



Controlling the Spontaneous Precipitation of Silver Nanoparticles in Sol-Gel Materials*

PU-WEI WU AND BRUCE DUNN[†]

Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095, USA
bdunn@ucla.edu

VINH DOAN AND BENJAMIN J. SCHWARTZ

Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095, USA

ELI YABLONOVITCH

Electrical Engineering Department, University of California, Los Angeles, CA 90095, USA

MASAYUKI YAMANE

Department of Inorganic Materials, Tokyo Institute of Technology, Tokyo 152-8552, Japan

Abstract. The mechanisms responsible for spontaneous silver precipitation in silver-doped sol-gel materials are identified. The chemistry of the solvent phase is found to be the critical factor in controlling this phenomenon. The addition of HCl as catalyst leads to the formation of AgCl and subsequent formation of silver upon light exposure. Another factor leading to silver precipitation is the reducing capability of methanol radicals. Silver precipitation is inhibited by simply washing out the pore solvents by a solvent exchange method.

Keywords: nanoparticles, solvent chemistry, silica sol-gel, silver-doped silica

1. Introduction

Sol-gel synthesis is a complex chemical reaction involving the presence of various intermediates during the synthesis step. There have been reports in the literature that the oxidation states for transition metals (vanadium, chromium) were altered during the sol-gel transition [1, 2] and spontaneous silver reduction has been reported [3–5]. The self-catalytic behavior of the gel matrix has been assumed, however there is relatively little research directed at identifying the responsible species and mechanisms. In our pursuit of fabricating three-dimensional silver patterns by high power laser pulses, the spontaneous precipitation of silver is un-

desirable since the plasma absorption band from the silver particles would interfere with the laser pulses resulting in poor contrast. Therefore, research was directed at identifying and controlling the spontaneous silver precipitation in sol-gel synthesis.

2. Experimental

Silver-doped silica gels were synthesized using two approaches. In one case a high concentration of silver salt solution was mixed with hydrolyzed silica precursor in various ratios. The second method involved synthesizing a pure silica gel and backfilling it with the silver salt solution. The precursors for the hydrolyzed silica sol were prepared by mixing TMOS (7.15 g) and deionized water (1.70 g) in a 1 : 2 molar ratio with small amount of acid (0.08 g) as catalyst. Acids (0.04 N) such as

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[†]To whom all correspondence should be addressed.

hydrochloric acid (HCl), nitric acid (HNO₃) and sulfuric acid (H₂SO₄) were used. The mixture was mixed ultrasonically for 15 minutes and became a homogeneous solution.

Aqueous solutions of silver nitrate (1.06 M) or silver perchlorate (0.49 M) were used as the silver source. These solutions were mixed with the hydrolyzed sol and the resulting one-phase solution was then poured into a cuvet and sealed with parafilm for gelation. The compositions prepared had a 2 : 1 weight ratio of silver salt solution : hydrolyzed silica sol.

The other synthesis approach employed solvent exchange. Rather than a silver salt solution, deionized water was mixed with the hydrolyzed sol in a 2 : 1 weight ratio and allowed to gel. After gelation, solvent exchange was carried out by immersing the wet gel in a large volume of deionized water to remove the methanolic pore solvent. Then, the washed gel was solvent exchanged with the silver salt solution. In this way, the resultant liquid phase in the pores of the wet gel contained nearly the same concentration of silver as that of the silver salt solution. The synthesized wet gel monoliths were typically 0.5 × 1 × 2 cm and did not exhibit any significant shrinking.

3. Results and Discussion

3.1. Effect of Catalysts

Previous research on sol-gel materials doped with silver salt solution demonstrated irreversible silver precipitation during the sol-gel transition [3–5]. The same behavior was observed in our samples as was evident from the gradual color changes after mixing the hydrolyzed sol and the silver salt solution. In addition, the precipitation occurred regardless of the catalysts used, silver salt concentrations or silver salt purity. Figure 1 shows representative absorbance curves of a gel sample with the hydrolyzed sol catalyzed by either HCl or HNO₃. The existence of silver nanoparticles is confirmed by the characteristic plasma absorption band centered at 410 nm. In the case of HCl catalysis, the absorption behavior initially exhibited a scattering dominated curve. Thereafter, the silver plasma absorption peak appeared and grew with time. For the HNO₃ case, after mixing for 30 min, there is a broad absorption band appearing at 415 nm which suggests an initial particle size of 14 nm [6]. The broad bandwidth (FWHM = 226 nm) of this absorption band suggests the presence of a wide distribution of particle sizes. After gelation, the absorption curves showed a strong absorption band

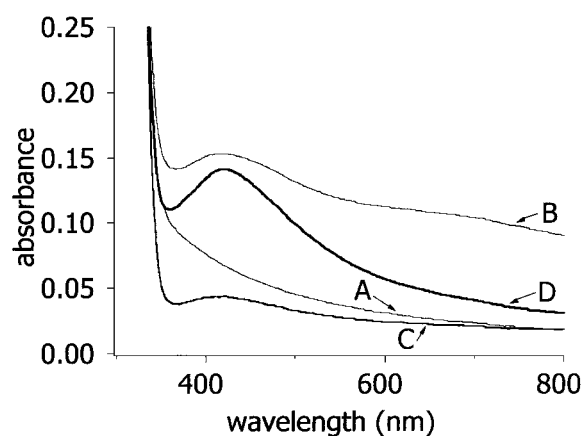


Figure 1. Representative absorption curves for samples containing 1.06 M AgNO₃/H₂O and the hydrolyzed silica sol. The hydrolyzed sol from (A) and (B) is catalyzed by HCl with (A) taken after mixing for 30 minutes (still in a liquid state) and (B) taken after 17 hours (in a gel state). The hydrolyzed sol from (C) and (D) is catalyzed by HNO₃ with (C) taken after mixing for 30 minutes (still in liquid state) and (D) taken after 17 hours (in a gel state).

around 430 nm. However, the scattering by internal pores renders the particle size estimation unreliable. TEM analysis (not shown here) showed that the gels contain silver particles with sizes between 5 nm and 30 nm.

The mechanism for silver precipitation in HCl catalyzed gels was elucidated in a series of control experiments where HCl solutions with different concentrations (0.2 M, 0.04 M and 0.004 M) were mixed with aqueous AgNO₃ solution (1.06 M) to produce aqueous silver salt solutions analogous to those used as the sol-gel precursors. Optical absorption showed a scattering-like behavior which was strongly dependent on the HCl concentration. The scattering was due to suspended particles which were formed immediately after mixing. These suspended particles precipitated to the bottom of the cuvet with time and X-ray diffraction indicated that the precipitates were silver chloride (Fig. 2).

The reason for silver chloride precipitation from solution is due to the low solubility of the AgCl in aqueous solution. The solubility for AgCl is 6.2×10^{-6} M in cold water and it is expected that the actual solubility in the sol-gel precursor solution is smaller [7]. The silver ion concentration in the final wet gel materials (0.70 M) is well above the solubility limit and thus the factor causing precipitation of AgCl is the concentration of HCl used as catalyst. The concentration of the chlorine ions in the sol-gel precursor solution is 4.1×10^{-4} M, which is two orders of magnitude greater

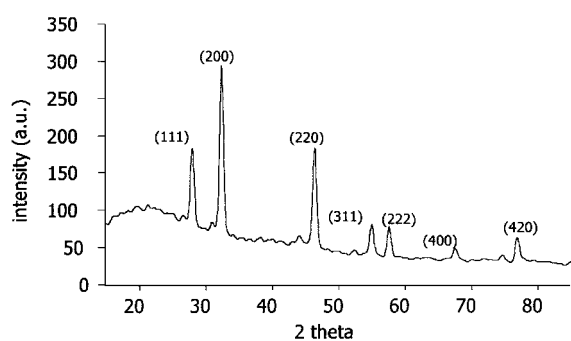


Figure 2. X-ray diffraction data of precipitates formed from the addition of HCl (0.04 N) to an aqueous AgNO_3 solution (1.06 M). The phase is identified to be cubic AgCl.

than the solubility limit of AgCl. It is for this reason that we observed scattering-like behavior immediately after mixing the silver salt solution with the hydrolyzed sol.

The AgCl microcrystals are known to be photosensitive and produced silver nanoparticles upon exposure to ambient light. This was observed in the absorbance data (Fig. 1) of the gel samples catalyzed by the HCl. Thus, the HCl-catalyzed gels changed from scattering-like absorbance at short times into a silver plasma absorption band.

3.2. Effect of Pore Solvent

The above description provides the reason for silver precipitation in gels catalyzed by the HCl, but does not explain precipitation observed for gels catalyzed by HNO_3 or H_2SO_4 . In order to clarify the reduction mechanism responsible for the silver precipitation, a solvent exchange method was developed to examine the role of the pore solvents in the silver reduction process.

The simple two-step solvent exchange method effectively eliminated the precipitation of silver particles. After washing in deionized water, the wet gel exhibits only a λ^{-4} Rayleigh scattering behavior resulting from the internal pores (Fig. 3). Subsequent washing with the AgNO_3 aqueous solution leads to only the absorption at 330 nm from the silver salt solution. Thus, there is no indication of the characteristic plasma absorption of Ag° nanoparticles at 410 nm as observed in Fig. 1.

From the solvent exchange results, it is evident that the reducing capability comes from the solvent phase (intermediates and methanol) encapsulated in the pores

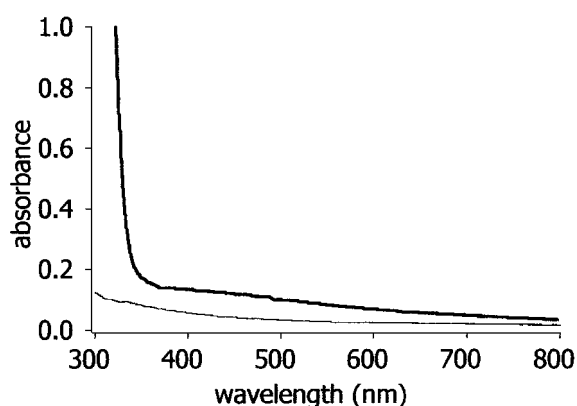
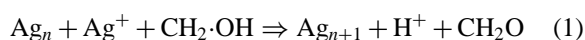


Figure 3. Absorbance curves for a pure silica gel (—) and a silver-doped gel after two-step solvent exchange (—). The absorption band at 330 nm is from the AgNO_3 aqueous solution.

and not from the silica network. The reduction of Ag^+ to Ag° requires a relatively high negative redox potential of -1.8 V in aqueous solution. The intermediates in the sol-gel transition primarily consist of partially hydrolyzed precursors $(\text{Si}(\text{OH})_x(\text{OCH}_3)_{4-x})$ and are not expected to have such a strong reducing potential.

The most likely source of reduction capability comes from the methanol generated from hydrolysis and condensation. In the synthesis of TEOS-derived silica gel, Wolf et al. have shown that prior to heat treatment, a variety of organic radicals are present (methyl radical; $\cdot\text{CH}_3$, and ethanol radical; $\text{CH}_3\text{CH}\cdot\text{OH}$) [8]. Similarly, in the TMOS-derived gel, it is expected that both the methyl radical and methanol radical ($\text{CH}_2\cdot\text{OH}$) would be present. The methanol radical is responsible for the formation of silver nanoparticles through the following reaction [9]:



with $n \leq 3$. Although, the $\text{CH}_2\cdot\text{OH}$ radical alone does not possess the required negative potential to reduce the silver ions, it has been suggested that the methanol radical complexes with silver ions and, upon absorption of an additional photon, the silver ion is then reduced to form Ag° [10].

References

1. J. Livage, *Chem. Mater.* **3**, 578 (1991).
2. W. Streck, E. Lukowiak, P.J. Deren, K. Maruszewski, I. Trabjerg, Cz. Koepke, and G.E. Malashkevich, *SPIE* **3176**, 249 (1997).
3. M. Mennig, H. Schmidt, and C. Fink, *SPIE* **1590**, 152 (1991).
4. M. Mennig, J. Spanhel, H. Schmidt, and S. Betzholz, *J. of*

- Non-Crystalline Solids **147/148**, 326 (1992).
5. B. Ritzer, M.A. Villegas, and J.M. Fernández Navarro, *J. of Sol-Gel Science and Technology* **8**, 917 (1997).
 6. G.W. Arnold and J.A. Borders, *J. Appl. Phys.* **48**, 1488 (1977).
 7. CRC Handbook of Chemistry and Physics, 62nd ed., edited by R. Weast (CRC Press, Florida, 1981).
 8. A.A. Wolf, E.J. Friebele, and D.C. Tran, *J. Non-Crystalline Solids* **71**, 345 (1985).
 9. T. Linnert, P. Mulvaney, A. Henglein, and H. Weller, *J. Am. Chem. Soc.* **112**, 4657 (1990).
 10. A. Henglein, T. Linnert, and P. Mulvaney, *Ber. Bunsenges Phys. Chem.* **94**, 1449 (1990).