

Formation and structural characterization of silver nanoparticles in ormosil sol–gel films

RENATA REISFELD*, TSIALA SARAIDAROV, VICTORIA LEVCHENKO

Department of Inorganic Chemistry, The Hebrew University, Jerusalem 91904, Israel

*Corresponding author: renata@vms.huji.ac.il

Silver nanoparticles were obtained *in situ* in ormosil sol–gel films with attached urethane groups. Optical spectra of the silver nanoparticles in the films show red shift of absorption maximum with increasing silver concentration from 2% to 10%. In the solutions λ_{\max} is shifted from 390 nm till 425 nm; in the films λ_{\max} is shifted from 438 nm till 456 nm. Structural characterizations of the composite sol–gel films incorporated by silver nanocrystals have been studied by: scanning electron microscopy (SEM), atomic force microscope (AFM), energy dispersion X-rays analysis (EDAX), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and scanning transmission electron microscopy (STEM). Two types of silver nanoparticles with sizes of 1–2 nm and 20–40 nm were observed. The crystal grow process and particle sizes depend on the starting concentrations of silver ions, reaction temperature and time. The small silver particles are arranged in micro pores of the matrix, as shown from STEM images. SAED confirms the silver face-centered cubic crystal lattice.

Keywords: silver nanoparticles, ormosil sol–gel composite, optical and structural characterizations.

1. Introduction

Nano-sized clusters of noble metals in a dielectric have attracted much attention due to their potential applications in many areas, including nonlinear optical devices, surface-enhanced Raman spectroscopy, near-field scanning optical microscopy, biological sensing, waveguides made of nanoparticle chains, in solar cells, light-emitting diodes and integrated optics. Metal nanoparticles dispersed in dielectric materials exhibit a strong characteristic extinction peak, due to plasmon resonance [1–4]. Surface plasmons are collective oscillations of the electrons of conductors, and have attracted intense interest recently due to their wide range of potential applications. These collective oscillations of the electrons lead to a resonant interaction between incident light and the conductor. Metal nanoparticles can result in strong scattering of incident light and greatly enhance local fields, and can also lead to enhanced

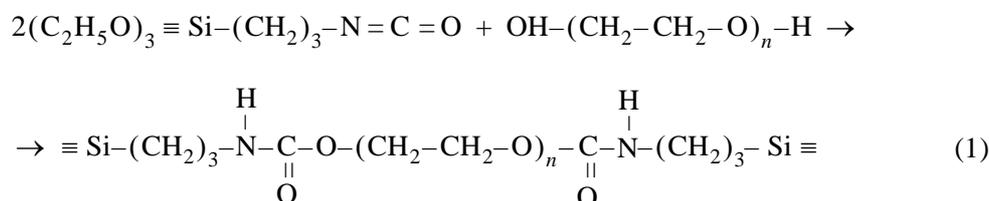
fluorescence. The shape, intensity and position of the peak depend on the size, shape, concentration, and chemical state of the nanoclusters and also the possible interaction between them [5–8]. Nanoparticles of noble metals can be prepared *via* different techniques, such as wet chemical synthesis, solvent exchange, chemical reduction with or without a stabilizing agent, thermal decomposition, in various polymers and sol–gel glasses [6–13]. Probably the most popular example on the reduction of noble metals salts by organic solvents is ethanol, which has been long used by Toshima and coworkers [14] for the preparation of metal nanoparticles suitable for catalytic applications. Another interesting example to obtain stable colloidal silver or gold particles is the reduction of Ag^+ ions by N,N-dimethylformamide (DMF) [8].

In this work we are using the new ormosil (organically modified silicate) sol–gel matrix for *in situ* formation of silver nanoparticles. Due to the low processing temperature, homogeneity as well as chemical purity of the resulting samples, and possibility of adding reducing and oxidizing agents in small concentrations, the sol–gel method has been considered as one of the most useful and versatile techniques for oxide film fabrication. Luminescence enhancement of rhodamine 6G dye in sol–gel films containing silver aggregates were investigated by REISFELD *et al.* [12]. The authors obtained Ag aggregates by means of reduction of ionic silver by a stannous ion. In this work we have obtained nano-sized particles of silver in diurethane-triethoxydisiloxane (DURS)-silica network. The connection between the porous structure of the ormosils matrix material of silica-polyurethane (SIPU) and the possibility of formation of silver nanoparticles is presented.

2. Experimental section

2.1. Preparation of the sol–gel ormosils matrix

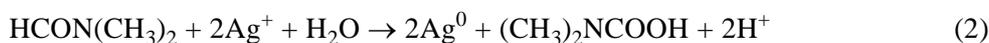
Sol–gel process is a method of material preparation by room temperature reaction of organic precursors and has been applied most often to the production of glasses and ceramics. The particles in the colloidal sol are linked to form a gel, which is subsequently dried to form a porous glass. The sol–gel process is based on hydrolysis and polycondensation reactions of metal-organic compounds, such as silicon alkoxide (tetramethyl orthosilicate – TMOS or tetraethyl orthosilicate – TEOS) mixed with water, catalyst (acid or base) and a solvent (such as methanol or ethanol) to achieve homogeneity on a molecular scale. In the case of organosilicate glasses (organically modified silicates or ormosils), the silicate network may be modified by organic substitute groups, such as alkyl (*e.g.*, methyl or ethyl) groups or other functional groups (*e.g.*, 3-glycidoxypropyl or 3-isocyanatopropyl) which may form organic copolymers that penetrate the silicate structure. In our experiments we used DURS-oligomer as modifier molecules of silica network and which was synthesized separately by reacting 3-isocyanatopropyltriethoxysilane (ICTEOS) and polyethylene glycol (PEG-600) with the molar ratio 2:1 [15, 16], as presented below:



The reagents were stirred in chloro-benzene at boiling temperature under reflux for 3 hours. The residual solvent was evaporated, whereas the DURS hybrid material oligomer was obtained. Isocyanate functionalized silane coupled with the polyol which forms urethane linkage is known as a system improving bond strength. On the other hand, DURS molecules act as a coupling agent, can complex with silver atoms through its secondary amine functionality and form stable dispersions.

2.2. Silver ion reduction process in sol-gel ormosils solution

Several routes have been proposed [8, 17] for the oxidation of DMF, which normally involve the evolution of H_2 or CO_2 gas. In our case, when silver ions are incorporated in the sol-gel ormosils solution, we do not observe any gas evolution for the reaction at room temperature, and we propose that the following reaction takes place during the process:



Actually, the carbamic acid formed can easily decompose as follows:



It is known that the reduction process of silver ion by DMF can proceed at room temperature, but this process is very slow. In our experiments we used two reaction temperatures: 40 °C and reflux at boiling temperature.

2.3. Ag nanoparticles preparation in sol-gel solution

Silica-ormosil sol-gel solution was obtained as follows: 2 ml of TEOS was mixed with 9 ml of ethanol and hydrolyzed using 2, 5 and 10 mol per cent of silver nitrate dissolved in 4 ml of water. After 30 min stirring to the solution was added 1.1 ml of DURS and allowed to hydrolyze additionally for 30 min. Then 5 ml of DMF was added and kept in a thermostat at 40 °C or was refluxed at boiling temperature.

2.4. Ag nanoparticles doped SIPU ormosils films

The crack-films were obtained using the dip-coating technique, then they were dried at 40 °C/1 hour and heated at 150 °C/1 hour. The use of DMF was found to be effective

in the sol-gel synthesis of silica glass. DMF is a drying control chemical additive (DCCA) which prevents the silica-ormosil gel cracking during drying.

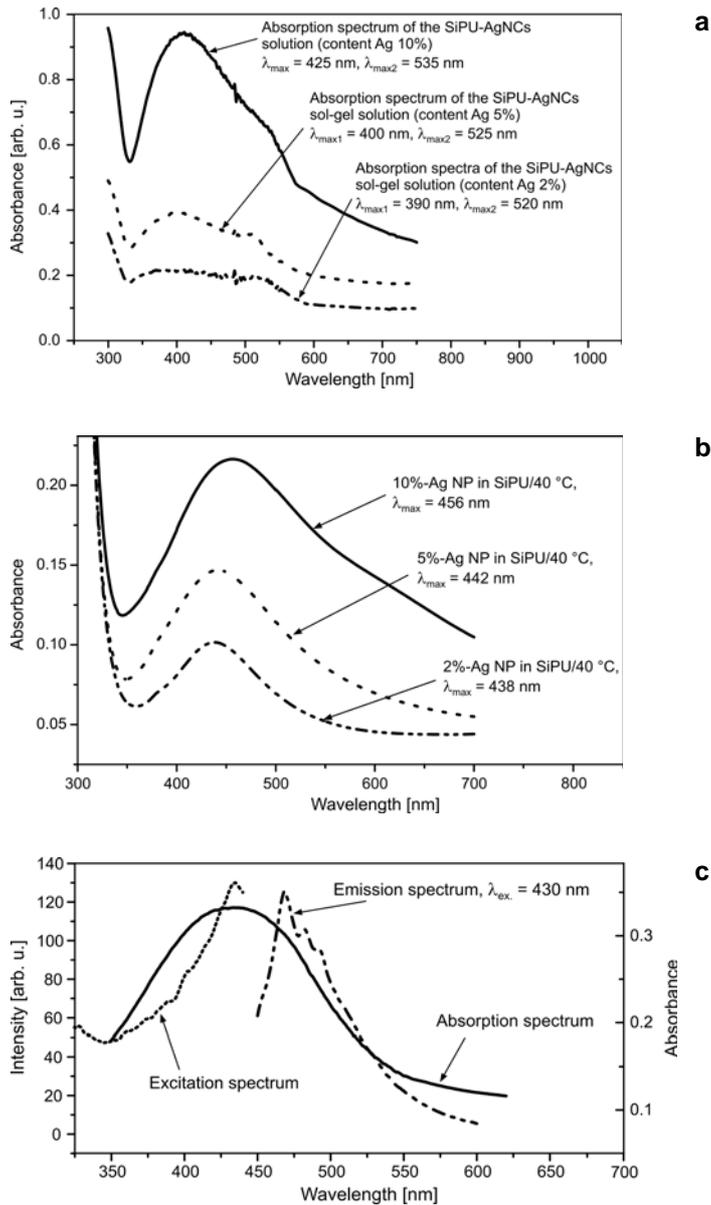


Fig. 1. Absorption and emission spectra of silver nanoparticles obtained in SIPU matrix: absorption spectra of 2, 5 and 10% of silver nanoparticles in solutions (a) and in ormosils films obtained at 40 °C/70 hours (b); excitation, emission and absorption spectra of silver nanoparticles in ormosils films obtained at 70 °C/30 min (c).

In the presence of strong acids and water, DMF is hydrolyzed to formic acid and dimethylamine, and as a polar aprotic solvent allows efficient hydrolysis followed by efficient condensation. The addition of DMF yields silica gel with large pores, which are even larger after aging at elevated temperature (150 °C) [18]. The same behavior was observed in our films, as shown in the results.

2.5. Optical and structural measurements

The absorption spectra in the UV–VIS region were recorded at room temperature on a Milton–Roy Spectronic M-3000 diode array spectrophotometer. Steady state luminescence and its excitation spectra were measured at room temperature using a JASCO FP770 spectrofluorimeter.

High resolution transmission electron microscopy (HRTEM) observations were carried out using a TECNAI F20 G² electron microscope (FEI Company) operated at 200 kV and equipped with an EDAX EDS detector. The film samples were deposited on 300-mesh copper grids. Selected area electron diffraction (SAED) was carried out by TEM electron beam at a distance of 310 mm. Energy dispersive X-ray spectroscopy (EDAX) was used for an elemental analysis of Ag-silica ormosil nanocomposite.

High resolution scanning electron microscopy (HRSEM) (Sirion FEI Company) uses Shottky-type field emission source and allows a wide range of accelerating voltages from 200 V to 30 kV. It is able to achieve resolutions of 1.5 nm at > 10 kV and 2.5 nm at 1 kV.

The Nanoscope Dimension 3100 Scanning Probe Microscope (SPM)/Atomic Force Microscopy (AFM) provides the ability to image the surface topography of both conducting and insulating samples, as well as adsorbed molecules and nanoparticles.

3. Results and discussion

3.1. Optical properties

Gray brown transparent sol–gel solution was formed at 40 °C during 70 hours and at reflux during 15–25 minutes. The change of the absorption spectra of silver nanoparticles, in solutions and in thin films, with various concentrations and temperatures is presented in Figs. 1a and 1b. The absorption maximum shows red shift with increasing silver nanoparticles concentration from 2% to 10%. In the solutions, the absorption peak is shifted from 390 nm till 425 nm; in the SIPU films the absorption peak is shifted from 438 nm till 456 nm.

The fluorescence peak of silver nanoparticles obtained at 70 °C/30 min in ormosils SIPU film is situated at 468 nm when the film is excited at 430 nm, as can be seen in Figure 1c.

3.2. Structural characterization

HRTEM characterizations (Fig. 2) of silver nanoparticles obtained in SIPU ormosils show two sizes of nanoparticles of 1–2 nm and 10–20 nm when the concentration is

10% and reduction is performed at reflux during 20 min. Figure 2a shows the part of the film containing big and small particles (bar 20 nm), Fig. 2b shows only small particles with sizes of 1.2–2.0 nm, Fig. 2c shows bigger particles of 20–40 nm and Fig. 2d presents HR-TEM of 10 nm crystal lattice image (bar 5 nm).

In the STEM picture (Fig. 3a) we can see silver nanoparticles (white) and the matrix pores (black) with sizes which are the same as the small silver

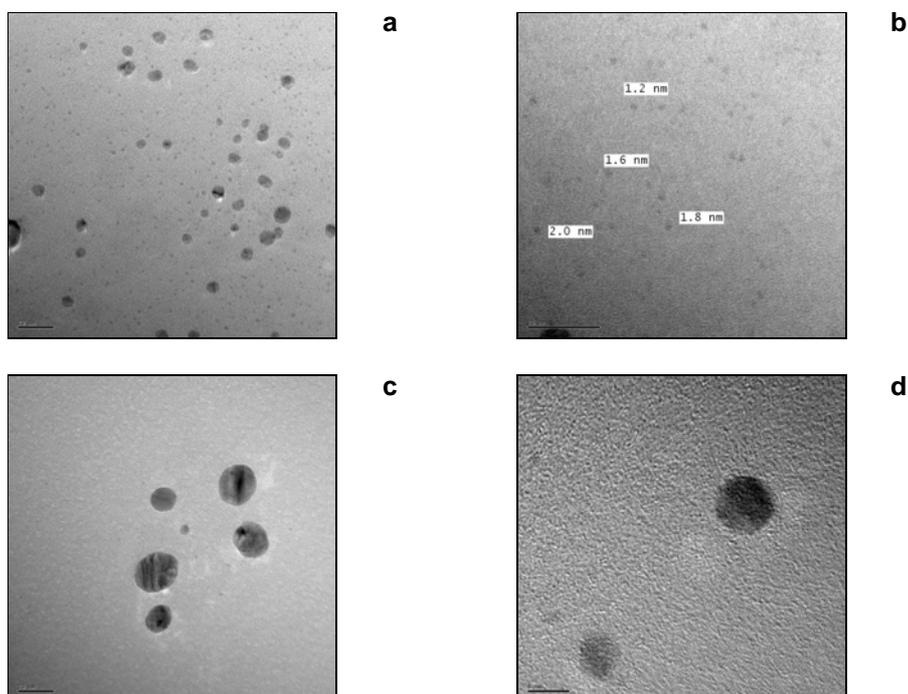


Fig. 2. HRTEM images of silver nanoparticles obtained in silica-polyurethane when the concentration is 10% and reduction is performed at reflux during 20 min.

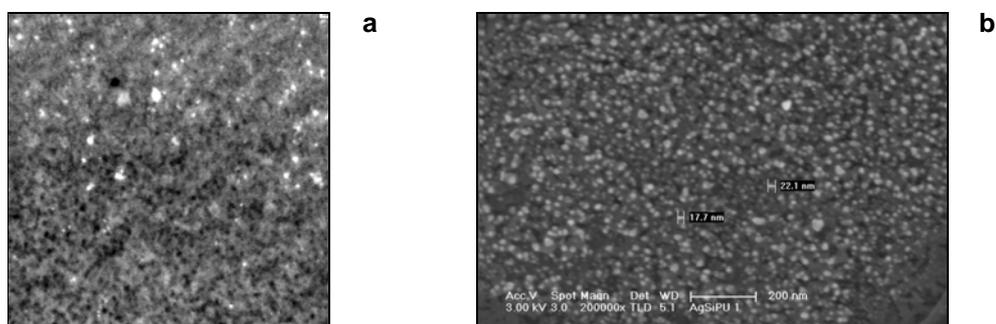


Fig. 3. STEM (a) and SEM (b) of silver nanoparticles obtained in silica-polyurethane when the concentration is 10% and reduction is performed at reflux during 30 min.

nanoparticles (~2 nm), which is the evidence that small silver particles are grown inside these pores. The SEM image (Fig. 3b) shows the homogeneity of bigger nanoparticles of 17–22 nm in the matrix. The STEM image of obtained sol–gel silica ormosils matrix treated by DMF during the silver reduction confirms the fact that

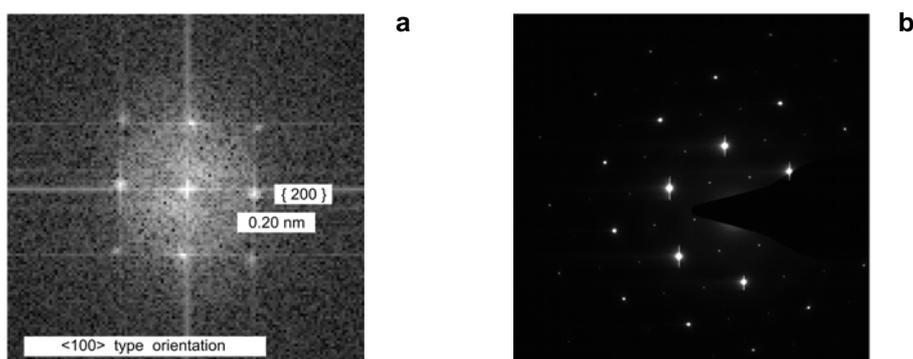


Fig. 4. Selected area electron diffraction (SAED) images of small (10 nm) and big (30 nm) silver nanocrystals obtained in silica-polyurethane when the concentration is 10% and reduction is performed at reflux during 20 min confirm confirm that silver forms face-centered cubic crystal lattice.

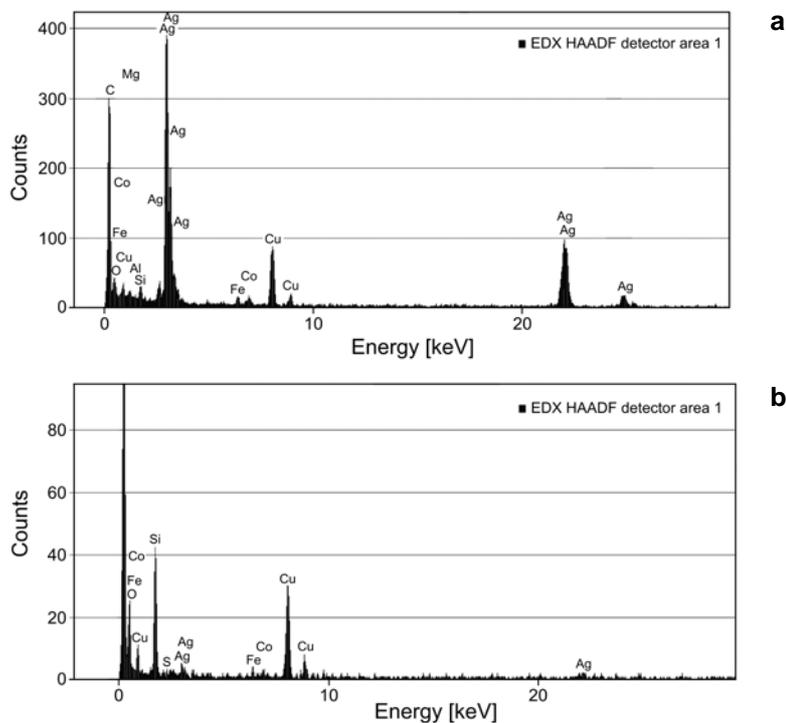


Fig. 5. Energy dispersion X-rays analysis of silver nanoparticle (a) and part of silica-polyurethane matrix (b).

the addition of DMF yields SIPU ormosil with large pores, and they are even larger after aging at elevated temperature (150 °C).

Selected area electron diffraction (SAED) images (Fig. 4) of small (10 nm) and big (30 nm) silver nanocrystals obtained in SIPU when the concentration is 10% and reduction is performed at reflux during 20 min confirm that silver forms face-centered cubic crystal lattice.

Energy dispersion X-rays analysis (EDAX) of big nanocrystals shows the presence of pure silver nanoparticles (Fig. 5a) and part of the matrix is identified as silica (Fig. 5b).

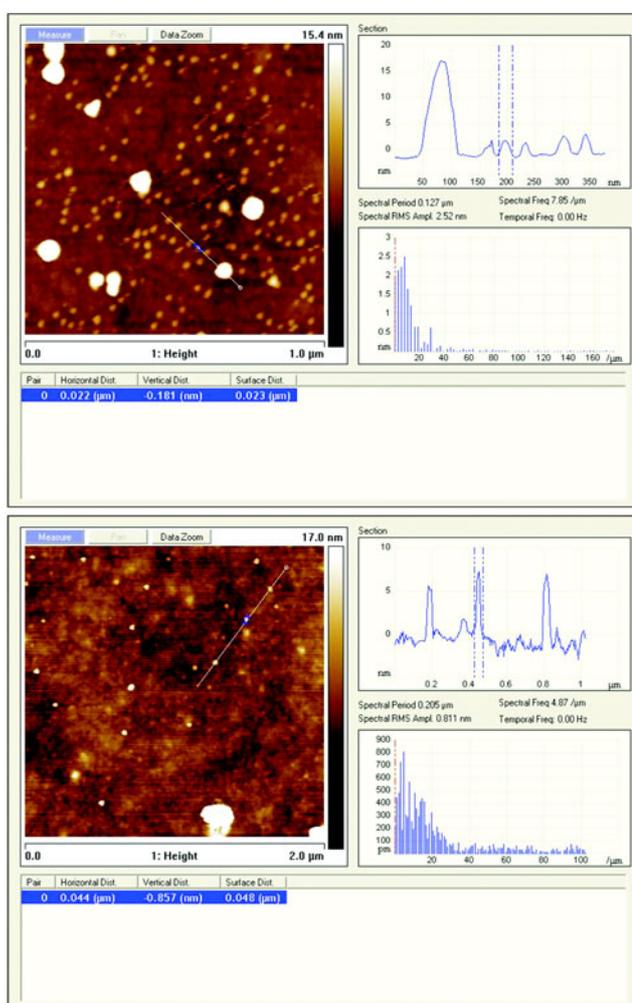


Fig. 6. AFM characterization of silver nanoparticles obtained in 10% of Ag in SIPU-sol-gel matrix with reflux in DMF/70 °C/30 min (a) and particles obtained using reduction reaction in DMF at 40 °C/72 hours (b).

AFM images (Fig. 6) show silver nanoparticles of sizes 22 nm obtained from 10% of Ag in SIPU-sol-gel matrix with reflux in DMF/70 °C/30 min (Fig. 6a) and particles of sizes 44 nm obtained using reduction reaction in DMF at 40 °C/72 hours (Fig. 6b). Pictures on the right show the particles size (nm) distribution of nanoparticles with distance on *x*-axis, and height on *y*-axis. AFM image (Fig. 6a) shows that the rapid reduction of silver nanoparticles occurs inside the solution of the SIPU ormosils after adding of DMF (at 70 °C/30 min), which leads to the formation of silver nanoparticles with the size of 22 nm. Figure 6b shows silver nanoparticles obtained in the matrix solution at 40 °C. It is clear that a decrease in the reaction temperature leads to bigger nanoparticles of 44 nm.

4. Conclusions

We present a new method of preparing silver nanoparticles in novel SIPU ormosil sol-gel glasses. The rapid reduction of silver nanoparticles occurs *in situ* solution after the hydrolysis of SIPU ormosils in the presence of DMF. Thin films of silica, with attached di-urethane groups which served as a coupling agent, were prepared using the sol-gel process.

HRTEM characterizations of silver nanoparticles obtained in SIPU ormosils show two sizes of nanoparticles of 1–2 nm and 20–40 nm when the concentration is 10% and reduction is performed at reflux during 20 min. Selected area electron diffraction (SAED) images confirm that silver forms face-centered cubic crystal lattice. Energy dispersion X-rays analysis (EDAX) of big particles shows the presence of pure silver nanoparticles; a part of SIPU matrix shows the Si-atom as a dominant atom and the traces of Ag.

We have shown that by reducing silver ions by dimethyl-formamide *in situ* in SIPU prepared by the sol-gel method, we obtain absorption and fluorescence spectra of silver plasmons. It is suggested that the mechanism is as follows: incident light excites surface plasmon resonance on the metal nanoparticles. The excited particles absorb in the visible spectrum and the width of the absorption depends on the multiplicity of sites of the plasmons.

Acknowledgments – We are grateful to Dr. Inna Popov, Dr. Evgenia Blayvas and Dr. Anya Radko, from the Unit for Nano Characterization for HRTEM, SEM and AFM measurements.

References

- [1] KALKMAN J., GERSEN H., KUIPERS L., POLMAN A., *Excitation of surface plasmons at a SiO₂/Ag interface by silicon quantum dots: Experiment and theory*, Physical Review B **73**(7), 2006, p. 075317.
- [2] CATCHPOLE K.R., PILLAI S., *Surface plasmons for enhanced silicon light-emitting diodes and solar cells*, Journal of Luminescence **121**(2), 2006, pp. 315–8.
- [3] KOKTYSH D.S., LIANG X., YUN B.-G., PASTORIZA-SANTOS I., MATTS R.L., GIERSIG M., SERRA-RODRIGUEZ C., LIZ-MARZÁN L.M., KOTOV N.A., *Biomaterials by design: layer-by-layer assembled ion-selective and biocompatible films of TiO₂ nanoshells for neurochemical monitoring*, Advanced Functional Materials **12**(4), 2002, pp. 255–65.

- [4] POPOV O., ZILBERSHTEIN A., DAVIDOV D., *Random lasing from dye-gold nanoparticles in polymer films: Enhanced gain at the surface-plasmon-resonance wavelength*, Applied Physics Letters **89**(19), 2006, p. 191116.
- [5] ZUSING YANG, YANG-WEI LIN, WEI-LUNG TSENG, HUAN-TSUNG CHAN, *Impacts that pH and metal ion concentration have on the synthesis of bimetallic and trimetallic nanorods from gold seeds*, Journal of Materials Chemistry **15**(25), 2005, pp. 2450–4.
- [6] JANA N.R., GEARHEART L., MURPHY C.J., *Wet chemical synthesis of silver nanorods and nanowires of controllable aspect ratio*, Chemical Communications 2001(7), pp. 617–8.
- [7] LIZ-MARZÁN L.M., LADO-TOURIÑO I., *Reduction and stabilization of silver nanoparticles in ethanol by nonionic surfactants*, Langmuir **12**(15), 1996, pp. 3585–9.
- [8] PASTORIZA-SANTOS I., LIZ-MARZÁN L.M., *Formation and stabilization of silver nanoparticles through reduction by N,N- dimethylformamide*, Langmuir **15**(4), 1999, pp. 948–51.
- [9] MAYER A.B.R., *Colloidal metal nanoparticles dispersed in amphiphilic polymers*, Polymers for Advanced Technologies **12**(1–2), 2001, pp. 96–106.
- [10] YUAN-HSIANG LEE, SHENG DAI, YOUNG J.P., *Silver-doped sol-gel films as the substrate for surface-enhanced Raman scattering*, Journal of Raman Spectroscopy **28**(8), 1997, pp. 635–9.
- [11] BALKIS AMEEN K., RAJASEKHARAN T., RAJASEKHARAN M.V., *Grain size dependence of physico-optical properties of nanometallic silver in silica aerogel matrix*, Journal of Non-Crystalline Solids **352**(8), 2006, pp. 737–46.
- [12] REISFELD R., EYAL M., BRUSILOVSKY D., *Luminescence enhancement of rhodamine 6G in sol-gel films containing silver aggregates*, Chemical Physics Letters **153**(2–3), 1988, pp. 210–4.
- [13] BABAPOUR A., AKHAVAN O., AZIMIRAD R., MOSHFEGH A.Z., *Physical characteristics of heat-treated nano-silvers dispersed in sol-gel silica matrix*, Nanotechnology **17**(3), 2006, pp. 763–71.
- [14] HIRAI H., NAKAO Y., TOSHIMA N., *Preparation of colloidal transition metals in polymers by reduction with alcohols or ethers*, Journal of Macromolecular Science, Part A: Pure and Applied Chemistry **13**(6), 1979, pp. 727–50.
- [15] REISFELD R., WEISS A., SARAIDAROV T., YARIV E., ISHCHENKO A.A., *Solid-state lasers based on inorganic-organic hybrid materials obtained by combined sol-gel polymer technology*, Polymers for Advanced Technologies **15**(6), 2004, pp. 291–301.
- [16] SARAIDAROV T., REISFELD R., SASHCHIUK A., LIFSHITZ E., *Synthesis and characterization of lead sulfide nanoparticles in zirconia-silica-urethane thin films prepared by the sol-gel process*, Journal of Sol-Gel Science and Technology **26**(1–3), 2003, pp. 533–40.
- [17] JAMES Y.YU., SCHREINER S., VASKA L., *Homogeneous catalytic production of hydrogen and other molecules from water – DMF solutions*, Inorganica Chimica Acta **170**(2), 1990, pp. 145–7.
- [18] BRINKER C.J., SCHERER G.W., *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, New York 1990, p. 500.

*Received September 18, 2007
in revised form December 23, 2007*