We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists



186,000

200M



Our authors are among the

TOP 1% most cited scientists





WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com



Chapter

Green Synthesis of Metal Nanostructures and Its Nonlinear Optical Properties

Emusani Ramya

Abstract

Simple green synthesis of metal nanoparticles (Ag NPs) was prepared by using Raphanussativus leaf extract. This extract acts as reduce and stabilizing agent. The formation of silver NPs was confirmed and characterized by XRD, UV–visible absorption spectrum, TEM, and FTIR. The luminescence enhancement and quenching of Eu³⁺ and Sm³⁺ ions were observed in the presence of silver NPs. The luminescence enhancement is owing to arise in the electric-dipole transition with alteration of the field around Ln³⁺ ions. Nonlinear studies in femtosecond (fs) and picosecond (ps) time scales have been studied by using the Z-scan technique. Thirdorder nonlinear optical susceptibility of silver nanoparticles was obtained with Degenerate Four-Wave Mixing (DFWM) in the fs regime. The lifetimes of lanthanum complexes were increased by the concentration of silver NPs and decreased for further silver. The high enhanced luminescence and nonlinear studies of green synthesized silver nanoparticles can be used in optics and bio applications.

Keywords: Metal Nanostructures, Green synthesis, Luminescence enhancement, Nonlinear optical properties

1. Introduction

Nanoparticles are the building blocks for many materials and contribute to the rapid growth of nanoscience [1]. There has been wide interest in silver nanoparticles (Ag NPs) due to their unique properties arising from shape, size and composition finding their applications in sensing devices, bio-labelling, catalyst, electronics, photonics, surface-enhanced Raman spectroscopy (SERS) and biomedicine, etc. [2–7]. For the applications of environmental friendly NPs in various fields, development of easy preparation methods using nontoxic and nonhazardous materials and methods is needed. Biosynthesis route has many advantages compared to other synthesis methods, as these routes do not use high temperature, pressure, energy and toxic elements. Recently, several groups reported on the synthesis of biocompatible Ag NPs using natural sources like fungi, yeast, bacteria [8–12] and plant extracts [13–16]. The properties of biosynthesized metal or bimetallic.

NPs are different from those synthesized from chemical methods and laser ablation methods [17, 18] because they are highly stable, nontoxic and biocompatible as the surfaces of the NPs are coated with biogenic surfactants. Biosynthesized metal NPs have biomedical applications like antimicrobial coatings (e.g. antibacterial, antifungal, antiviral activity, antiparasite) [19–22], drug deliveries [23], medical imaging [24], anticancer NPs [25], medical diagnostics, sensors [26], catalytic degradation of organic pollutants to enhance membrane treatment processes [27] and also as optical limiters [28, 29] in the field of optics.

The *Raphanussativus* leaves belong to the Brassicaceae family, call it Radish and it is root vegetable. Derivatives and various components of *Raphanussativus* consist of 2- Hexen -1- al (leaf aldehyde) 3- hexane -1- ol (leaf alcohol) and n- isobutyr-aldehyde and isovaleraldehyde, sapogenin, methin, levon, phosphatase, histamines and spasmolytic components, lysine, polyphenolic, Sulphoraphene, vanillic acids and raphanin, those are having various medicine utilities. These bio-molecules consist in the extract are binding on the surface of nanoparticles and reduce the ions to NPs, additionally keeping stabilize the nanoparticles.

Lanthanide (Ln³⁺) complexes are of great interest due to their large Stoke shifts, long emission lifetimes, and narrow emission bandwidths. Metal-enhanced luminescence of rare-earth ions is of great interest because of their applications in laser materials, nano-photonics, LEDs, and biosensors [30]. Few groups investigated that enhancement or quenching of luminescence is depending on the concentration, shape, and size of metal nanoparticles based on the interaction of metal nanoparticles and luminescence centres [31, 32]. In the presence of metallic nanostructures, the field around the rare-earth ions can alter the emission and excitation [33, 34]. The literature reported that luminescence enhancement is because of energy transfer between Ln³⁺ complexes and metal NPs [35]. Quantum yields and lifetimes are influenced by changing the decay rate of radiative and nonradiative transitions [36]. Nevertheless, the process elaborated in Ln³⁺ ion luminescence with Ag NPS is not clear and hence, essential to address which is a promising and fascinating challenge.

Here, we have synthesized silver nanoparticles by using *Raphanussativus* leaf extract. The aim of the work is to discuss the origin of the effect of Ag NPs on enhancing and quenching the luminescence intensity of Ln³⁺ complexes and their nonlinear optical properties.

2. Experimental details

2.1 Materials and methods

AgNO₃ (Silver nitrate, 99.99%) was procured from Sigma Aldrich. *Raphanussativus* leaves were got from the market. Lanthanum complexes Eu (TTFA)₃ and Sm(TTFA)₃ were obtained from Soltech BioScience and Rare Earth products Inc., USA.

2.2 Preparation of Raphanussativus leaf extract

First Raphanussativus leaves were wiped using distilled water. 10 grams of *Raphanussativus* leaves have taken into 100 ml of distilled water and heated for 5 minutes and grinded in a pestle. The mixture solution was filtered with Whatman no. 1 filter twice to get rid of granules and refrigerated at 4°C.

2.3 Synthesis of Ag NPs using Raphanussativus leaf extract

1.5 ml of freshly prepared leaf extract was poured into 30 ml of silver nitrate (1 mM) aqueous solution with stirring at room temperature. Then, the solution changed from transparent to ash color in 5 minutes, which represents the formation



2.4 Sample preparation for luminescence studies

Rareearth ions europium and samarium of weight ratio of 0.28% were dissolved. Various concentrations of silver nanoparticles (0.16, 0.33, 1, 1.6, 2.32, 3.32 and 6.64 μ M) were added to 0.10, 0.13, 0.20 μ M of europium and 1.32, 1.45, 1.58 μ M of samarium for luminescence studies.

3. Characterization techniques

The green synthesized silver nanoparticles and Lanthanide complexes with silver nanoparticles were characterized using XRD, TEM, FT-IR, UV-visible absorption, luminescence studies, Z-scan, degenerate four-wave mixing (DFWM), and decay measurements techniques. XRD pattern of silver nanoparticles was measured on Cu-K_{α} X-ray radiation with λ = 1.5406 Å over the range of 2 θ = 5–50° at 1° min⁻¹. A transmission electron microscope (TEM) on FEI TECHNAI G² S-Twin was used to measure the diameter and morphology of nanoparticles. FT-IR spectrum was performed using Thermo-Nicolet 6700 spectrophotometer with a 500–4000 cm⁻¹ range. UV–Vis spectra were carried out by JASCO-V670 UV/VIS/ NIR spectrometer with 1 nm resolution and 200-800 nm range. Luminescence emission spectra of Ln³⁺ complexes with silver nanoparticles were performed on HORIBA JOBIN YVON spectrophotometer with 262 nm and 350 nm excitations. Nonlinear absorption and optical limiting studies were performed using the Z-scan with laser source of Nd: YAG laser at 532 nm, 30 ps and 10 Hz repetition rate; and 1 kHz, 110 fs pulses of Ti: sapphire at wavelength 800 nm. Degenerate four-wave mixing (DFWM) measurements were studied with Ti: sapphire laser in box-car geometry. Luminescence decay studies were performed on FLS980 with an excitation source as a Xenon lamp.

4. Results and discussions

4.1 X-ray diffraction (XRD)

XRD spectrum of Ag NPs confirms the crystalline nature in **Figure 2**. Diffraction patterns of silver nanoparticles at 38.1°, 43.9°, 64.6° and 77.3° and corresponding the planes (111), (200), (220) and (311) are compared with standard spectrum [37]. Which showed the silver nanoparticles are having FCC formation. The diffraction reflection at (111) is sharp and high intensity as compared to the planes at (200),



Figure 2. *X-ray diffraction spectrum of silver nanoparticles.*

(220), and (311). It demonstrates that silver nanocrystals were oriented along the (111) plane. The unassigned reflections at marked with #, 27.7° and 32.2° were related to the biological phase appearing on the silver nanoparticles' surface. Therefore, these results indicate that the silver nanoparticles were formed. Both the TEM results and XRD results are in good agreement.

4.2 Transmission electron microscope (TEM)

The morphology, size distribution, and selected area electron diffraction (SAED) circular patterns of silver nanoparticles were exhibited in **Figure 2**. From **Figure 3(a–c)**, the Ag NPs are nanospheres in shape, crystalline, and size is about 7 nm respectively. The planes (111), (200), (220), and (311) from the SAED pattern were exhibiting FCC structure from **Figure 3(d)**.

4.3 UV-Vis absorption spectroscopy

UV–Vis linear absorption of silver nanoparticles with 240–800 nm range areas displayed in **Figure 4**. The absorption spectra were measured at various concentrations of silver nanoparticles added to 3 ml of distilled water and silver nanoparticles with Eu and Sm complexes at various concentrations.

UV–visible absorption spectrum of various concentrations are (0.16, 0.33, 1.0, 1.60, 2.32, 3.32, 6.64 and 9.96 μ M) of silver nanoparticles as depicted in **Figure 3(a)**. The band at 262 nm is becoming strong as increase the concentration because the number of organic compounds absorption is increasing, which helps to reduce the silver ions. The plasmonic band of silver nanoparticles at 460 nm is increasing with an increase in the concentration from 0.16 μ M to 9.96 μ M. The inset shows the absorption of silver NPs is increasing linearly at 460 nm i.e. the nanoparticles are not agglomerating with concentration.

The absorption spectrum of europium complex with various concentrations (0.13, 0.20, 0.26, 0.33, 0.99, 1.98 and 3.3 μ M) as displayed in **Figure 4(b)**. The linear absorption peaks at 262 nm and 342 nm corresponding to $\pi \rightarrow \pi^*$ transition



Figure 3.

(a) TEM figures (b) high-resolution TEM (HRTEM) image (c) particle size distribution and (d) SAED circular patterns of silver nanoparticles.

due to complex absorbance and $n \rightarrow \pi^*$ transition of europium and occurrence of the shoulder at (1.99 and 3.3 μ M) higher concentrations due to strong interaction among the europium molecules [38].

The absorption spectrum of europium complex $(0.13 \ \mu\text{M})$ with various concentrations $(0.16, 0.33, 1.0, 1.60, 2.32, 3.32, \text{ and } 6.64 \ \mu\text{M})$ of silver nanoparticles (Ag NPs) and the absorption bands appeared at 262 nm, 342 nm, and 460 nm as seen in **Figure 4(c)**. The absorption band in the range of 300–400 nm is shifted to red slightly because the interaction of silver nanoparticles and europium molecules i.e. the Plasmon field of silver nanoparticles is influencing the europium ions but the surface plasmonic peak of Ag NPs at 460 nm is not altering. The inset shows a linear increase in absorption with silver NPs, suggesting that nanoparticles are not agglomerating in the complex solution.

Absorption spectrum of samarium complex (1.45 μ M) with various concentrations (0.16, 0.33, 1.0, 1.60, 2.32 and 3.32 μ M) of silver nanoparticles as depicted in **Figure 5**. The absorption band at 265 nm corresponds to the $\pi \rightarrow \pi^*$ transition of the samarium complex and biological components in the extract, and bands at 342 nm and 460 nm correspond to the $n \rightarrow \pi^*$ transition of samarium and plasmonic peak (SPR) of silver nanoparticles. Samarium complex concentration (1.45 μ M) is more as compared with silver nanoparticles so the bands of samarium (265 nm and 342 nm) are predominating the SPR.

4.4 Fourier transform infrared (FTIR) technique

FT-IR spectrum displays the *Raphanussativus* leaf extract used for biosynthesis of Ag NPs in **Figure 6**. The Silver suspension was loaded on a potassium bromide (KBr) pellet and dried. The FT-IR peaks of silver nanoparticles appeared at



Figure 4.

UV–visible spectra of (a) silver nanoparticles with various concentrations: a) 0.16, b) 0.33, c) 1.0, d) 1.60, e) 2.32, f) 3.32, g) 6.64 and h) 9.96 μ M. Inset displays the linear absorption of silver nanoparticles at 460 nm with increasing silver. (b) Various concentrations of europium ions in ethanol are: i) 0.13, ii) 0.20, iii) 0.26, iv) 0.33, v) 0.99, vi) 1.98 and vii) 3.3 μ M. (c) Various concentrations of Ag NPs with 0.13 μ M europium solution: A') 0.16, b') 0.33, c') 1.0, d') 1.60, e') 2.32, f') 3.32 and g') 6.64 μ M. Inset figure exhibits the absorption of silver nanoparticles at different concentrations in (0.13 μ M) europium solution at 460 nm.

3315 cm⁻¹ indicate hydroxyl –OH stretching; 2929 cm⁻¹ and 2834 cm⁻¹ assigned to stretching C-H modes of methyl groups; 1636 cm⁻¹ assigned to carbonyl (–C=C) stretching; 1382 cm⁻¹ attributed to –C-O stretching mode of water-soluble organic components like polyphenols, alkaloids, and flavonoids in *Raphanussativus* extract; 1040 cm⁻¹ indicate the C-O alcoholic stretching group. These results concluded that the organic compounds of the extract are responsible for making nanoparticles [39–42].

4.5 Photoluminescence studies

The excitation spectra of europium complex ($\lambda_{em} = 614 \text{ nm}$) at various concentrations (0.03, 0.07, 0.13, 0.20, 0.26, 0.66, 1.99 and 3.3 µM) as shown in **Figure 7**. The bands in the range 250–400 nm are due to $\pi \rightarrow \pi^*$ transitions of Eu. At very low concentrations of europium (0.03 µM and 0.07 µM), the broadband appears at 340 nm. As increase the concentration (0.13–0.66 µM), the new band appeared at 270 nm and 340 nm band splits into two bands which results, strong interactions among the europium complex in the solution phase and depend on the



Figure 5.

Linear absorption spectrum of samarium complex (1.45 μ M) with various concentrations are a) 0.166 b) 0.33 c) 1.0 d) 1.60 e) 2.32 f) 3.32 and g) 9.96 μ M of Ag NPs.



Figure 6. FT-IR Spectrum of Raphanussativus leaf extract used for biosynthesized silver nanoparticles.

concentration of europium. As increase the concentration further (1.99 μ M and 3.3 μ M), 270 nm and 340 nm bands shifted to the blue region, and the 270 nm band has vanished. Even for further concentrations, the 370 nm band shifted to the red region, which indicates that the interaction among europium ions enhanced.

The emission spectra of the europium complex excited with 262 nm as shown in **Figure 8**. The band at 614 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) is a hypersensitive electric-dipole



Figure 7. Excitation spectra of europium complex ($\lambda_{em} = 614 \text{ nm}$) at various concentrations (0.03, 0.07, 0.13, 0.20, 0.26, 0.66, 1.99 and 3.3 μ M).



Figure 8.

Emission spectra of europium complex (λ_{exc} = 262 nm). The inset figure displays the ${}^{5}D_{o} \rightarrow {}^{7}F_{2}$ transition on various silver nanoparticle in europium complex (0.13 μ M).

transition, a dominant peak. The magnetic dipole transitions are at 577 nm and 590 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$). Inset displays the figure of concentration of silver nanoparticles with the intensity of electric dipole transition (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) in

europium complex. As increase, the concentration of silver nanoparticles, affect the ligand field surrounding the europium ions, consequently enhance the electric dipole transition rate. The ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition enhanced its intensity 25 times up to the 6.64 μ M of silver nanoparticle and quenching slowly exceeding 6.64 μ M in 0.13 μ M europium solution. Hence, we emphasize the effect of silver on the europium luminescence emission intensity of electric dipole transition (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$).

The emission spectra of europium (λ_{exc} = 350 nm) with various (0.16, 0.33, 1.0, 1.60, 2.32, 3.32 and 6.64 μ M) of silver nanoparticles as seen in **Figure 9**. The luminescence emission intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition starts enhanced and maximum at 1.6 µM of silver NPs and gets quenched for further increase the silver in europium (0.13 μ M) and the enhancement factor is ~5. In the spectra of excitation, Ag NPS cannot intensify the europium ions excitation at 262 nm and 350 nm, nanoparticles absorption (400–550 nm) is uncertain at excitation wavelengths, although it enormously affects the luminescence centers of europium ions in the emission. At excitation wavelength around absorption of silver (350 nm), the intensity of the electric field increased certain times induce an intensification in luminescence intensity by a few hundred times. The enhancement of luminescence intensity because of the overlap of europium emission and the scattering of nanoparticles which bank on the gap of NPS [33, 43, 44]. The distance of NPS reduces, the scattering at 612 nm overlay on the emission enlarges appearing in the increment of luminescence intensity. Similarly, the intensity decreases with the distance of nanoparticles increases. The luminescence increment was observed only at 0.13 µM concentration of europium and at other concentrations of 0.10, and 0.20 µM, the luminescence is quenching. That means, the enhancement of luminescence intensity purely depends on the concentration, distance, size, and shape of nanoparticles.



Figure 9.

Emission spectra of europium with various silver nanoparticles: a) 0.16, b) 0.33, c) 1.0, d) 1.60, e) 2.32, f) 3.32 and g) 6.64 μ M excited with 350 nm. Inset figure shows dependence of luminesce intensity with silver concentration. Eu concentrations are (a) 0.1 (b) 0.13 and (c) 0.2 μ M.

At 260 nm excitation, the enhancement factor is high as compared with 350 nm excitation, which is caused by the biological components in extract and ligand enhance the luminescence effectively and the overlap of emission europium and scattering of silver, luminescence efficiency will be high.

To understand the luminescence enhancement alteration on various lanthanides, we also obtained the emission of the samarium complex. The emission spectra of samarium with different concentrations of silver nanoparticles (0.16, 0.33, 1.0, 1.60, 2.32, 3.32, and 6.64 μ M) at 350 nm excitation as can be seen in **Figure 10**. The inset picture exhibits the luminescence emission versus silver concentration with varying samarium concentrations (1.32, 1.45, and 1.58 μ M). The luminescence intensity is noticed at 1.45 μ M of samarium. The transitions at 645 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$) electric dipole, 566 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$), and 602 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$) are magnetic dipole transitions. The enhancement factor of electric dipole transition is 7.4 at 2.32 μ M of silver. For more increases in silver, the enhancement factor decreases [45, 46]. The enhancement factors for magnetic dipole transitions at 566 nm are 1.9 and 602 nm is 5.2. The scattering can alter by altering the distance of nanoparticles. Hence, the change in luminescence intensity overlay on the scattering and emission spectra as in the case of europium. So this is the reason for emission intensity quenched at 1.32 μ M and 1.58 μ M of samarium as depicted in the inset.

4.6 Nonlinear optical properties

Nonlinear absorption coefficients were obtained by using the Z-Scan technique with Nd: YAG laser, repetition rate 10 Hz, 30 ps pulses with 532 nm, and Ti: Sapphire laser, 1 kHz, 110 fs pulses with 800 nm. The nonlinear absorption studies of the biosynthesized silver nanoparticles solution were studied using an open aperture Z-scan set up (**Figure 11**) [29, 47]. In the Z-scan setup, the Gaussian



Figure 10.

Emission spectra of samarium 1.45 μ M with silver nanoparticles: a) 0.16, b) 0.33, c) 1.0, d) 1.60, e) 2.32, f) 3.32 and g) 6.64 μ M excited with 350 nm. Inset shows the dependence PL intensity on silver concentration at various samarium concentrations (a) 1.32 (b) 1.45 and (c) 1.58 μ M.



Figure 11. *Z-scan experimental set up a) open aperture b) closed aperture.*

profile of the laser beam is concentrated with the lens. The silver solution in a 1 mm thickness quartz cuvette is moving along the Z-direction through-beam-focused direction. A focus point, the silver sample undergoes maximal intensity and slowly reduce from the focal point in both directions and the f/40 configuration is operated here. The width of the sample undergoes less than the Rayleigh range (3 mm). For beam, shaping apertures are used, and to change the intensity of laser neutral density filters are used. The experimental data is measured by examining the sample along with the focus and saving the data by boxcar averager (model SRS 250) with an analog-to-digital (ADC) card to a computer. The absorption coefficient (α_2) for open aperture Z scan is measured by fitting the transmittance equation

$$T_{OA(2PA)} = 1 - \frac{\alpha_2 I_0 L_{eff}}{2^{3/2} (1 + z^2/z_0^2)}$$
(1)

Where, I_0 - intensity at focus on the sample, z - sample position, λ - laser wavelength, $z_0 = \pi \omega_0^2 / \lambda$ is Rayleigh range, ω_0 - beam waist at the focus (Z = 0), α_2 nonlinear absorption coefficient, and L_{eff} - effective path length is $L_{eff} = \frac{1-e^{-\alpha_0 L}}{\alpha_0}$, L sample length, α_0 is the linear absorption coefficient.

Figure 12(a) displays the Z-scan data of open aperture and varying input intensities of silver nanoparticles. The symbols are the experimental data, those are fitting theoretically (solid curves) using Eq. 1. These curves showed reverse saturable absorption (RSA) behavior in biosynthesized silver nanoparticles, which are ascribed to the excitations from the plasmonic band to the free carrier absorption band of silver nanoparticles and two-photon absorption (TPA) from the ground state. We determined α_2 is 10.2×10^{-9} cm²/W at various intensities 1.2 GW/cm²– 3.9 GW/cm². These coefficients are not altering much at input intensities.

Optical limiting experimental curves of silver nanoparticles as shown in **Figure 12(b)**. The threshold optical limiting value is 4 mJ/cm². Nonlinear scattering is not observed so optical limiting is due to two-photon absorption (TPA) and excited-state absorption (ESA) from SPR.

Similarly, **Figure 13(a)** illustrates the open aperture Z-scan data measured for silver nanoparticles with a wavelength of 800 nm at different input intensities from



(a) Z-scan of silver nanoparticles with various input intensities and (b) optical limiting curve with 532 nm.



Figure 13. *(a) Z*-scan of silver nanoparticles with various input intensities and (b) optical limiting curve with 800 nm.

 4.7×10^{11} – 7.7×10^{11} W/cm². Solid lines give the fits theoretically acquired by Eq. (2). RSA behavior of open aperture data gives the two-photon absorption (TPA). The two-photon absorption coefficients are $1.6 \times 10^{-9} - 3.8 \times 10^{-9}$ cm²/W measured from theoretical fitting. The optical limiting data of silver nanoparticles with femtosecond laser is shown in **Figure 13(b)**. The optical limiting threshold value is 1.2 mJ/cm². So bio-reduced silver nanoparticles displaying good optical limiting behavior in both regimes and silver nanoparticles can behave as broadband optical limiters [29, 48].

4.7 Degenerate four-wave mixing technique (DFWM)

By using Ti: Sapphire laser with 800 nm, the third-order nonlinear susceptibility was obtained. Carbon disulfide (CS₂) has taken reference to the same input powers to measure third-order nonlinear susceptibility $\chi^{(3)}$ of silver nanoparticles using Degenerate Four Wave Mixing set up (**Figure 14**). The temporal profile of biosynthesized silver nanoparticles is shown in **Figure 15**. The cubit fit of the DFWM signal provides the nature of the third-order susceptibility. The inset picture gives the slope of silver nanoparticles, it is approximately ~4. It shows that the DFWM signal has the contribution of two-photon absorption due to the electronic polarizability of the ground state alone. The $\chi^{(3)}$ was obtained as 2.95 X 10⁻¹⁴ esu for silver nanoparticles by the following equation



Figure 14. *Four wave mixing experimental set up.*



Figure 15.

Temporal response of DFWM signal of silver nanoparticles with 0.9 mg/l. inset picture gives the DFWM signal versus input intensity at zero delays. The solid line gives linear fit.

Nonlinear Optics - Nonlinear Nanophotonics and Novel Materials for Nonlinear Optics

$$\chi_{sample}^{(3)} = \left(\frac{n_{sample}}{n_{ref}}\right)^2 \left(\frac{I_{sample}}{I_{ref}}\right)^{1/2} \left(\frac{L_{ref}}{L_{sample}}\right) \alpha L_{sample} \left(\frac{e^{\frac{\alpha L_{sample}}{2}}}{1 - e^{-\alpha L_{sample}}}\right) \chi_{ref}^{(3)}$$
(2)

Where L - path length of the sample, n - refractive index, I - DFWM signal intensity, and α - absorption coefficient.

The second-order hyperpolarizability (γ) is measured by the equation.

$$\chi_{sample}^{(3)} = T^4 \left[N_{solvent} \gamma_{solvent} + N_{sample} \gamma_{sample} \right]$$
(3)
ocal field factor, $T = \frac{n^2 + 2}{2}$

T - local field factor, $T = \frac{n^2+2}{3}$. Where, n - refractive index, N- number density of the solvent and the sample, and γ is the second-order hyperpolarizability. The Number density N can be written as $N = N_0 C_s / 1000$

Where N_0 -Avogadro number and C_s -concentration of the solution

Second-order hyperpolarizability is obtained as 2.1×10^{-32} esu for silver nanoparticles. The nonlinear refractive index is measured from $\chi^{(3)}$ as 6.57 x $10^{-16} \text{ cm}^2/\text{W}$. For reproducibility, the experiment was repeated twicely [49].

4.8 Decay measurements

The decay curve of europium ions (${}^{5}D_{0}$ level) in various concentrations of silver nanoparticles was obtained with 350 nm excitation. The decay profile of 0.13 μ M of europium ions with silver nanoparticles (1.60 μ M) was measured by monitoring the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 612 nm as shown in **Figure 16(a)**. The decay curves are having single exponential behavior. Average decay time (τ) is obtained by below equation

$$\tau = \frac{\int tI(t)dt}{\int I(t)dt} \tag{4}$$

From the data, it is clear that the lifetime increase with the concentration of Ag NPs (1.60 μ M) then decreases rapidly for further increase the silver at a particular concentration of europium. The lifetime was increased from 275 μ s to 361 μ s, from 0 to 1.60 μ M concentration of Ag NPs, then decreased lifetime for further increase the nanoparticles. The alteration of a lifetime follows the same tendency as the emission



Figure 16.

Fluorescence decay rate of (a) europium and (b) samarium complexes monitoring at 612 nm and at 645 nm bands excited with 350 nm in 1.60 and 2.32 μ M of silver nanoparticles respectively.

intensity in the presence of Ag. As the increase in the asymmetric ratio $({}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1})$, the decay rate of radiative transition increases than the decay rate of non-radiative transition of europium [50]. This shows that the presence of nanoparticles reduces the loss of energy due to non-radiative decay [51].

Similarly, the decay profile of the ${}^{4}G_{5/2}$ level samarium (1.45 µM) ions in the presence of silver NPs (2.32 µM) excited at 350 nm and monitoring 645 nm emission band as shown in **Figure 16(b)**. The decay is also single exponential with silver. Average decay τ values for samarium increases from 16 µs to 31 µs for 0 to 2.32 µM of silver and then reduces with an additional increase of silver. This behavior is due to enhancing in radiative decay rate. The samarium ions transmit energy to nanoparticles, then excited SPR converted into emission with enhancing luminescence efficiency consequently increase in lifetime. This is assigned to the luminescence emission intensity enhancing and quenching exhibited by samarium ions with silver. The lifetime of samarium ions is smaller as compared with europium ions may be because higher concentrations reduce the nonradiative decay rates.

5. Conclusions

- Introduced fast, simple, economic, and eco-friendly biological synthesized silver nanoparticles using *Raphanussativus* leaf extract.
- The Luminescence enhancement factor for europium ions is high compared to samarium ions. Rare-earth ions displaying luminescence emission intensity enhancement and quenching with silver nanoparticles are assigned to local field enhancement and decay processes.
- Third-order nonlinear optical properties of biosynthesized silver nanoparticles were studied in femtosecond and picosecond regimes.
- Nonlinear susceptibility was measured by the DFWM technique.
- Ag NPs show good nonlinear optical absorption and optical limiting properties.
- These non-toxic NPs show many applications such as luminophores in biomedical and the strong reverse saturable absorption make them be good optical limiters.

IntechOpen

IntechOpen

Author details

Emusani Ramya Department of Science and Humanities, CMR Institute of Technology, Hyderabad, Telangana, India

*Address all correspondence to: eramya29@gmail.com

IntechOpen

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

[1] Geddes C D, Lakowicz J R (2002) Metal-Enhanced Fluorescence. *J Fluoresc*. 12:121-128

[2] Frederix F, Friedt J M, Choi K H, Laureyen W, Campitelli A, Mondelaers D, Maes G, Borghs G
(2003) Biosensing based on light absorption of nanoscaled gold and silver particles. *Anal Chem* 75: 6894-6900

[3] Wang J (2003) Nano particle-based electrochemical DNA detection. *Analytica Chimica Acta*. 500: 247-257

[4] Tripathi G N R (2003) P-Benzosemiquinone Radical Anion on Silver nanoparticles in water. *J Am Chem Soc* 125:1178-1179

[5] Tian Z Q, Ren B (2004) Adsorption and reaction at electrochemical interfaces as probed by surfaceenhanced Raman spectroscopy. *Annu Rev Phys Chem* 55:197-229

[6] Parak W J, Gerion D, Pellegrino T, Zanchet D, Micheel C, Williams S C, Boudreau R, Le Gros M A, and Larabell C A, Alivisatos A P (2003) Biological Applications of Colloidal Nanocrystals. *Nanotech* 14:15-27

[7] Mansoori G A, George T F, Zhang G, Assoufid L (**2007**) Molecular building blocks for nanotechnology. Springer, New York

[8] Nair B, Pradeep T (2002) Coalescence of Nanoclusters and Formation of Submicron Crystallites Assisted by Lactobacillus Strains. *Cryst Growth Des* 2:293-298

[9] Klaus T, Joerger R, Olsson E, Granqvist C G (2001) Bacteria as workers in the living factory: metalaccumulating bacteria and their potential for materials science. Proc *Trends in Biotechnol* 19:15-20 [10] Mukherjee P, Ahmad A, Mandal D, Senapati S, Sainkar S R, Khan M I, Ramani R, Parischa R, Ajaykumar P V, Alam M, Sastry M, Kumar R (2001) Bioreduction of $AuCl_4$ Ions by the Fungus, Verticillium sp. and Surface Trapping of the Gold Nanoparticles Formed. *Angew Chem Int Ed* 40: 3585-3588

[11] Ahmad A, Mukherjee P, Senapati S, Mandal D, Khan M I, Kumar R, Sastry M (2003) Extracellular Biosynthesis of Silver Nanoparticles using the Fungus *Fusarium oxysporum. Colloids Surf B Biointerfaces* **28:**313-318

[12] Shiv Shankar S, Ahmad A,
Pasricha R, Sastry M (2003)
Bioreduction of Chloroaurate ions by
Geranium leaves and it's Endophytic
Fungus yields Gold Nanoparticles of
Different Shapes. J Mater Chem 13:
1822-1826

[13] Begum N A, Mondal S, SaswatiBasu, Laskar R A, Mandal D (2009) Biogenic Synthesis of Au and Ag Nanoparticles using Aqueous Solutions of Black Tea Leaf Extracts. *Colloids Surf B Biointerfaces* 71:113-118

[14] Philip D (2009) Biosynthesis of Au, Ag and Au–Ag nanoparticles using edible mushroom extract. *Spectro Chim Acta Part A* 73:374-381

[15] Badri Narayanan K, Sakthivel N(2008) Coriander Leaf MediatedBiosynthesis of Gold Nanoparticles. *MatLett* 62:4588-4590

[16] Awwad A M, Salem N M, Abdeen A O (2012) Biosynthesis of Silver
Nanoparticles using Olea
europaeaLeaves extract and its
Antibacterial Activity. Nanosci
Nanotechnol 2:164-170

[17] Youyi Sun, Zhi Zheng, Qing Yan, Jiangang Gao, Hongfang Jiu, Qijin Zhang (2006) Effects of Ag colloidal nanoparticles on luminescent properties of Eu(III) β -diketone. *Mat Lett* **60**: 2756-2758

[18] Kuladeep R, Jyothi L, Prakash P, Mayank Shekhar S, Durga Prasad M, and Narayana Rao D (2013) **Investigation of optical limiting properties of Aluminium nanoparticles prepared by pulsed laser ablation in different carrier media**. J Appl Phys **114**:243101

[19] Vigneshwaran N, Kathe A A, Varadarajan P V, Nachane R P, Balasubramanya R H (2007) Silver protein (core shell) nanoparticle production using spent mushroom substrate *Langmuir* **23:**7113–7117

[20] Katrin Quester, Miguel Avalos-Borja, Ernestina Castro-Longoria (2016)
Controllable Biosynthesis of Small
Silver Nanoparticles Using Fungal
Extract. J Biomater Nanobiotechnol 7: 118-125

[21] Raheman F, et al (2011) Silver nanoparticles: Novel antimicrobial agent synthesized from an endophytic fungus *Pestalotia* sp. isolated from leaves of *Syzygium cumini* (L). *Nano Biomed Eng* **3:**174-178

[22] Santhoshkumar T, Rahuman A, Rajakumar G, Marimuthu S, Bagavan A, Jayaseelan C, et al (2011) Synthesis of silver nanoparticles using *Nelumbo nucifera* leaf extract and its larvicidal activity against malaria and filariasis vectors. *Parasitol Res* **108:**693–702

[23] Venkatpurwar V, Shiras A, Pokharkar V (2011) Capped gold nanoparticles as a novel carrier for delivery of anticancer drug: in vitro cytotoxicity study. *Int J Pharm* **409:**314–320

[24] Vahabi K, Dorcheh S K (2014) Biosynthesis of silver nano-particles by trichoderma and its medical applications. In: Gupta VK, Schmoll M, Herrera- Estrella A, Upadhyay RS, Druzhinina I, Tuohy MG, editors (2014) *Biotechnology and biology of trichoderma*. Elsevier, London, UK 393–404

[25] Jeyaraj M, Sathishkumar G, Sivanandhan G, MubarakAli D, Rajesh M, Arun R, et al (2013) Biogenic silver nanoparticles for cancer treatment: an experimental report. *Colloids Surf B Biointerfaces* **106**:86–92

[26] Basha K S, Govindaraju K, Manikandan R, Ahn J S, Bae E Y, Singaravelu G (2010) Phytochemical mediated gold nanoparticles and their PTP 1B inhibitory activity. *Colloids Surf B Biointerfaces* **75:** 405–409

[27] Pradeep T, and Anshup (2009) Noble metal nanoparticles for water purification: A critical review. *Thin Solid Films* **517**:6441-6478

[28] Sathyavathi R, Bala Murali Krishna M, and Narayana Rao D (2010) Biosynthesis of Silver Nanoparticles Using *Moringa oleifera* Leaf Extract and Its Application to Optical Limiting. *J Nanosci Nanotechnol* **10:**1–5

[29] Feifei Chen, Junwen Cheng, Shixun Dai, Zhe X, and Qinyuan Zhang, Wei Ji, Ruiqin Tan (2014) Third-order optical nonlinearity at 800 and 1300 nm in bismuthate glasses doped with silver nanoparticles. *Opt Exp* **22**:13438-13447

[30] Nabika H, and Deki S (2003) Enhancing and Quenching Functions of Silver Nanoparticles on the Luminescent properties of Europium Complex in the solution phase. *J Phys Chem B* **107:**35

[31] Mock J J, Barbic M, Smith D R, Schultz D A, and Schultz S (2002) Shape effects in plasmon resonance of individual colloidal silver Nanoparticles. *J Chem Phys* **116**:6755-6759

[32] Qingru Wang, Shangxin Lin, Chengguo Ming, Hongyan Zhao, Jiadong Liu, Chao Zhang, Feng Song,

Edwin Y B Pun (2011) Plasmonenhanced luminescence of Eu complex by using silver nanocubes for different excitations. *Mat Lett* **65**:905–907

[33] Fang X N, Song H W, Xie L P, Liu Q, Zhang H, Bai X, Dong B, Wang Y, Han W (2009) Origin of luminescence enhancement and quenching of europium complex in solution phase containing Ag nanoparticles. *J Chem Phys* **131**: 054506

[34] Novotny L, Hecht B (2006) Principles of nano-optics. Cambridge University, London

[35] Gagandeep K, Verma R K, Rai D K, Rai S B (2012) Plasmon-enhanced luminescence of Sm complex using silver nanoparticles in Polyvinyl Alcohol. *J Lumin* **132:**1683–1687

[36] Ringler M, Schwemer A, Wunderlich M, Nichtl A, Ku rzinger K, Klar T A, and Feldmann J (2008) Shaping Emission Spectra of Fluorescent Molecules with Single Plasmonic Nanoresonators. *Phys Rev Lett* **100**: 203002

[37] Philip D, Unni C, Aswathy Aromal S, Vidhu V K (2011) MurrayaKoenigii leaf-assisted rapid green synthesis of silver and gold nanoparticles. *Spectrochim Act Part A* **78:**899–904

[38] Mirgorod Yu A, Borodina V G, and Borsch N A (2013) Investigation of Interaction between Silver Ions and Rutin in Water by Physical Methods. *Biophysics* **58**:743–747

[39] Preeti Singh, and Jaspal Singh (2013) MEDICINAL AND THERAPEUTIC UTILITIES OF *RAPHANUS SATIVUS. Int J Pl An and Env Sci* **3**:2231-4490

[40] Philip D (2011) MangiferaIndica leaf-assisted biosynthesis of welldispersed silver nanoparticles. *Spectrochim Act Part A* **78:**327–331 [41] Elemike Elias Emekaa, Oseghale Charles Ojiefoha, Chuku Aleruchib, Labulo Ayomide Hassana, Owoseni Mojisola Christianab, Mfon Rebeccac, Enock Olugbenga Darea d, Adesuji Elijah Temitope (2014) Evaluation of antibacterial activities of silver nanoparticlesgreen-synthesized using pineapple leaf (*Ananas comosus*). *Micron* **57:1**–5

[42] Agasti N, KaushikAmerican N K(2014) One Pot Synthesis ofCrystalline Silver Nanoparticles. *JNanomater* 2:4-7

[43] Tam F, Goodrich G P, Johnson B R, and Halas N J (2007) Plasmonic enhancement of molecular fluorescence. *Nano Lett* **7:**496–501

[44] George Z, and Barnes W L (2008) Fluorescence enhancement through modified dye molecule absorption associated with the localized surface Plasmon resonances of metallic dimmers. *New J of Phys* **10**:105002

[45] Wang Q, Song F, Lin S, Liu J, Zhao H, Zhang C, Ming C, and Edwin Y B Pun (2011) **Optical properties of silver nanoprisms and their influences on fluorescence of europium complex c.** *Opt Exp* **19:**6999-7006

[46] Pascal A, Palash B, and Lukas N (2006) Enhancement and Quenching of Single-Molecule Fluorescence. *Phys Rev Lett* **96:**113002

[47] Bala Murali Krishna M, Praveen Kumar V, Venkatramaiah N, Venkatesan R, and Narayana Rao D (2011) Nonlinear Optical Properties of Covalently Linked Graphene-Metal Porphyrin Composite Materials. *Appl Phys Lett* **98:**081106

[48] Shukla V, Singh C P, Mukherjee C, and Bindra K S (2013) Investigation of optical limiting in Cobalt nanoparticles synthesized by laser ablation. *Chem Phys Lett* **555**:149-153 [49] Ramya E, Jyothi L, Narayana Rao D (2018) Influence of Optical Properties of Ag NPs from Raphanussativus Leaf Extract on Lanthanide complexes. Plasmonics 12:1601

[50] Felicia T, Glenn P, Goodrich Bruce R J, and Naomi J H (2007) Plasmonic Enhancement of Molecular Fluorescence. *Nano Lett* **7:**496-501

[51] Fang H, Song H, Xie Liu Q, Zhang H, Bai X, Dong B, Wang Y, and Han W (2009) **Origin of luminescence enhancement and quenching of europium complex in solution phase containing Ag nanoparticles.** *J Chem Phys* **131:**054506

