

Photoluminescence Behaviour of Sm³⁺ Ions in presence of Ag Nanoparticles in Methanol

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Abstract. In the present work, capped Ag NPs prepared by reduction of Ag (NO₃)₃ by Dimethyl Formamide is doped with Sm³⁺ in methanol and its photoluminescence behavior is studied. Significant modifications of the Sm³⁺ ions' emission as well as quantum yield, were observed with the concentration of Ag NPs. Local field enhancement induced by neutral Ag NPs were found to be responsible for enhancement in efficiency of the Sm³⁺ ions.

1. Introduction

Photoluminescence (PL) of rare earth (RE) ions is one of the principal technologies that support laser amplification, optical communication, sensing, display systems etc. However, the small absorption cross section of RE ions has spawned numerous attempts to enhance the PL efficiency of these ions [1]. Coupling of RE ions with metal nanoparticles (NPs) have been emerged as a novel technique to enhance the PL intensity of RE ions [2].

Metal NPs possess fascinating optical and electronic etc. properties compared to their bulk counterparts. Electromagnetic excitations induce noble metal NPs to exhibit the Surface Plasmon Resonance (SPR), which is the collective oscillation of the free conduction band electrons in the visible region. SPR generates enhanced localized electric field around the metal NPs. RE ions, when present within the close proximity of such NPs, experience a drastic increase in their excitation rates by the induced electric field and thereby their spectroscopic properties get modified [3]. The shape, size, number density of metal NPs and the coupling distance between the NP and RE ion also have a crucial role on the PL enhancement from the RE ions [4].

In the present work, the effect of Silver (Ag) NPs on the PL behavior of Samarium (Sm) ions in methanol has been investigated.

2. Experimental

Stock solutions of Silver Nitrate (AgNO₃) (Acros Organics, 99.85%) and Polyvinylpyrrolidone (PVP) (SRL, research grade) were first prepared separately by dissolving AgNO₃ in Dimethyl Formamide (DMF) (Acros Organics, 99%) and PVP in distilled water respectively at room temperature. Both the solutions were then mixed and kept for four hours. Samarium Nitrate hexahydrate (Aldrich, 99.99%) was mixed with the solution containing the other precursors methanol, distilled water and nitric acid in



the volumetric ratio of 2: 3: 0.4. This solution was mixed with the stock solution of AgNO₃ and magnetically stirred for 30 minutes. Altogether four sets of samples were prepared for fixed concentration of Samarium Nitrate hexahydrate and varied concentrations of AgNO₃. Composition of the samples used for the study is shown in Table 1.

Table 1. Composition of the prepared samples.

Sample Name	SmNO ₃ .6H ₂ O (wt%)	AgNO ₃ (wt%)
S	2.24	-
SA1	2.24	0.003
SA2	2.24	0.03
SA3	2.24	0.3

The UV-Vis-NIR absorption spectra of the prepared samples were recorded by using Scinco PD Array (S-3100) UV-Vis spectrophotometer in the wavelength range of 200-1100nm. PL and PL excitation spectra were recorded by Fluoromax 4P spectrofluorometer equipped with 150W CW xenon lamp as excitation source and photomultiplier tube detector. The samples were excited at 402nm keeping the excitation and emission slits both at 3nm. All the measurements were done at room temperature.

3. Results and discussions

Fig.1 shows the UV-Vis-NIR absorption spectra for AgNO₃ doped with Sm ions in methanol. Absorption spectrum for AgNO₃ singly doped sample (with different scale) is also incorporated in the figure for comparison. To show the resolved Sm³⁺ peaks, the enlarged view of the absorption spectra for samples S, SA1 and SA2 in 350-550 nm range are shown in Fig. 2.

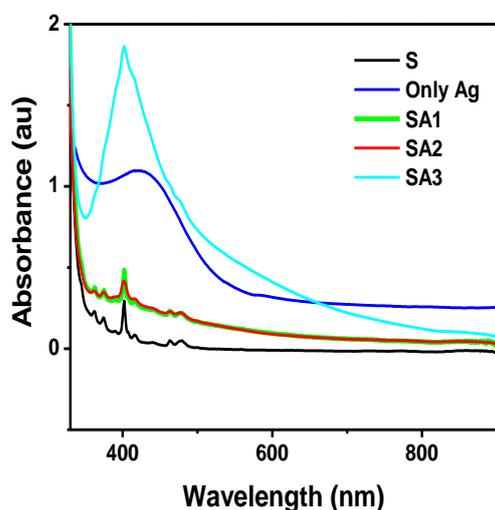


Figure 1. Absorption spectra for samples S, SA1, SA2, SA3 and singly doped AgNO₃.

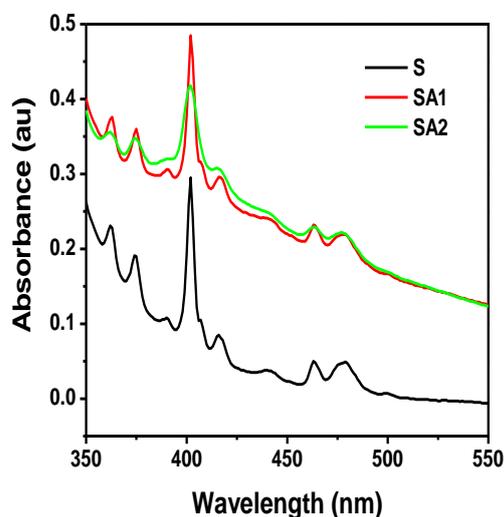


Figure 2. Enlarged absorption spectra for samples S, SA1 & SA2.

The spectra for S, SA1 and SA2 show seven absorption peaks located around 362, 374, 388, 402, 416, 463 and 479nm respectively arising due to the f-f transitions from the ground state ⁶H_{5/2} of Sm³⁺ [5]. It is observed that the absorption intensity as well as FWHM for Sm³⁺ peaks first increases with the addition of AgNO₃. The enhancement was observed till the AgNO₃ concentration of 0.03 wt%. With

further increase in the concentration of AgNO₃ to 0.3 wt% (SA3), the SPR band of Ag at 416 nm broadened, became asymmetric and the tail extended upto 800nm [6].

Fig. 3 illustrates the PL spectra of the samples under the excitation wavelength of 402 nm. The spectra show two intense PL bands around 596nm and 642nm in the visible region together with a weak band at 560nm and are assigned as ⁴G_{5/2}→⁶H_{5/2} (green), ⁴G_{5/2}→⁶H_{7/2} (orange), ⁴G_{5/2}→⁶H_{9/2} (red) transitions respectively [5].

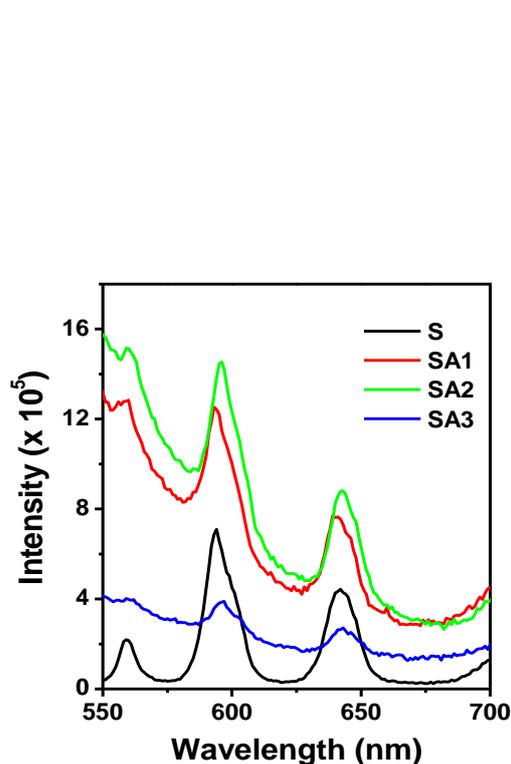


Figure 3: PL spectra for samples S, SA1, SA2 & SA3 under 402nm excitation.

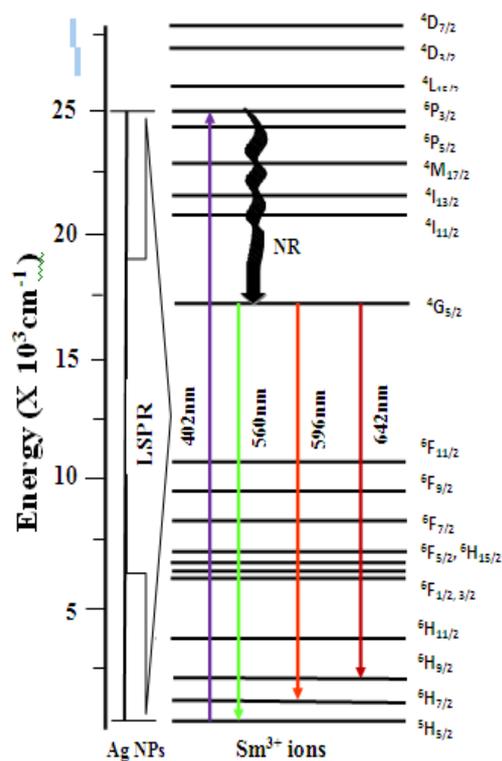


Figure 4. Schematic energy level diagram of Sm³⁺: Ag NPs under 402nm excitation.

It is seen from Fig. 3 that the PL intensity first increases with the increase in concentration of AgNO₃ (till 0.03 wt%). Further increase in concentration to 0.3 wt% results decrease in the emission intensity. The PL enhancement of the Sm³⁺ ions in the presence of Ag NPs may be attributed to the Local field enhancement (LFE) around the Ag NPs induced by the SPR. Consequently, the electric field around the RE ions, lying within the proximity of metal NPs enhances. This in turn increases the rate of excitation of the RE ions and hence the PL intensity of Sm³⁺ ions is enhanced. Moreover, with the increase in concentration of AgNO₃, the electric fields of the NPs overlap and produce hot spot regions that lead to stronger surface enhanced fluorescence. However, beyond certain concentrations of Ag NPs (0.3 wt% for present case), an undesired back transfer of energy from Sm³⁺ to the nanoparticles might occur causing the decrease in emission intensities. Also, since a fraction of Ag NPs may still remain as Ag⁺ ions, dimers and multimers in the system, energy absorbed by Sm³⁺ may get transferred to the Ag⁺ ions resulting in the quenching of PL [7].

Fig. 4 shows the schematic energy level diagram for Sm³⁺ ions in the vicinity of Ag NPs. Under 402nm excitations, the 4f electrons of Sm³⁺ ions at the ground state are excited to the ⁶P_{3/2} state by single step ground state absorption (GSA). The electrons then decay non-radiatively and populate the

lower $^4G_{5/2}$ level. Radiative transitions from $^4G_{5/2}$ level to $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ produce respectively the observed green emissions at 560nm, orange emission at 596nm and red emission at 642 nm.

Table 2. Comparison of PL intensities, quantum yields and FWHMs for Sample S, SA1, A2 & SA3.

	PL Intensity			
	S	SA1	SA2	SA3
560	1.19×10^5	1.28×10^6	1.51×10^6	3.98×10^5
596	7.1×10^5	1.25×10^6	1.45×10^6	3.89×10^5
642	1.77×10^5	7.65×10^6	8.81×10^5	2.71×10^5
Relative Yield				
560	2.04×10^6	1.08×10^7	1.44×10^7	4.26×10^6
596	1.04×10^7	2.1×10^7	2.52×10^7	6.07×10^6
642	7.12×10^6	1.38×10^7	1.5×10^7	4.8×10^6
FWHM (nm)				
560	8	9	10	11
596	14	21	22	19
642	14	23	22	22

4. Conclusions

In the present work, absorption and PL behavior of Sm^{3+} ions in presence of Ag NPs in methanol medium were studied. An enhancement of the PL intensities by two times and yields by 2.4 times with the addition of 0.03 wt% of $AgNO_3$ were observed which shows a decrement when the concentration was further enhanced to 0.3 wt%. The study reveals that localized SPR is responsible for the enhancement of the absorption and PL efficiencies of the Sm^{3+} ions whereas the decrement in efficiency is attributed to the back energy transfer from Sm^{3+} ions to the Ag NPs in the studied medium.

References

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