Blueshift Plasmonic effect in photonic crystal cavity with gold nano-structure

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Research Article

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Abstract

In this research article, we reportthe plasmonic effect exhibited by a self-assembled photonic crystal cavity in nanostructures using asecond harmonic laser exposure. The photonic nanostructures composed of goldnanoparticles (AuNPs),enhancedthe fluorescence properties which undergo into lattice planesand thereby affect thenonlinearproperties.The newlyfabricated colloidal structures exhibited a strong plasmonicinteraction with different laser powersdensity.The outcome of this research presentsthe self-assembled nano-photonic cavity as a suitable plasmonic nanostructure for optoelectronic applications. These nanostructurescan be fabricated using high power lasers source,e.g. dye laser and solid-state laser.

Introduction

Much interest has been shown in the field of colloidal spheres (CS)during the past few years, by the scientific community,because of their unique, challenging and potential applications in optoelectronics[1]. The dependence of optical, magnetic, physical and chemical properties on the size and shape of opticalnano-materials have drawnsignificant attention for new applications of photonic crystals and colloidal spheresfor severaldifferent technological areas[2].Laser light interactionwith the colloidal sphere (CS) increases the high-quality factors for optical devices and the efficiency of lasers[3, 4]. CS has proved there wide applications in several optoelectronic fields[5-7]. The resultant or the collective oscillations of available free electronswithin nanoparticles, along with localized surface plasmon resonance (LSPR) band, may tune the optical characteristicsof metal nanoparticles. According to previous findings, the skillful variation of the size and shape of the nanoparticles may tunethe LSPR band in visible and near-infrared[8].Attachment of colloidal spheres with gold nanoparticles (AuNPs) may also highlymanipulatethefluorescence intensity of dye[9].Some exceptionalproperties originating from surface modification and quantum confinementprove CSa useful candidate in nanotechnology[10, 11]. The AuNPs caninduce self-organization into lattice planes [12-14]. This system isrequiredtocontrol the positioning of the metal nanoparticles in the crystal plane[7, 15]. According to literature, nonlinear responses are reported to be enhanced because of the strong interaction of plasmonic AuNP[16, 17]. This variety of nanoparticle assemblies is wholly different and paves a new way for new possible meta-materials having the desired optical and electronic properties, which can be tuned by the size of colloidal particles and LSPR[18].Within these LSPRs, the oscillations of collective electrons fallin the metal conduction band and can be modified by an external field by employing closely spaced metallic nanoparticles (MNPs).

LSPR is the exceptional optical properties of MNPs. As compared to the identical dimensions of dielectricNPs, MNPs possess a larger cross-section of scattering than that of the NPs. The surface plasmon resonance (SPR) is a unique characteristic property of MNPs, by which the light waves can be confined close to the surface of nanoparticles and a high gain can be achieved.[19]. The nature of the material, it's shape and size along with the nearby environment of NPs, can decide the position of SPR. The NPs canmodify the transition rates (non-radiative and radiative) of the dye molecules in the vicinity[20-23].

Within the present work, we have examined the laserinteraction performance with polymer-based colloidal spheres (CS),attached with AuNPs, doped with dye pigment Rhodamine6G (Rh6G). A blue plasmonic shift at high tuning laser power density was obtained. The Colloidal spheres CS-Rh6G attached with AuNPs exhibitedstronginteraction with fluorescence and peak broadening, which in turn, clearly indicatesblue plasmonic behavior. This behaviordepends on laser powerdensity instead of CS-Rh 6G. The CS-Rh 6G-AuNPs also demonstrated peak broadening and improved spontaneous emission properties. These resultssuggested thatthe self-assembled CS-Rh6G-AuNPs nano-photonics systems can be used for the future application ofseveral optoelectronic areas.

Materials And Methods

Synthesis & attachment of colloidalspheres with gold nanoparticles:

Monodisperse polymer-based colloidal spheres weresynthesized by emulsion polymerization method. Polymethyl methacrylate (PMMA) spheres were chemically synthesized by adding 25mLmonomer and 200mL water in athree-necked flaskcontaining dye solution ($10x10^{-4}$Mm) at 900 rpm stirring speed. The mixture was rinsed to reflux, and after reaching to90^{o}C of the mixture, potassium persulfate powder (0.02gm to 0.2gm) was dissolvedin the solution. After 120 minutes, the reaction was paused.The solution was cooled down untilroom temperature thensilica wool was used to filter the colloidal solution.Chemical reduction method was used to synthesizeAuNPs, in which, 5 ml solution of chloroauric acid ($HAuCl_4.3H_2O$) having a concentration of 10 mMwas heated until boiling in 100 mL beaker with 90 mL di-ionized water and stirring at 400rpm. 5mL of $3.8x\ 10^{-2}$ M trisodium citrate dihydrate ($Na_3C_6H_5O_7.2H_2O$)was further added into the solution. The solution changed color within 15 minutes similar tored wine, while at continuous stirring. 10 mL of colloidal spheres and some amount of PVP was added into the solution, it was continuously stirredovernight and then was washed with water 3 times. AuNPs were attached to photonic crystals by adding some amount of the AuNPs after centrifugation.Finally,the mixture was aged for 24 hrs.

Results

For characterization, we synthesized CS with dye molecules, some amount of AuNPs was added and after that, a continuous stirring for 10 hours was done. Finally, the solution of CS and Au NPs werespread over the silicon substrateand left for getting a dry surface in figure 1.

Figure 2, showing scanning electron microscope images, which are typical close packing arrangements. The self-assembly of CS well ordered.In addition, their diameters as 300 nm for CS-Rh6G and 20 nm AuNPs. AuNPs distributed in superlattice plane on CS. **Fig.2a** showswell-ordered PMMA CS with few defects and **fig.2b** shows well organizedAuNPs on PCs.Bright tiny particles are AuNPs.

Experiment set-up for laser characteristic

Optical effect was observed by the second harmonicgeneration laser such as Nd:YAG at a repetition rate of 20 kHz and pulse duration of 1ns. The sample was fixed ata circular platformto allowthe detectionofthe luminescence around the particles. A notch filter filtered the collected emission.

The measurements were performedby changing the excitation power from small to large values. The energy transferbetween the dye molecule and metal nanoparticles(Förster resonance energy transfer, FRET) [24, 25]and surface energy transfer (SET) [26-28] was explained using Förster elegant theory.

$$E = \frac{1}{1+(r/R_0)^6} (1)$$

The value ofE depends on the separation distance {\displaystyle r}r between donor-to-acceptor and varies with an inverse 6th-power law because ofthe dipole-dipole coupling mechanism. R_0denotes {\displaystyle R{0}}RrRthe Förster distance of this donor-acceptor pair[29, 30]. However, the conventional FRET technique suffers from many limitations and can be employed only on dye molecules as donor and acceptor. Theenergy-transfer beyond this distance becomes too weak to measure[31, 32]. In this process, dye molecules take part in the resonance energy transfer and affect the optical traits of donor and acceptor molecules.

MNPsare reported to influence the radiative rate of a chromophore [33, 34]. Fluorescence intensity can be enhanced by a modification of the chromophore radiation rate by the AuNPs. Thevariation of the radiative rate of chromophore has already been explained in the context of the coupling of the molecular and nanoparticle dipoles. The rates of decay for radiative and non-radiative decaydependonthe chromophore dipole related to the surface of the particle[35].During the enhancement of laser power, the radiative transition enhanced anda little shift towards the lower side[36]was observed.Timmerman et al. reported the power dependence shift of spectral peaks with different sizes of particles[37].In this paper, laser light interactionwith CS attached with dye molecules, attached with Au-NPsatdifferent powersisstudied.The more is the power of laser; the more energy is absorbed by CS and hence the more is the emissionby the composite. The blue shift in the spectrum is attributed to the absorption at higher energy radiation and emission from the adjacent attached CS and AuNPs.However, for increased power (50 to 275mW) of laser, with Rh 6G dye-doped CS, neither blue shift at high power nor peak broadening was observed (**Fig. 4**).This effect clearly showstheplasmonic optical effects on CS-Rh6G+AuNPs, peak shift and peak broadening associated withthe attachment of the AuNPswith CS.The peak broadening is recorded to augment first, a reduction after aspecific power of the laser, followed by a saturation[38, 39].

Table 1. Comparativestudy of spontaneous Emission spectrum in colloidal spheres with dye molecules and withoutthe attachment of metal nanoparticles.

Power (X-Axis)	FWHM (Y-Axis) With dye	FWHM (Y-Axis) With Au-NPs
50 mW	53 nm	90 nm
75 mW	53 nm	90 nm
100 mW	53 nm	90 nm
125 mW	53 nm	94 nm
150 mW	53 nm	97 nm
175 mW	53 nm	99 nm
200 mW	53 nm	102 nm
225 mW	53 nm	102 nm
250 mW	53 nm	102 nm
275 mW	53 nm	98 nm

In table 1, the variation in FWHM (Y-Axis) with laser power (X-Axis) has been shown. The emission spectrum at different pump powers was recorded, and changes in FWHM of the spectrum was observed.

Colloidal based self-assembly film wasexcited by laser radiation, the probability of radiative transition increases at higher energy edge of the spectrum, creating a blue shift in the recorded spectrum [40], while enhancing the pump power from 50 to 275 mW. It indicates that the laser powers affect the peak broadening and peak shift [41], as has been shown in **fig. 3**. With the increased pump power, the gain in the proximity of peak emission wavelength increases, attributing to a blue shift towards the maximum of the emission spectrum.This gain, for an inhomogeneous medium, at any wavelength equals to the product of cross-section of stimulated emission and difference of population density, as follows:

$$g_{\lambda}^{D} = \Delta N_{ul} \sigma_{ul(\lambda)}^{D} \quad (2)$$

Where g_{λ}^{D} is the gain at any wavelength, ΔN_{ul} is the difference in population density, and $\sigma_{ul(\lambda)}^{D}$ is the cross-section of stimulated emission.

CS-RhB+AuNPs are involved in the emission process; hence, the difference in population density is higher for higher pump powers. This will enhance the gain in the proximity of the peak wavelength of the emission, which in turn leads to a relative blue shift in the emission spectrum towards the maximum of emission. The increment in pump power beyond does not produce any further blue shift in the emission spectrum, probably because of gain saturation. In various studies, almost identical relative blueshifts have been observed towards the peak of emission cross-section, while increasing the pump power. Within this study,the CS surface was modified with AuNPs and photoluminescence, higher than without AuNPs was observed (**Fig. 5**). Gontijo et al. reported that the modification in the density of surface plasmon states is necessary to increase the rate of spontaneous emission andsimultaneously toenhance the quantum efficiency of the semiconductor materials being used in the reaction [38]. The excitation of plasmons can be controlled by surface Plasmon density of states and this configuration is essential to increase the properties of luminescence[42].

The emission spectrum in **fig.5a** indicates a high PL intensity with and without AuNPsin the CS RH6G surface.This PL enhancement is due to the attachment of AuNPs.Experimental and theoretical compression UV spectrum are shown in **fig.5b.** **Fig. 5d** shows, energy level diagram ofCS-Rh 6G AuNPs,excited bythe wavelength of 532 nm.Thelowershift occurs due to the Intersystem crossing (ISC).The peak shifting and peak broadening are attributed tothe plasmonic effect due to AuNPs self-assembly.

Experimental and simulation study of absorption spectrumCS-Rh6G and CS-Rh6G AuNPs (**a**and **b**). Simulation studies and experimental data are following each other and show a good fitting. The distinct gold surface plasmonic peak is observed at ~522 nmin gold attached samples(**c).** Time-resolved fluorescence spectrum of the Rh6G-CS and presence of AuNPs, and energy transfer diagram (**d**).

$$k_T(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6 (3)$$

where $\tau_D$is the lifetime of the donor in the absence of the acceptor, r is the distance between the donor-acceptor pair, and R_0 is the Förster distance, at which the transfer rate $k_T(r)$ becomes equal to the decay rate of the donor while the donor is absent.Chance et al.[44]termed the rate of energy transfer from a dye molecule to the surface of the metal as surface energy transfer (SET).

The average size of AuNPs was calculated to be 20 nmby SEM. All of the AuNPs were spherically symmetric.Blueshift occurrence is indicative of the capping ofnanoparticles with the stabilization molecule[45]. The plasmonresonance band for gold nanoparticle is not onlydependent onthe particle size but alsothe surrounding medium's dielectric constant. Whenwe change the stabilization molecule, probably the dielectric constant also changes and therefore, it causes ashift at the band.

Conclusions

In summary, this research explained theencapsulationof dye molecules with colloidal spheres and AuNPsusing a self-assembly approach. Further, the blue shift plasmonic effect exhibited by plasmonic nano-cavity fabricatedwas investigated to be due to the self-assembly of AuNP. It is observed that by varying the laser powers, colloidal spheres with AuNPs exhibited ashiftfrom shorter to greater wavelengthsat high poweralong-with a peak shifting as compared to CS-Rh 6G specimen. This new 3D-CS material maybesuitablefor several nonlinear optical devices and otherlaser applications.

Abbreviations

colloidal spheres (CS), Polymethyl methacrylate (PMMA), localized surface plasmon resonance (LSPR), goldnanoparticles (AuNPs),

Declarations

Availability of data and materials:

All data generated or analyzed during this study are included in this article

Authors' contributions

AY carried out plasmonic behavior in nanostructures and drafted the manuscript. VA synthesized metal nanoparticles part of this manuscript. AK, YW, ZH and SR discussed and helped draft the manuscript. All authors read and approved the final manuscript.

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Competing interests:

The authors declare that they have no competing interests.

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Figures

Figure 1

Schematic diagram of the fabrication processand attachment of Au-NPs with self- colloidal spheres.

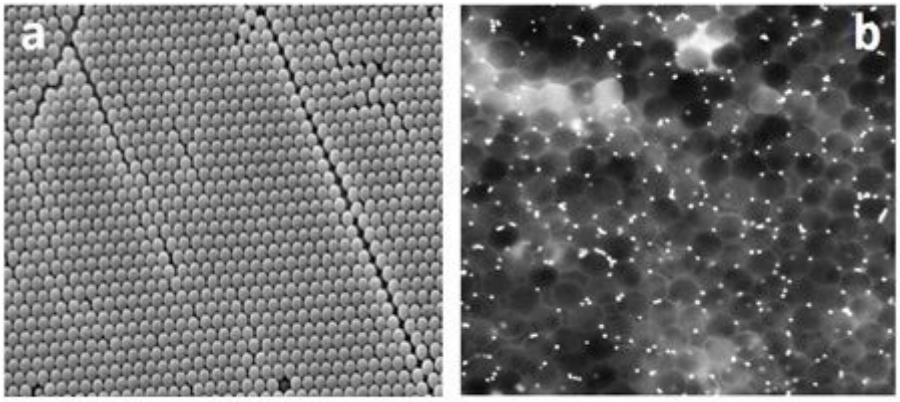

Figure 2

SEM micrograph: PMMA Rh6G spheres (300 nm) and attached with gold nanoparticles20nm (a), and (b).

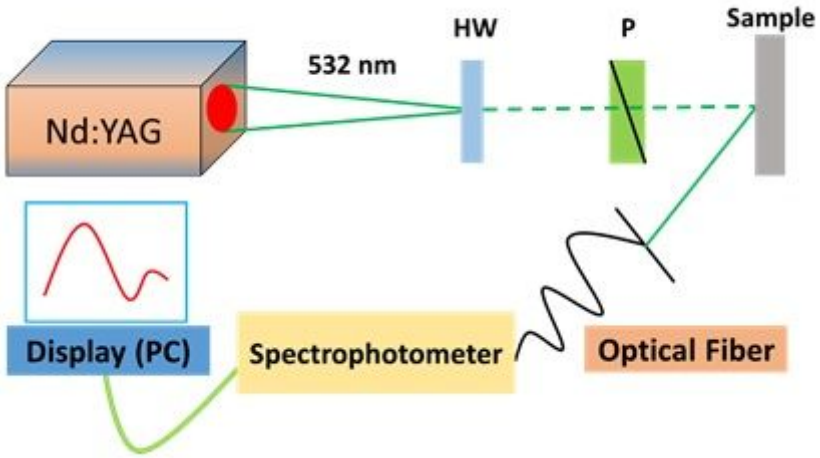

Figure 3

Schematic diagram of the laser set-up for measurements

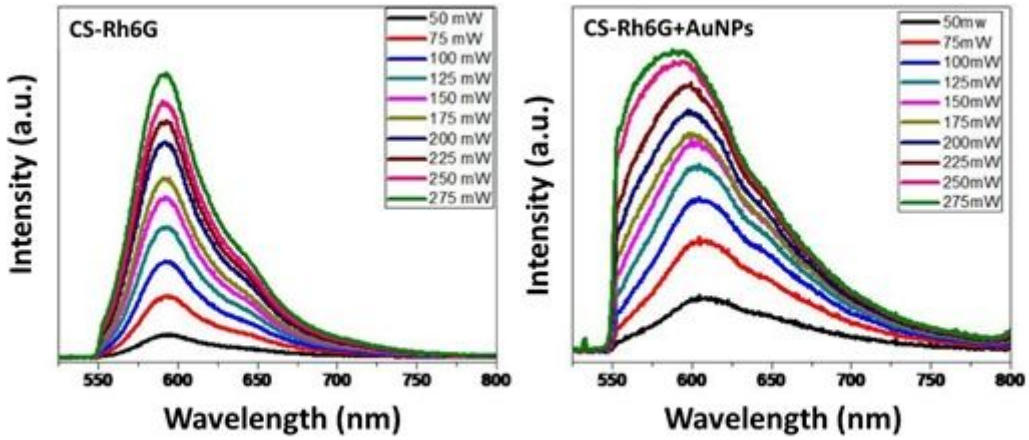

Figure 4

PMMA CS with dye molecule emission spectrum at different powersshowing the variation ofPL spectra of PMMA CS + AuNPs with various excitation powersof the laser.

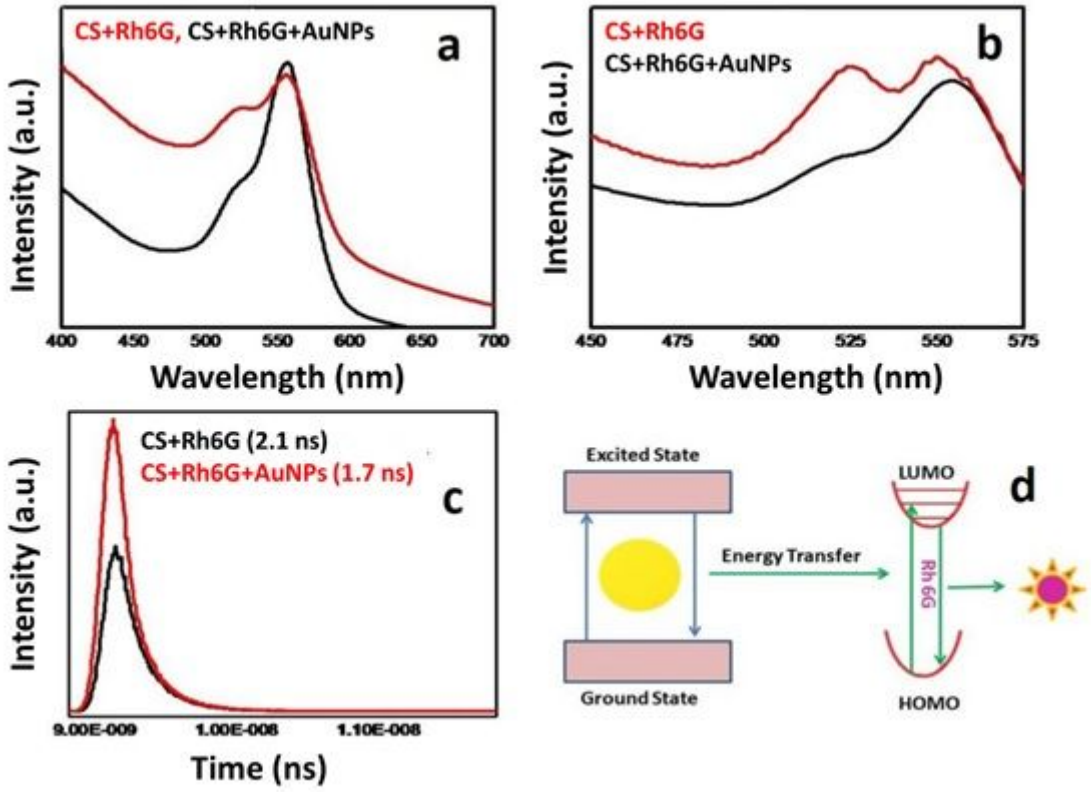

Figure 5

Experimental and simulation study of absorption spectrumCS-Rh6G and CS-Rh6G AuNPs (aand b). Simulation studies and experimental data are following each other and show a good fitting. The distinct gold surface plasmonic peak is observed at ~522 nmin gold attached samples(c). Time-resolved fluorescence spectrum of the Rh6G-CS and presence of AuNPs, and energy transfer diagram (d).