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Using silicon-coated gold nanoparticles to enhance the fluorescence of CdTe quantum dot and improve the sensing ability of mercury (II)

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ABSTRACT

The effect of silicon-coated gold nanoparticles with different gold core diameter and silica shell thickness on the fluorescence emission of CdTe quantum dots (QDs) was investigated. For gold nanoparticles with a diameter of 15 nm, silica coating can only result in fluorescence recovery of the bare gold nanoparticle-induced quenching of QDs. However, when the size of gold nanoparticle is increased to 60 nm, fluorescence enhancement of the QDs could be obtained by silica coating. Because of the isolation of the silica shell-reduced quenching effect and local electric field effect, the fluorescence of QDs gets intense firstly and then decreases. The maximum fluorescence enhancement takes place as the silica shell has a thickness of 30 nm. This enhanced fluorescence from silicon-coated gold nanoparticles is demonstrated for sensing of Hg²⁺. Under optimal conditions, the enhanced fluorescence intensity decreases linearly with the concentration of Hg²⁺ ranging from 0 to 200 ng/mL. The limit of detection for Hg²⁺ is 1.25 ng/mL. Interference test and real samples detection indicate that the influence from other metal ions could be neglected, and the Hg²⁺ could be specifically detected.

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1. Introduction

In recent years, much attention has been focused on the modulation of fluorescence emission from dye molecule or quantum dots (QDs) using noble metallic nanoparticles [1,2]. The main physical origin is based on the non-radiative energy transfer-induced fluorescence quenching or local field effect-induced fluorescence enhancement [3,4]. Because of the localized surface plasmon resonance (LSPR), which is kind of collective oscillation of conduction-band electrons on the particle surface, gold and silver nanostructure can concentrate optical electromagnetic field into subwavelength regions close to the surface of the particles [5]. Thus intense resonance light absorption and local electric field enhancement could be generated. When a single quantum emitter, such as a fluorescent dye molecule or a quantum dot, is coupled to a plasmonic nanostructure, the resonance absorption-induced quenching and local field effect-induced enhancement will greatly affect the fluorescence emission [6,7].

In the competition between non-radiative energy transfer-induced quenching and local field effect-induced fluorescence enhancement, the distance between the metal surface and fluorescent emitter plays an important role in tuning the fluorescence intensity [8–11]. When the fluorescent emitter is directly contacted with the metal particle, the nonradiative decay is the dominating effect and the fluorescence

quenching occurs [12,13]. Whereas when the distance between the metal surface and fluorescent emitter has been enlarged, the nonradiative energy transformation-induced quenching fades down rapidly, and then the local field enhancement will take the dominating effect and the fluorescence enhancement occurs. However, the local field enhancement is also a kind of local effect, thus the fluorescence enhancement will be weakened as the distance is too large [14]. Therefore, the maximum fluorescence enhancement only takes place when the distance has an appropriate value. In order to modulate the distance between the fluorescent emitter and metal surface, a dielectric separate layer, such as a silicon shell, has been coated on the metal nanoparticles [15]. In the report of Jia et al., Au/Ag@SiO₂ nanoparticles with different silica layer thicknesses have been used to modulate the emission of CdSe/CdS quantum dots [16]. Their experimental results demonstrated that the fluorescent emission of CdSe/CdS QD can be either obviously quenched or enhanced, depending on the spectral overlap and local distance control between QDs and Au/Ag nanoparticles. Using the dye-doped silica-coated silver nanoparticles with shell thicknesses ranging from 8.6 to 75.4 nm, Blake-Hedges et al. studied the plasmon-enhanced fluorescence [17]. It has been found the fluorescence enhancement is positively correlated to the dye-metal distance, with ~19 nm separation producing the greatest fluorescence enhancement. In the report of Niu et al., silica-coated gold nanobipyramids with distance-dependent plasmon-enhanced fluorescence has been studied and been applied in biologic sensing [8]. In their study, silica shell was chosen as the rigid spacer to regulate the distance between the metal surface and dyes. Maximum fluorescence enhancement was observed at a distance of approximately

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17 nm. Recently, silica-shell isolated Au-Ag alloy nanoparticle has also been used for investigating the metal-enhanced fluorescence effect [3]. They found the fluorescence enhancement effect is separation-layer sensitive, and the optimal phenomenon occurs for the surface enhancement effect when the shell thickness is at around 8 nm.

Besides the separation distance, the size of metal particle and the overlap between the emission spectrum and LSPR also greatly affect the fluorescence modulation [18–20]. In the study of Lin and Chen, varied sizes of gold nanoparticles with controlled thickness of silica shell were synthesized to investigate the effects on metal-enhanced fluorescence of rose bengal fluorophores [11]. The maximum fluorescence enhancement factor is 2.4, 3.8, 4.6, and 5.5 at spacer separation ~10 nm when the diameters of silica-coated gold nanoparticles are 45, 65, 80, and 100 nm, respectively. Thus, the fluorescence enhancement could be obtained more easily when the gold core has a larger size. Could fluorescence enhancement always be observed from gold nanoparticles by silica coating? The spectral overlap between the emission bands of the fluorophores and the plasmon band of the metal nanoparticles is the other important factor affecting the intensity of fluorescence. A strong correlation between the fluorescence intensity of the emitter and the degree of spectral overlap with the LSPR of the metal nanoparticle has already been observed [19]. Thus the metal nanoparticles or fluorescence emitter with tunable peak wavelength contributes to the spectral overlap of the emission of fluorophore with the absorption of the metal nanoparticle. QDs have size-dependent fluorescence emission wavelength. Therefore, by changing the particle size, we can obtain suitable fluorescence wavelength to match the LSPR of metal nanoparticles in this study.

Ultra-sensitive Hg^{2+} detection based on fluorescent QDs is also a hot topic in recent years [21–25]. In these detection methods for Hg^{2+} , the fluorescence of QDs can usually be quenched by Hg^{2+} through an effective electron energy transfer process. The mechanism of the remarkable quenching effect of Hg^{2+} could be attributed to the electron transfer process between the capping ligands and mercury ions, and the non-radiation recombination of holes and excitation electrons [21,26]. The detection limit and linear range depend on the fluorescence intensity decrease of the QDs. So we think, could the detection sensitivity be improved by increasing the fluorescence intensity of the QDs? In this paper, by using gold nanoparticles with large diameter and optimal silica shell thickness, and CdTe QDs with appropriate size and wavelength, which is coupled with the SPR of silica-coated gold nanoparticles, the enhanced fluorescence of CdTe QDs has been obtained. Then this enhanced fluorescence has been used to detect Hg^{2+} , which improves the quenching range and the corresponding sensing ability. This fluorescent probe based on silica-coated gold nanoparticles could be used for selective detection of Hg^{2+} with a linear range of 0–200 ng/mL and a detection limit of 1.25 ng/mL.

2. Experimental

2.1. Materials and Chemicals

Chloroauric acid (HAuCl_4) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Sodium citrate, Te powder, cadmiumchloride, sodium hydroxide, sodium borohydride, tetraethyl orthosilicate (TEOS) and (3-aminopropyl)-trimethoxysilane (APTES) were obtained from Aladdin Industrial Corporation. 16-mercaptohexadecanoic acid (MHA) was purchased from Sigma. Anhydrous ethanol was purchased from Tianjin Hedong Hongyan Reagent Factory. Dimethylamine (40 wt%) was obtained from Tianjin Kemiou Reagent Co., Ltd. 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) was purchased from Bio Basic Inc.. N-hydroxysuccinimide (NHS) was purchased from Beijing lark technology Co., Ltd. All chemicals used in this work were analytical grade and deionized water (18.0 $\text{M}\Omega \cdot \text{cm}$) was used throughout the experiments.

2.2. Synthesis of Citrate-Stabilized Gold Nanoparticles

Gold Nanoparticles were synthesized using the seeded growth method according to the literature with a slight modification [27]. Firstly, we prepared the Au seeds. Typically, 150 mL 2.2 mM sodium citrate was heated to boiling under vigorous stirring. Then 1 mL HAuCl_4 (25 mM) was injected. The colour of the solution changed from yellow to soft pink and then to wine red. Afterwards, deionized water was added to make the whole volume of the solution 150 mL. Immediately after the synthesis of the Au seeds, the seeds solution was heated to boiling in the same process, then 1 mL 25 mM HAuCl_4 solution was added into the boiled seeds solution. After 15 min, another 1 mL 25 mM HAuCl_4 solution was added, and the reaction was finished after 15 min. After that, the sample was diluted to 152 mL using deionized water. Afterwards, a new seeds solution was synthesized by extracting 55 mL of the above sample and adding 53 mL deionized water and 2 mL 60 mM sodium citrate. Then the whole process was repeated again. Greater sizes of Gold Nanoparticles were obtained by addition of the times of the seeded growth.

2.3. The Preparation of Silicon-Coated Gold Nanoparticles

Au@SiO_2 NPs were synthesized via a modified method reported [28]. Typically, 10 mL freshly prepared gold nanoparticles were centrifuged and redispersed in 10 mL deionized water. An ethanolic solution of MHA (400 μL , 4 mM) was added into the colloidal solution, and the mixture was reacted for 15 min under vigorous stirring. The obtained solution was then centrifuged and resuspended in 10 mL anhydrous ethanol. Subsequently, the TEOS in anhydrous ethanol (10 wt%) was added followed by the addition of dimethylamine (40 wt%, 1.1 mL). Finally, it was allowed to stir for 12 h at room temperature before being centrifuged and redispersed into ethanol. Silica shells of varied thickness were obtained by controlled TEOS addition.

2.4. Preparation of Amino-Functionalized Au@SiO_2 Nanoparticles

Au@SiO_2 nanoparticles with different silica shell thickness were functionalized with amino groups. Briefly, 20 μL APTES was added to 10 mL Au@SiO_2 nanoparticles solution dissolved in anhydrous ethanol, and the mixture was shaken at room temperature for 12 h followed by heating at 70 °C for 1 h. The resulting amino-modified Au@SiO_2 nanoparticles were purified by centrifugation at 10000 rpm for 10 min and redispersed with 10 mL ethanol three times. Eventually, the amino-modified Au@SiO_2 nanoparticles were dispersed in 10 mL water for further use.

2.5. The Covalent Attachment of QDs to the Amino-Modified Au@SiO_2 Nanoparticles

Firstly, TGA-coated CdTe QDs were synthesized according to the previous approach [29]. To activate the carboxyl group of TGA on the surfaces of CdTe QDs, the mixed solution containing 1 mL freshly prepared CdTe solution and 3 mL anhydrous ethanol were centrifuged at 5000 rpm for 5 min and then the precipitate was redispersed in 1 mL deionized water. Whereafter, 0.5 mL 40 mg/mL EDC and 0.5 mL 40 mg/mL NHS solution was respectively added into the QDs solution, and the mixture was stirred for 20 min at room temperature. Then 6 mL anhydrous ethanol was added into the reaction solution and the centrifugation was operated to remove the excess EDC and NHS, and the precipitate was redispersed in 10 mL deionized water. Finally, amino-functionalized Au@SiO_2 colloidal solution was mixed with 0.1 mL the above QDs solution. The solution was shaken in ultrasonic cleaner at room temperature for 4 h and finally the QDs were attached to the surface of Au@SiO_2 nanoparticles.

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