

Covalently modified Silica Nanoparticles – Synthesis and electrochemical Investigations into the Mobility of Surface-bound redox Centers.

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The objective of this work is the immobilization of redox-active molecules on a simplified interphase system with a controlled geometry in order to investigate their interactions in such environments with, among other, electrochemical tools^[1]. This will later allow to study the mobility and accessibility of such molecules on the surface. Since the product resulting from the standard silylation modification procedure^[1] is not suitable for the preparation of the desired systems, the surface modification via a stable Si-C bond from a modified Si-H surface became the main synthetic challenge.

The spherical particles necessary as solid matrix for the simplified interphase system were synthesized by a modified Stöber process^[2, 3]. The synthetic strategy involves high water concentrations as well as post-synthesis high-temperature treatment in order to reduce the microporosity. The characterization with scanning electron microscopy (SEM, Figure 1) and dynamic light scattering (DLS) demonstrates that the silica particles are monodisperse and non-agglomerated spheres. Also, gas physisorption isotherms show that the materials can be considered as non-porous. The diameter of the particles can be tuned in the sub-micrometric range by a precise control of the reaction conditions. The non-porosity is necessary to ensure a homogeneous environment for and a good accessibility to the redox-active molecules. The monodispersity and the well-defined properties makes them suitable for quantitative analyses in electrochemical investigations.

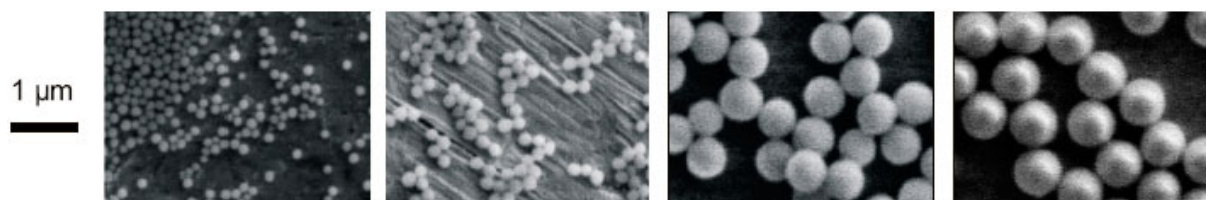


Figure 1: Spherical silica particles produced from the modified Stöber process.

For the silica surface modification via stable Si-C bonds, a Si-H terminated surface is desired as starting material. The chlorination-reduction sequence at high temperatures introduced in this work, opens a new route for the synthesis of Si-H modified silica surfaces^[4]. According to a quantitative analysis of the evolved hydrogen from the reaction of the modified surface with ethanol/KOH, a high Si-H surface concentration is achieved. Also the procedure is reproducible for many types of silica materials. IR as well as ²⁹Si CP/MAS NMR spectroscopy (Figure 2) demonstrate that T³_H groups are the main product while the reaction of Si-OH groups by reduction or dehydroxylation is almost quantitative.

The high degree of cross-linking of the Si-H groups with the silica matrix as well as the absence of silanol groups are desired for the stability, homogeneity and inertness of the matrix. This contrasts with Si-H modifications obtained from low temperature methods where silanol groups remain after the reaction and a large proportion of T²_H groups are produced.

The characterization of the Si-H modified materials also makes it possible to propose the assignment of the ν_{SiH} band at 2283 cm⁻¹ in IR spectroscopy to the T³_H groups.

The chlorination is the key step to achieve a high Si–H coverage, and the optimal temperature for the reduction step is about 900 °C. Under these reaction conditions, as shown by the SEM and DLS measurements as well as by the BET and BJH analysis of gas physisorption data, the physical properties, such as shape, pore size and surface area, remain essentially unchanged. Only micropores are lost due to the high temperatures employed during the procedure.

Thus, the chlorination-reduction sequence represents an ideal strategy to provide the starting material for further silica surface modification with redox-active molecules by reaction of the Si–H groups. Moreover, the simple and efficient access to Si–H terminated silica may also open new modification routes and further applications of such materials, e.g. in separation science and catalysis. To the best of our knowledge, this is the first procedure enabling a silicon hydride surface modification that may be applied to all types of silica surfaces, producing a high surface concentration, possibly allowing large scale ups and leaving the surface free of any other functionalities beside the Si–H groups.

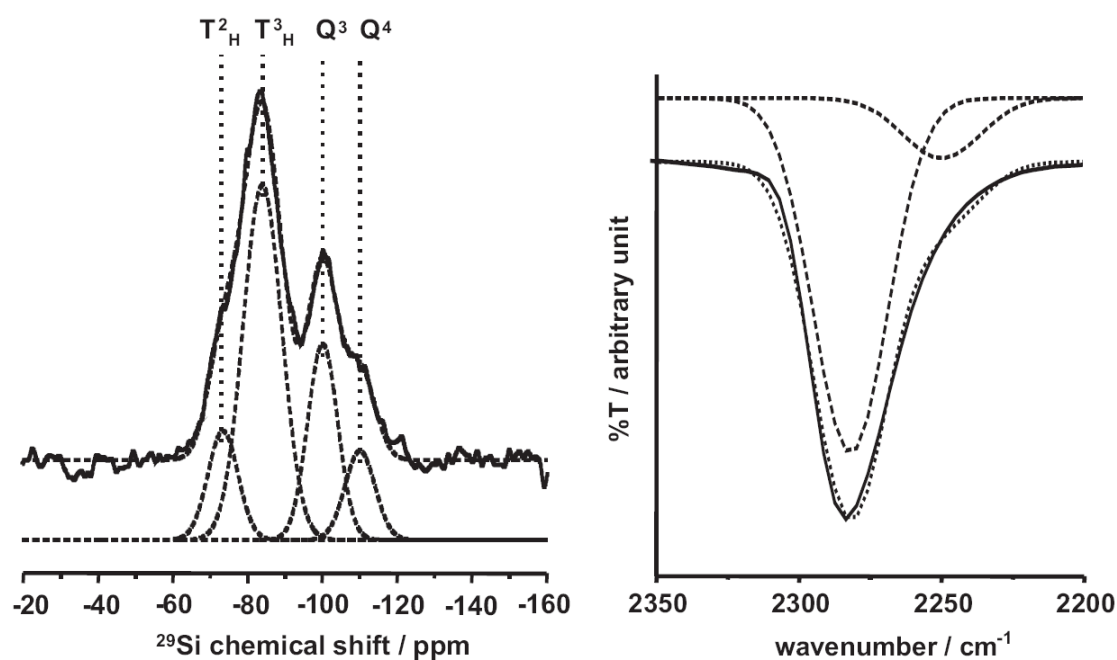


Figure 2: ^{29}Si CP/MAS NMR spectrum (left) and ν_{SiH} signal from the DRIFT spectrum (right) with Gaussian deconvolution of Si-H modified silica surface.

Free radical initiated hydrosilylation reactions were developed to produce a Si–C bond on Si–H terminated silica surfaces. Both photochemical and thermal initiation^[5,6] was employed. A strong attachment of the organic molecules on the silica surface is obtained. Indirect evidence, like decrease in the Si–H surface concentration, absence of C=C signals in the IR and NMR spectra of the modified materials (Figure 3) are in agreement with the formation of a Si–C bond.

The reaction occurs exclusively on the silica surface according to NMR investigations of the reaction solution. However, direct evidence for the Si–C bond formation could not be established with ^{13}C or ^{29}Si solid state NMR spectroscopy, because of weak signal intensity and signal overlapping, respectively. Moreover, the possibility for a radical initiated surface telomerization as well as Markovnikov addition during the hydrosilylation reaction can not be excluded. The free radical hydrosilylation has the advantage over the transition metal catalysed or radical initiator induced reactions that it leaves the silica surface free of impurities. A C18 as well as a terminal C=C bond modified surface were obtained from this route.

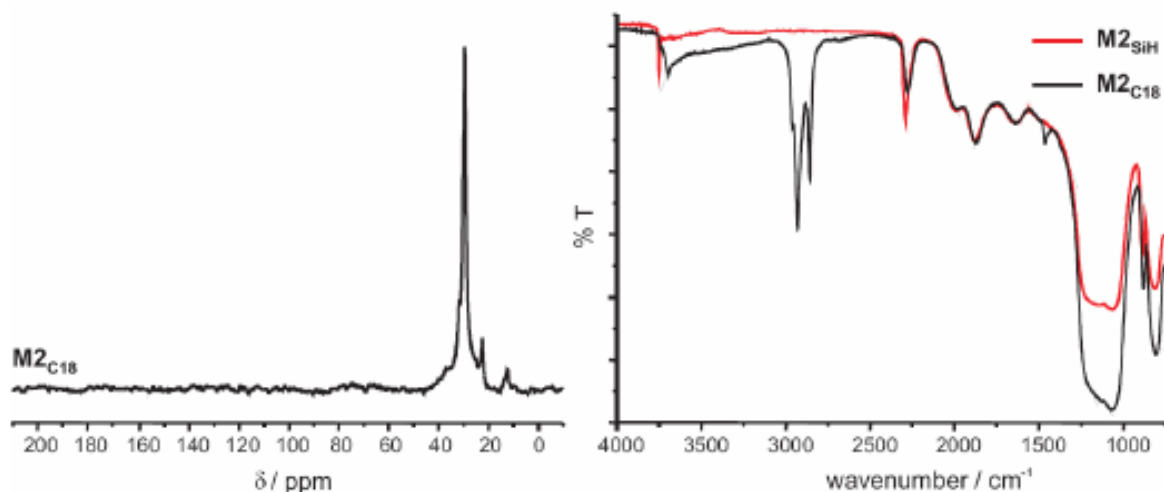


Figure 3: ^{13}C CP/MAS NMR (left) and DRIFT (right) spectra of C18 modified silica surfaces.

The photochemical induction is also advantageous with regard to its mild reaction conditions for the modification of non-porous materials. A carboxylic acid functionalized surface was obtained via this method.

As an alternative to the radical hydrosilylation methods, a base catalyzed dehydrogenative coupling reaction of a terminal alkyne with Si-H groups was tested. The reaction performed on soluble model compounds shows two valuable advantages: side reactions are not found, and direct spectroscopic evidence for the formation of the Si-C bond is obtained. The kinetics of the reaction were investigated with ^1H NMR spectroscopy (Figure 4). The reaction needs several days to complete, but a high yield is achieved.

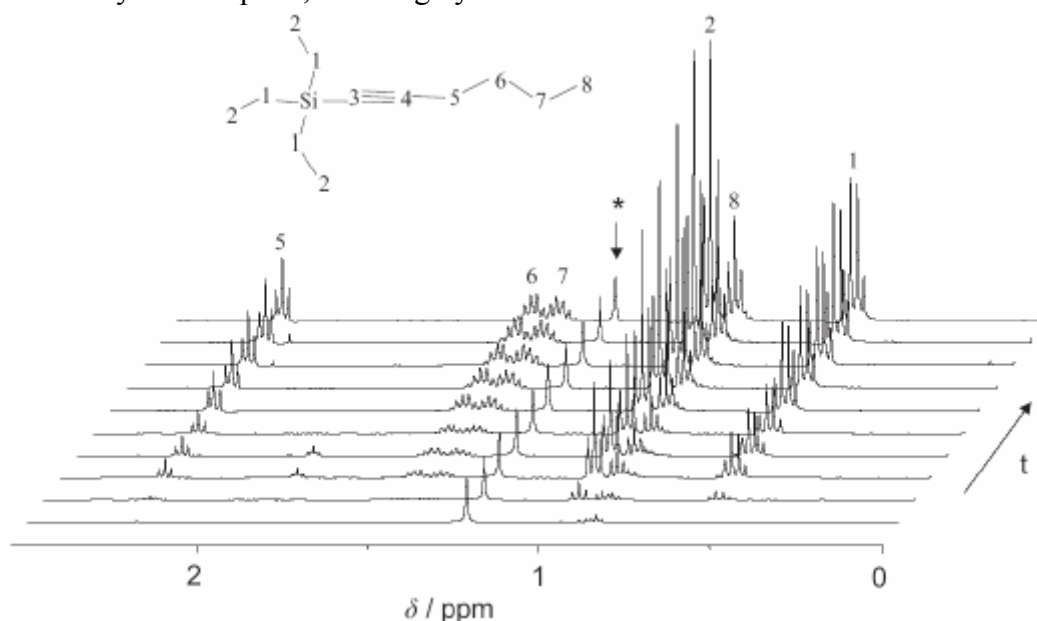


Figure 4: Time resolved ^1H NMR spectroscopic investigation of the production of triethylhex-1-ynylsilane in THF; $[*]\text{CH}_2$ resonances of hexadecane (internal standard).

A dehydrogenative coupling mechanism was proposed and supported by experimental observations: No reaction occurs in the absence of 1-hexyne, whose acidic proton is believed to act as a Lewis acid to make the hydride a better leaving group. This is confirmed by the experimental detection of H_2 when the reaction is performed in presence of a proton source. The optimization of this reaction on the silica surface and the attachment of redox-active

molecules via this route are still needed at this point. However, this reaction is promising as a general modification method for silica surfaces.

The direct attachment of terminal C=C bond functionalized redox-active molecules was not achieved by photochemical or thermal hydrosilylation reactions because of the poor stability under the reaction conditions and / or the need for high concentration of the olefin. On the other hand, the carboxylic acid modified surface prepared by the free radical induced hydrosilylation can be converted easily into the corresponding acyl chloride, and then be used in a subsequent reaction to immobilize ferrocene units bearing an amine functional group. A surface concentration similar to the one expected for a ferrocene monolayer is obtained.

The terminal C=C bond modified silicas obtained by thermal hydrosilylation may also be further functionalized by radical hydrobromination. Characterization by DRIFT and NMR spectroscopy shows that the silica bound C=C groups have fully reacted. Indirect evidence on the outcome of the reaction is obtained from low molecular weight model compounds: the fact that the C=C bonds of 1-octene and of octavinylsilsequioxane are fully hydrobrominated and that the anti-Markovnikov products are obtained under homogeneous conditions, suggests that C=C bonds on the silica surface may react in the same manner. Furthermore, the use of a silsequioxane as model compound led to the production of the bromoethyl substituted octasilsequioxane by radical hydrobromination in better yield and purity than the previously published procedures.

However, the application of the brominated spacer for the immobilization of active molecules has several limitations. Therefore, the reactive acyl chloride modified silica surface was preferred for the immobilization of the ferrocene derivatives.

As a first application of the Si-H terminated silicas modified by radical hydrosilylation, their performances as HPLC separation phases were tested. The chlorination-reduction sequence followed by C18 surface modification opens a new synthetic strategy for the preparation of low silanol activity C18 HPLC phases compared to the conventional silylation method. At the early stage of their development, the C18 modified phases already match their silylated equivalent for the separation of organic bases (Figure 5). On the other hand the peak tailing of chelating analytes may still be improved. The source of metal impurities is not determined at this point. The solvent used during modification and HPLC tests as well as the original silica materials are two potential sources. Finally, the methylene selectivity of the C18 modified phase is low. Optimization of the thermal hydrosilylation reaction, in order to achieve higher surface concentration and lower the extent of possible side reactions, may further improve the separation quality.

The HPLC investigation of the Si-H and C18 modified silicas delivers additional information on the surface chemistry of these materials. The peak asymmetry of organic bases after separation with Si-H modified materials demonstrates that the chlorination-reduction sequence produces a material almost free of surface isolated silanol groups. On the other hand, according to the peak tailing of organic bases after separation with C18 modified particles, some silanol groups are produced during the hydrosilylation reaction. However, their effect on the HPLC separation is moderate, indicating that their surface concentration remains low.

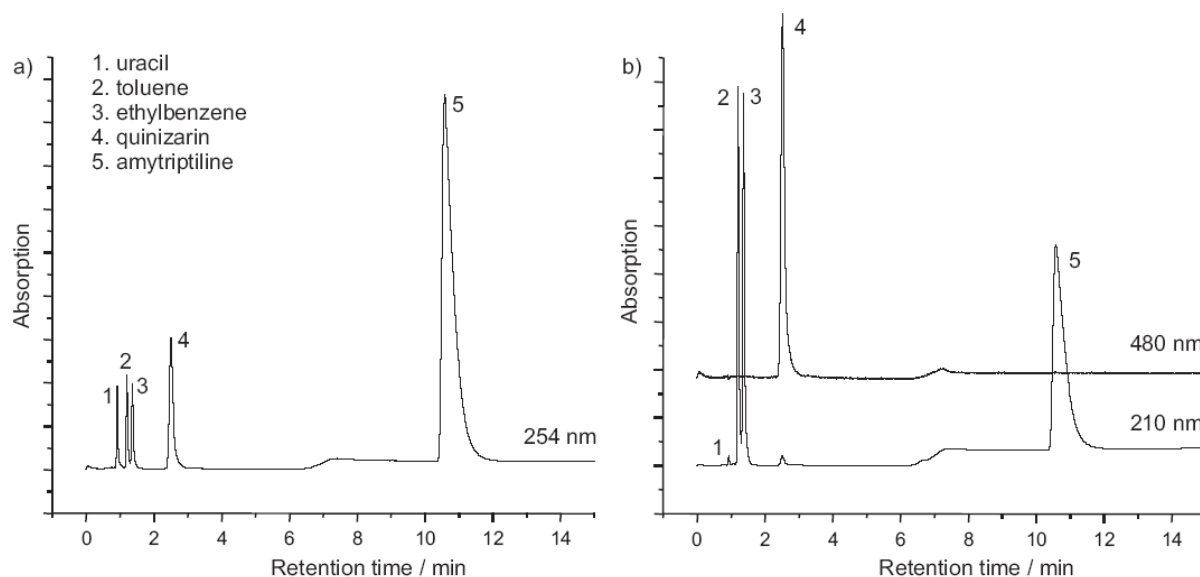


Figure 5: Separation of SRM 870 with C18 modified silica a) UV detection at 254 nm, b) UV detection at 210 and 480 nm: Gradient elution: 60 % methanol/ 40 % aqueous potassium phosphate buffer, pH 7.0 (v/v) hold 5 min to 80 % methanol/ 20 % buffer (v/v) between 5 min to 6 min.

The second application of the silicon hydride terminated silicas modified with redox-active molecules by radical hydrosilylation is their electrochemical investigation.

In order to support a precise quantitative analysis of the electrochemical results, a two dimensional particle assembly on an electrode surface was carried out. Dip-coating experiments with bare hydrophilic silica particles yield the desired monolayer coverage on hydrophilic platinum surfaces. However, the hydrophobic character of the ferrocene modified particles results in weak particle-electrode interactions. The spontaneous adsorption of isolated particles on the electrode surface^[1, 2] (Figure 6) is preferred for the qualitative analysis of the charge transfer mechanism and quantitative analysis of the redox-active molecules' accessibility.

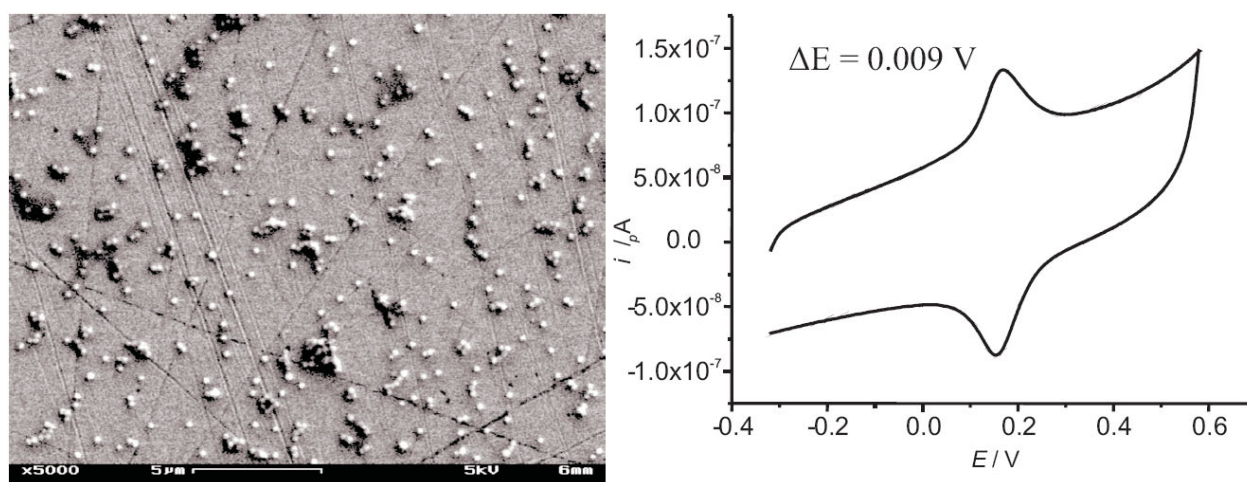


Figure 6: Ferrocene-modified silica particles on a platinum electrode: SEM images (left) and cyclic voltammogram in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ (0.1 M) at 0.02 V s^{-1} (right).

The electrochemical investigation makes it possible to elucidate the mechanism of the charge transfer within the simplified interphase system: Cyclic voltammetry of the ferrocene modified particles (Figure 6) indicates that ferrocene units over a large part of the particle surface are electrochemically accessible by an electron hopping mechanism^[2, 7]. In addition to the intermolecular charge transfer between ferrocene units on the surface of a single particle, an interparticle charge transfer between adjacent particles within large agglomerates is also taking place. Moreover, the proportion of active molecules that are accessible to the redox reaction were determined from the comparison of the ferrocene surface concentration obtained from cyclic voltammetry with the one obtained from atomic absorption spectroscopy. The accessibility of more than half of the ferrocene units to the redox process is a further evidence for a charge transfer occurring along the particle surface. These redox-active molecule interactions and the charge transfer by electron hopping observed for the ferrocene as a model system are important requirements for the scope of electrochemical investigation and control of immobilized catalyst in interphases, which should be the subject of future work.

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