Applied Surface Science 255 (2009) 9447–9452

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Surface plasmon resonance in nano-gold antimony glass–ceramic dichroic nanocomposites: One-step synthesis and enhanced fluorescence application

Tirtha Som, Basudeb Karmakar *

Glass Technology Laboratory, Glass Division, Central Glass and Ceramic Research Institute (Council of Scientific and Industrial Research), 196 Raja S.C. Mullick Road, Kolkata 700 032, India

ARTICLE INFO

Article history:
Received 6 March 2009
Received in revised form 10 June 2009
Accepted 18 July 2009
Available online 25 July 2009

PACS:
42.70.Ce
42.70.−a
73.20.Mf
81.05.Pj

Keywords:
Surface plasmon resonance
Nano gold
Antimony glass–ceramic
Nanocomposite
Enhanced fluorescence

ABSTRACT

A single-step melt-quench in situ thermochemical reduction technique has been used to synthesize a new series of Au° nanoparticles embedded antimony glass–ceramic (K_2O–B_2O_3–Sb_2O_3–ZnO) dichroic nanocomposites. X-ray and selected area electron diffractions manifest growth of Au° nanoparticles along (2 0 0) planes. The particle sizes obtained from X-ray diffraction patterns are found to vary in the range 4–21 nm. Dichroic behavior is attributed to the elliptical shape gold nanoparticles having aspect ratio 1.2, as observed from the transmission electron microscopy (TEM) images. The Au° nanoparticles exhibit surface plasmon resonance band (SPR) around 600 nm, which experiences red-shifts with increasing Au concentration. These nanocomposites when co-doped with Sm_2O_3 and excited at 949 nm, exhibit 2-fold intensification of 636 nm red emission transition ($^4G_{5/2} \rightarrow {}^6H_{9/2}$) due to SPR induced local field enhancement of Au° nanoparticles and are promising materials for display applications.

1. Introduction

An obligatory intermediate step involving the synthesis of metallic nanoparticles (NPs) and their utilization in practical appliances is their organization within solid dielectrics (glasses and glass–ceramics), which in turn can be developed into real devices. Composite materials synthesized by metal clusters embedded in glass matrices have occupied a very unique position in materials science since the millennia due to their striking optical and electronic properties [1–5]. Consequently they are widely used for optoelectronic applications, as part of all-photonic devices, optical communications, switching and sensing devices [1,6]. Enhancement of the fluorescence properties of rare earth (RE) containing glasses and glass–ceramics by the introduction of metal nanoclusters is of the most recent upsurging photonic application of such nanocomposites [4,7,8].

Surface plasmon resonance is a unique optical phenomenon occurring at the surfaces of metal particles in the nanometer size regime. It is the collective oscillation of the outer conduction electrons upon electromagnetic excitation [9]. SPR is intimately dependent on the nanoparticle's size, shape, refractive index of the dielectric environment and other proximal nanoparticles (NPs) [3,10,11]. Precise tuning of the SPR peak across a wide spectroscopic range can be accomplished by varying any of the aforesaid parameters. Besides absorption and scattering, SPR also generates intense local electric fields around the metal nanostructures [4,7–9]. Rare-earth (RE) ions when present in close vicinity of such plasmonics nanoparticles experiences enhanced excitation rate leading to an enormous increase in their fluorescence intensity.

In this regard, anisotropic nanoparticles with sharp edges (ellipsoids, nano-rods, etc.) are more potential candidates for plasmon enhanced fluorescence studies [8,12]. Upon electromagnetic excitation the local surface charge densities are drastically increased and confined near the sharp edges of anisotropic nanostructures which act as light-harvesting nano optical antennas converting visible light into large localized electric field ("lightning-rod effect") [9]. Although glass–ceramic-based nanocomposites play a significant role in the newly emerging nanophotonics technology due to the low production cost, ease of processing, mechanical strength and high transparency but the production of anisotropic nanostructures in a controlled fashion

* Corresponding author. Tel.: +91 33 2473 3469; fax: +91 33 2473 0957.
E-mail address: basudebk@cgcri.res.in (B. Karmakar).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.07.053

embedded in glass–ceramics being a great challenging task, has been met with hindered success.

Fabrication metal–glass and metal–glass–ceramic nanocomposites by conventional techniques are not simple and involves intricate multi-step pathways like ion-implantation, ion-exchange, melting at high temperatures with small quantity of reducing agents, photosensitive nucleating agents, and then subsequent laser, ion or X-ray bean irradiation and long time heat treatment in reducing atmosphere (H_2), UV-light /Co γ-radiation to precipitate and grow the metal nanoparticles [1–5]. Moreover, dichroic glasses are generally produced by deformation of embedded spherical NPs into ellipsoidal NPs by intense irradiation with ultrashort laser pulses [13–15]. So, large scale production requires simplification of production methods.

Most of metal–glass–ceramic composites to date have been comprised of spherical nanoparticles inserted within silicate and phosphate matrices. Hence it would be quite interesting to study the unusual optical (plasmonics) properties of anisotropic metal nanoparticles embedded within heavy metal oxide glass–ceramic matrices, like antimony(III) oxide. Heavy metal oxide glass–ceramics as hosts offer some inherent advantages over silicate, borate and phosphate systems. These are high refractive index, large transmission windows, large non-linear optical (NLO) properties for NLO-based applications, and low phonon energy which is advantageous to diminish the multiphonon relaxation and non-radiative loss and to obtain high upconversion efficiency in the case of metal–RE hybrid nanocomposites [7,8].

Earlier reports on preparation of high Sb_2O_3 containing glasses and glass–ceramic show they all yielded in very tiny pieces or pulverized form [16–18]. The low field strength (0.73) of Sb^{3+} makes it poor glass former [18]. Consequently, the area of nano metal-doped and RE-doped Sb_2O_3-based glasses, glass–ceramics and nanocomposites (NCs) have remained totally unexploited because of their difficulties in preparation particularly in the bulk monolithic form which is very much essential for practical applications. It is only in recent times that we first exploited the remarkable upconversion luminescence of RE ions (Sm^{3+}, Er^{3+} and Nd^{3+}) in (mol%) $15K_2O$–$15B_2O_3$–$70Sb_2O_3$ monolithic oxide glass [19–21]. Sb_2O_3 being a heavy metal oxide, Sb_2O_3 glasses have lower phonon energy (around 600 cm^{-1}) which would increase the upconversion and quantum efficiency of luminescent RE ions [19–21]. But, the most interesting aspect of antimony oxide-based glass–ceramics over conventional systems is that Sb_2O_3 is a mild reducing agent (reduction potential, E° = 0.649 V) [22]. This mild reduction property enables in-situ reduction of Au^{3+} ($HAuCl_4{\cdot}xH_2O$) to Au° than RE ion (Sm^{3+} ion) in a single-step during the melting process thereby providing for a straightforward, low cost strategy for the fabrication of bulk nanophotonic materials.

We are the first to demonstrate here: (i) the Au-embedded antimony glass–ceramics (mol%) $15K_2O$–$15B_2O_3$–$55Sb_2O_3$–15ZnO (KBSZ) nanocomposites and (ii) Au:Sm^{3+} co-embedded hybrid antimony glass–ceramic nanocomposites. The Au°-embedded nanocomposites are characterized by UV–visible absorption spectroscopy, X-ray diffraction (XRD) analysis, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analysis. To explore the photonic (plasmonics) application, we have used the same single-step methodology to prepare novel Sm^{3+}:Au° co-embedded antimony glass–ceramic nanocomposites. The effect of Au° NPs on the upconversion fluorescence emission (visible) of Sm^{3+} under photoexcitation at longer wavelength NIR radiation (949 nm) is also investigated.

2. Experimental

2.1. Synthesis of glass–ceramic nanocomposites

Potassium metaborate, $KBO_2{\cdot}xH_2O$ (15.7% H_2O, Johnson Matthey); antimony(III) oxide, Sb_2O_3 (GR, 99%, Loba Chemie); zinc oxide, ZnO (GR, 99%, Fluka) and chloroauric acid, $HAuCl_4{\cdot}xH_2O$ (49% Au, Loba Chemie), and samarium(III) oxide, Sm_2O_3 (99.99%, Indian Rare Earth) were used as raw materials.

All the raw materials were mixed thoroughly in isopropyl alcohol medium in an agate mortar followed by drying. The base glass of composition (mol%) $15K_2O$–$15B_2O_3$–$55Sb_2O_3$–15ZnO (KBSZ) was prepared in a 20 g melt size using above mixed raw materials in a high purity silica crucible at 900 °C in air for 10 min in a raising hearth electric furnace followed by intermittent stirring of 0.5 min. The molten glass–ceramics was cast into a carbon plate and annealed at 260 °C for 3 h. The Au°-doped nanocomposites (NCs) were prepared in a similar technique using respective dopant concentrations (in excess) as shown in Table 1. To study the photonic application, a Sm_2O_3 and Au° co-doped (0.3 and 0.003 wt% respectively) NCs were synthesized similarly. The melting and annealing times were kept constant for all the samples. Samples of about 2.0 ± 0.01 mm thickness for optical measurements were prepared by cutting, grinding and polishing with cerium oxide.

2.2. Characterization of glass–ceramic nanocomposites

Archimedes method using toluene as the immersion liquid was used to measure the density of the samples (accuracy of ±0.7%). The XRD patterns of the bulk samples were recorded in X'pert Pro MPD diffractometer (PANalytical) operating at 40 kV and 30 mA using Ni-filtered Cu Kα radiation with the X'celerator with step size 0.05° (2θ) step time 0.5 s, from 10° to 80°. FESEM images were taken with a Gemini Zeiss Supra™ 35VP Model using an accelerating voltage of 4.9 kV. TEM was done using a Jeol (model JEM 2010) operating at an accelerating voltage of 200 kV. The UV–vis–NIR absorption spectra in the range 300–1100 nm were recorded with a double-beam spectrophotometer (PerkinElmer, Lambda 20) at the error of ±0.1 nm. Fluorescence spectra were measured, at the error of ±0.2 nm, with a fluorescence spectrophotometer (Spex, Fluorolog 2) in which a Xenon lamp is attached as an excitation source and a photomultiplier tube as detector. The excitation slit (1.25 mm) and emission slit (0.5 mm) was kept same for all the samples so that the excitation intensity was as nearly as

Table 1
Composition and some properties of Au–antimony glass dichroic nanocomposites.

Sample identity no.	Concentration of Au (wt%)[a]	Density ($g\,cm^{-3}$)	Color of transmitted light	Color of reflected light	SPR band position (±1, nm)	Particle size of Au from Scherrer's Eq. (±1, nm)
B	–	4.522	Yellow	Yellow		
NCG1	0.003	4.527	Green	Brown	597	4.5
NCG2	0.007	4.536	Greenish-blue	Brown	616	7.2
NCG3	0.03	4.542	Blue	Brown	625	12.3
NCG4	0.1	4.549	Blue	Brown	632	16.7
NCG5	0.3	4.553	Blue	Brown	685	21.0

[a] Base glass (B) composition (mol%): $15K_2O$–$15B_2O_3$–$55Sb_2O_3$–15ZnO.