PHOTOINDUCED FORMATION AND CHARACTERIZATION OF METALLIC SILVER AND GOLD PARTICLES IN VYCOR® GLASS

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ABSTRACT

The formation of metallic nanoparticles in Vycor® glass has been demonstrated via photoreduction of $AgClO_4$ and $NaAuCl_4$. Spectroscopic measurements are reported to confirm the formation of the nanoparticles. The chemical mechanisms of particle formation are presented and are supported by characterization of the formed metallic particles.

1. INTRODUCTION

In both the military and the private sector, there is a growing need for flexible displays. To address this need, the Army has initiated a Flexible Displays Initiative (FDI) to synthesize new materials, develop new techniques and build new systems to advance the state of the art in display technology. In general, materials that undergo reversible color changes in the solid state have applicability in this technology area.

The synthesis and characterization of metallic nanoparticles has been well-documented in the literature.[1,2] Typically, a colloidal suspension of particles is formed from a metal salt precursor solution that is treated with a reducing agent such as citric acid or sodium borohydride. Other systems have been studied in which polymers such as poly vinyl alcohol/poly acrylic acid or sol-gels are used as a matrix for nanoparticle formation. Fewer researchers study the formation of metallic nanoparticles in glasses. Glasses tend to be more thermally robust than polymers and can be cleaned by vigorous methods to eliminate impurities that can affect particle formation chemistry.

In this summary, we describe the preparation of gold and silver nanoparticles within a high surface area Vycor® glass substrate. Wet and solid-state chemistries are described for gold and silver treatments, respectively. Dramatic color changes using low metal loadings suggest that these materials may have utility in display applications. Spectroscopy was employed to track the photoreduction and species present to aid in the proposed chemical mechanisms.

2. EXPERIMENTAL

Silver doped Vycor® samples were prepared in the following manner. Typically, a clean Vycor® substrate measuring 1 cm × 1 cm × 2 mm was placed in a quartz tube furnace at 700 °C for 24 hrs. The annealed samples were then soaked for 72 hrs in a solution of 1.0×10^{-2} M $AgClO_4$ that contained either 3.0%, 0.3% or 0% (aqueous only) H_2O_2. The samples were then put in a vacuum oven at room temperature at 30 Torr for 2 hours. Samples were irradiated with 350 nm light using a Rayonet photoreactor with a light intensity of 10 mW/cm^2.

Gold particles were formed in Vycor® samples by soaking samples in methanolic solutions of sodium tetrachloroaurate with a concentration of 0.01 M. The samples were removed from the solution and the solvent was slowly evaporated while illuminating at 350 nm in a Rayonet photoreactor. This process minimized the formation of gold particles at the surface of the Vycor®. The preparation of the silver-doped Vycor®, however, resulted in substantial formation of silver particles on the Vycor® surface.

3. RESULTS

Upon irradiation of the metal ion doped samples, various color changes were noted. While color changes were apparent both visibly and spectroscopically, the samples remained transparent as can be seen in Figure 1.

The transparent Vycor® began to tint yellow in the Ag^+ doped samples after ~ 20 min irradiation indicating the formation of small Ag particles. The UV-VIS spectra of the irradiated Ag doped Vycor® is depicted in Figure 2. Two absorption bands appear upon irradiation of the sample; one band at ~ 275 nm and another band at ~ 410 nm corresponding to Ag clusters and particles, respectively. At all times the signal associated with the surface plasmon resonance band of large silver particles, 410 nm, predominates. Based on the spectroscopy studies, the formation of

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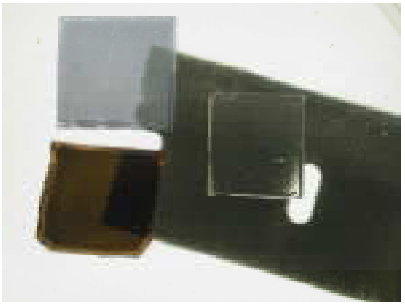

Figure 1: Photograph of blank and treated Vycor® samples. The gold-treated sample is blue-gray and the silver-treated sample is brown.

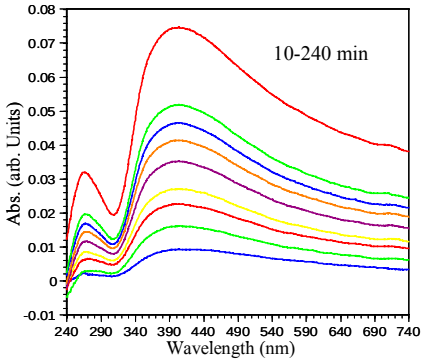

Figure 2: Evolution of the UV-VIS absorbance spectra resulting from the irradiation of Ag^+ doped Vycor® (from 10 min to 240 min irradiation).

silver particles is consistent with the mechanism shown in Scheme 1.

Scheme 1:

$$\text{—OH} + Ag^+ \rightarrow \text{—O—Ag} + H^+ \quad [1]$$

$$\text{—O—Ag} + h\nu \rightarrow \text{—O}\bullet + Ag \quad [2]$$

$$Ag + Ag^+ \rightarrow Ag_2^+ \quad [3]$$

$$2Ag_2^+ \rightarrow Ag_4^{2+} \quad [4]$$

$$Ag_2^+ + Ag \rightarrow Ag_3^+ \quad [5]$$

$$Ag_i + kAg \rightarrow Ag_{(i+k)} \quad [6]$$

The formation of particles is initialized by the silanol groups of the surface of the Vycor®.

The Au^{3+} doped samples are irradiated in the presence of methanolic solutions of the dopant, $NaAuCl_4$. The UV-VIS spectra of the Au^{3+} doped methanolic Vycor® sample are shown in Figure 3. The spectra were taken at various irradiation times. The inset is the same sample showing the initial photoinduced reduction of the dopant, $NaAuCl_4$ which has an absorption band centered at ~ 320 nm. As the sample is irradiated, this signal at 320 nm bleaches and the surface plasmon resonance band for large Au particles, ~ 525 nm, begins to appear. The peak is not well resolved due to the scattering properties of the formed particles.

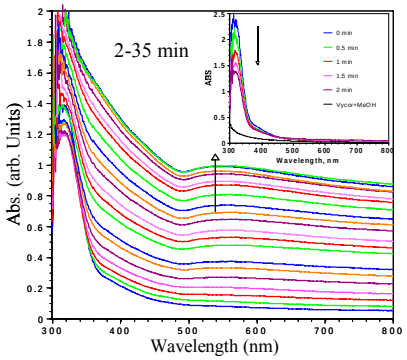

Figure 3: Evolution of the UV-VIS absorbance spectra resulting form the irradiation of Au doped Vycor® (from 10 min to 240 min irradiation). Inset - initial stages of the photo- reduction of Au^{3+}, showing the bleaching of the Au^{3+} precursor.

In Scheme 2, the mechanism that describes the formation of the gold particles is presented.

Scheme 2:

$$Au^{(III)}Cl_4^- + h\nu \rightarrow \{Au^{(III)}Cl_3....Cl\} \rightarrow Au^{(II)}Cl_3^- + \bullet Cl \quad [7]$$

$$Au^{(III)}Cl_4^- + h\nu + CH_3OH \rightarrow Au(II)Cl_4^{2-} + \bullet CH_2OH + H^+ \quad [8]$$

$$2Au^{(II)}Cl_4^{2-} \rightarrow Au^{(III)}Cl_4^- + Au^{(I)}Cl_2^- + 2Cl^- \quad [9]$$

$$AuCl_2^- + h\nu + CH_3OH\ \{Au^{(III)}Cl_4^-\} \rightarrow Au + 2Cl^- + \bullet CH_2OH + H^+ \quad [10]$$

$$Au + AuCl_2^- \rightarrow Au_2Cl_2^- \rightarrow\rightarrow\rightarrow (Au)_n \quad [11]$$

$$\bullet Cl + MeOH \rightarrow \bullet CH_2OH + HCl \quad [12]$$

$$O_2 + \bullet CH_2OH \rightarrow HO_2\bullet + CH_2O \quad [13]$$

$$O_2 + \bullet CH_2OH \rightarrow \bullet O_2CH_2OH \quad [14]$$

$$2\bullet O_2CH_2OH \rightarrow 2H_2CO + H_2O_2 + O_2 \quad [15]$$

$$2\bullet CH2OH \rightarrow (CH_2OH)_2 \quad [16]$$

4. DISCUSSION

The photoreduction of Ag^+ and Au^{3+} has been demonstrated within the pores of Vycor® glass. Detailed characterization of the formed particles will be discussed, which include: X-ray Photoelectron Spectroscopy (XPS), Rutherford Backscattering Spectroscopy (RBS), and prompt gamma-ray activation analysis (PGAA).

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