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NEW CONCEPT FOR LUMINESCENT SOLAR CONCENTRATORS

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ABSTRACT: We have studied the excitation rate of Lumogen Red dye molecules by enhanced local electromagnetic field of Au nanoparticles for thin film luminescent solar concentrator (LSCs). The localized enhanced electromagnetic field of Au nanoparticles leads to an increase the excitation rate, and consequently in emission rate of dye molecules. By varying the distance between Au nanoparticles and dye film we showed transition from quenching to enhancement in edge emission and resultant I_{SC} current output of thin film LSCs. When dye molecules were placed in the range of enhanced electromagnetic field of Au nanoparticles. Two competing factors affected the edge emission of thin film LSC; increased excitation rate (by enhanced local electromagnetic field of Au nanoparticles) and distance between Au nanoparticles and dye molecules.

Keywords: Concentrators, Au Nanoparticles (Au NPs), SPR.

1 Introduction

The luminescent solar concentrator (LSCs) was suggested in late 1970s to concentrate and convert solar power into monochromatic light to increase the output of solar cells and decrease the cost of solar power [1-2]. Thin film LSC was proposed to reduce the re-absorption and scattering loss [3-4]. A thin film LSC consists of heavily doped luminescent species (organic dye, quantum dots, and rare earth materials) matrix material thin film placed on a highly transparent substrate of relatively large thickness and of same refractive index for optical matching. Luminescent materials absorb the incident solar radiation and re-emit isotropically in the matrix material. The emission is guided via total internal reflection to the sheet edges where solar cell is attached. The amount of luminescent materials in the film is intended to be same as in a comparable homogeneously doped thick LSCs, but concentrated in small volume. The effect reduced re-absorption and scattering loss has been debated [5]. It has been argued that the gain in path length in the substrate is compensated by the loss within the optically dense film. Thin film LSCs have several other advantages [6]. They allow to stacking of LSCs plates which are containing different types of luminescent species to utilize full solar spectrum, they reduce the fabrication cost as less doped material is required and allow for more flexible employments of thin films with appropriate optical properties on any host substrate. A disadvantage is that in thin film the volume to absorb the solar radiation decreased consequent may lead to a decrease in overall output of LSC device. This problem could be solved using the plasmonic properties of noble (Au, Ag) metal nanoparticles (MNPs).

When MNPs have dimension smaller than the wavelength of the excitation light, energy can be confined in the small spatial regions through the excitation of localized surface plasmon resonance (SPR). SPR is a collective oscillation of conduction band electrons can not be excited in metal by ordinary plane wave light due to momentum mismatching of the SPR dispersion relation and the excitation light photon. MNP thus overcome the momentum mismatching and SPR can be excited by ordinary plan wave [7]. SPR induced enhanced localized electromagnetic field intensity (E_{loc})

or equivalently the photon mode density (PMD) [8]. Decays exponentially away from the surface and decay length are on the order of half the SPR wavelength [9].

When luminescent species is placed in the range of enhanced E_{loc} field, it can modify absorption and excitation rate and consequently changed in radiative and non radiative decay rate and quantum yield. When SPR wavelengths overlap to absorption spectra of luminescent species, both, the absorption and excitation are increased [10]. These interactions have been subject to theoretical [11] as well as experimental [12-15] investigation.

This mechanism provides a possibility for extending the range of luminescent species which could be used in LSCs to harvest longer wavelength light. In this paper a composite material model for thin film LSCs is presented. Au NPs with controlled surface structures and Lumogen Red are employed to maximize the emission in thin film LSC by adjusting the enhanced local electromagnetic field intensity E_{loc} (or equivalently the PMD) at dye molecules.

2 Experimental

2.1 Materials

Gold precursor gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) of high purity $\geq 99.9\%$, Poly vinylpyrrolidone (PVP) of M_w 10 000 and HPLC grade toluene, and sodium hydroxide (NaOH) of molecular weight 40.00 g/mol (Sigma Aldrich) and analytical grade ethanol (Lennox). Plexit55 is pre-polymerized mixture of MMA and PMMA with polymerization initiator catalyst Katalysator 22 (100:1) (Carl Roth GmbH + Co.KG) used as polymer matrix for thin film LSCs. Lumogen F Rot 305 (Lumogen Red) dye (BASF) was used as luminescent species for thin film LSCs. All glassware were scrupulously cleaned with detergent, acetone, and ethanol and finally rinsed with deionised water from a Millipore system.

2.2 Synthesis of PVP-stabilized Au NPs their thin film

A general procedure for the synthesis of the PVP-stabilized Au NPs in ethanol is described as follows. The initial step is reduction of 2 mM HAuCl_4 solution in ethanol in the presence of PVP ($M_w=10000$ g/mol) and aqueous NaOH. The PVP plays a dual role of reducing and stabilizing agent for nanoparticles. The NaOH used as initiator for the chemical reduction of AuCl_4^- by PVP. The mass ratio of PVP to HAuCl_4 was 12:1. The solution was refluxed at 80 °C for 30 minutes while stirring. After a sequence of colour changes finally it turned dark-red colour which shows the formation of stable nanoparticles. The resulting colloidal Au NPs solution was spin coated on cleaned glass substrate of 25mm×25mm×1mm (refractive index $n\approx 1.5$) by using G3 P-8 spin coater (Specialty Coating System) at 1500 rpm for 30 sec. and dried in air.

2.3 Fabrication of Au NPs and Lumogen Red dye samples

To demonstrate the phenomena of increased absorption and excitation of Lumogen Red dye molecules by enhanced local electromagnetic field intensity (E_{loc}) of Au nanoparticles (Au NPs). The following structures were prepared; Lumogen Red dye molecules placed in the range of enhanced local electromagnetic field of Au NPs by varying spacing thickness between dye molecules and Au NPs. Sample configuration is shown in figure 1 where the spacing layer thickness was varied. Plexit 55 was used as polymer matrix for thin film LSCs. For spin coating purpose it was further diluted with 25 wt % toluene and mixture to refer as 25 wt % Plexit 55. Lumogen F Rot 305 of 0.7 wt% concentration was dispersed in 25 wt % Plexit 55, in ultrasonic bath for one hour. First the dye film of 500nm thickness was deposited on glass substrate by spin coating at 2000 rpm for 30 sec. then spacer film of thickness 0, 30, and 60nm by spin coating of 2 wt % Plexit at 3000 rpm for 30 sec and finally Au NPs film top layer that has optimized separately. In each step dyes and spacer film were dried at 60 °C for two hours in vacuum oven to remove evaporating solvent. Au NPs film was dried in air.

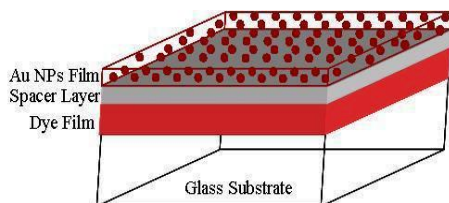


Fig. 1: Schematic drawing of the sample configuration; spacing layer thickness was varied.

3. Characterization

The size and morphology of Au NPs and their spin coated film were observed using a field emission scanning electron microscope (Hitachi, SU 6600FE-SEM) operated at 25 kV. Samples for Au NPs were prepared on holey carbon-coated 300 mesh copper grid

(Agar Scientific); diluting the parent Au NPs solution in ethanol 1: 5 ratio, then dropped on the mess grid and subsequently dried in a desiccator. The optical properties of Au NPs and samples were analyzed by measuring the absorbance spectra in UV-Vis spectrophotometer (Perkin Elmer Lambda 900 UV/Vis/NIR spectrometer). Edge emission measurements were made by the excitation-detection system shown in figure 2. A fiber optic AvaSpec-2048 (Avantes Company) spectrometer was used to measure the edge emission of illuminated samples. Samples were illuminated by halogen lamp solar simulator combination with yellow subtractive filter which cut off above 510nm to well separate the excitation and emission wavelength. Emission was collected at 90° relative to the excitation.

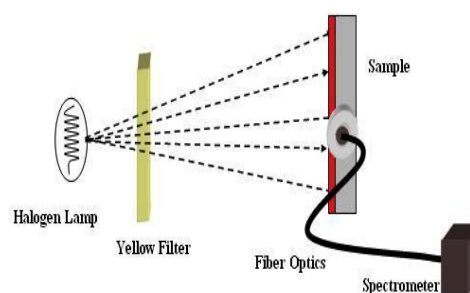


Fig. 2: Experimental set for edge emission measurement.

For electrical characterization a PV mount containing a solar cell (Solaronix) of 25×1 mm was used. The short-circuit current (I_{sc}) was measured of the LSCs, illuminated by halogen solar simulator with intensity 1kWm^{-2} .

4. Results and Discussion

In typical Au NPs synthesis process; when designated amount of NaOH was added to the mixture solution of PVP/ HAuCl_4 , a sequence of colour changes observed during the course of the reaction in just a few minutes.

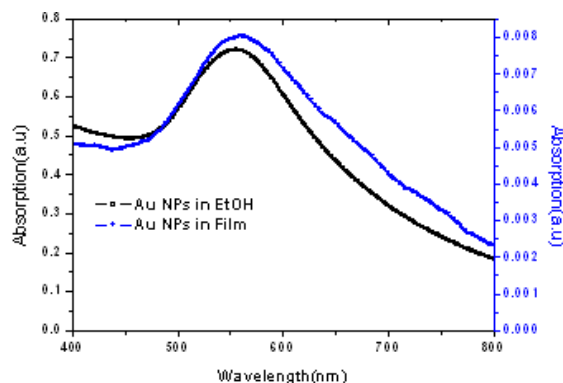


Fig. 3: Absorption spectra of spherical 10±1nm Au nanoparticles in solution and in spin coated film.

The initial light yellow solution became colourless, indicating the AuCl_4^- was reduced to form Au atom then turned dark-red colour within 5 minutes and that

remained constant, indicating formation of stable gold nanoparticles. The absorption spectra of Au NPs in ethanol and in spin coated thin film are shown in figure 3.

The SPR peak was observed at 556 and 562 nm in ethanol and film, respectively. Synthesized nanoparticles appeared nearly spherical with an average diameter 10 ± 1 nm as determined by STEM characterization, shown in figure 4.

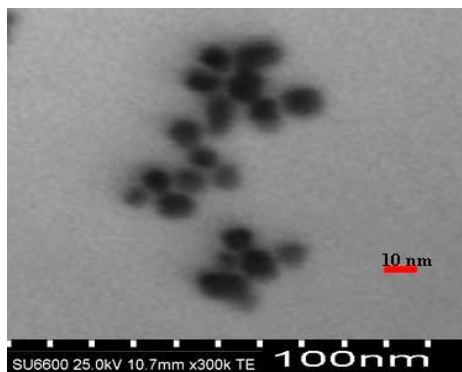


Fig.4: STEM image of Au spherical nanoparticles synthesised through reduction of HAuCl_4 in a PVP/EtOH mixture, in the presence of NaOH.

The linear absorption phenomenon of the spin coated Au NPs film reveals that nanoparticles were successfully assembled without any agglomeration with good surface coverage demonstrated. That is confirmed by the SEM image of coated film in figure 5. The SPR peak was slightly red-shifted in thin film. This phenomenon is probably due to change in size distribution when nanoparticles assembled in thin film during spin coating [16].

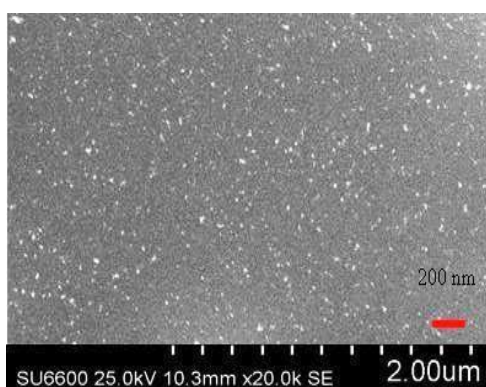


Fig.5: SEM images of spin coated Au NPs film at 1500 rpm for 30 sec.

Absorption measurement were performed by acquiring a transmission measurement of samples with respect to a reference, are shown in figure 6. The absorption peak for Lumogen Red dye was observed at 575 nm. It is observed that absorption increases for Au NPs and dye film samples and independent of spacing thickness. This increased absorption can be explained by

the SPR phenomena in MNPs. SPR increases the optical cross-section and consequently the extinction coefficient, and lead to increased scattering of light into high refractive index [17] dye film. Due to significant overlap between SPR wavelength and the absorption peak of Lumogen Red dye the magnitude of absorption increase. The results in figure 6 show the absorption is independent of the spacing layer thickness.

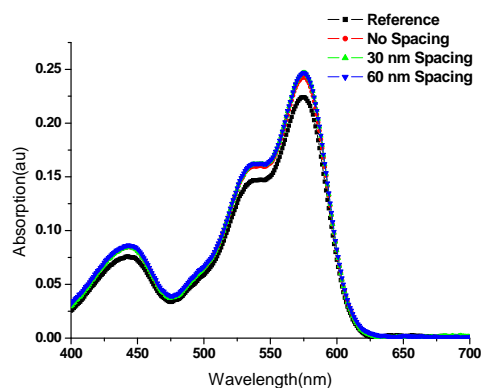


Fig.6: Absorption spectra of samples.

Edge emissions photons were recorded with a fiber optic spectrometer, shown in figure 7. It is observed that edge emission intensity does depend on spacing layer thickness. In figure 8 the integrated edge emission, normalized to reference as a function of spacing layer thickness, is shown. We have shown that absorption is independent of spacing layer thickness so the absorption alone is not responsible for the variation in edge emission intensity. The other important factor is the excitation rate of dye molecules located in the range of enhanced electromagnetic field. It is known that excitation rate is directly proportional to the square of the electric field amplitude around the luminescent species.

We control the volume of dyes molecules located in the enhanced local electromagnetic field intensity by placing the spacing layer between Au NPs and dye film.

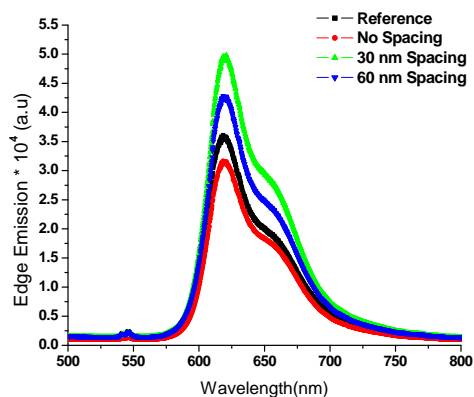


Fig.7: Edge emission for four types of samples In the case of zero spacing samples the edge emission was decreased even though a large number of dyes molecules located in the range of enhanced field. This is due to quenching of emission; mechanism may include chemical bonding and nonradiative energy transfer from

luminescent dye molecules to the Au nanoparticle through near field component and compensate the effect of enhanced emission rate. This is a short range effect less than 10 nm [18] it weakens with distance much faster than the enhanced local electric field intensity and responsible for the expected enhancement for 30 and 60 nm spacing layer thickness samples. The maximum edge emission was recorded for 30 nm spacing thickness. Further increase in spacing leads to decrease the volume of dye within enhanced electric field and edge emission started to decrease for 60 nm spacing.

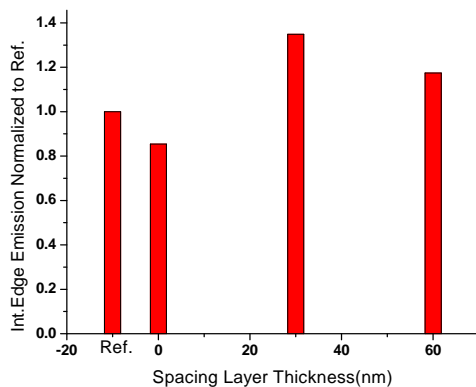


Fig. 8: Reference normalized integrated edge emission as function of spacing layer thickness.

The short circuit current, I_{SC} was measured for thin film LSCs by placing one of its edges on the solar cell and illuminated at 1 kWm^{-2} by solar simulator. The results are shown in figure 9. Reference samples, only dyes film on glass substrate. There is good agreement between electrical and spectroscopy characterizations confirmed the spacing layer optimization.

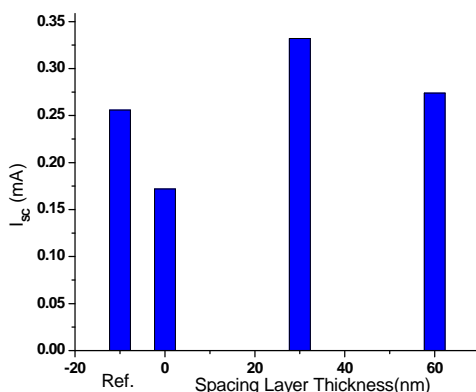


Fig.9: Electrical measurement for thin film LSCs as function of spacing layer thickness.

5. Concluding Remarks

We observed that a localized SPR phenomenon of Au NPs is responsible for both increased absorption and excitation rate of Lumogen Red dyes in thin film LSC. The excitation rate of luminescent species can be increased by placing the dye molecules in the range of enhanced localized electric field of Au NPs. It has been

verified that quenching of luminescence is a short range effect and weakens with distance much faster than the enhanced localized electric field. To achieve the largest possible enhancement, one must create a structure where the luminescent species are located in the range of optimum enhanced localized electromagnetic field of the metal nanoparticles. The development of plasmonic structures with controlled metal nanoparticles–luminescent species spacing opens the possibilities for plasmonic applications in the solar energy field.

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