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Quantum and dielectric confinements of sub-10 nm gold in dichroic phosphate glass nanocomposites

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HIGHLIGHTS

- We fabricated Au^0 embedded nanocomposites in P_2O_5–SnO–ZnO glass matrix.
- Au^0 synthesized by a single step in-situ thermochemical reduction technique.
- We have reported the blue shifts of the SPR band of sub-10 nm Au^0 NPs.
- The optical property has been explained on the basis of electrodynamics theories.

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ABSTRACT

Blue shifts of the surface plasmon resonance band of sub-10 nm gold in dichroic phosphate glass nanocomposites are observed with increase in both size of gold nanoparticles and refractive index of the medium, which are contrary to the common trends. These phenomena have been enlightened with the electrodynamics theories (Mie and Drude models) and happened due to quantum and dielectric confinements. Nanocomposites have been synthesized by in-situ thermochemical reduction technique in reducing phosphate glass matrices. The plasmon bands are characterized by the UV–vis spectrophotometer, and shape and size of the nanogold by the transmission electron microscopy. All the nanocomposites are dichroic in nature.

1. Introduction

Metal nanocomposites exhibit a variety of novel optical and electrical properties of immense technological and intellectual prospects which have attracted scientists over the last two decades [1–3]. The interaction of light with matter in nanostructured metallic structures has led a new branch of photonics called “plasmonics” [4]. Surface plasmon-based photonics or plasmonics are very promising for new solutions of nanophotonics and nano-optoelectronics [1–5]. The optical properties of metal nanocomposites depend mainly on its surface plasmon resonance (SPR) phenomenon where the plasmon refers to the collective oscillations of the free electrons when excited by an electromagnetic field [1,2]. Again surface plasmon resonance (SPR) band position depends on various factors such as the size of the nanoparticles, shape, refractive index of the dielectric medium and also the metallic species [6–10]. So, by controlling the above parameters it is possible to develop metal dielectrics nanocomposites (here glass) with unusual properties which make them widely applicable in optical memory devices, laser sources [11–15], as well as create a new avenue for biological labels, energy transfer pairs and so on [16–19]. The dichroic property is exhibited by some metal nanocomposites i.e., they transmit and reflect different lights. It is an interesting property which is very useful for various types of dichroic applications such as dichroic polarizers, display (LCD) devices [11–19]. Besides, nanocomposites with nanometal size in the quantum confinement regime (2–10 nm) provide various exciting properties which are of great importance in various fundamental research as model materials and novel technological applications as well [19–26]. It has also initiated a new branch of nanophotonics called “nanometal enhanced photoluminescence” [1,5,9–11,13,14].

The dielectric medium and the size of the nanoparticles are the most important factors those govern the SPR band location of nanometal nanocomposites. In most of the cases, SPR bands show a red-shift (increase in wavelength) with the increase in refractive

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index of the dielectric medium [9] and also with the increase in nanoparticle size [6,11–14]. But in some cases, the blue-shifting (decrease in wavelength) of the SPR bands is observed for the particle size having diameter less than 20 nm [21–27]. This anomaly from the general behavior is due to electromagnetic field enhancement, called the dielectric confinement of the medium and quantum confinement (decrease in electron density) which is the direct consequence of the wave nature of the electrons.

The synthesis of nanometal dielectric (here glass) nanocomposites is not simple. The traditional methods of their preparation comprise of multi-step techniques like sol–gel route fabrication followed by heat-treatment in reducing atmosphere, ion-exchange and subsequent laser, ion or X-ray beam irradiation and heat treatment in reducing atmosphere (e.g., hydrogen) for long time at high temperatures to generate nanometal embedded glasses [28–30]. On the other hand, the synthesis of metal dielectric (glass) nanocomposites by melt-quench technique [9,11,31] is much simple. It provides a straightforward low cost strategy. Recently, Som and Karmakar [13,14] have reported a single-step methodology for the synthesis of nanogold-glass nanocomposites, characterization and nanogold enhanced photoluminescence of rare-earths. However, the synthesis and properties of nanogold embedded phosphate glass nanocomposites have not reported previously. Further, anomalous behavior like plasmon blue shifting instead of common red shifting have also not been reported until now.

In view of the above facts, here, we report the fabrication of Au^0 embedded nanocomposites in phosphate glass matrix (P_2O_5–SnO–ZnO) using a new melt-quench in-situ thermochemical reduction technique. We emphasize here on the study of their optical properties with nanostructuring using the UV–visible absorption spectroscopy, transmission electron microscopy (TEM) and selected area electron diffraction (SAED).

2. Experimental

The raw materials used were tin (II) oxide, SnO (99.9%, Alfa Aesar), ammonium dihydrogen phosphate, $NH_2H_2PO_4$ (98%, Alfa Aesar), zinc oxide, ZnO (99%, Fluka), and chloroauric acid, $HAuCl_4.xH_2O$ (49% Au, Loba Chemie). The glasses of the compositions (mol %): $35P_2O_5$–xSnO–$(65-x)$ZnO (where $x = 30$, 40, and 50) were melted for 30 min in a high purity silica crucible at 1000 °C in air in a raising hearth electric furnace with an intermittent stirring and cast onto a carbon plate. All the glasses were powdered by using a mortar grinder (RM 200, Retsch). Then the required quantity of $HAuCl_4 \cdot xH_2O$ (in excess) was added with the above mentioned glass powders. Detailed compositions of base glass and nanocomposites are given in Table 1. They were mixed thoroughly in alcohol medium and dried. It was then re-melted as following the procedure mentioned above, cast and annealed properly. Samples of about 3.0 mm ± 0.1 mm thickness were prepared by cutting, grinding and polishing with cerium oxide and used for optical and other measurements.

The UV–visible spectra were acquired using a double-beam UV–vis spectrophotometer (Lambda 20, Perkin Elmer) at the error of band position of ±0.1 nm. TEM images of very finely powdered samples were taken using an FEI instrument (Technai G^2) operating at the accelerating voltage of 300 kV. The refractive indices were determined by using SciGlass (Glass Properties Information System, Version 6.7) software following the Priven-2000 method.

Table 1
Composition and some properties of base glass and nanocomposites.

Sample identity	Glass composition (mol %)			Au (mol %) (in excess)	Refractive index	SPR maxima, λ_{max} (nm), ±0.1 nm
	P_2O_5	SnO	ZnO			
NC0	35	30	35	–	1.666	–
NC1	35	30	35	0.001	1.666	–
NC2	35	30	35	0.01	1.666	612.0
NC3	35	30	35	0.02	1.666	604.7
NC4	35	30	35	0.04	1.666	595.4
NC5	35	30	35	0.07	1.666	593.4
NC6	35	30	35	0.10	1.666	592.8
NC7	35	40	25	0.04	1.699	594.4
NC8	35	50	15	0.04	1.732	588.0

3. Results and discussion

The composition of the all the nanocomposites and some of their properties are listed in Table 1. All the Au^0 embedded nanocomposites are dichroic in nature, that is, they transmit blue light whereas reflect brown to brownish-red lights attributable to the formation of nanogold. The intensity of these lights increases with the increase in gold concentration. These facts are depicted in Fig. 1. The homogeneous coloration of the nanocomposites implies the uniform distribution of the Au^0 nanoparticles and the uniform dielectric network formation of the nanocomposites. The larger particles bring about reflection and scattering due to which they exhibit brown to brownish-red coloration in the reflected light. On the other hand, smaller particles exhibit the blue coloration due to transmission of light of lower wavelengths [32]. Several researchers have observed that soda lime silicate glasses containing reducing agents and gold ions (Au^{3+}) on heat-treatment at high temperature exhibit dichroic behavior. They ascribed the dichroic nature to the formation of smaller and larger gold particle formation [33].

The probable mechanism of selective thermochemical reduction of Au^{3+} to Au^0 by Sn^{2+} can be explained by considering the standard reduction potentials (E^0) of the respective redox system [34]. It is necessary to mention here that the redox potential data in glass melts at the melting temperature (1000 °C) are not available, so we have considered the standard reduction potential (E^0) values at room temperature (25 °C) in equilibrium with air.

$$Sn^{4+}/Sn^{2+},\ E^0 = 0.15\ V \quad (1)$$

$$Au^{3+}/Au^0,\ E^0 = 1.5\ V \quad (2)$$

$$Zn^{2+}/Zn^0,\ E^0 = -0.76\ V \quad (3)$$

Thus, Sn^{2+} is expected to reduce Au^{3+} to Au while itself being oxidized to Sn^{4+}. The overall reaction

$$3Sn^{2+} + 2Au^{3+} \rightarrow 3Sn^{4+} + 2Au^0 \quad (4)$$

has the $E^0 = 2.55$ V and the free energy ($\Delta G = -nFE^0$) value around −1476 kJ. Therefore, the reaction (4), that is, the reduction of Au^{3+} to Au^0 is spontaneous. On the other hand, in the case of Zn^{2+}/Zn^0 system the ΔG is positive, so reduction of Zn^{2+} is not thermodynamically feasible.

The UV–vis absorption spectra of the Au^0 embedded nanocomposites as shown in Fig. 2, display broad surface plasmon resonance (SPR) absorption bands characteristics of nano Au^0. The intensity of the SPR absorption bands increases and shifts towards lower wavelength from 612.0 nm to 592.8 nm (a blue shifting) with increasing concentration of Au [35]. It is reported that the SPR band position shifts toward higher wavelength with increasing refractive index of the encapsulating medium [9]. The characteristic plasmon band of Au^0 nanoparticles in soda lime silicate glasses with a