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Distance-dependent metal enhanced fluorescence by flowerlike silver nanostructures fabricated in liquid crystalline phase

Ying Zhang [a, b], Chengliang Yang [a, *], Guiyang Zhang [a, b], Zenghui Peng [a], Lishuang Yao [a], Qidong Wang [a], Zhaoliang Cao [a], Quanquan Mu [a], Li Xuan [a]

[a] State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin, 130033, China

[b] University of Chinese Academy of Sciences, Beijing, 100049, China

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ABSTRACT

Flowerlike silver nanostructure substrates were fabricated in liquid crystalline phase and the distance dependent property of metal enhanced fluorescence for such substrate was studied for the first time. The distance between silver nanostructures and fluorophore was controlled by the well-established layer-by-layer (LbL) technique constructing alternate layers of poly (allylamine hydrochloride) (PAH) and poly (sodium 4-styrenesulfonate) (PSS). The Rhodamine 6G (R6G) molecules were electrostatically attached to the outmost negative charged PSS layer. The fluorescence enhancement factor of flowerlike nanostructure substrate increased firstly and then decreased with the distance increasing. The best enhanced fluorescence intensity of 71 fold was obtained at a distance of 5.2 nm from the surface of flowerlike silver nanostructure. The distance for best enhancement effect is an instructive parameter for the applications of such substrates and could be used in the practical MEF applications with the flowerlike nanostructure substrates fabricated in such way which is simple, controllable and cost-effective.

1. Introduction

Metal enhanced fluorescence (MEF) is an approach for enhancing the fluorescence intensity of probe molecules nearby the metallic surfaces [1–3]. It is a complex phenomenon combined the effects of enhancement in the emission intensity and quenching of the probe molecules emission. The enhancement is due to the enhanced excitation and radiative decay rate which is induced by the metal nanostructures [1,3]. The quenching of the probe molecules emissions is due to the fact that nonradiative energy transfers to the metal. The probe molecules nearby metallic nanostructures experience enhancement and quenching depend on distance between metallic nanostructures and probe molecules. The distance dependent metal enhanced fluorescence has been theoretically and experimentally studied [4,5]. Lakowicz et al. bound the fluorophores on the 7 nm thick cell membranes, resulting fluorescence signals were enhanced significantly by silver islands films (SIF), while the fluorophores intercalated in the cell nuclei were not influenced significantly by SIF [6,7]. Ginger et al. controlled the distance between silver nanostructures and fluorophores by changing the bond length of complementary deoxyribonucleic acid sequences, and the fluorescence emission intensity was enhanced 13 fold rather than 7 fold with the silver nanostructures without complementary deoxyribonucleic acid sequences [8]. Lakowicz et al. employed multilayer polyelectrolyte of PSS and PAH nanostructures to control the distance. When the distance was 9 nm, the fluorescence intensity was enhanced for 6 fold. However, when the distance was 30 nm, the enhancement was decreased to 1.5 fold [9]. And also, some publications show that the optimal distance should be as large as 60 nm [10]. From above studies we can see that the appropriate distance at which the fluorescence enhancement is the best varies depending on the morphology, shape and size of metallic nanostructures. More and more researchers devoted to flowerlike nanostructure substrates' study owing to its highly effective surface enhanced effects. So far, there are many studies about the best effective distances of silver nanoparticles and silver islands, but there are still little studies about such kind flowerlike silver nanostructure substrate which is a good candidate in the field of MEF. The study of appropriate distance for flowerlike silver nanostructures is still needed especially for applications such as

* Corresponding author.
E-mail address: ycldahai@ciomp.ac.cn (C. Yang).

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optical imaging, biotechnology and material detections [11–14].

In this work, highly effective surface-enhanced fluorescence substrates with roughened 3D flowerlike silver nanostructures were fabricated by electrodeposition in liquid crystalline template which is stable, simple, controllable, reproductive and cost-effective. Comparing with the silver colloid nanostructures, flowerlike silver nanostructures on substrates are more stable because the silver colloid nanostructures are easy to aggregate under light or heating conditions which vastly influences its applications in optics and material detection. The existing fabrication processes of flowerlike nanostructure substrates in former work are either complicated with expensive machines or instable, while our method needs only one step and very simple machines. We studied the distance-dependent property of MEF from R6G assembled on our flowerlike silver nanostructured substrates using the polyelectrolyte LbL assembly to control the distance from R6G to nanostructures for the first time. In the LbL assembling process, PAH (polycations) and PSS (polyanions) from dilute aqueous solution were sequentially adsorbed onto our silver flowerlike nanostructure substrates by electrostatic interaction. We choose R6G as the fluorophore to investigate the MEF effect which is a kind of very common fluorescence dye in the research field of metal enhanced fluorescence and also be used as laser dye. In order to ensure that the quality of the assembled layers is good, absorption spectra of the assembled layers were measured. And the emission spectra of R6G were also measured. The study shows that fluorescence enhancement factor of flowerlike nanostructure substrate compared with glass substrate experienced an increasing firstly and then decreasing as the distance increases. The best enhancement effect was obtained at the distance of 5.2 nm, which is an instructive parameter for the future applications of such substrates and should be considered in all MEF applications similar in this work.

2. Theory

Fluorescence is a character for a material to absorb light at a wavelength and emit light of longer wavelength, which is due to the radiative relaxation from an electronically excited state [1]. The process includes two parts which are absorption and emission of light. The two aspects were quantified by excitation efficiency and fluorescence quantum yield, respectively. According to the Jablonski diagram, the final fluorescence emission intensity is determined by the product of these two factors mentioned above. Excitation efficiency is influenced by the intensity of excitation light and fluorescence quantum yield (Q_o) is determined by the radiative (Γ) and nonradiative decay rates (k_{nr}) [1] which can be described by

$$Q_o = \frac{\Gamma}{\Gamma + k_{nr}}. \tag{1}$$

Metal enhanced fluorescence is an approach for enhancing the fluorescence intensity of fluorophores nearby the metallic surfaces which is due to the localized surface plasmon resonance from the collective oscillation of electrons. The fluorescence enhancement can then be described by

$$\frac{\gamma_{em}}{\gamma^o_{em}} = \frac{\gamma_{exc}}{\gamma^o_{exc}} \frac{Q}{Q_o} \tag{2}$$

where γ_{em} and γ^o_{em} are the fluorescence rates of a single molecule with and without metal nanostructures, respectively. γ_{exc} and γ^o_{exc} are the excitation rates with and without metal nanostructures, respectively. γ_{exc} is proportional to $|\mathbf{E}\cdot\mathbf{p}|$, in which $\mathbf{E}$ is the local electric field and $\mathbf{p}$ is the transition dipole moment. Q and Q_o are the quantum yields with and without metal nanostructures, respectively. Q can be expressed as

$$Q = \frac{\Gamma + \Gamma_m}{\Gamma + \Gamma_m + k_m + k_{nr}} \tag{3}$$

where Γ_m and k_m are additional radiative and nonradiatvie decay rates of the excited molecule in the presence of metal nanostructures. In summary, the enhancement effect could be attributed to three competing effects: (1) local field enhancement on the surface of metal nanostructures enhanced the excitation rate leading to enhanced excitation efficiency. (2) surface plasmon-coupled emission from coupling of the fluorescence emission with the metal nanostructures causes increase of radiative decay rate (Γ_m), which leads to the increased quantum yield. (3) the non-radiative energy transfer from the fluorophores to metal nanostructures leading to increased non-radiative decay rate (k_m) which results in fluorescence quenching [1,2,15,16]. These three effects fall off when the distance between fluorophore and metal nanostructure increases. According to studies before, the non-radiative energy transfer effect dominates at the surface and drops off with inverse third power of distance, while the local field effect decays exponentially from the surface [15]. Therefore, an appropriate distance can be found at which the enhancement of local field and the quenching effect could achieve a balance to realize the best fluorescence enhancement effect.

3. Experimental methods

3.1. Materials

Anionic surfactant sodium bis (2-ethylhexyl) sulfosuccinate (AOT) (98wt %), oil phase p-xylene (99wt %), silver nitrate (99wt %) and PSS were from Sigma-Aldrich. PAH and Silver foil (2.0 mm 99%) were obtained from Alfa Aesar. Cysteamine (95wt %) was obtained from Macklin. R6G was purchased from J&K (China). Deionized water was obtained from the Millipore Elixir 100 and the resistivity is over 18MΩ·cm. All of the materials were used as received.

3.2. Preparation of flowerlike silver nanostructure substrates

In the past decades, lyotropic liquid crystal have been investigated because of its remarkable effects on structure and morphology of desired nanomaterials [17,18]. Flowerlike silver nanostructures grown on the ITO glass by means of electrodeposition in liquid crystalline phase was reported previously by us [19]. The liquid crystalline phase was prepared according to the ternary phase diagram [20] consisting of AOT, oil phase of p-xylene and water which was replaced by $AgNO_3$ aqueous solution for the growth of silver flowers. In the electrodeposition process, a silver foil was mounted as the anode with an indium tin oxide (ITO) glass ($15 \times 40\ mm^2$) whose surface was very smooth was mounted as the cathode to collect the flowerlike silver structure. And the liquid crystalline phase was used as the electrolyte. The applied 3.0 V potential was controlled by a DC voltage-stabilized power supply. After the deposition, the negative electrode ITO glass was softly washed by ethanol and dried by a gentle flow of N_2.

3.3. Adsorption of polyelectrolyte layers and R6G

Negatively charged PSS and positively charged PAH were used as the spacers between nanostructures and R6G. It was realized through layer by layer assembling owing to electrostatic interaction between oppositely charged polyelectrolytes. Cysteamine was used to functionalize the silver nanostructure substrates with amines and positively charge the substrates before PSS/PAH multilayer