

Novel technique for engineering the structural and optical properties of metal-doped nanocomposite glasses

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We introduce a novel technique for engineering the structural and optical properties of metal-doped nanocomposite glasses, which relies on the electric-field-assisted dissolution of metal nanoparticles embedded in glass. Using this technique we demonstrate the bleaching of the visible-range absorption associated with the surface plasmon resonance of silver nanoparticles in soda-lime glass host.

Introduction

The Lycurgus cup (4th century A.D.), which can be seen at the British Museum, is a striking example of the early (artistic) use of metal nanoparticles embedded in glass: the vessel appears green in daylight (reflected light), but red when it is shone from the inside (transmitted light) (Fig. 1). This peculiar color display is due to the presence of metal nanocrystals (~70 nm) containing silver and gold [1]. Actually, the surface plasmon resonance (SPR) – i.e. the collective motion of the free electrons of the metal in response to an electromagnetic field radiation – is responsible for a wavelength-selective absorption of the incident light [2]. Spherical particles produce a single SPR band, which is located in the visible range in the case of Ag, Au or Cu, whereas elongated (e.g. ellipsoidal) particles give rise to two spectrally separated SPR bands corresponding to transverse and longitudinal electron oscillations (with respect to particle main axes) [2]. The latter property is exploited for making dichroic glass polarizers [3]. Metal nanoparticles have also interesting nonlinear optical properties such as enhanced third-order nonlinear susceptibility near SPR frequency [2]. In general, surface plasmon resonances can be tailored in a wide spectral range by selecting appropriately both the metal and the host material, but also by controlling the shape, the size and the spatial arrangement of the particles [4]. Complex systems of metal nanoparticles with nonspherical shape (rods, triangles) and special spatial arrangement (arrays) can be produced using sophisticated technologies (electron beam lithography, ion implantation, wet chemistry, etc.) [1]. However, the simple system consisting of uniformly distributed spherical nanoparticles, which is technologically easy to produce, is worth to be studied because it already possesses interesting optical properties. Among various host materials, glass is obviously the most interesting one for

applications in photonics. Ion exchange combined with annealing is probably the most straightforward way to produce spherical silver nanoparticles embedded in glass [5]. Techniques have been reported for engineering the structural and optical properties of these *simple* metal-doped nanocomposite glasses. Low temperature tensile deformation can be used to produce dichroic samples as a result of particle deformation from spherical shape to ellipsoidal shape [5]. Dichroic patterns can be engineered in metal-doped nanocomposite glass through ultrafast particle shape deformation by means of femtosecond laser pulse irradiation [6]. Recently, we discovered that electric-field treatment at moderately elevated temperature – known as thermal poling – was able to dissolve silver nanoparticles embedded in glass [7, 8]. Here, we introduce a novel technique for engineering the structural and optical properties of metal-doped nanocomposite glasses, which relies on the electric-field-assisted dissolution of metal nanoparticles. Using this technique we demonstrate the bleaching of the SPR absorption in soda-lime glasses containing ellipsoidal or spherical silver nanoparticles and we discuss spatial features and dynamics of the bleaching.

Experimental set-up and results

Aggregation of spherical silver nanoparticles (30~40 nm diameter) was realized within a 6- μm thick near-surface layer by thermal annealing of $\text{Ag}^+\text{-Na}^+$ ion-exchanged soda-lime glass samples in H_2 reduction atmosphere. The volume filling factor of metal clusters ($f = V_{\text{Ag}}/V$) decreased exponentially with depth from $f \approx 0.8$ (surface) to 10^{-3} (layer edge). Tensile deformation and simultaneous heating of 1-mm thick samples with spherical nanoparticles produced 0.2-mm thick samples with elongated (ellipsoidal) nanoparticles in 1- μm thick near-surface layer. The samples were subject to thermal poling which consisted in applying a high voltage to the heated sample and cooling it down to room temperature with the voltage applied. Poling was carried out at 280 °C inside an oven using pressed-contact steel electrodes (6 \times 9 mm), with the metal-doped layer facing the anode. The voltage had to be applied in small amplitude steps (typically 0.2 kV) because of the high ionic conductivity of the soda-lime glass substrate [7]. As a result of the poling treatment, bleaching (i.e. increase of glass transmission in the visible range) was observed in the region under the anode with sharp edges corresponding perfectly to the electrode size: in a sample containing ellipsoidal Ag nanoparticles, the treated region became completely transparent after poling treatment up to 1 kV (Fig 1). Scanning electron microscope (SEM) images of the cross section of one half of the treated sample showed that silver clusters had disappeared, leaving nano-scale porous structure instead [8]. Thermal annealing of the other half of the treated sample led to re-aggregation of Ag nanoparticles, as it was indicated by the partial recovery of the original glass colour. The latter result gave us evidence that thermal poling caused the dissolution of Ag clusters into Ag^+ ions in the depth of the glass matrix. In a sample containing spherical Ag nanoparticles, the treated region became yellowish after poling treatment up to 1 kV (Fig. 1). This result indicated that not all the clusters were dissolved and that remaining ones were present with a low volume filling factor. Incomplete bleaching can be explained in terms of the roles that are played by the filling factor and the thickness of ion-depleted layer in the dissolution process [7, 8]. In order to study the dynamics of the bleaching, a sample containing spherical Ag nanoparticles was subject to successive poling steps at 280 °C and its optical transmission spectrum

was measured between each steps. Fitting the measured absorption spectra (between 350 nm and 550 nm) to the theoretical absorption given by Maxwell-Garnett effective medium theory allowed us to estimate corresponding changes in the Ag volume filling factor as a function of poling time and voltage. The SPR band (around 420 nm) was bleached progressively but only after the last poling step the bleaching was strong enough so that the SPR peak could be measured (Fig. 2). At a voltage of 200 V, the filling factor decreased with cumulated poling time but saturation was observed after ~40 min; poling at higher voltages for 10 min led to further decrease of the filling factor (Fig. 3).



Fig. 1. Photographs of Lycurgus cup (4th century A.D.) and silver-doped nanocomposite glass samples (21th century A.D.) after poling treatment. Metal nanocrystals (~70 nm) containing silver and gold are responsible for the peculiar color display of the Lycurgus cup: the vessel appears green in daylight (reflected light), but red when it is shone from the inside (transmitted light) (Fig. 1). The original colour of nanocomposite glass samples (green or orange) is due the wavelength-selective absorption of light associated with the surface plasmon resonance of ellipsoidal (left) or spherical (right) silver nanoparticles. After poling treatment (280 °C, 1 kV), the surface plasmon resonant absorption has been bleached underneath the rectangular electrode area to such an extent that the treated sample is completely transparent (left) or displays a colour different from the original one (right).

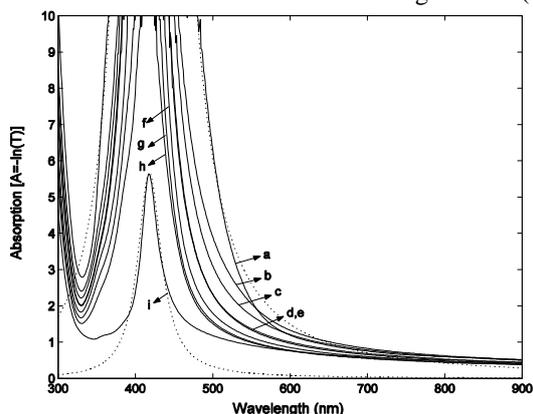


Fig. 2. Absorption spectra of Ag-doped nanocomposite glass: as-received (a); after each of the following poling steps: 200 V - 10 min (b), 200 V - 10 min (c); 200 V - 20 min (d); 200 V - 40 min (e); 400 V - 10 min (f); 600 V - 10 min (g); 800 V - 10 min (h); 1 kV - 15 min (i). Dotted lines are best fits to theoretical absorption of embedded metal nanoparticles given by the Maxwell-Garnett effective medium theory.

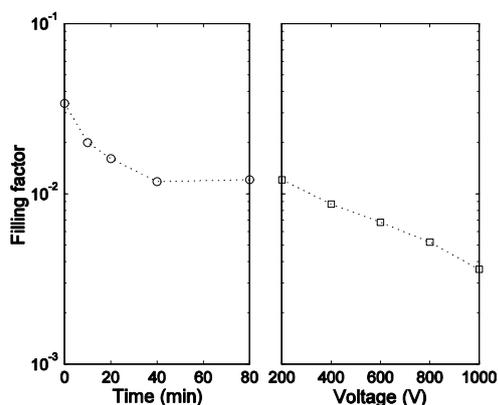


Fig. 3. Volume filling factor of Ag nanoparticles as a function of cumulated poling time (left) and voltage (right), for fixed voltage (200 V – left) and time (10 min – right, except datum at 1 kV: 15 min). The filling factor values were determined from best fits of measured absorption spectra (between 350 nm and 550 nm) to Maxwell-Garnett effective medium theory, assuming uniform distribution of the filling factor across the depth.

Discussion

The physical phenomenon responsible for bleaching is the electric-field-assisted dissolution of metal nanoparticles embedded in glass [7, 8]. The dissolution process is intimately related with the depletion of positively charged ions which takes place underneath the anode during thermal poling. As ion depletion proceeds, the resistivity of the glass host increases considerably in a thin near-surface layer where a high electric

field builds up; this internal field is further enhanced in the vicinity of silver clusters. The thickness of the ion-depleted layer ranges typically from 1 μm to 5 μm (depending on poling voltage) so that spatial distributions of internal electric field and Ag particles overlap when the metal-doped layer faces the anode. At some time during that process the threshold for ionisation of the silver clusters is exceeded so that silver ions are ejected from the ionised clusters due to strong Coulomb forces and drift away in the depth. The silver ions, in turn, are involved in the ion depletion process. A voltage as low as 200 V turns out to be sufficient to initiate the dissolution of spherical Ag nanoparticles. Bleaching increases for longer poling times (at 200 V) until saturation takes place, higher voltages being required to increase it further. Incomplete bleaching is likely due to the presence of Ag nanoparticles which are located deeper in the depth with smaller filling factor, where the electric field strength is not high enough to cause their dissolution. The filling factor plays a critical role here as the uppermost layers (with larger filling factor) are expected to be dissolved first. As the voltage is increased, the electric field gradient which results from ion depletion increases in strength and extends deeper in the host. Both the higher local field strength and the extension of the depletion layer contribute to dissolve those silver particles which remain deeper in the glass.

Conclusion

A novel technique was introduced for engineering the structural and optical properties of metal-doped nanocomposite glasses, which relies on the electric-field-assisted dissolution of metal nanoparticles embedded in glass and is easy to implement. Using this technique we were able to bleach the visible-range absorption associated with the surface plasmon resonance of embedded silver nanoparticles to an extent that was controlled by the poling treatment conditions. Control of the bleached area by the electrode geometry is another key point of the technique, which could be useful for the realization of patterned glass polarizers.

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