Surface Plasmon Enhanced Fluorescence Emission inside Metal Nanoshells

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Abstract: We study the surface plasmon enhanced fluorescence where an emitter is embedded in a metal nanoshell. Both simulation and experimental results are presented.

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The potential to locally enhance the excitation strength and increase the emission rate using metal nanostructures provides promising routes for creating ultra-bright fluorescence emitters[1]. Fluorescence control using a metal nanostructure is typically realized by attaching an emitter outside of the nanostructure[2]. This approach limits the flexibility of integrating the composite nanoparticle into a cellular system without perturbing cellular functions. In addition, it is difficult to precisely control the emitter location with respect to the metal surface to achieve a large fluorescence enhancement instead of quenching. To address this challenge, we study a new configuration in which the emitter is embedded in a dielectric core and enclosed in a metal nanoshell as shown in the inset of Fig 1(a). Because the electric field inside a metal nanoshell is relatively uniform, the placement of the emitter is not critical. To keep the emitter away from the metal surface, we use a genetically driven assembly approach to synthesize the nanoshell-emitter composite particle where the core radius and shell thickness can be precisely controlled. This approach ensures particle size uniformity, in contrast to previous approaches[3]. These nanoshell encapsulated emitters are expected to find important applications in the development of ultra-bright fluorescence labels, laser sources at the nanoscale, etc. In this paper, we report simulation results on the fluorescence emission of the nanoshell encapsulated emitters as well as experimental results on their synthesis.

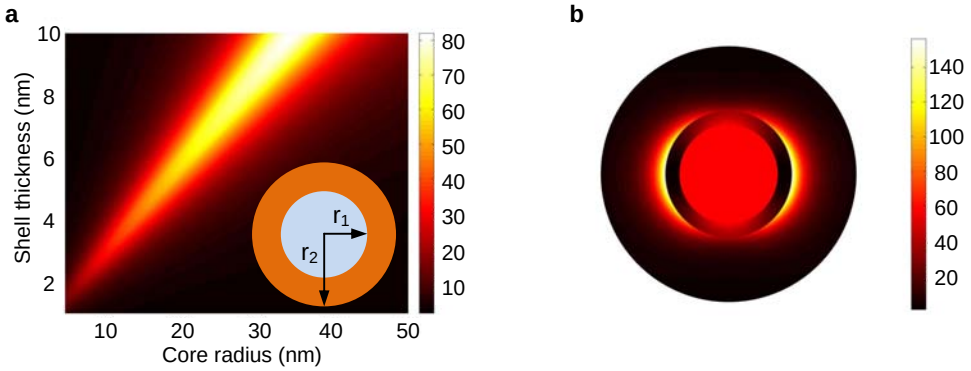

Fig. 1 (a) Internal field intensity enhancement versus core radius and shell thickness. The shell material is assumed to be gold with a modified dielectric function including the electron-surface scattering effect; the core material is assumed to have a refractive index as 1.46, and the excitation wavelength is 632 nm. The inset shows the schematic structure of the nanoshell. (b) Cross section of the field intensity distribution around a nanoshell with a core radius of 20 nm and shell thickness of 6 nm. (Excitation wavelength = 632 nm)

To maximize the light absorption of an emitter inside a nanoshell, it is desired to optimize the design of the nanoshell so that the resonant wavelength for internal field enhancement coincides with the absorption peak of the emitter, and then use a laser source at this particular wavelength for fluorescence excitation. In order to illustrate how to choose core radius and shell thickness, we use Alexa Fluora®633 from Invitrogen with an absorption peak at 632 nm as an example dye. The field intensity enhancement inside the nanoshell with 632-nm excitation as a function of core radius and shell thickness was calculated using the quasi-electrostatic theory[4] and shown in Fig. 1(a). It can be seen that there is a narrow region associated with strong field intensity enhancement, where the ratio between shell thickness and core radius is approximately 0.3. Figure 1(b) shows the field intensity cross section around a nanoshell with an optimized design (core radius: 20 nm, shell thickness: 6 nm). The field enhancement in

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the core region is not as high as that at the outside of the nanoshell near the metal surface. However, the electric field in the core region is much more uniform than that at the outside of the nanoshell, which decays rapidly with the distance from the metal surface. Therefore, when the emitter locates inside the nanoshell, it can still experience a substantial field enhancement while being kept away from the inner metal surface.

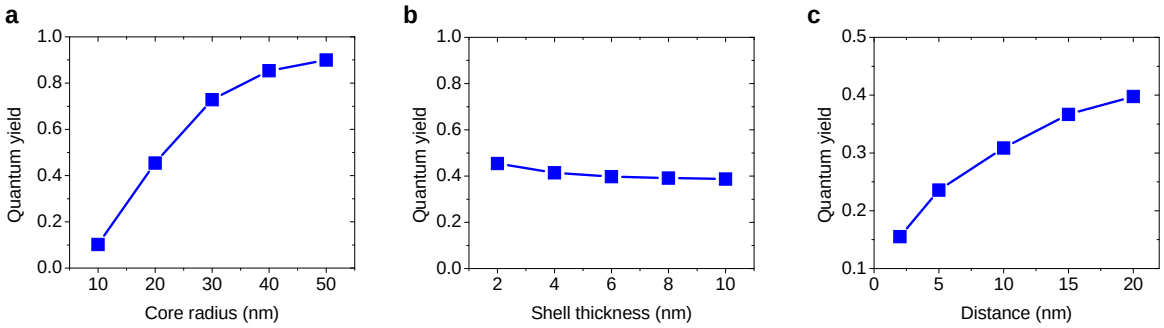

Fig. 2 (a) Quantum yield as a function of core radius when the shell thickness is fixed at 2 nm and the emitter locates at the center. (b) Quantum yield as a function of shell thickness when the core radius is fixed at 20 nm and the emitter locates at the center. (c) Quantum yield as a function of the distance from the emitter to the inner metal surface when the core radius is 20 nm and shell thickness is 6 nm.

Next we calculate the quantum yield of an emitter inside a nanoshell using finite-difference time-domain (FDTD) simulations. The fluorescence emitter is assumed to be an ideal electric dipole source, which has an infinitely small size and a radiative quantum yield of 1. In the simulation, we use two sets of detectors, which are closed surfaces on which the flux of the Poynting vector is integrated. One set of detector takes only the FDTD cell of the dipole source and it implements the calculation of total power radiated by the dipole P_{tot}. The other set of detector locates outside of the nanoshell and measures the power radiated into the far field P_{rad}. The difference between P_{tot} and P_{rad} represents the energy being absorbed by the metal shell. The quantum yield of the emitter-nanoshell complex can therefore be calculated by P_{rad} / P_{tot}. In Fig. 2(a) the quantum yield increases from 0.1 to 0.9 when the core radius increases from 10 nm to 50 nm while the shell thickness is kept at 2 nm. In Fig. 2(b) the quantum yield barely changes when the shell thickness increases from 2 nm to 10 nm while the core radius is kept at 20 nm. The comparison between Fig. 2(a) and (b) suggests that the main factor which influences the quantum yield is the distance from the emitter to the metal surface instead of the shell thickness. This conclusion is further supported by the result shown in Fig. 2(c), where the quantum yield decreases as the emitter approaches the inner metal surface.

The ratio of fluorescence signal with and without metal nanostructure in the low intensity illumination regime can be determined by $K \times (\eta/\eta 0)$, where K is the local field intensity enhancement leading to increased light absorption in the emitter, η and η_0 are the quantum yield with and without the presence of metal nanostructure, respectively[1]. When the product between K and (η/η_0) is larger than 1, the fluorescence is enhanced. Otherwise, the fluorescence is quenched. For an ideal emitter with the absorption peak at 632 nm and located at the center of the nanoshell with a core radius of 20 nm and shell thickness of 6 nm, the field intensity enhancement K is 60 and the ratio of quantum yield η/η_0 is 0.4. This predicts that the fluorescence detected in the far field is enhanced 24 times by encapsulating the ideal emitter in the nanoshell. Notice this is only the lower-bound estimate of the fluorescence enhancement since in reality the quantum yield of a fluorescence emitter is always smaller than 1.

Experimentally we synthesized the gold-nanoshell encapsulated quantum dot (QD) by attaching single QDs to hairpin RNA that directs the formation of icosahedra virus-like particles (VLPs) from 120 copies of a protein building block, thereby conjugating gold binding peptides on the VLP surface which results in the formation of single crystal gold-shell. Figure 3 shows the TEM image of such nanocomposite particles. Fluorescence measurements are ongoing and will be presented at the conference along with comparisons between simulation and experiment.

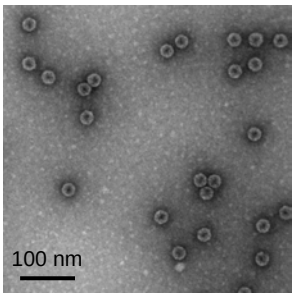

Fig. 3 TEM image of gold coated VLPs with CdSe QDs encapsulated.

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