Metallic Nanoparticles Enhanced Surface Plasmon Resonance in Tellurite Glass

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Abstract

The role of gold NPs in the luminescence enhancement of tellurite glass is presented. We use the concept of localized surface plasmon resonance (LSPR) from metallic nanoparticles (NPs) in rare earth (RE) ions doped tellurite glass to modify their optical properties. The LSPR has the ability to encounter problem related to the decrease in emission intensity caused by nonradiative decay of excited levels and thereby enhance the luminescence. Incorporating gold NPs inside the glass matrix by dispersing or arranging as arrays, the plasmon can be excited that modify the radiative decay rates. The emission wavelength, intensity and lifetime of the excited energy levels is found to depend both on the RE ions and the chemical environment of the RE ions excited state that interacts with the surrounding NPs. The strength of the local electric field around the metal NPs is greatly affected by the metallic screening and concentration of light in NPs. The optical properties of the glass depend on the size and shape of NPs. In addition, different annealing time of glass formation also contributes to the photoluminescence enhancement due to the growth of NPs. The photoluminescence enhancement or quenching effect can is understood by the energy transfer between the NPs and RE excited states through coupled multiple dipole theory. The study and exploitation of LSPR and local field properties of metallic NPs embedded in glasses matrix may show different levels of enhancement in fluorescence.

Keywords: LSPR**,** Nanoparticles, Up-conversion, Photoluminescence

1. Introduction

Recently, nanotechnology is developed in wide area to encounter the ever growing challenges in human needs. The NPs contribute to the elements that build up the nanotechnology application today. It can exist as nanopowder, nanocluster or nanocrystal among many other forms. A great scientific interest is discovered through NPs since they effectively play a dramatic role in bridging the gap between bulk materials and atomic or molecular structures. Currently, metallic nanostructures is a subject of considerable interest because they are endowed with unique optical properties and functionalities contrast to their bulk counterparts as reported by Som et al. (2010). It is established that the properties of the clusters can vary depending on whether they are free, deposited on a surface or embedded in

a matrix of another material. The methods of diffusion and aggregation of atoms can be used to form the clusters on the surface.

Tellurite glass is a good candidate in manufacturing field because they exhibits a good chemical durability, low glass transition, high refractive index and high transmittance especially in near (NIR) to middle infrared (MIR) regions as studied by Sahar et al. (1997). Previous study showed that these glasses are excellent in hosting rare-earth ions since they provide a low phonon-energy environment to minimize the non-radiative losses as well as possessing good optical properties. Glasses doped with RE ions and metallic NPs has the ability to enhance the RE luminescence and improved nonlinear optical properties as demonstrated by Carmo et al. (2009). The presence of plasmonic metal NPs in the vicinity of RE ions affects and triggered the RE-luminescence.

In this work the modification of optical properties of RE ions doped tellurite glass containing NPs is investigated by means of SPR. The luminescence is found to be sensitive to different processes such as excitation by the incident field. In addition, the local environment and emission of radiation is influenced by the competition of radiative and nonradiative decay. The role of NPs in enhancing the SPR and optical performance are examined and understood.

2. Nanoglass Preparation

Tellurite glasses overcome the limit application of phosphate and borate glasses where they posses relatively low transformation temperatures, high densities and non hygroscopic properties. The glass preparation based on conventional melt-quenching method including melting, quenching, annealing and cooling down to room temperature are performed. In the glass formation, the RE concentration is kept higher than the concentration of NPs to maximize the luminescence intensity. The ratio between NPs and RE concentration is considered less than one. The probability of multi-poles formation increases (RE ions: NPs) as the concentration of NPs become higher than RE ions. This condition is extremely unfavorable for the system. Recently, Rivera et al. (2011) reported that the quenching rate is increased due to energy transfer by the excited RE ions to the surface of metallic NPs.

2.1. Gold Nanoparticles

NPs have a very high surface area to volume ratio. The shape, the size, the number density of the metal NPs, host matrix environment, and distance between the RE ion and the metallic surface have a dominant effect on the fluorescent enhancement as reported by Som et al. (2009). The properties of materials change as their size approaches the nanoscale and the percentage of atoms at the surface become significant. Gold NPs display special characteristics in electrical and optical properties. Electrons in metallic NPs are not bound to individual atoms instead forming a cloud around the atomic cores. This cloud of electrons is mobile allowing metallic NPs to transport charge (electrons) easily. The SPR usually occurs at the surface of the materials.

NPs can experience SPR in the visible region of the spectrum. In this phenomenon, certain part of the visible wavelengths is absorbed, while another portion gets reflected. The reflected portion lends the material a certain colour. Small NPs absorb light in the blue-green region of the spectrum (~400-500 nm) while red light (~700 nm) is reflected, yielding a deep red color. As particle size increases, the wavelength of SPR related absorption shifts to longer and cause a formation of redder wavelengths. If particle size continues to increase toward the bulk limit, SPR wavelengths move into the infrared portion of the spectrum and most visible wavelengths are reflected.

Previous work reports the embedment of silver NPs close to the emission centers of TeO_2-PbO-GeO_2 glass improved the luminescence efficiency of the Pb^{2+} clusters. Silva et al.

(2011) used glasses doped with NPs to increase the radiative and nonlinear properties as compared with the undoped counterparts. The effects of gold NPs and silver NPs incorporation in Er^{3+} doped tellurite glasses and the coupling of optically active Er^{3+} ions with plasmon modes of silver NPs or gold NPs are investigated by Rivera et al. (2011). Meanwhile, Kassab et al. (2011) used the operation of energy transfer (ET) between metallic NPs and rare-earth ions leading the enhancement of local field that acts on the RE ions located in proximity of the NPs specifically when the wavelength of the incident light beam, or luminescence wavelength is close to the SPR wavelength of the NPs.

2.2. Role of Annealing Time

The annealing time during glass preparation is controlled the growth of gold NPs and interaction of SPR with Er^{+3} inside materials as demonstrated by Rivera et al. (2011). Mertens et al. (2006) showed that different heat treatment during preparation of glass to reduce Au^{+} or Au^{3+} ions to Au^{0} and to nucleate gold NPs. The average diameter of gold NPs is reduced due to thermal fragmentation of the larger particles for longer heat treatment. The concentration of the smaller gold NPs is increased due to effect of fragmentation. The amplitude of SPR increases for longer heat-treatment times due to the increase of the NPs volume fraction. Kassab et al. (2009) reported the occurrence of larger surface plasmon bandwidth is due to the varieties of shapes and sizes of the NPs and the presence of aggregates of NPs.

Similar results are achieved by Singh et al. (2010), where the size of NPs depends on different parameters including annealing temperature and the duration of annealing. Rivera et al. (2010) showed the annealing time dependence of the formation of different NPs sizes with different distances between them dispersed in the vitreous matrix. The size of NPs found to increase as the annealing duration is increased. The presence of metallic NPs enhance up-conversion (UC) emission intensity is also evidenced. The concentration of NPs grows with the annealing time annealing as temperature become higher and leads to enhancement of the intensity of surface plasmon band. The RE ions Er^{3+} are mostly used in glass to perform this action. Metallic NPs can enhance the intensity of Er^{3+} bands in different ways either by ET from NPs plasmon band to Er^{3+} ion or through local field of NPs on Er^{3+} ions.

2.3. Mechanism of Nanoparticles Thermochemical Reduction

In annealing process, the glass viscosity is sufficient to promote the Ag^{0} diffusion. Different sizes of NPs will be dispersed throughout the glass with different annealing times. In this condition, the sizes of NPs will be changing with different mobility of Au^{0}. Previous study performed by Rivera et al. (2011) showed a complete reduction of Au^{3+} to Au^{0} with annealing time and there is no formation of gold oxide Au_2O (Au^{+}) or Au_2O_3 (Au^{3+}). Melting process involves the formation of Ag^{+} and Au^{3+} ions. Meanwhile, both the NPs growth and the thermal reduction occur during the glass annealing (above T_g), where T_g is transition temperature. The thermal reduction can be described as in Equation (1):

$$Au^{3+} + 3e^{-} \rightarrow Au^{0} \quad , \qquad (1)$$

The glass viscosity is sufficient to promote the Au^{0} diffusion in this condition. Osorio et al. (2011) in their plasmonic coupling study showed the formation of gold NPs taking several steps described by,

$$Au^{+3} \rightarrow Au^{+} \quad (2)$$

$$Au^{+} \rightarrow Au^{0} \quad (3)$$

In comparison, the annealing time for the gold NPs formation must be longer than for silver NPs in order to obtain comparable sizes.

2.4. The Role of Er^{+3} ions

The RE ions are capable to perform the lasing action in glassy hosts. The Er^{3+} -doped tellurite glass are a major attractive research subjects for the UC emission due to their low phonon energy as showed by Sahar et al. (2008). The effect of Er^{3+} environment to glass has extensively been studied by Souza et al. (2002). The atomic-like luminescence emitted by Er^{3+}. This luminescence arises from electronic transitions within its incomplete internal 4f shell. The photons with a wavelength close to 1.55 μm will be emitted due to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition from the first excited to the fundamental state. The outer filled $5s^2$ and $5p^6$ shield the internal 4f shell. Therefore, the transition wavelength has a small dependence on the details of the host. The local site around Er^{3+} can be used to obtain information about the shape and intensity of the luminescence line. The surrounding dielectric environment of the metal structure has a significant influence on the plasmon peak wavelength. In this system, tellurite glass can be modeled as dielectric environment. Fu et al. (2010) discovered that the plasmon peak shift observed due to the binding of an analyte to the metallic surface.

However, there is some problem need to be considered. In Er-doped dielectrics, the Er concentration needs to be kept low to avoid concentration quenching and cooperative UC. In certain situation, if the distance between the RE ion and the NPs (or metallic aggregate) is very small the dipole-dipole interaction between them may contribute for ET from the RE ion to the metallic structure and the luminescence band is quenched as in study performed by Kassab et al. (2009). In other study of Mertens et al. (2006) reported that the temperature quenching is the main constraint for device applications in Er-doped Si. There is alternative methods are introduced to eliminate the quenching effect by modifying the dielectric environment. This method will enhance the spontaneous emission rate of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. For emitters positioned in close proximity of metal NPs, very strong effects of the environment on the emission rate are predicted. Previous work shows that the photoluminescence (PL) intensity of Er^{3+} ions positioned close to gold NPs is significantly enhanced.

The Er^{3+} ions show capability in UC luminescence at 550 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) and 660 nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$), as in Figure 1. This characteristic very important in solids state UC lasers. The luminescence intensity depends nonlinearly on excitation power since the UC luminescence is multiphoton process. In order to achieve high intensity of UC luminescence in study performed by Ueda et al. (2009), low phonon energy host and high-power-density excitation are required. Erbium doped tellurite glass with embedded metallic NPs can be used to achieve effective observation of the SPR evidence.

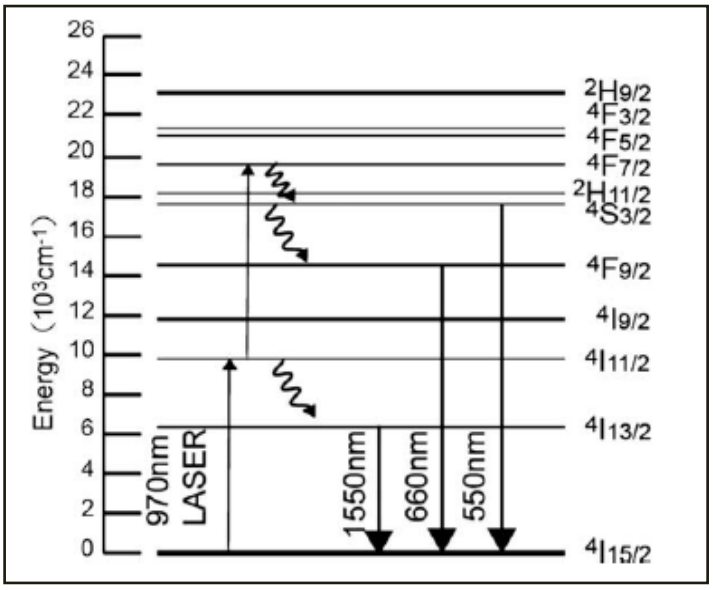

Fig 1: Energy level diagram of Er^{3+} and UC luminescence processes corresponding to 970 nm two-photon excitation.

3. Theory of Surface Plasmon Resonance (SPR) interaction

The SPR is localized near the boundary between the metal nanostructures and the surrounding (dielectric) matrix. It will produce an enhanced electric field at the interface. This phenomenon is applied for the physical basis of absorption of light by metallic NPs and results the coherent oscillation of the conduction band electrons upon interacting with the electromagnetic radiation. Som et al. (2010) in their study demonstrated a study of strong SPR band of Au NPs which exhibit red-shifts with increasing Au concentration. More light will be absorbed by plasmonic metal NPs if compared to their geometrical cross section. These NPs can improve many applications such as fluorescence enhancement since they act as "photon catchers", concentrating a significant quantity of electromagnetic energy into a very small region around them. Research based to the monometallic: RE hybrid composites are introduced due to their flexible properties as color displays, optical amplifiers, as well as optical sensors.

Plasmonic can be used in Osorio et al. (2011) study to modify the radiative decay properties of RE ions with NPs. The weak photoluminescence emissions from NPs contribute to the excitation energy and increasing the photonic density around the ion if a RE ions is situated in close proximity from the NP surface. This process resulting more photons are captured by the ion and increasing its excited state population. According to Fermi's golden rule, the transition probability to the ground state is proportional to the photonic mode density. Thus, there is enhancement in the rate of radiative decay. But, the Fermi's golden rule is not discussed in this study.

Significant enhancement of the erbium fluorescence can be induced in tellurite glass doped Er^{3+} with embedded with NPs as investigated by Rivera et al. (2010). This is due to long-range electromagnetic interaction between the plasmons of the metallic NPs in the host medium. In nonlinear optics effects, this strong enhancement of electromagnetic fields play a crucial role to allows an achievement in high values of electromagnetic field enhancement through the SPR excitation. Size and shape of the particle tuned the resonance frequency which is known as plasma frequency (w_p). A SPR applied a free electrons oscillation of a metallic particle. These oscillations as are dependent on the shape and size of NPs and the dielectric medium containing them. The interaction between incident radiation and the NPs

triggered the oscillation. Fu et al. (2010) investigate the changing of dielectric constant of the surrounding material will have an effect on the oscillation frequency. The surface will vary the ability to accommodate electron charge density from the NPs.

The changes in local electric field cause the enhancement (or quenching) of photoluminescence. An oscillating electric field is created using a collective excitation of the conduction electrons when a light beam irradiates the NPs. The change of local electric field due to the presence of the NPs can be described as Equation (4) below.

$$\vec{E}_{eff} \propto \vec{E}_0 E(\omega_P, \gamma), \tag{4}$$

where γ is the damping of the resonance. This damping γ represents the contribution of the conduction electrons and it can be described as:

$$\gamma = \frac{1}{\tau^{NP}} = \frac{1}{\tau_0} + 2\frac{g_S V_F}{D}, \tag{5}$$

The term $1/\tau_0$ is associated to the bulk electron scattering process in the particle while the second term is a consequence of the quasi electron-free interaction with the surface of the sphere. V_F is the Fermi velocity and g_s is the surface factor. The limitation on the mean-free path of the free electrons by the particle dimensions can be described by this last term. Thereby, the shape and size of NPs give a significant effect to magnitude of the quantum efficiency enhancement due to resonant coupling with plasmon modes.

Rivera et al. (2010) in their study showed that the energy transfer is due to the electric coupling (type electric dipole) of the NPs with the Erbium be a influence in improvement or a quenching in the luminescence of Er^{3+} ions. The distance of separation of this dipole with concomitant changes in excited state lifetime determine the performance of this coupled. In their study, the other possibility for the ET mechanism is due to the part of metallic NPs (small metallic NPs aggregates) remained under the form of ions, atoms, charged or neutral dimmers and multimers. This resulting to the contribution of the latter species to the Er^{3+} luminescence enhancement and band shape features cannot be excluded. The strong modification of the glassy network and to the Erbium local environment is caused by the insertion of metallic NPs. The effective electric can be written as Equation (6):

$$\vec{E}_{eff} = \frac{(\varepsilon_0 + 2)}{3}\left(1 + \frac{q\omega_P^2}{3\varepsilon_0\left[(1-q)\left(\omega_P^2/3\varepsilon_0\right) - \omega^2 + i\gamma\omega\right]}\right)\vec{E}_0, \tag{6}$$

where $q = \pi d^3/6$ is the NP specific volume, γ is the damping resonance, ω_p is the plasma frequency, ε_0 is the dielectric constant in the presence of an external electromagnetic field of amplitude E_0. LSPR forms electric dipoles separated by distance r in the presence of an electromagnetic field. The oscillator strength, $P_{strength}$, of a spectral line is modified by the local field induced by NPs. It corresponds to a determined transition from the ground level *i* to the excited level *f* as follows:

$$P_{strength} = \chi\left[\frac{8\pi^2 m\nu}{3h(2J+1)}\right]\left(\sum\left|\left\langle 1\left|D^{(1)}_{q_{nearest-neighbor}}\right|f\right\rangle\right|^2 + \sum\left|\left\langle 1\left|D^{(1)}_{q_{Au-NP}}\right|f\right\rangle\right|^2\right). \tag{7}$$

The second term in the parenthesis is added to represent the electric dipoles due to LSPR of NPs (gold is used in this study), where *m* is the mass of an electron, *h* is the Planck constant, *v* is the frequency of the line. The factor χ is an adjustable factor that depends on the

refractive index of the medium in which Er^{3+} ions are embedded, and J is the total angular momentum.

4. Conclusion

The role of metallic NPs embedded in tellurite glass in enhancing the optical behavior through the effect of SPR is investigated. The interaction between NPs and Er^{3+} ion and their dependence on certain conditions such as size, shape of NPs and annealing time are analyzed and understood. It is asserted that the SPR are capable in enhancing the luminescence properties of glass. The SPR coupled enhancement is these glass is a very promising way to fabricate high optical performance photonic devices. It is important to calculate the Judd-Ofelt intensity parameters for quantifying the mechanism involved in the enhancement process.

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