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Spectroscopic investigations on metallo-dielectric Gold@silica composites

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HIGHLIGHTS

- Spectroscopic study on metallo-dielectric composites is presented.
- Bragg reflection peak red shifts with shell growth.
- PL spectra show two PL bands in visible and IR region.
- Study reveals that metallo-dielectric particles are good candidate for SERS.

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ABSTRACT

Optical properties of metallo-dielectric (Gold@silica) composites were measured using different characterizing techniques viz. UV–Visible and photoluminescence (PL) spectroscopy. Reflection spectra showed the Bragg reflection peak shifted to longer wavelength and was broadened with the shell growth. The PL spectra showed the presence of visible and infrared bands. While the visible emission is explained by radiative recombination caused by interband transitions, the infrared emission is accounted for by the intraband transitions. Raman spectroscopy of methyl red (MR) indicator dye adsorbed on metallo-dielectric films has shown an enhancement in the Raman signals on incomplete shells. The enhancement is ascribed to the surface roughness and nanogaps making the synthesized metallo-dielectric particles a potential substrate for surface enhanced Raman spectroscopy (SERS).

Introduction

Metallic nanostructures encapsulating a dielectric core have attracted the attention of researchers because of their peculiar properties [1–7]. In core–shell geometry, dependence of optical properties on shell thickness combined with chemical stability of silica core results in a good candidate for applications in the field of optics [8], photonics [9], surface enhanced Raman spectroscopy (SERS) [10], catalyst [11], sensors [12], drug delivery [13], etc. Surface plasmon resonance (SPR) of these composites can be tuned from visible to infrared region of electromagnetic spectrum by varying the core to shell thickness ratio [14,15]. These composites can be assembled to form an ordered structure called photonic crystals to realize complete photonic band gap (PBG) in the desired frequency range [16,17]. The photoluminescence of gold surfaces was reported by Mooradian with a low quantum yield [18] but anisotropic particles have shown enormous enhancement in the PL signals [19,20]. However, no apparent study has been conducted on the core–shell geometry. Metallo-dielectric composites have also served as brilliant substrates for SERS [21] but there is a very little attempt to study the SERS with incomplete shells.

In the present work, we demonstrate the spectroscopic investigations on metallo-dielectric composites. Opal structures were fabricated on the glass substrate using vertical deposition technique. The photonic properties were studied by varying the shell thickness. Photoluminescence study on the same samples was conducted. The synthesized samples were also demonstrated for amplifying Raman signals of methyl red indicator by using substrate coated with it.

Materials and methods

Materials used

Hydrogen tetrachloroaurate tri hydrate ($HAuCl_4{\cdot}3H_2O$), Tetrakis-hydroxymethyl phosphonium – chloride (THPC), Sodium

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hydroxide (NaOH), Aminopropyl-tri-methoxy silane (APTMS) and Hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) were obtained from Acros, Fisher Scientific and Potassium Carbonate (K_2CO_3) was purchased from Merck-India. Methyl red indicator ($C_{15}H_{15}N_3O_2$) was obtained from Lobachemie. All the chemicals were used as received without any further purification. Deionized (DI) water used in the preparation had a resistivity of 18.2 MΩ obtained from Lab Pure Andel BIO-AGE.

Metallo-dielectric particles were prepared by chemical reduction growth procedure in a multistep process [22]. In this approach, firstly silica microspheres of diameter ~450 nm were synthesized via sol gel method (denoted as S sample), the detailed procedure is given elsewhere [23]. The surface of the dielectric core (S) was functionalized with APTMS, such that AuNPs could be attached to it (denoted as sample AS) and then additional gold was reduced onto the seeded particles to get a shell around silica core. This process was repeated four times to achieve a gradual shell growth (the samples are denoted as AS1, AS2, AS3 and AS4). The detailed sample preparation is given in the following section.

Shell growth

For the shell growth, gold hydroxide (K-Gold) solution was prepared by adding $HAuCl_4$ and potassium carbonate solution in water and keeping this solution in dark for 24 h, initial yellow solution turned white, which indicated the formation of gold hydroxides. The K-Gold solution was divided into four equal parts. Seeded silica microspheres were added to the first part of K-Gold solution with constant stirring. To this mixture, a freshly prepared Hydroxylamine hydrochloride solution (130 mg/L; 1.87 mM) was added drop-wise in 45 min, and this final solution was stirred for 3 h. After the completion of reaction, the solution was centrifuged thrice to remove all the free un-attached gold particles so that the growth would only take place at the seeded particles over the silica surface. This shell growth process was repeated thrice with other three parts of K-Gold solution to get a complete shell of gold nanoparticles around the silica surface. The samples were centrifuged and redispersed in DI water for further characterizations.

Metallo-dielectric opals

Ordered structures from the synthesized metallo-dielectric particles were prepared on glass substrate (having dimension 5 mm × 5 mm) using vertical deposition technique. The detailed procedure is given elsewhere [23–25].

All the samples were characterized with Scanning electron microscopy (SEM, FEI Quanta FEG 450) for morphological properties and the optical properties were characterized with UV–Visible spectroscopy (PerkinElmer, LAMBDA 750, in absorbance and reflection modes) and Raman Spectrometer (in Via Raman spectrometer, Renishaw). 325 nm wavelength was used for PL measurements while SERS spectra were obtained using 514 nm wavelength.

Results and discussion

Scanning electron microscopy

Fig. 1(a) and (b) show the SEM micrographs of bare silica and initial attachment and seeding of AuNPs onto the silica spheres. We could see a remarkable difference in the images, as the seeded silica micrograph showed a rougher surface (although the nanostructures on the surface were sparsely present) in contrast to the smooth silica surface. Fig. 1(c)–(f) show the gradual growth of shell with each coating step. With initial coatings, the voids in between the already existing particles were filled and then the particles grew in unison to form an almost complete shell of larger thickness. Some un-attached gold clusters were also seen in the micrographs because of the improper washing. Fig. 2 shows the SEM micrograph of ordered metallo-dielectric composites on glass slides. It shows that the particles have self-assembled into a face centered cubic (fcc) lattice.

UV–Visible spectroscopy

Optical characterization of as-synthesized metallo-dielectric particles, in the form of ordered structures was conducted by measuring normal reflection, using UV–Visible spectroscopy in reflection mode, along the (1 1 1) direction in 400–1100 nm range, as shown in Fig. 3.

It is noticed that the first order Bragg's reflection, originated from the complete photonic band gap (PBG), is shifted from 820 to 882 nm as the shell thickness increased. Intensity is decreased which shows that photonic band gap effect becomes weaker as the shell thickness increases. The second order Bragg's reflection peak is shifted from 426 nm to 474 nm for AS2 and then to 452 nm for AS4. Bragg's reflection originated from the face centered cubic (fcc) (1 1 1) in the IR region also showed red shift behavior i.e. from 954 to 1000 nm. Bragg's reflection positions are summarized in Table 1.

The red shift in the spectra may be attributed to the change in the dielectric constant of the surrounding medium and increase in the particle size. The peaks are almost consistent with the Bragg's law, since the photonic crystals diffract light according to the Bragg equation [23]:

$$\lambda_{\max} = 2d_{hkl}\sqrt{n_{eff}^2 - \sin^2\theta}, \tag{1}$$

where $\lambda_{\max}$ is the Bragg's reflection wavelength, n_{eff} is the refractive index, θ is the incident angle and d_{hkl} is the interplanar distance between the two consecutive layers along the incident direction. In case of fcc structure along (1 1 1) plane, $d_{111} = 0.816D$, D is the diameter of the microsphere. The deviation between the experimental and theoretical values of $\lambda_{\max}$ may be attributed to polydispersity of the silica core and presence of unattached gold nanoparticles in the samples.

The relative forbidden photonic band gap around the center wavelength for each Bragg's reflection is calculated as:

$$W_{PBG} = \frac{\Delta\lambda}{\lambda_{\max}}, \tag{2}$$

where $\Delta\lambda = \lambda_+ - \lambda_-$, is the full width at half maximum.

Table 1 summarizes the percentage of relative forbidden photonic band gaps for different compositions.

Photoluminescence spectroscopy

PL measurements on the ordered structures were performed at room temperature with a 325 nm laser. Fig. 4 shows the PL spectra of metallo-dielectric composites and pure silica. PL from pure silica can be attributed to the presence of hydrogen related species, such as Si—H and Si—OH, at the surface of the silica spheres [26]. For the metallo-dielectric composites, a broad band ranging from 500 to 620 nm in the visible region is seen. Luminescence in gold nanoshells arises from radiative recombination of electron hole pairs at selected symmetry points in the Brillouin zone. Usually, emission peaks of gold crystal are expected to occur at 520 and 650 nm. These emission peaks originate from the interband transitions near the X- and L-symmetry points of first Brillouin zone due to large density of states near the symmetry points. So the PL band in this region may occur as a combined band in response to these emission peaks, which results from radiative recombination of