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Solution-based metal enhanced fluorescence with gold and gold/silver core–shell nanorods

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ABSTRACT

Metal enhanced fluorescence of Oxazine720 fluorophore with gold and gold/silver core–shell nanorods is investigated experimentally in aqueous solution system. Metallic nanorods are synthesized for providing proper localized surface plasmon resonance and necessary enhancement to the fluorophore molecule. The experimental observation shows that the fluorescence enhancement increases firstly and then decreases when the concentration of metallic nanorods increases, which is resulted by the competition between enhanced emission and inner-filtering effect. Further investigation with different amounts of metallic nanorods shows that the relationship between metal enhanced fluorescence and spectral correlation strongly depends on the concentration of metallic nanorods.

1. Introduction

Fluorescence emission can be enhanced when fluorophores are around noble metallic nanostructures and under proper light excitation. This phenomenon is known as metal enhanced fluorescence (MEF) or surface enhanced fluorescence (SEF) [1–3]. The previous study suggests that the MEF originates from the near-field interaction between the fluorophore and localized surface plasmon resonance (LSPR) of metallic nanostructure [4–7]. It is generally accepted that spectral correlation between metallic substrate and fluorophore plays an important role in the MEF effect. The proper overlap of LSPR with excitation spectrum of fluorophore can effectively increase the fluorophore excitation efficiency due to local field enhancement effect [8,9], while the overlap of LSPR with the fluorophore emission may alter the quantum yield by changing the radiative and nonradiative decay rates [10]. Therefore, an optimized MEF effect might be obtained by tuning the overlap of LSPR with excitation or emission of the fluorophore molecule [10–14]. In a solution-based system, the dependence of MEF intensity on the distance between metallic nanoparticle and fluorophore has been studied [15–17], but the relationship between MEF and spectral correlation is barely reported [18]. It is noticed that gold/silver nanoparticles with a spherical shape are frequently used as enhancement substrates in MEF, for which the tuning ability in LSPR is poor. M.D. Furtaw investigated the MEF with silver nanoparticle solution, where four kinds of fluorophores with different overlaps between absorption/or emission and LSPR were employed [19]. A negative relationship between fluorescence enhancement and spectral overlap was demonstrated at high concentration of silver nanoparticles, but the influence of the fluorescence quantum yield was not considered, which may have a significant impact on the MEF.

In current work, MEF of gold (Au) and gold/silver (Au/Ag) core–shell nanorods (NRs) is studied with Oxazine720 as fluorescence emitters. It is found that with tunable longitudinal LSPR in a large range, Au and Au/Ag core–shell NRs can provide different kinds of overlap between LSPR and emission of Oxazine720. The relationship between MEF and spectral correlation is also investigated systematically with various metallic nanoparticle concentrations.

2. Experimental details

2.1. Sample preparation

Gold chloride tetrahydrate ($HAuCl_4 \cdot 4H_2O$) and silver nitrate ($AgNO_3$) were purchased from Shanghai Chemical Reagent Co. Cetyltrimethylammonium bromide (CTAB), sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH), ascorbic acid and glycine were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All reagents were used without further purification. Deionized water was used throughout the experiment.

A modified seed-mediated growth method was used to prepare Au nanorods [20,21]. The precipitates were divided into three

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equal parts due to the requirement of the experimental study. One part was diluted into deionized water that was denoted as Au NRs, the other two parts were redispersed in CTAB solution for the preparation of Au/Ag core–shell NRs.

Au/Ag core–shell nanorods were fabricated with chemical reduction of $AgNO_3$ on Au nanorod surface according to the reported method with minor modification [22]. To begin with, 17.8 ml of 0.4 M glycine buffer solution at pH=8.5 (adjusted with NaOH solution) was mixed with the prepared CTAB solution containing Au nanorods under vigorous stirring. Then 400 μl of 0.01 M $AgNO_3$ was added to the solution, and followed by injecting 200 μl of 0.1 M ascorbic acid to start the reduction. The reaction was fulfilled in 50–60 min. After centrifugation, the core–shell nanorods solution was prepared with deionized water, denoted as Au@Ag NRs1.

Au/Ag core–shell nanorods with different longitudinal LSPR can be fabricated by following the same procedure with adjustment of the amount of $AgNO_3$ and ascorbic acid [23]. In this part, 1200 μl $AgNO_3$ and 600 μl ascorbic acid were used to obtain bimetallic nanorods that were denoted as Au@Ag NRs2.

To investigate MEF of Oxazine720 with metallic nanorods, a certain volume of Au NRs, Au@Ag NRs1 and Au@Ag NRs2 solutions were injected into Oxazine720 molecule solution (5.0×10^{-7} mol/L). The same volume of water without any nanorods was also added into the Oxazine720 molecule solution to get a reference system for the enhancement study. In order to homogenize the mixed solution of fluorophore and metallic NRs, an ultrasonic process was applied for the sample before each MEF measurement.

2.2. Characterization

The size and morphology of the synthesized nanoparticles were measured with a JEOL 2100 transmission electron microscope (TEM) at 200 kV. UV–visible absorption spectra were obtained by using a UV–vis spectrophotometer (Hitachi, U-3010). Fluorescence spectroscopic measurements were performed with a spectrometer (Acton, SP2750i) coupled with CCD (Acton, PIXIS100) system. A CW laser with 325 nm output was used as excitation source. The fluorescence emission was collected in a direction that is perpendicular to the excitation laser beam. Also, a properly selected long-pass filter was used to block the scattering light. All the spectroscopic measurements were conducted at room temperature.

3. Results and discussion

3.1. Morphological and optical property of metallic NRs

TEM images of Au NRs, Au@Ag NRs1 and Au@Ag NRs2 are presented by Fig. 1(a)–(c). It can be seen that Au nanorods have a "dog bone" shape with an average length of 62.8 ± 4.7 nm, end-cap diameter of 19.8 ± 2.1 nm, and central diameter of 17.4 ± 1.6 nm. As illustrated by Fig. 1(b) and (c), the overall nanorod turns into a regular cylinder shape after the silver coating. The final dimension of Au@Ag NRs1 is 64.2 ± 5.0 nm in length and 22.3 ± 2.3 nm in width, which has an aspect ratio of 2.9 ± 0.3. While for Au@Ag NRs2, the length is 72.4 ± 7.4 nm and the width is 28.7 ± 3.5 nm, its aspect ratio is 2.6 ± 0.3.

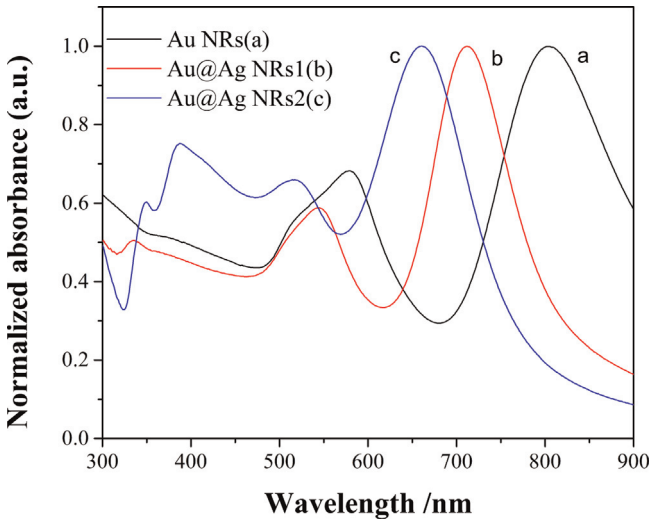

Fig. 2. Normalized absorption spectra of metallic NRs. (a) Au NRs, (b) Au@Ag NRs1, and (c) Au@Ag NRs2.

Normalized UV–visible absorption spectra of metallic nanorod solution are shown in Fig. 2. Au NRs have a longitudinal plasmon absorption band centered at around 805 nm and some transverse plasmon absorptions at shorter wavelength side. For transverse plasmon absorption band, an unexpected spectral broadening is observed that may be resulted from the non-rod-like nanoparticles including the square-shape nanoparticles as shown in Fig. 1(a) [24,25]. The longitudinal plasmon absorption bands of Au@Ag NRs1 and Au@Ag NRs2 sit at 712 nm and 661 nm respectively, which are blue-shifted comparing with that of Au NRs. It is also noticed that except for the regular longitudinal and transverse plasmon bands, some additional absorption bands at 335 nm for Au@Ag NRs1, 350 nm and 388 nm for Au@Ag NRs2 are also appeared in the spectra of Fig. 2. These spectral features are considered as typical for Au/Ag core–shell nanorods according to the study of Refs. [23,26].

3.2. Fluorescence enhancement with Au and Au@Ag NRs

The fluorescence enhancement of Oxazine720 with Au and Au@Ag NRs is studied in solution system with excitation at 325 nm. The corresponding fluorescence emission spectra observed experimentally are shown in Fig. 3(A), in which the obvious

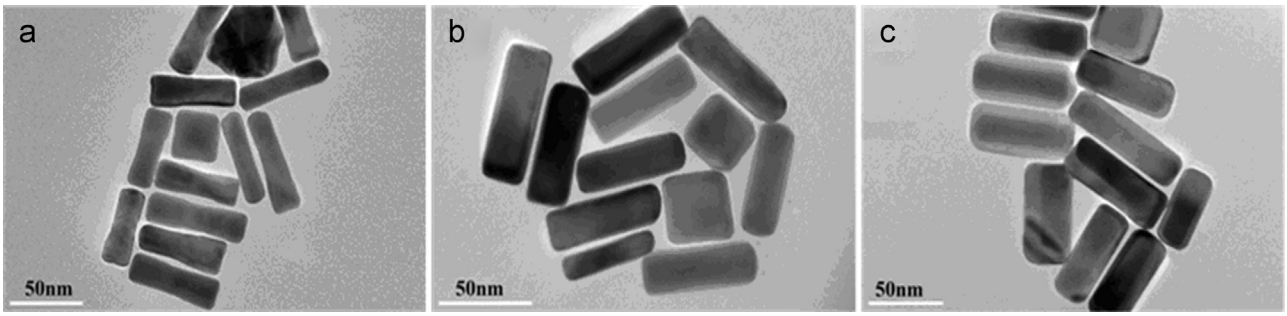

Fig. 1. TEM images of metallic nanorods. (a) Au NRs, (b) Au@Ag NRs1, and (c) Au@Ag NRs2. The scale bar corresponds to 50 nm.