Enhanced Light Emission Using Plasmonic Gold Nanoparticles

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Abstract/Introduction:

Gold nanoparticles with diameters of approximately 5-100 nm can exhibit localized surface plasmons, which are quantizations of oscillations in the electric field and charge distribution of the particles. We attempted to use such "plasmonic" nanoparticles to enhance the emission intensity of two phenomena: quantum dot fluorescence and light emission from metal-insulator-metal (MIM) tunnel junctions (TJs), as elaborated below.

(1) One goal of this project was to enhance the fluorescence of quantum dots, which hold promise for medical imaging, by taking advantage of the strong local electric field around metallic nanoparticles. In this project, enhancement was attempted using 50 nm gold nanoparticles, ~ 5 nm CdSe/ZnS quantum dots and a 10 nm SiO_2 spacer layer between the two to minimize fluorescence quenching. The intensity and rate of fluorescence was observed to increase by approximately two-fold.

(2) In a tunnel junction, electrons tunnel through a thin oxide layer placed between two metals with a potential difference. Lambe and McCarthy [1] observed light emission from Al/Al_2O_3/Au junctions roughened with the use of a MgF_2 layer, due to coupling of surface plasmons generated by tunneling electrons to light.

In this project, gold nanoparticles (Au-NPs) were investigated as a means of increasing the surface roughness of TJs to enhance light emission. Several Au-NP deposition methods were attempted, but in all cases the emission intensity was insufficient to obtain spectra before or after deposition. Nevertheless, unusual light emission characteristics were observed from TJs roughened with MgF_2.

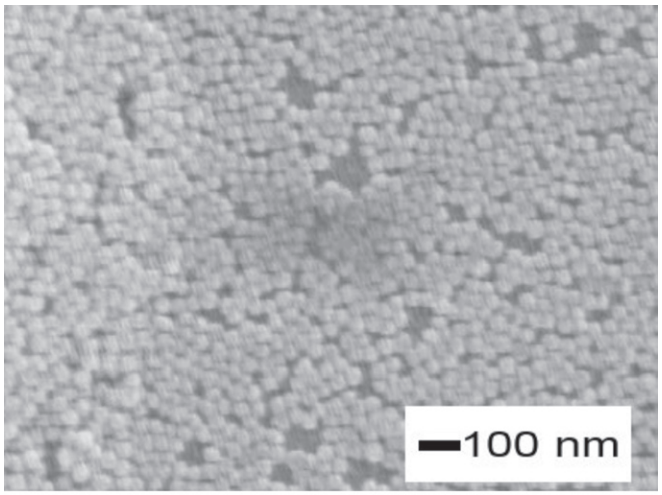

Figure 1: SEM of a 50 nm Au nanoparticle layer deposited by a droplet evaporation method.

Experimental Procedure:

To enhance quantum dot fluorescence, arrays of quantum dots and nanoparticles were built. First, cadmium selenide (CdSe)/zinc sulfide (ZnS) quantum dots with an absorption peak of 522 nm were spin-coated onto a glass slide. Next, a 10 nm spacer layer of silicon dioxide (SiO_2) was deposited on top of the previous layer using evaporative deposition. Finally, a layer of 50 nm gold nanoparticles (Au-NPs) was deposited using several different methods. The simplest successful method consisted of putting a droplet of Au-NPs in ethanol solution on the desired surface and evaporating the solvent quickly using a microwave oven. Figure 1 shows a scanning electron microscope (SEM) image of such a deposited layer (using 50 nm Au-NPs).

Fluorescence spectra were measured using a monochromator, photomultiplier tube (PMT) and a lock-in amplifier. The fluorescence rates were also measured in order to verify enhancement. To accomplish this, phase fluorometry was used: a blue (465 nm) light-emitting diode (LED) was modulated at frequencies of 1-5 MHz, and the phase shift between the modulated excitation light and the resulting fluorescence was used to calculate the fluorescence rate.

To test tunnel junction light enhancement, Al/Al_2O_3/Au TJs were constructed using the same procedure as Lambe and McCarthy [1]. 10 nm nanoparticles were deposited onto several TJs using two methods. In the first method, a droplet of nanoparticles in ethanol solution was simply placed onto the junction. The second method involved using a method developed by Pang et. Al [2] in which nanoparticles in poly-(dimethylsiloxane) (PDMS) form a monolayer on a water

interface. Other TJs were "roughened" by first evaporating a rough MgF_2 layer (with an rms period of ~ 100 nm) onto the substrate and constructing the TJ on top of this "roughened" substrate.

The junctions were connected to a voltage source, with a positive bias applied to the gold side, and light emission was observed. Light emission spectra were measured at different excitation voltage.

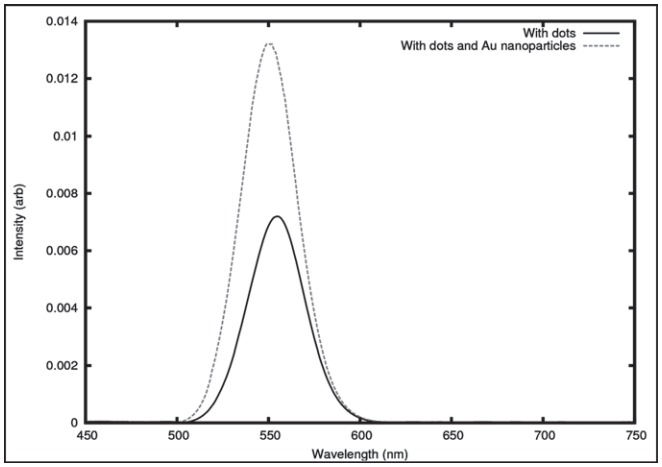

Figure 2: Fluorescence spectra of 522 nm CdSe/ZnS quantum dots (QDs) with and without 50 nm Au nanoparticles (Au-NPs) and a 15 nm spacer layer between the QDs and the Au-NPs.

Results and Conclusions:

Figure 2 shows fluorescence spectra of the quantum dots with and without the Au-NP layer. An approximately two-fold increase in fluorescence intensity is evident. Additionally, preliminary phase fluorometry results indicate that the fluorescence rate of the quantum dots increased from approximately 8×10^7 s^{-1} to approximately 13×10^7 s^{-1}, presumably due to increased coupling to the Au-NPs.

Measurement of tunnel junction emission enhancement was less successful; the intensity of the light outputs from "nominally" smooth junctions with Au-NPs was too low to measure reliably. However, as stated above, the brighter light emission obtained from junctions roughened with MgF_2 was easier to quantify with spectral measurements. Some of these junctions exhibited an interesting phenomenon; their light output intensity and spectra changed drastically as the excitation voltage increased to 4.1 V, as seen in Figure 3. However, the shape of the spectra characteristics did not revert back to the originally observed spectra when the voltages were subsequently lowered, suggesting a permanent change, possibly caused by heat or high current density.

Future Work:

Further enhancement of quantum dot fluorescence should be achievable by optimizing the SiO_2 spacer thickness or the type and sizes of quantum dots and Au-NPs used. Moreover improved theoretical models need to be developed.

Further methods of nanoparticle deposition on tunnel junctions should be evaluated in order to attempt to obtain spectra. In addition, the spectral shift observed on some junctions should be investigated in order to determine the structural changes involved.

Acknowledgments:

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References:

[1] Lambe, J. and McCarthy, S.L; "Light Emission from Inelastic Electron Tunneling"; Phys. Rev. Lett. 37, 923 (1976).

[2] Pang J. et. al; "Free-Standing, Patternable Nanoparticle/ Polymer Monolayer Arrays Formed by Evaporation Induced Self-Assembly at a Fluid Interface"; J. Am. Chem. Soc. 130, 3284 (2008).

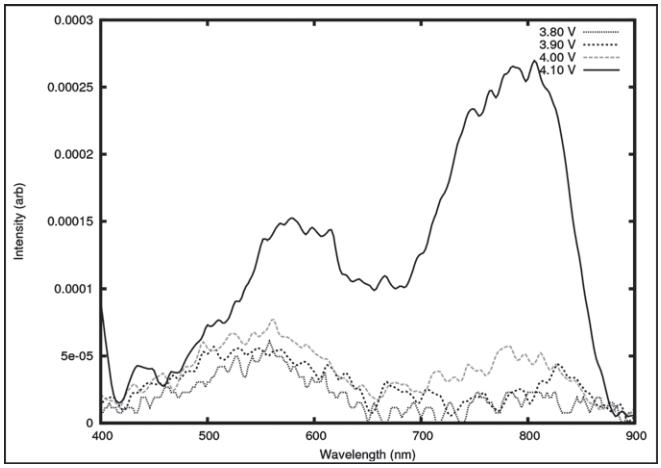

Figure 3: Emission spectra of a MgF_2 roughened Al-Al_2O_3-Au tunnel junction as a function of the voltage applied across the junction.