In-Situ Thiol-Modified Silica Nanoparticles

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Citation

Abstract

In situ organically-modified silica nanoparticles were produced by the co-reaction of TetraMethOxySilane (TMOS), a standard sol-gel precursor and organofunctional alcoxysilanes. The hydrolysis and condensation reactions, as compared to those of pure silica, were followed by Dynamical Light Scattering and FTIR, showing stable sols with extended regimes, prior to gelation, and chemically active surface sites.

INTRODUCTION

Chemical incorporation of functional organic groups on silica gels is an area of great potential and activity ([1],[2],[3]), due to the possibility of tailoring the chemical behavior of the surface of otherwise inert nanoparticles, through, for instance, the anchoring of metalorganic complexes or even catalytic active organic groups. In principle, one straightforward way to prepare organically-modified sols is by co-hydrolyzation and/or co-condensation during a sol-gel processing of a known material ([4]). However, this requires the hydrolysis and condensation of the organically-modified alcoxide to be slower that that of the unmodified precursor. Thus, the details of how an organic group is bonded to the surface of a nanoparticle must be determined, if one is to produce chemically-active nanostructures.

The complex kinetics of the particle size during the initial stages of these reactions, for the case of unmodified silica, for example, has been revealed by DLS (Dynamic Light Scattering) ([5],[6],[7]), mainly. As for the chemical structure during the hydrolysis-condensation process, 29Si NMR, FTIR and Raman have been employed to characterize sol-gel intermediates at different pH or thermal treatments ([8],[9],[10],[11]). However, scarce information is available on the details of the initial stages of the hydrolysis-condensation of organically-modified nanoparticles prepared via sol-gel, in terms of the particle size and chemical structures present.

Accordingly, in the present study, the initial stages of thiol-modified silica sols are studied with DLS and FTIR, as compared to those unmodified nanoparticles under the same conditions. The DLS studies allow determining the gelation point ([12]), key information to ensure the long-term stability of the modified nanoparticles, whereas the FTIR allows to follow the chemical changes during the production of the sols and the details of how the thiol group gets attached to their surface. Thiol groups are known to have a great affinity to metal ion, so their presence on oxide sols could lead either to the production of in-situ nanocomposites or the develop ion sequestrates for various applications ([13]).

EXPERIMENTS

The organically-modified sols were prepared from methanolic solutions of TetraMethOxySilane (Aldrich 99%) TMOS, a well known precursor for silica gels, and 3-mercptopropyl-Trimethoxysilane (Aldrich 99%) $RSi(OMe)_3$, by co-reaction in a standard sol-gel procedure as reported previously ([13]). The thiol- modified silica particles were prepared by synthesizing first pure silica particles, followed by a containing process with a sell of silica – thiol molecules. The silica particles were prepared by mixing with agitation magnetic, TMOS with on half of the methanol; separately, water with the pH=7 was mixed with the other half of methanol. These two solutions were mixed together drop wise with strong agitation and kept under reflux conditions (around 67 °C) these particles were used as a reference to evaluate the properties of the silica- thiol particles, TMOS: water : methanol, of the silica particles, was 1:4:12.

Silica particles refluxed during 30 min produce, when they are chemically modified with thiol groups, particles with a size larger that those obtained for pure silica particles. Once the silica cores were prepared, a solution of MPTS in methanol was added drop wise with agitation vigorous to produce the silica- thiol shells. This suspension was kept

under reflux conditions for different periods between 60 and 120 min depending at pH=7 and the molar ration Si: S; in this work a 1:1 molar ration for Si: S was used. The final composition of the thiol- modified particles, TMON:MPTS: water: methanol, was 1:1:4:15.

With this procedure it is possible to obtain core shell type particles with the core made of pure silica and the shell of silica-thiol the particle size of silica sol changed with time during the sol gel reaction ([13]); these particle size profiles were determined by DLS as a function of the reaction time by sampling the system at regular time intervals from the beginning of the sol-gel reaction and during the coating procedure of the silica particles. Because DLS measures the diffusion coefficients of the scattering particles and this depends on temperature, all samples were cooled to room temperature prior to the determination of the particle size. The DLS measurements were performed using an apparatus (Brookheaven BI-90) equipped with a digital correlator (BI-9000). From the correlation function it is possible to obtain the mean and the standard deviation of the particle size distribution; in this work, only the mean of the particle size is reported. The experimental error obtained from the DLS measurements is of ±3%. The light source was a laser operated at 488 nm an the scattering angle was set to 90°.
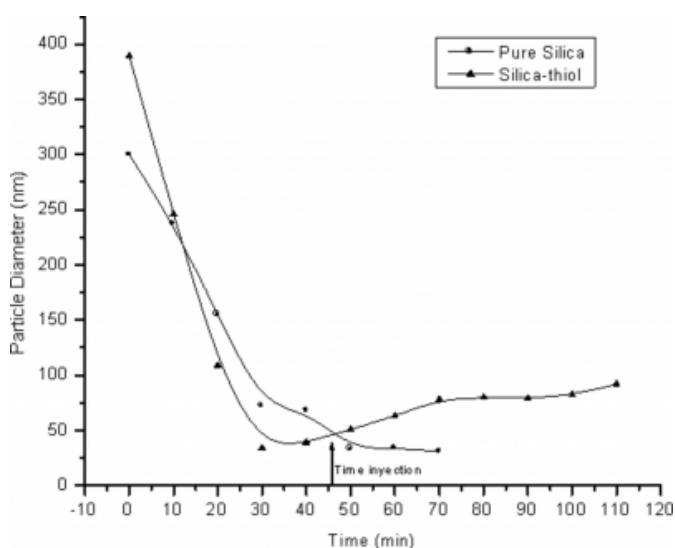
Particle size profiles were determined by DLS in a Brookhaven BI-90, equipped with digital correlator (BI-9000) and through a neon laser emitting at at 488 nm and at a scattering angle of 90 °. The FTIR was carried out in a Nicolet 910 apparatus, by the diffusive reflectance technique.

RESULTS AND DISCUSSION

Figure 1 shows the effect of the thiol group on the sols kinetics, at a pH=7, as compared to the equivalent result for a standard silica nanoparticle. At the early stages of the reaction, an unstable regime appears, as revealed by the oscillations in the particle size. Pure silica sols reach a stable regime after 30 minutes, with an average particle size of 97 nm, whereas the thiol-modified ones require up to 80 minutes to reach a steady state in terms of the particle size variations, with a mean value of 110 nm, indicating that, in fact, some groups have been bonded to the surface of the nanoparticles, increasing their effective diameter. Obviously, after reaching the stable state, longer reaction times would lead to gelation of the system.
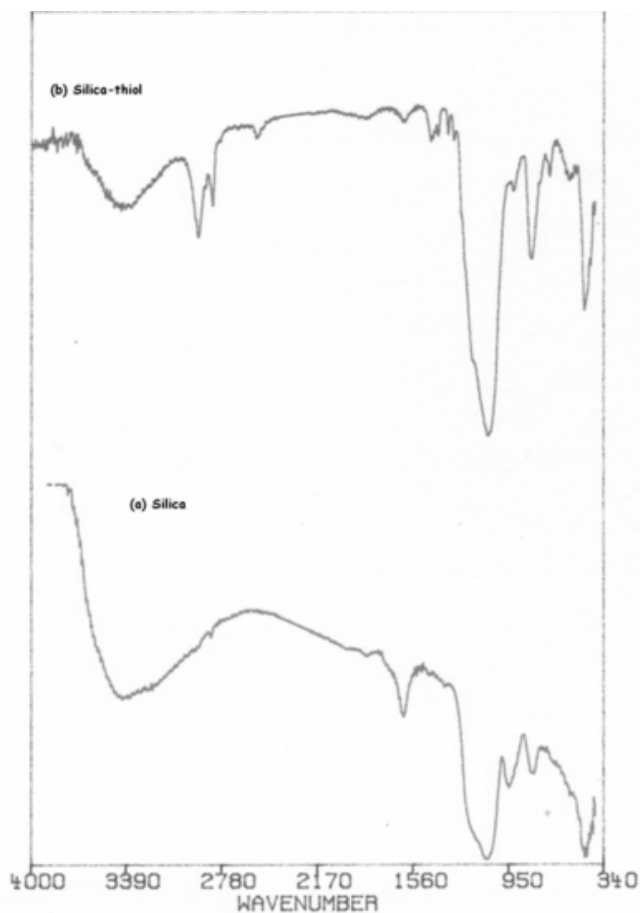
Figure 1

Figure 1: Particle size as a function of time for (a) pure silica ans (b) silica – thiol.

During the reaction of TMOS and water in an alcoholic medium, IR bands appear at 950 and 1090 cm^{-1}, due to the vibrations of Si-OH and Si-O-Si bands, respectively. These bands are very intense and correspond to the formation of the SiO_2 network. The chemical reactions between adsorbate molecules and available surface sites are clearly demonstrated by a new band ([14,15,16]), along with the decrease of the original above bands, as clearly seen in Figure 2, where the difference between pure silica and thiol-modified silica is obvious. For the unmodified silica, dried at 50 °C in vacuum (Figure 2a) the broad absorption band between 4000 and 3000 cm^{-1} corresponds to the fundamental stretching vibrations of different types of hydroxyl groups ([13,14,15,16,17]). The combination of the SiO_2 vibrational modes are generally located at 1960, 1870 and 1640 cm^{-1}.

Figure 2

Figure 2: FT-IR spectra of a (a) pure silica and (b) silica – thiol, heat treated at 50 °C and pH=7
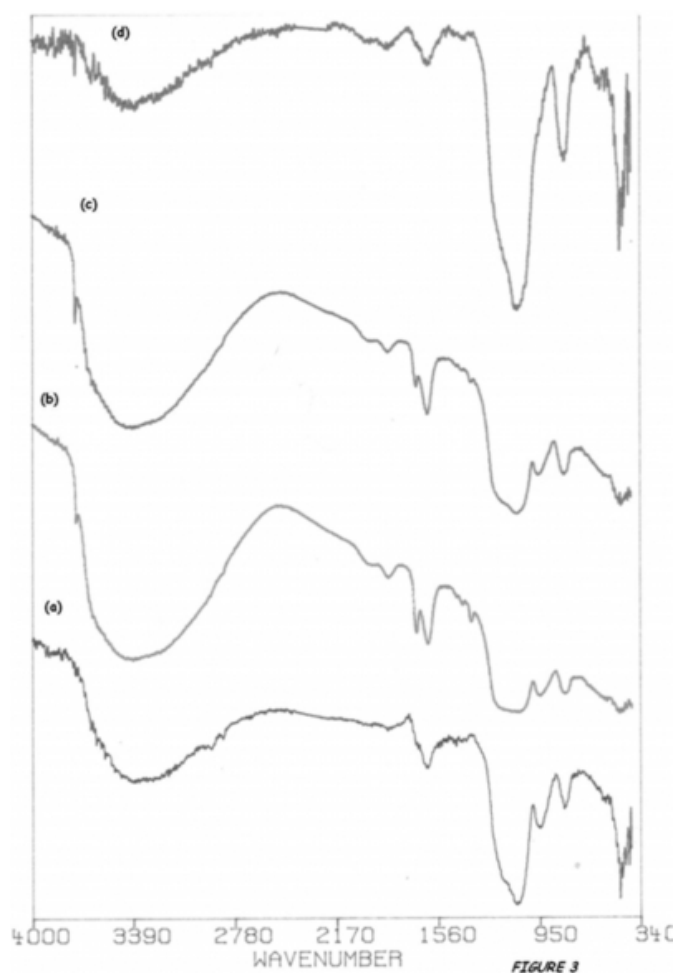

For the case of the thiol-modified silica samples (Figure 2b), one can observe, on the high frequency side, a broad band centered at around 3000-3600 cm^{-1}, corresponding to free Si-OH groups. On the low frequency side of this broad band, there exists a weak shoulder, near 2860 cm^{-1}, which indicated the presence of methanol. If the TMOS is not fully hydrolyzed, the IR spectrum will show bands at 2958, 2853 and 152 cm^{-1} [15]. The first such bands cannot be distinguished from those of ethanol, whereas the 1456 cm^{-1} band can be easily appreciated in the spectrum. This indicates that the sample contains Si-OCH$_3$ bonds, from the incomplete TMOS reaction. The band at 2569 cm^{-1} corresponds to the thiol group. The hump around 1859 cm^{-1} corresponds to Si-O groups and the bands 1343 and 1307 cm^{-1} are attributed to CH$_2$ on the surface, demonstrating that thiol groups are indeed on the surface of the nanoparticles, since the tripping, intensification or disappearance of this band indicates that a molecule is absorbed on the surface on in the immediate vicinity of each functional group [16].

Figure 3 corresponds now to the pure silica sample dried at

(a) 100, (b) 300, (c)700 and (d) 800 °C. generally speaking, the spectra show changes in water-related bands in the samples with temperature. The stretching modes of silanol appear at 3750 cm^{-1}, for free silanols, at 3660 cm^{-1} for vicinal silanols and 3440 cm^{-1} for internal silanol. The range 300-2750 cm^{-1} corresponds to the symmetric and antisymmetric fundamental stretching vibrations of the CH$_3$ groups. For the 300 °C sample, a hump at 1968 cm^{-1} appears, corresponding to SiO$_2$ vibrational modes.

Figure 3

Figure 3: FT-IR spectra of a pure silica heat treated at (a) 100, (b) 300, (c) 500 and (d) 700 °C


FIGURE 3

As for the thiol-modified silica samples, Figure 4 shows the IR spectra for (a) 100, (b) 300, (c) 700 and (d) 800 °C heat treatments. As in the pure silica case, water-related bands decrease with temperature. There is first a rapid loss of water below 200 °C and then the removal of bonded water, at a slower rate, between 400 and 800 °C. The band at 1621 cm^{-1} corresponds to molecular water. As heating takes place, the 3750 cm^{-1} can be observed, corresponding to the stretching vibrations of the free Si-OH groups. When a hydrogen bond

is formed between the surface silanols and any other compound, new bands appears at lower frequencies and the intensity of the band at 3750 cm^{-1} decreases. This band begins to form at 400 °C. The 1452 cm^{-1} band is not present now, except for a small hump, which does not change significantly with temperature. The 2565 cm^{-1} thiol band disappears after 300 °C, due to the decomposition of organic groups at relatively high temperatures. It can be observed that the addition of organic groups favors the formation of free silanol groups, very convenient feature for potential uses as anchoring sites.

Figure 4

Figure 4: FT-IR spectra of a pure silica – thiol heat treated at (a) 100, (b) 400, c) 700 and (d) 800 °C
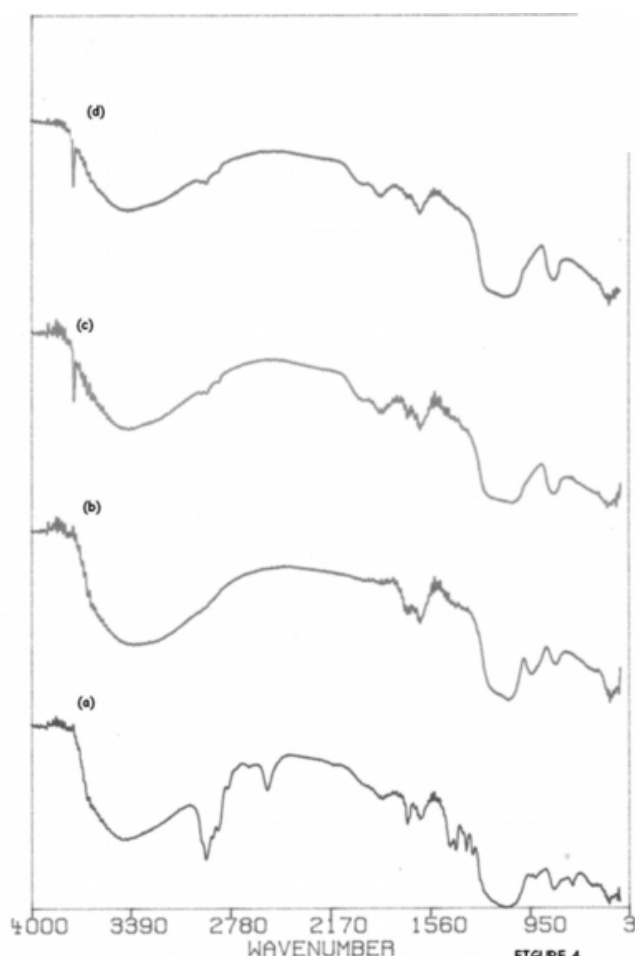
CONCLUSIONS

Organically-modified silica nanoparticles were obtained in-situ by co-reaction of standard silica precursors (TMOS) with thiol-containing chemicals. The incorporation of thiol groups did not show a significant change on the structure of the final gel produced, in terms of their porosity, but allowed to have longer gelation times and, most importantly, stable reactive nanoparticles. The use of these materials, for water purification and biomedical technologies, will be reported separately.

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