidth ($\Delta\Gamma$, B), both measured on the 5 (□) and 15 MHz (○) overtone, current density (j, C), and Sauerbrey thickness (d_S, D), monitored during the electrochemically triggered deposition of VTMOS at −1 V vs. SCE. A pH gradient in front of the electrode surface induces the hydrolysis and condensation of the silane precursor.

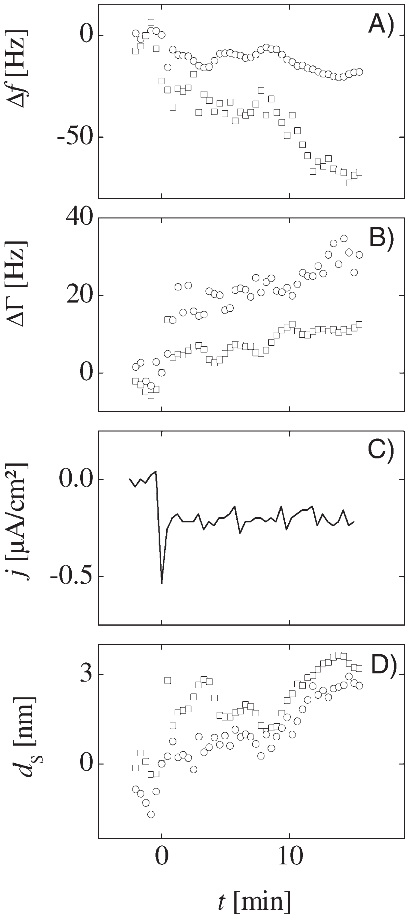

Figure 5.
Shifts of frequency (Δf, A), and bandwidth ($\Delta\Gamma$, B), measured on the 5 (□) and 15 MHz (○) overtone, current density (j, C), and film thickness (d_S, D) detected during electrochemically induced polymerization of NIPAm on a gold electrode modified with VTMOS.

density (panel C) is large in the beginning and drops when the gel is deposited. Presumably, the silica film blocks the surface and lowers the amount of water being reduced.

The modification of VTMOS films with NIPAm using electrochemically induced polymerization was tested, as demonstrated in Figure 5. The frequency shifts (panel A) in response to application of −0.8 V were very small. The film thickness was about 3 nm after 15 min deposition (panel D). The bandwidth shift increased slightly (panel B). The current density (panel C) was very small, indicating that the VTMOS layer blocks the access of the reactants to the surface. Blocking of the surface was evidenced by cyclic voltammetry in a potassium ferricyanide solution, as shown in Figure 6.

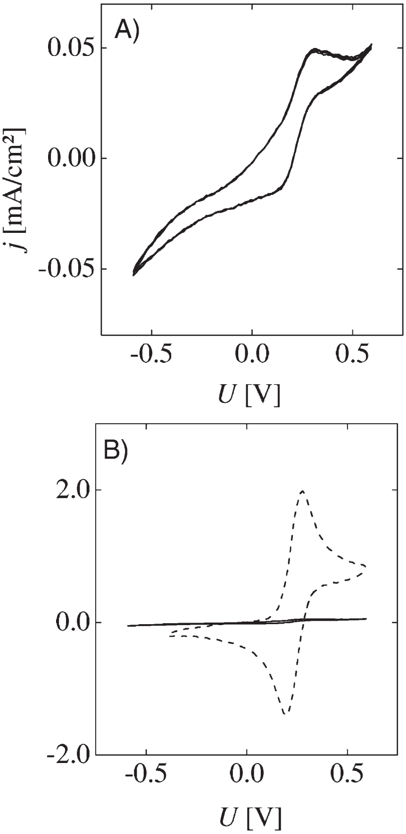

Figure 6.
Cyclovoltammograms acquired in a 5 mmol/L $K_3[Fe(CN)_6]$ solution with a vinylsilica coated electrode (A, B, straight line) and with a bare electrode (B, dashed line). The current density is dramatically decreased by the presence of the inorganic film. Note that the scaling in panel A and B is different.

The cyclovoltammograms acquired on an electrode coated with vinylsilica (panel A, B) show a strong decrease of the current density as compared to the bare electrode (panel B). The vinyl-modified silica film is an efficient barrier to the diffusion of ferricyanide ions. Hindrance of the penetration of reactants into the VTMOS film may be useful for the preparation of two-layer structures with a silica sub-layer covered by a polymer coating. In this case, the polymerization must be initiated thermally or photochemically in the bulk phase because the electrode surface is blocked.

Conclusion

We demonstrate two routes to the electrochemical formation of hydrogel-silica hybrid films on conducting surfaces. Both routes make use of an electrochemically induced pH gradient in front of an electrode surface. Hydrolysis and condensation of the alkoxysilane precursor result in the deposition of a silica structure on the surface. Producing the pH gradient in front of a polymer coated electrode induced the deposition of a rigid silica structure into the polymeric hydrogel. Typical silica film thicknesses were in the range of 100 nm. Another approach exploits the deposition of silica films that contain vinyl groups. The film thickness was in the range of 250 nm, here. Electrochemically triggered polymerization in the presence of the vinyl groups yielded very low hydrogel film thicknesses which could be attributed to the good barrier properties of the dense silica film. This route may be useful to produce two-layer structures composed of an inorganic sub-layer with a polymer layer on the top.

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