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SOL-GEL SYNTHESIS OF METAL NANOCOMPOSITES

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ABSTRACT

Gold nano composites with ORMOCER matrices have been prepared by a controlled precipitation process from $HAuCl_4$ solutions, using silanes of the type $NH_2[(CH_2)_2NH]_x(CH_2)_3Si(OR)_3$ (with x = 1,2) as a stabilizing agents. In the first step, formation and properties of the ligandstabilized colloidal suspensions was investigated. The different ligands are influencing the absorption spectra, showing surface plasmon bands between 380 and 700 nm. With the diamo silane, photoreduction is required for the colloid formation, whereas in the case of triamo silane, the colloid formation occurs spontaneously. In the second step, the formation of colloid films on glass substrates was investigated.

INTRODUCTION

Size and aggregation effects in colloidal gold systems are known to be responsible for a broad variety of observed optical absorption spectra (1,2). More recently, third order optical nonlinearities of gold-doped glasses have been reported (3,4). In order to exploit the linear and nonlinear optical properties of gold particles in potential applications, flexible material processing conditions are needed to control the material parameter such as particle sizes, aggregate shapes, particle surface chemistry, refractive index of the surrounding matrix etc. The sol-gel technique as a soft chemistry route offers appropriate means for flexible processing conditions, and in this paper, we address the synthesis of gold doped inorganic-organic composites. The sol-gel route for the fabrication of inorganic-organic composites has already been successfully applied to design materials with high abrasion and mechanical resistance (5), to fabricate patterned coatings for integrated optics (6), as well as to synthesize semiconductor quantum dot composites (7). The main tool of this study was to prepare colloidal gold particles carrying multifunctional polymerizable ligands, and to transform them subsequently to nanocomposites by ligand reactions. In order to form inorganic networks and/or organic chains, bifunctional silanes of the general formula $L\sim\sim Si(OR)_3$ were used where L represents complexing groupings for Au^{3+} (e.g. L = $-NH_2$, -SH,) or polymerizable ligands (e.g. L = -vinyl, -methacryloxy, -epoxy). The $-Si(OR)_3$ groupings undergo conventional sol-gel reactions. This contribution focusses on a photoinduced and spontaneous gold formation using differently functionalized silanes, preparation of gold doped sol-gel films and on the characterization of their UV/VIS optical properties.

EXPERIMENTAL

1 g $H[AuCl_4]$ was dissolved in 100 ml ethanol solution containing 0.5 mole amino grouping functionalized propyl triethoxysilane (the silanes used in the preparations are shown in Figure 1 and 2). These stock solutions were diluted with ethanol to give 0.001 molar solution (with respect to gold) and further used in photochemical gold formation experiments (polychromatic irradiation using a high pressure Hg-Xe lamp and a 280 nm cut-off filter).

In the second step, prehydrolysed methacryloxypropyl trimethoxy silane was added (the molar concentration ratio silane/Au was 20) to the freshly prepared coating sol. The hydrolysis and condensation was performed under CO_2 atmosphere, the molar silane/H_2O being 2 (inorganic network formation). After solvent removal (desireable for the formation of sol-gel films via dip-coating technique), glass substrates have been coated using the freshly prepared gold colloids. The curing of the films was performed in a oven at 60 °C and under ambient air conditions. As the catalyst for the formation of the organic network, azo-bis-isobutyronitrile was used.

The photothermal synthesis of gold doped films containing gold diamine complexes was performed by diping glass substrates in non-irradiated stock solutions and by subsequent UV/IR treatment of the coated glass slides using BELTRON UV/IR curing machine. The curing procedure took usually 1 - 2 minutes.

Optical absorption spectra from the colloidal solutions and cured sol-gel films on glass substrates were taken with an OMEGA 30 spectrophotometer (Bruins Instruments). Cluster sizes were determined using a JEOL 200CX TEM and a Siemens XRD - diffractometer 5000. Film thicknesses were determined by profilometry.

RESULTS AND DISCUSSION

Metallic particles can be prepared photolytically in solutions containing acetone, isopropanol and metal cations (8). UV-light absorption generates ketone triplets which react with alcohol to give strongly reducing alcohol radicals. Subsequently, colloidal metals are formed. In our preparations, Au^{3+} complexed with diamine grouping functionalized silanes in ethanolic medium was UV irradiated in the presence of methyl ethyl ketone and isopropanol. The results of an UV-VIS spectroscopically followed gold formation is summarized in Figure 1 depicting changes in optical absorption spectra as a function of the irradiation time. The spectra of non-irradiated solutions showed a weak absorption around 400 nm. After 3 minutes of irradiation, the characteristic plasmon band of the colloidal gold (spherical particles with sizes ranging between 3 and 10 nm as determined by transmission electron microscopy) at 520 nm is evident along with a less intense band at 380 nm. With increasing irradiation time, an additional increasingly intense band appeared at longer wavelengths.

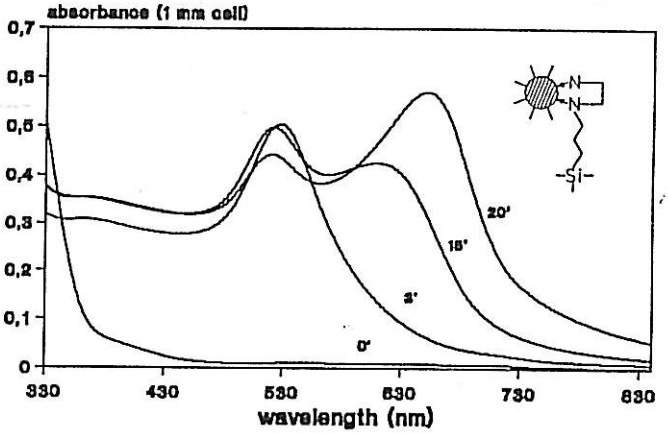

Figure 1. Photoinduced gold formation in ethanolic diamine silane containing solutions under ambient laboratory conditions. Changes in optical absorption (corrected for the solvent) with increasing irradiation time.

Its maximum continuously shifted to 670 nm after 20 minutes. Although the integrated absorption intensity increased with longer irradiation time and reached a plateau after 20 minutes, indicating complete reduction of metal cations, further investigations are needed. Transmission electron micrographs of the solutions irradiated for 30 minutes showed similar particle size distribution as those irradiated for 3 minutes. These results suggest that at irradiation times above 3 minutes, new small particles are formed and due to increrasing particle concentration, aggregates are created resulting in the activation of additional optical absorption bands at longer wavelengths. Similarly structured optical spectra as those presented in Figure 1 have also been calculated (based on plasma resonance coupling in Au particle pairs) and experimentally observed in other studies (2, 9). After coating and thermal curing of the glass substrates using these precursor gold sols, the resulting optically transparent films possess the same optical absorption spectrum as the precursor gold sol. These observations indicate a diamine ligand shielding effects from the ORMOCER matrix on the gold particle interface.

In contrast to diamine silane stabilized colloids, triamine silane based preparations do not require the photolytical reduction step. In this case, the gold colloids are spontaneously formed under ambient laboratory conditions. Figure 2 depicts optical absorption spectra (corrected for the solvent) taken at different times after mixing triamine functionalized silane and Au^{3+} in ethanol.

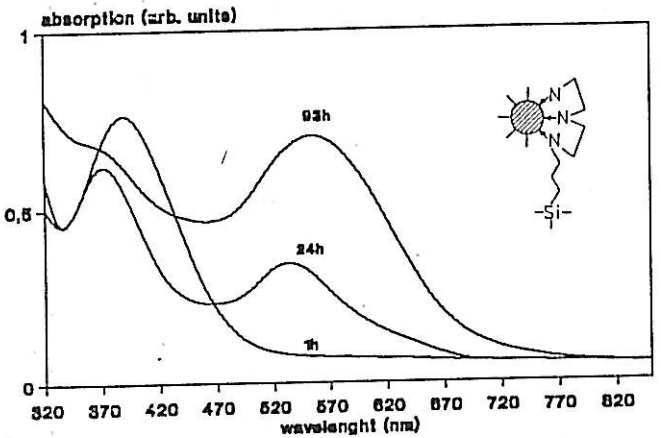

Figure 2. Spontaneous gold formation in triamine silane contaning ethanolic Au^{3+} solutions kept in the dark under ambient laboratory conditions. Changes in optical spectra with time.

After one hour, a pronounced absorption band at 380 nm could be seen. After 24 hours (kept in the dark), a plasmon band of colloidal gold around 540 nm was detected while the 380 nm band became less intense and slightly blue shifted. After 93 hours, the 540 nm band became more pronounced and slightly red shifted. In time resolved pulse radiolysis studies on aqueous gold and silver colloids (10,11) it was shown that during the metal particle growth, short-lived clusters composed of a few atoms are initialy formed exhibiting high energy optical absorption bands, followed by development of the characteristic plasmon bands after larger metallic particles are formed. Considering these results, the initial appearence of the high energy [illegible] nm band could be similarly attributed to the formation of long-lived nonmetallic gold clusters. Again, the cured sol-gel films, prepared via dip-coating using the above triamo silane stabilized gold sols, exhibit the same optical spectral response as the corresponding precursor sol.

The reduction mechanism in the triamine based system causing a spontaneous gold formation in opposition to the results obtained with the diamine systems could be given considering the following possible reaction equilibria (eqs (1) and (2)):

$$Me^{n+} + (R)_2HC\text{-}OH \leftrightarrow Me^{(n-2)+} + (R)_2C{=}O + 2H^+ \quad (1)$$

$$Me^{n+} + (R)_2HC\text{-}OH + LB \leftrightarrow Me^{(n-2)+} + (R)_2C{=}O + H_2LB^{2+} \quad (2).$$

It is of note, that silver and other metal colloids are also spontaneously formed when alcoholic solutions containing metal cations Me^{n+} are exposed to a strong Lewis base (equilibrium shift to the right (2)) whereas in acidic alcoholic solutions, the spontaneous metal formation is blocked (12). On the other hand, the missing gold cation reduction in the diamine case could be explained considering a stronger ligand field effect on the gold redox potential in the triamine case, a possible autocatalytical effect where the nonmetallic gold clusters initially formed serve as catalytical centers or a stronger Lewis base character of the triamine silane.

A question arises whether is it possible to synthesize the diamine based gold films by an one step process during the curing procedure. The possibility of this procedure has been in detail investigated and involved two major steps. In the first step, non-irradiated Au^{3+} containing prehydrolysed silane stock solutions were directly used to coat commercial glass substrates via dip coating techniques. In the second processing step, the photoinduced metal particle growth and the thermal curing (organic network forming step) of the films could be achieved simultaneously. By this technique, glass substrates can be repeatedly coated and photo-thermally treated to synthesize crack-free films of variable optical density, the optical spectra of which are depicted in Figure 3.

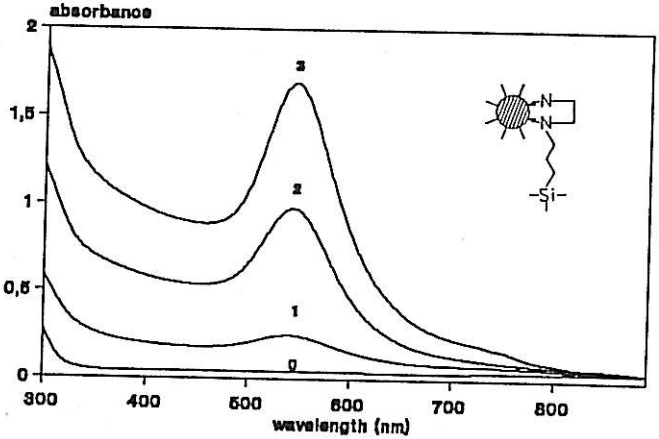

Figure 3. UV/VIS spectra of photothermally treated gold doped sol-gel films on glass substrates after repeated coating (number in the spectra indicates the number of coating steps).

The photo-thermally prepared inorganic-organic glassy films are optically transparent, but show remarkable differences in the absorption spectra compared to the colloidal solutions (see Figure 1). The gold particle size of these composites has been determined to be 15 nm, in contrast to 5 nm particles obtained by photochemically prepared coating sols. The thicknesses of

these films were detemined to be of about 8 microns after the first coating and up to 20 microns after three times repeated coating. The volume fraction of gold particles has been calculated from the optical spectra to be $3 \cdot 10^{-4}$ using Maxwell - Garnett approximation (3,4). At present, we are engaged in nonlinear optical measurements on these composite films which will be the subject of a future publication.

CONCLUSIONS

Based on previous results from studies on solutions and molten glasses it has been shown that gold doped sol-gel films on glass substrates can be prepared. With this sol-gel technique, transparent coatings of variable spectral response and optical density can be prepared. It has been also shown that amine functionalized silanes can be used to stabilize photochemically prepared metallic gold colloids as well as to induce spontaneous formation of long-lived nonmetallic gold clusters. The chemical nature of the nanocomposite matrix could be widely varied including the use of other ligands than amines. These soft chemistry routes enable efficient variation of reaction parameter and synthesis under moderate conditions which suggests further work in this field.

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