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Growth of Metal Nanoparticles in a Sol-Gel Silica Thin Film

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Silica films on glass substrates with homogeneously dispersed platinum, gold or silver nanoparticles were prepared by sol-gel processing mixtures of tetraethoxysilane and {3-[(2-aminoethyl)amino]propyl}triethoxysilane complexes of the corresponding metal ions, followed by dip-coating and hydrogen treatment of the films at elevated temperatures.

Introduction

Numerous work has been published on the synthesis of metal oxide or metal nanoparticles[1] in polymeric,[2] inorganic,[3] or hybrid organic-inorganic matrices.[4] Independent of the type of matrix material, the principles of introducing the nanoparticles are rather similar. Thus, the matrix can be formed around pre-formed (stabilized) nanoparticles, the particles can be generated in the pre-formed matrix, or matrix and nanoparticles can be synthesized concomitantly. All methods, when properly controlled, can lead to homogeneously dispersed materials.

We have previously developed a sol-gel method by which nanometer-sized metal oxide or metal particles with narrow size distributions are generated within a silica matrix.[5–7] The nanoparticles prepared by this method are not agglomerated and are homogeneously distributed in the SiO_2 matrix, even in materials with high metal loading. The high metal dispersion in the nanocomposites was achieved by tethering metal ions to the matrix generated during sol-gel processing. To this end, trialkoxysilyl-substituted metal complexes of the type $[(RO)_3Si(CH_2)_nA]_nMX_m$, formed in situ by reaction of a metal salt (MX_m) with alkoxysilanes $(RO)_3Si(CH_2)_nA$ (A = a coordinating group), were used as precursors for sol-gel processing. Metal coordination is retained during gel formation, and the metal complexes are tethered to the gel network through the $(CH_2)_nSiO_{3/2}$ groups. The metal loading can be adjusted by using $Si(OR)_4$ as a co-precursor. The resulting gels with the idealized composition $[O_{3/2}Si(CH_2)_nA]_nMX_m{\cdot}xSiO_2$ had the typical color of the corresponding metal complexes. When the metal complex containing gels were subsequently heated in air, all organic moieties were oxidized and/or pyrolyzed, i.e. carbon-free materials were obtained, and nanosized metal oxide particles [i.e., the nanocomposites $MO_y{\cdot}(x+n)SiO_2$] were formed in the silica matrix. In the final step, the oxide particles were reduced by hydrogen, resulting in metal/silica nanocomposites, $M{\cdot}(x+n)SiO_2$. Since the nanoparticles are formed during the *oxidation* step, the reaction conditions during this step, including the nature of the organic groups (counterion, tethering groups) being burnt, determine the size of the obtained metal oxide nanoparticles.[7] The particle size is not changed significantly during the subsequent reduction step.

This procedure results in nanocomposite *powders*, due to the removal of the organic groups. Although we have previously shown that the synthesis of metal/silica nanocomposite powders by the coordination/oxidation/reduction protocol can also be applied to the coating of porous silica pellets with Pt nanoparticle-containing gels,[6] this synthesis protocol is not suitable to prepare coherent nanoparticle-containing *films*. Such sol-gel films are interesting for a variety of applications.

It was recently shown for aerogels that metal nanoparticles are also formed by direct reduction of tethered metal complexes without prior removal of the organic groups.[8] Since removal of the organic groups is detrimental to good film properties, this modification of the synthesis protocol may also allow to obtain metal nanoparticle containing films. However, this is not at all a straightforward modification of the existing procedure, because the *metal* particles will not be formed by reduction of existing metal oxide particles, but instead by nucleation and growth during the reduction step. Since nucleation and growth of the nanoparticles occurs under completely different conditions, one cannot assume that the modified approach necessarily also results in nearly monodisperse, highly dispersed metal particles as were obtained by the described coordination/oxidation/reduction route.

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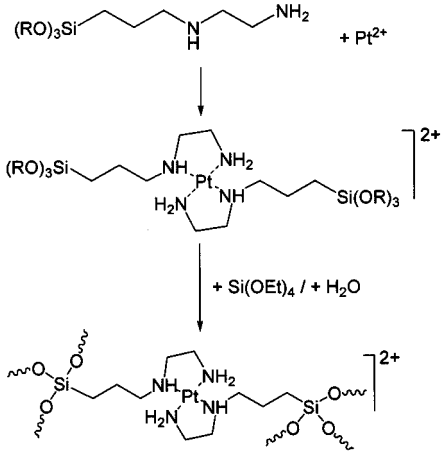
We now show that metal particle containing sol-gel films can be prepared by exposing the films to hydrogen at elevated temperatures without prior calcination. Gold/silver alloy particles with diameters of 2.5–7 nm in a silica film were already obtained by UV irradiation of sol-gel films.[9] The work reported in this contribution has proof-of-concept character, without optimization of the reaction conditions, the metal particle sizes or the properties of the silica matrix.

Results and Discussion

The metal nanoparticle containing sol-gel films were synthesized in three successive steps. In the first step (Scheme 1 for Pt^{2+}), metal complexes substituted by {3-[(2-aminoethyl)amino]propyl}triethoxysilane (AEAPTS), a trialkoxysilyl-substituted derivative of ethylenediamine, were prepared in situ. In the second step (Scheme 1), a sol was formed by hydrolytic polycondensation of the (AEAPTS) metal complex and $Si(OEt)_4$. This sol was dip-coated on glass slides resulting in thin, transparent films of the metal complex containing inorganic-organic hybrid material. In the final step, the metal ions in the sol-gel film were reduced by exposure to hydrogen at elevated temperatures, resulting in the formation of metal nanoparticles.



Scheme 1.

The advantage of this approach is that films can be prepared by standard coating technologies. The presence of the organic groups not only renders possible an atomic dispersion of the metal component during film formation, but also allows, in principle, to adjust the properties of the coating sol in the same way as for other well-known applications of alkoxysilane mixtures.

The reduction of the metal was followed by X-ray diffraction (Figure 1), which confirms the "postsynthesis reduction" in the last synthesis step, i.e. after formation of the silica film. Only a broad bump corresponding to amorphous silica was observed before the films were exposed to hydrogen and after the films were heated in hydrogen up to 200 °C. Only when the reduction temperature was increased to 400 °C, did reflections of elemental Pt emerge additionally. An average diameter of 6.8 nm was calculated by Scherrer's equation from the half-height widths of the reflections. When the reduction temperature was raised to 500 °C, the reflections became sharper, as expected, and the average particle diameter increased to 22 nm.

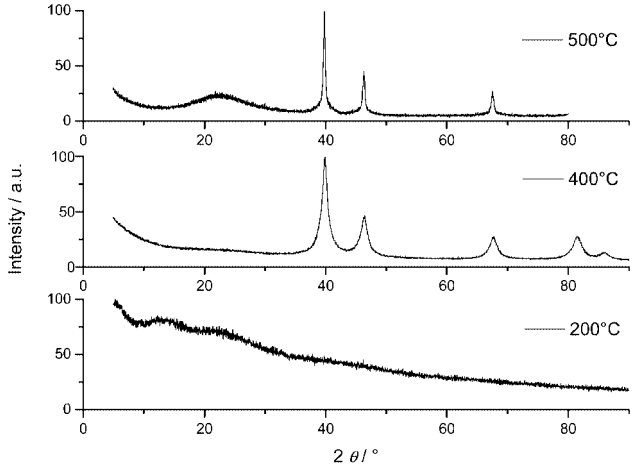


Figure 1. Temperature-dependent XRD on the reduction of platinum in the sol-gel films. The films were kept at each temperature in hydrogen for 2 h before the diffractogram was taken.

Silica films containing gold or silver nanoparticles were similarly prepared. The diffraction patterns (Figure 2) showed both the broad bump for amorphous silica and the characteristic reflections of the reduced gold or silver particles. An average diameter of 7.9 nm was calculated for the Au particles by Scherrer's equation, and of 13.1 nm for the silver particles.

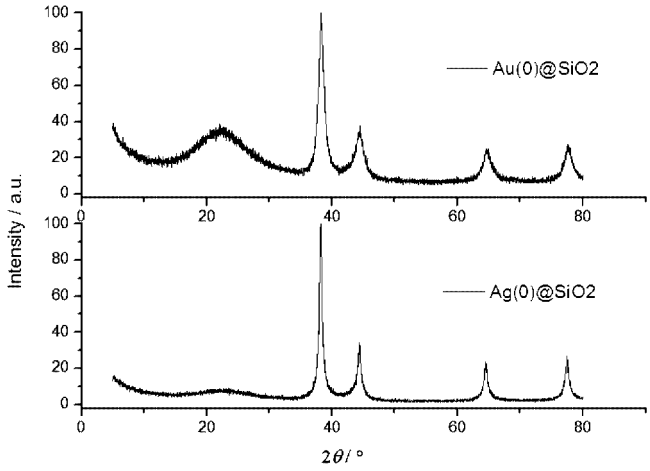


Figure 2. XRD of silica films containing gold or silver nanoparticles after reduction at 500 °C.

As a consequence of the tethering of the metal complexes, the metal ions are perfectly dispersed in the film before being reduced. During reduction of the metal ions, growth of the resulting metal particles is limited by the sur-

rounding silica matrix. This leads to a homogeneous dispersion of the metal nanoparticles. Figure 3 shows the TEM of the silica film with platinum nanoparticles in the range 10–100 nm (average ca. 30 nm). The metal particle size is of course also dependent on the reduction temperature, and larger average particle sizes were consequently obtained when the temperature was increased.

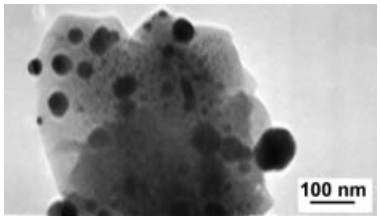


Figure 3. TEM of Pt^0 nanoparticles dispersed in the silica film after reduction at 500 °C.

A key issue in this work was also the film properties. Even after hydrogen treatment at 500 °C for 2 h, the film remained transparent. Adhesion of the film after reduction was as good as before, and the films were crack-free.

Conclusions

The present work shows the feasibility of preparing silica *films* with dispersed noble metal nanoparticles by sol-gel processing. Reduction is performed after coating, i.e. in the deposited sol-gel film, in which the metal cations are chelated by the amino groups and thus linked to the silica network. Contrary to synthesis protocols for carbon-free nanocomposite *powders*, the organic tethers and the counterions of the employed metal salts were not oxidatively removed prior to reduction. This had a beneficial influence on the quality of the final coating.

The metal nanoparticles obtained are highly dispersed in the silica film. However, the obtained metal particles have a much broader particle size distribution than those prepared by the coordination/oxidation/reduction protocol. This may be due to different nucleation and growths mechanisms in the reduction step and/or the influence of the substrate. This will be subject to further work.

The possibility to generate metal nanoparticles without completely destroying the organic groups of the gel opens the possibility of optimizing the properties of the coatings, e.g. adhesion to substrates or compliance of the films, by using organically substituted trialkoxysilanes $R'Si(OR)_3$ as co-reactants.

The goal of the work reported here was a proof of principle. We have neither optimized the reduction conditions nor the film or particle properties. Future work also needs to address the fate of the organic groups during hydrogen reduction at elevated temperatures and their influence on the particle growth and the film properties.

Experimental Section

General: {3-[(2-aminoethyl)amino]propyl}triethoxysilane (AEAPTS) and ethanol were distilled before use and kept under inert gas. Ethanol was kept over molecular sieves under an inert gas.

Preparation of the Coating Solutions: An amount of 0.1 mmol of $AgNO_3$, $HAuCl_4$, or $Pt(acac)_2$ (acac = acetylacetonate), was dissolved in 10 mL of freshly distilled, dried ethanol. An amount of AEAPTS was added to the solution of the metal salt which corresponded to a metal/AEAPTS molar ratio of 1:2, 1:3, and 1:4 for silver, gold and platinum, respectively. The mixture was stirred at room temperature until the color of the solution did not change any more, which indicated the formation of the metal complexes $[Ag(AEAPTS)_2]^+$, $[Au(AEAPTS)_2]^{3+}$, or $[Pt(AEAPTS)_2]^{2+}$.[5,7] An amount of 0.2 mmol of tetraethoxysilane (TEOS) was added to the metal complex solution and sol-gel reactions were started by addition of 40 mL of 0.2 N aqueous NH_4OH. The resulting colloidal suspensions, which had the typical color of the corresponding metal complexes, were heated to 70 °C for 72 h.

Dip-Coating: Glass sides were cleaned by treatment with a concentrated sodium hydroxide solution followed by successive rinsing with ethanol and deionised water and then coated by dip-coating with a withdrawal speed of 24 $cm\,min^{-1}$.

Metal Reduction: The coated glass plates were put in an oven flushed with hydrogen. The temperature was then raised to 500 °C at 10 $°C \cdot min^{-1}$ and kept at this temperature under hydrogen for 2 h.

Characterization: The obtained films were characterized by transmission electron microscopy (TEM) with a JEOL 200CX. X-ray analyses were carried out with a Philips X'Pert diffractometer using Cu-K_α radiation. For both investigations, the films were scraped off from the glass slides.

Acknowledgments

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