

## Tuning luminescence intensity of RHO6G dye using silver nanoparticles

SUCHITA KALELE, APARNA C DESHPANDE, SHASHI BHUSHAN SINGH and S K KULKARNI\*

DST Unit on Nanoscience and Nanotechnology, Department of Physics, University of Pune, Pune 411 007, India

**Abstract.** The photoluminescence (PL) from rhodamine (RHO6G) dye dispersed in ethanol has been studied in the presence of different amounts of citrate stabilized silver nanoparticles of size, ~10 nm. Enhancement as well as quenching of luminescence intensity has been observed and it was found that luminescence intensity can be tuned by adding various amounts of silver nanoparticles to the RHO6G dye dispersion. The luminescence spectra of dye consist of two peaks at 440 nm and 550 nm. Peak at 440 nm shows an enhancement in intensity at all the concentrations of added silver nanoparticles with the maximum intensity for dye with 0.25 ml silver nanoparticles (82% enhancement in the luminescence intensity). PL intensity of intense peak at 550 nm of dye molecules was found to be quenched in presence of silver nanoparticles and maximum quenching was found to be 41% for the dye with 1 ml silver nanoparticles. However, for lowest concentration of silver nanoparticles viz. (0.01 ml), enhancement in intensity was observed (13% enhancement than the dye molecules). The quenching as well as enhancement in the intensity can be understood by considering the possibility of three different phenomena. It has been reported earlier that when metal nanoparticles are in close proximity to the fluorophores, quenching of luminescence occurs, whereas when metal nanoparticles are located at certain distance, enhancement in luminescence is observed. This effect has been explained by coupling of surface plasmon resonance from metal nanoparticles with fluorophore, resulting in the increase of excitation and emission rate of the fluorophore in the localized electromagnetic field. The quenching and enhancement of luminescence intensity of the dye molecules can also be explained as the transfer of electrons from dye to the silver nanoparticles and to an extent it can be attributed to the aggregation of dye molecules upon addition of silver nanoparticles.

**Keywords.** Luminescence; optical properties; metal nanoparticles.

### 1. Introduction

Organic dyes have been studied extensively due to their luminescence properties and possibility to tune their properties by coating with another material (encapsulating shell) or by localizing near metal surfaces (Geddes *et al* 2003; Ethiraj *et al* 2005). Among organic dyes, rhodamine 6G (RHO6G) dye is one of the most important dyes. This dye has remarkably high photostability and high quantum yield (0.95), therefore, often used as a laser dye. However, this dye photobleach very fast upon exposure to the light source and efforts have been dedicated to overcome this problem by doping them in polymer matrix (George *et al* 1999).

Earlier, the luminescences of dye molecules have been studied by encapsulating them with silica shell (Imhof *et al* 1999; Ethiraj *et al* 2005). It was found that coating these molecules with silica, photostabilizes them. Tuning the luminescence intensity of dye molecules near a metal surface was studied by Drexhage in as early as 1970,

leading to various reports on interaction of fluorophores with metal nanoparticles or surfaces (mostly silver) displaying various spectral changes such as enhancement in luminescence intensity, photostability, quantum yield etc (Lakowicz 2001). It has been found that when metal nanoparticles are in close proximity to the fluorophores, quenching of luminescence occurs, whereas when metal nanoparticles are located at certain distance, enhancement in luminescence is observed (Zhang and Lakowicz 2006). These effects have been explained by coupling of surface plasmon resonance from metal particles and fluorophore. Zhang and Lakowicz (2005) studied the fluorescence of phenyl phenanthridine dye on silver nanoparticles and could notice an enhancement in the luminescence by a factor of two. Geddes *et al* (2003) examined the effect of metallic silver colloids on the luminescence properties of indocyanine green dye and found a 30 fold increase in the intensity of dye molecules with decreased life times and increased photostability. Ishikawa and Okubo (2003, 2005) have investigated the spectrally narrowed emission from rhodamine 6G infiltrated in synthetic opals. Synthetic opals have interconnected nanoscale voids in which silver nanoparticles can be anchored. When dye molecules are

\*Author for correspondence (skk\_surface@yahoo.com)

dispersed in these opals, they are within a distance of only few tens of nanometer from metal surface. Effect of surface plasmon resonance of silver nanoparticles on dye molecules have been studied and narrowing of spectral line width (one tenth lower than without silver) in the emission spectra from the dye molecules was observed.

Theoretical studies have been carried out on absorption and luminescence of dye molecules adsorbed on silver and gold nanoparticles or surfaces. Wang and Kerker (1982) found that due to interaction of metal and dye in core shell particles splitting of extinction bands occurs. Enhancement also has been reported due to such interaction. Quenching of the luminescence of dye molecules adsorbed on a smooth Ag surface was observed by Ritchie and Burstein (1981).

However, all these reports are limited to metal surfaces and thin films and study of the behaviour of dispersion of dye molecules in presence of colloidal metal nanoparticles would be interesting. Here, in this report, enhancement as well as quenching of luminescence intensity of RHO6G dye upon interaction with 10 nm size citrate stabilized silver nanoparticles is discussed. It was found that luminescence intensity can be tuned by adding various amounts of silver nanoparticles in the ethanolic dispersion of dye molecule.

## 2. Experimental

Silver nanoparticles were synthesized by chemical reduction method using tri-sodium citrate. In a typical synthesis procedure, 50 ml of  $2 \times 10^{-3}$  M silver nitrate ( $\text{AgNO}_3$ ) was heated at  $80^\circ\text{C}$  for 15 min. To this warm solution, 50 ml of  $2 \times 10^{-2}$  M tri-sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) was added and the resulting mixture was refluxed at  $80^\circ\text{C}$  for 30 min. After about 15 min, initially clear solution of silver nitrate turned pale yellow and finally to golden yellow colour indicating the formation of silver nanoparticles. TEM analysis revealed that the silver nanoparticles

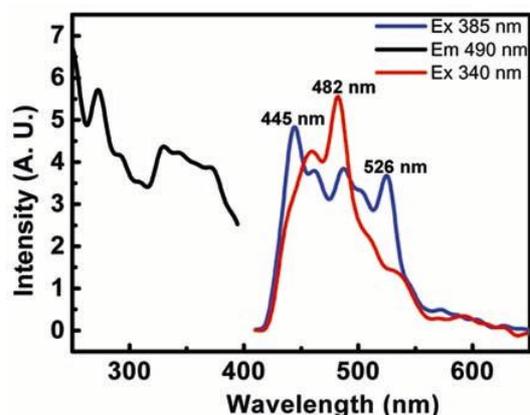


Figure 1. Luminescence spectra of Ag nanoparticles.

synthesized by this procedure had a size of  $\sim 10$  nm. These particles were stabilized by the formation of electric double layer of adsorbed citrate and/or nitrate ions and their corresponding cations around them, hence they were very sensitive to charge transfer interactions.

Rhodamine (RHO6G) dye ( $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$ ) was dispersed uniformly in ethanol and to this solution measured amount of aqueous dispersion of silver nanoparticles was added viz. 1 ml, 0.5 ml, 0.25 ml, 0.2 ml, 0.1 ml and 0.001 ml. Photoluminescence spectra (PL) were recorded using Perkin Elmer LS 55 spectrophotometer and UV-Vis absorption spectra were recorded using Ocean Optics (model DT 1000 CE 376) spectrophotometer.

## 3. Results and discussion

First report on luminescence from metals has been given by Mooradian (1969). The band structure of metal has been represented by a simplified model which includes an  $s-p$  conduction band and two sets of occupied  $d$  bands. The excitation involves a transition from states in the upper  $d$  bands to unoccupied levels in the  $s-p$  band at and above the Fermi energy. The emission arises from direct recombination of conduction band electron below the Fermi energy with holes in the  $d$ -band. Emission and excitation spectra for silver nanoparticles are shown in figure 1. Excitation of silver nanoparticles with 385 nm results in broad emission band consisting of several peaks between 445 and 550 nm. Excitation of the same sample with photons of high energy (340 nm) results in narrowing of the spectra with a sharp peak at 482 nm.

Interaction of rhodamine dye molecule with silver nanoparticles is schematically shown in figure 2. This molecule has two amine (NH) groups with which it can bind to silver nanoparticles. Among these two amino groups, one group is more electropositive and can bind to silver nanoparticles preferentially to form dye silver nanoparticles complex. Due to affinity of dye molecule with silver nanoparticles, electron transfer mechanism becomes easier as can be noticed from luminescence measurements.

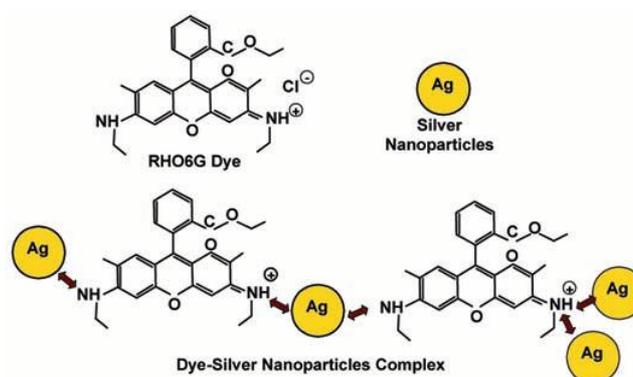
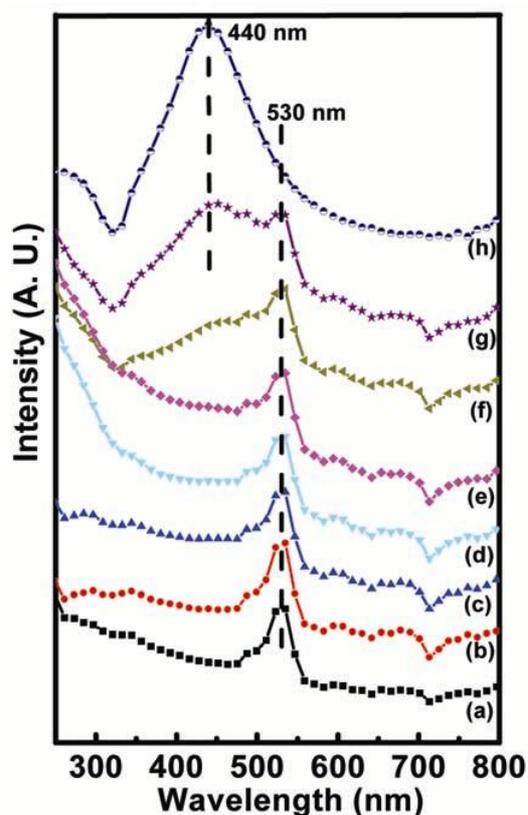


Figure 2. A schematic representation of the formation of dye-Ag nanoparticles complex.

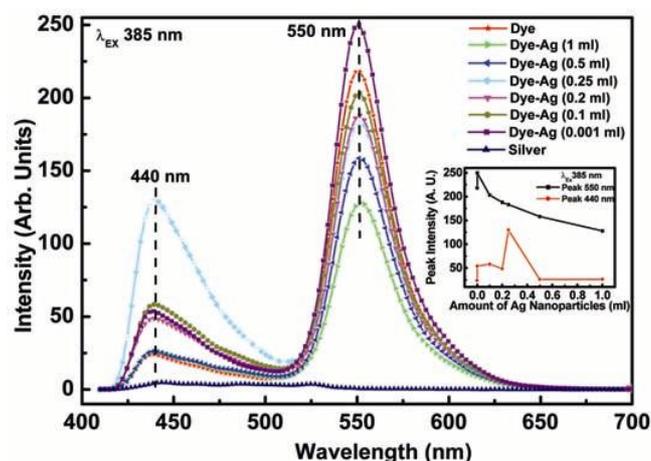
UV-Vis absorption spectra from dye and dye molecules with silver nanoparticles are shown in figure 3. Citrate stabilized silver nanoparticles show an intense absorption peak also known as surface plasmon resonance peak at 440 nm (as shown in figure 3), presence of which is explained as the resonance between the collective oscillations of conduction electrons with incident electromagnetic field (Mulvaney 1996). Dye molecules show an intense peak at around 530 nm, position and intensity of the same remain unchanged at addition of lower concentration of silver nanoparticles. For higher concentration of silver nanoparticles viz. 0.5 ml and 1 ml, presence of broad hump at 440 nm along with a peak at 530 nm could be noticed. The absorption spectra of dye molecules with higher concentration of silver nanoparticles (0.5 ml and 1 ml) are found to be the sum of the spectra recorded for dye and silver nanoparticles separately. Similar results could be noticed by Franzen *et al* (2002) while studying the optical properties of various dye molecules (such as crystal violet, methyl green, indocynine green, rhodamine B etc) adsorbed on citrate stabilized gold nanoparticles.

Figure 4 shows luminescence spectra from dye and dye molecules with variable concentration of silver nanopar-



**Figure 3.** UV-Vis absorption spectra of (a) bare dye, (b) dye-Ag (0.001 ml), (c) dye-Ag (0.1 ml), (d) dye-Ag (0.2 ml), (e) dye-Ag (0.25 ml), (f) dye-Ag (0.5 ml), (g) dye-Ag (1 ml) and (h) bare Ag.

ticles in the solution at excitation wavelength, 385 nm. The emission spectra consist of two distinct peaks at 550 nm and 440 nm. Peak at 440 nm shows an enhancement in intensity at all the concentrations with the maximum intensity for dye with 0.25 ml silver nanoparticles. It was found that on addition of 0.25 ml silver nanoparticles in RHO6G dye, can enhance the luminescence intensity by 82%. For peak at 550 nm enhancement in intensity for only one concentration viz. 0.001 ml and quenching of peak intensity for all other concentrations was observed. This peak at 550 nm shows 13% enhanced intensity for dye with 0.001 ml silver nanoparticles, whereas 41% quenching of luminescence intensity for 1 ml silver nanoparticles was observed. A graph of peak intensity as a function of amount of silver nanoparticles is plotted in inset of figure 4. The graph for peak at 550 nm shows a gradual reduction in intensity as the amount of added silver particles increases whereas for 440 nm peak intensity it was found to be maximum for 0.25 ml silver nanoparticles. Earlier, enhancement of luminescence was observed by Zhang *et al* (2004) for fluorophores in the vicinity of silver nanoparticles due to aggregation. At the same time enhancement and quenching of luminescence has been explained in terms of electron transfer from fluorophore to the silver nanoparticles (Lakowicz *et al* 2004). Luminescence behaviour of fluorophores also gets affected by SPR, arising from metal nanoparticles. The plasmon resonance of the metal nanoparticles represents the existence of a localized electromagnetic field near the metal nanoparticle. In case of spherical nanoparticles of size between 10 and 200 nm, 100–10,000 times enhancement of the electric field is observed near the particle surface (Haes *et al* 2005). When a fluorophore is placed in the close vicinity of metal nanoparticle, increase in excitation and emission rate is observed due to the pre-



**Figure 4.** Emission spectra from dye and dye molecules with variable concentration of silver nanoparticles at 385 nm excitation wavelength. (Inset: a plot of peak intensity as a function of amount of silver nanoparticles added).

sence of this localized electromagnetic field as can be seen from the emission spectra. Similar trend in emission spectra from dye and dye molecules with variable concentration of silver nanoparticles at 340 nm excitation wavelength is observed.

Luminescence properties of dye molecule can be tuned by adding small quantities of colloidal silver nanoparticles. Coupling of dye molecules with silver nanoparticles can lead to many interesting optical and electronic properties and exploited in a variety of applications such as biological sensing, light emitting diodes etc.

### Acknowledgements

Authors would like to thank DST India, CSIR India and UGC India, for constant support.

### References

- Drexhage K H 1970 *J. Lumin.* **12** 693  
 Ethiraj A, Hebalkar N, Kharrazi S, Urban J, Sainkar S R and Kulkarni S K 2005 *J. Lumin.* **114** 15  
 Franzen S, Folmer J C W, Glomm W R and O'Neal R 2002 *J. Phys. Chem.* **A106** 6533  
 Geddes C D, Cao H, Gryczynski I, Gryczynski Z, Fang J and Lakowicz J R 2003 *J. Phys. Chem.* **A107** 3443  
 George N A, Aneeshkumar B, Radhakrishnan P and Vallabhan C P G 1999 *J. Phys. D: Appl. Phys.* **32** 1745  
 Haes A J, Haynes C L, McFarland A D, Schatz G C, Van Duyne R P and Zou S 2005 *MRS Bull.* **30** 368  
 Imhof A, Megens M, Engelberts J J, De Lang D T N, Sprik R and Vos W L 1999 *J. Phys. Chem.* **B103** 1408  
 Ishikawa K and Okubo T 2003 *Appl. Phys. Lett.* **83** 2536  
 Ishikawa K and Okubo T 2005 *J. Appl. Phys.* **98** 043502  
 Lakowicz J R 2001 *Anal. Biochem.* **298** 1  
 Lakowicz J R, Geddes C D, Gryczynski I, Malicka J, Gryczynski Z, Aslan K, Lukomska J, Matveeva E, Zhang J, Badugu R and Huang J 2004 *J. Fluorescence* **14** 425  
 Mooradian A 1969 *Phys. Rev. Lett.* **22** 185  
 Mulvaney P 1996 *Langmuir* **12** 788  
 Ritchie G and Burstein E 1981 *Phys. Rev.* **B24** 4843  
 Wang D -S and Kerker M 1982 *Phys. Rev.* **B25** 2433  
 Zhang J and Lacowicz J R 2005 *J. Phys. Chem.* **B109** 8701  
 Zhang J and Lacowicz J R 2006 *J. Phys. Chem.* **B110** 2387  
 Zhang J, Malicka J, Gryczynski I and Lakowicz J R 2004 *Anal. Biochem.* **330** 81