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Distance dependent fluorescence enhancement of silver nanowires deposited on AAO

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ABSTRACT

Metal nanoparticls deposited on substrate are usually used for the enhancement of fluorescent molecules. In this article, AAO template was introduced into the reaction solution during the preparation of silver nanowires. Then the AAO template with deposited silver nanowires was suspended in RhB solution to study its fluorescence enhancement effect. The results showed that the uneven surface of AAO template caused a series of distances between silver nanowires and RhB molecules which were happen to be below 10 nm that can effectively enhance the fluorescence of RhB solution. Our research is helpful to the study of fluorescence enhancement of metal nanostructures deposited on substrate.

1. Introduction

Metal - enhanced fluorescence has attracted significant attention recent years due to their effective fluorescence enhancement based on surface Plasmon effect [1–7], therefore has tremendous potential applications in medical detection, biosensors, spectroscopy and so on [8–12]. In addition to the metal surface plasmon effect, the morphology of nanoparticles [13,14], the distance between the fluorescent molecules and the surface of metal nanoparticles also play an important role in the fluorescence enhancement of fluorescent molecules [15–17]. The direct adsorption or bonding of fluorescent molecules on the surface of metal nanoparticles could have fluorescence quenching due to the non radiative energy transfer between the excited state and the metal. However the energy transfer can be eliminated when the distance between the molecules and metal is far enough. Meanwhile the fluorescent molecules can still be affected by the electromagnetic field enhanced by the metal nanoparticles, and thus achieve the enhancement of the fluorescence. Therefore, the distance between the fluorescent molecules and metal nanoparticles has a great influence on the fluorescence enhancement of the fluorescent molecule. Based on this, recent years, some core-shell structures such as $M@SiO_2$ structures were widely fabricated to study the effect of distance on fluorescence enhancement [18–22]. In these core-shell structures, SiO_2 is usually coated on the surface of noble metal and thus forms a certain distance between the metal nanoparticles and dye molecules. By controlling the thickness of SiO_2 layer, the fluorescence enhancement of fluorescence molecules can be obtained.

In the above study, the distance between the metal and the fluorescent molecules was mostly achieved by the thickness of the shell in the core-shell structures. The maximum enhancement of the fluorescent species was achieved by adjusting the thickness of the shell. However the preparation of core-shell structures and the adjustment of the thickness of the shell bring some complexity to the application of fluorescence enhancement.

In this article, silver nanowires were prepared using a simple solvothermal method with the assist of AAO template [23]. Silver nanowires were prepared in the solution and directly formed on the surface of AAO template. Then AAO template as a substrate with deposited Ag nanowires was suspended in rhodamine B (RhB) solution to study the fluorescence enhancement. The unique concave and convex structure of the AAO surface formed a series of distances between the silver nanowires and RhB dye molecules, and thus effectively enhanced the fluorescence effect of RhB.

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2. Material and methods

2.1. Materials

Silver nanowires were prepared by solvethermal method using DMF to reduce $AgNO_3$ with the assistance of AAO. We have reported the preparation method in detail in Ref. [23]. Anodic Aluminum oxide (AAO, Andisc 25 with pore diameter 200 nm) was obtained from Whatman International Ltd. The used fluorescent molecule is rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$, analytical pure), Sinopharm Chemical Reagent Co., Ltd., reagent, without any purification treatment.

2.2. Characterization methods

UV–Vis absorption spectra (UV-1601, Shimadzu Corporation) were used to characterize the UV–Vis absorption properties of dye RhB solutions. The fluorescence spectra of AAO substrate with deposited silver nanowires were measured by fluorescence spectrophotometer (RF-5301PC, Shimadzu Corporation). The morphologies of AAO template and silver nanowires were observed by Hitachi S4800 field emission scanning electron microscope (FE-SEM), made in Japan.

3. Experimental

To prepare the silver nanowires on AAO template, $AgNO_3$ is reduced by DMF in a solvethermal method with a piece of AAO template added in the reaction solution [23]. After the reaction, AAO template was removed from the reactor kettle, and was washed with distilled water several times. Silver nanowires formed directly on the surface of AAO during the preparation. In this work, a blank glass substrate with deposited Ag nanowires was also used in the contrast experiment. A certain amount of silver nanowires prepared in the same reaction were deposited onto the blank glass substrate uniformly. The samples were dried sufficiently to remove the alcohol from the sample. Then AAO template and glass substrate with deposited silver nanowires were suspended into RhB solution to study the fluorescence enhancement properties of RhB. RhB dye solution with uniform concentration of 0.01 mM, 0.1 mM and 1.0 mM were prepared in order to select the most suitable concentration. The solvent of RhB dye solutions is distilled water.

4. Results and discussion

4.1. The optical propeties of RhB

The molecular structure of RhB is shown in Fig. 1. RhB molecules usually show self-quenching in the resonant energy transfer process. This resonant energy transfer is related to the distance (r) between the donor and acceptor. The greater the concentration of the donor and receptor, the smaller the r value and the greater the efficiency of resonance transfer. Therefore, with the increased concentration of biomarkers in the process of detection, the fluorescence intensity decreased gradually. If it is used in a low concentration range, the detection sensitivity will be low due to the weak fluorescence intensity. In order to select the proper RhB concentration and suitable excitation wavelength, the optical properties of RhB were analyzed firstly. Three different concentration of 0.01 mM, 0.1 mM and 1.0 mM of RhB solution were prepared and the UV–Vis absorption spectra were determined in Fig. 2.

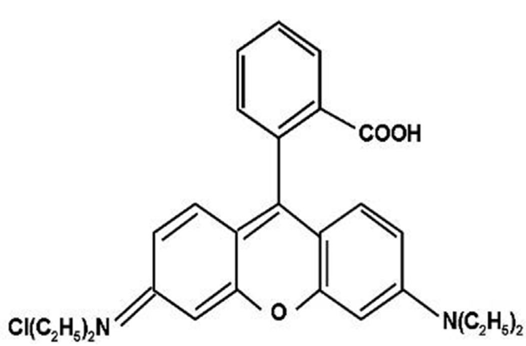

Fig. 1. The molecular structure of RhB.

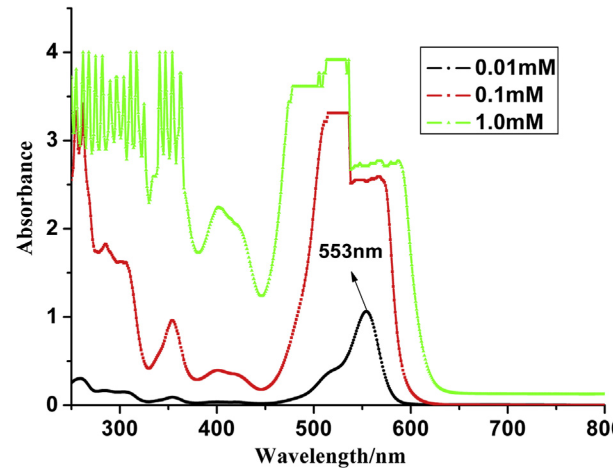

Fig. 2. UV–Vis absorption spectra of RhB solutions with different concentrations.

We can see that with the increase of RhB concentration, the UV–Vis absorption increases gradually. When the concentration of RhB is 0.01 mM, the maximum absorption occurs at about 553 nm. When the concentration increases to 1.0 mM, many interference peaks appear in the absorption curve, while the accurate absorption peak cannot be obtained. In our experiment, we found that RhB solution with high concentration (1.0 mM) is easily quenched which is ascribed to the collisions among the dye molecules, resulting in the energy loss and fluorescence quenching. The fluorescence intensity of RhB solution with high concentration is very low. So in this article, we chose high concentration (1.0 mM) in order to observe effective fluorescence enhancement and offset the effect of fluorescence quenching, and thus to prove the effective enhancement of our materials. Therefore, in the following fluorescence enhancement measurements, the concentration of RhB is chosen to be 1.0 mM. Fig. 3 shows the fluorescence emission spectrum of RhB (1.0 mM) solution at different excitation wavelengths.

It can be seen that the fluorescence peak is mainly distributed between 616 nm and 630 nm. As the excitation wavelength increases, the

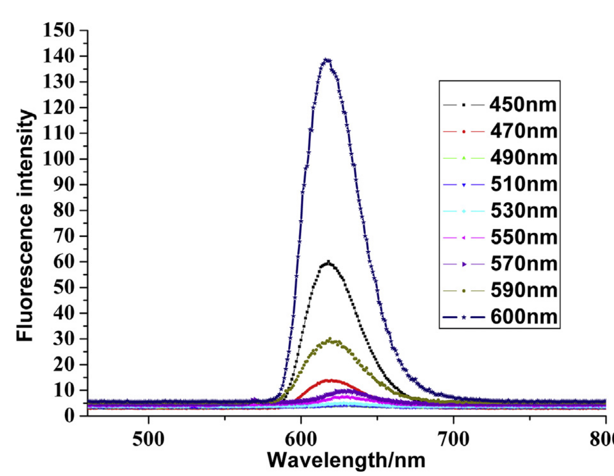

Fig. 3. Emission spectra of 1.0 mM RhB solution excited at various wavelength.

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