



# Etching-dependent fluorescence quenching of Ag-dielectric-Au three-layered nanoshells: The effect of inner Ag nanosphere

Jian Zhu, Zai-jie Xu, Guo-jun Weng, Jing Zhao, Jian-jun Li, Jun-wu Zhao \*

The Key Laboratory of Biomedical Information Engineering of Ministry of Education, School of Life Science and Technology, Xi'an Jiaotong University, Xi'an 710049, China

## ARTICLE INFO

### Article history:

Received 21 January 2018

Received in revised form 31 March 2018

Accepted 8 April 2018

Available online 10 April 2018

### Keywords:

Fluorescence quenching

Etching-dependent

Ag-dielectric-au three-layered nanoshells

Rhodamine 6G

## ABSTRACT

In this report, Ag-dielectric-Au three-layered nanoshells with controlled inner core size were synthesized. The fluorescence emission of the rhodamine 6G (R6G) could be quenched by the three-layered nanoshells distinctly. What's more, the fluorescence quenching efficiency could be further improved by tuning the etching of inner Ag nanosphere. The maximum fluorescence quenching efficiency is obtained when the separate layer just appears between the inner Ag core and the outer Au shell. Whereas the fluorescence quenching efficiency is weakened when no gaps take place around the inner Ag core or the separate layer is too thick and greater than 13 nm. The fluorescence quenching properties of the Ag-dielectric-Au three-layered nanoshells with different initial sizes of the Ag nanoparticles are also studied. The maximum fluorescence quenching efficiency is obtained when the three-layered nanoshells are synthesized based on the Ag nanoparticles with 60 nm, which is better than others two sizes (42 and 79 nm). Thus we believe that the size of initial Ag nanospheres also greatly affects the optimized fluorescence quenching efficiency. These results about fluorescence quenching properties of Ag-dielectric-Au three-layered nanoshells present a potential for design and fabrication of fluorescence nanosensors based on tuning the geometry of the inner core and the separate layer.

© 2018 Published by Elsevier B.V.

## 1. Introduction

The unique optical characteristics such as resonance light absorption, scattering, fluorescence quenching, surface-enhanced Raman scattering of the metal nanoparticles and their widely applications have been intensive studied in recent years [1–6]. These attractive optical properties are mainly resulted from the localized surface plasmon resonance (LSPR), which is contributed from the collective oscillation of conduction band electrons in the surface of the metal nanoparticles [7–9]. By changing the particle size, geometry and local dielectric environment, the LSPR properties could be fine tuned [10]. Because of the LSPR and LSPR-induced intense resonance light absorption, the fluorescence emission of the signal molecule adsorbed on the metal surface has been greatly quenched when the fluorescence band is overlapped with the wavelength of LSPR [11–14].

As we know, fluorescence resonance energy transfer (FRET) and inner filter effect (IFE) are two kinds of mechanism of metal nanoparticle-induced fluorescence quenching [15]. FRET is a kind of photonic energy transfer from the donor to the acceptor without light emission [16]. IFE can also greatly reduce the intensity fluorescence emission. In this optical effect, light is first emitted and then re-absorbed

by the absorber, thus the second absorber is simply filtering off the fluorescence emission [17]. In order to quantize the ability of fluorescence quenching, the equation  $\eta = (F_0 - F)/F_0$  has been defined as the key parameter of the fluorescence quenching effect for the metal nanoparticles act on signal molecule [18]. Here, the fluorescence intensity of the signal molecule is recorded as  $F_0$  with no metal nanoparticles addition, and  $F$  denotes the fluorescence intensity of the mixed solution. In recent years, improving the fluorescence quenching efficiency of metal nanoparticles has been extensive investigated.

Gold nanoparticles with different sizes had been studied to quench the fluorescence of fluoroquinolones including norfloxacin, ciprofloxacin, danofloxacin and ofloxacin [19]. In agreement with the obtained quenching constants of Stern-Volmer, it has been found that the size increasing of Au nanoparticles (AuNPs) is advantage to the fluorescence quenching effect, and the thiols also have the great influence on the fluorescence of the fluoroquinolone-AuNPs systems. Besides particle size, morphology and construction of the nanostructure also affect the fluorescence quenching ability [20]. In the report of Horimoto et al., enhancement or quenching of fluorescence was also found to be strongly dependent on the particle shape [21]. It has been found that the gold nanorods with high aspect ratios showed distinct quenching effects. Fluorescence quenching properties of hollow porous gold nanoshells with roughened surface have also been reported recently [22]. It has been found the fluorescence emission of carcinoembryonic antigen (CEA) could be greatly quenched by the hollow porous gold nanoshells.

\* Corresponding author at: School of Life Science and Technology, Xi'an Jiaotong University, Xi'an 710049, China.

E-mail address: [nanoptzhao@163.com](mailto:nanoptzhao@163.com) (J. Zhao).

What's more, the fluorescence quenching efficiency would be further enhanced when the gold nanoshells have a larger particle size, surface hole size and roughened surface. Under the optimized conditions, CEA could be detected with an ultralow detection limit of 1.5 pg/mL.

Fluorescence quenching ability of gold nanoparticles could also be effectively enhanced by silver coating. The interactions of bovine serum albumins with silver-coated gold nanorods have been studied by Zhang et al. [23]. The fluorescence quenching efficiency could be greatly improved by increasing the aspect ratio or silver shell thickness of the gold nanorods. The fluorescence quenching abilities of gold triangular nanoplates with silver coating have also been studied recently [24]. By comparing with the bare gold triangular nanoplates, the gold nanoplates with silver coating exhibit greater fluorescence quenching efficiency and could be further improved by increasing the silver coating thickness. By using this gold silver bimetallic fluorescence quenching nanoprobe, the CEA could be detected with an ultra low detection limit of 10 pg/mL [25].

As a new type of nanostructure, multi-layered metal nanoshells with their plasmonic optical properties have been extensively studied recently [26–28]. The excellent optical features are resulted from the plasmon coupling between the inner metal core and outer metal shell. In the study of Zhu et al., the triple-bands LSPR has been adjusted according to the optimization of the geometric construction of the three-layered Au–Ag bimetallic nanoshells [27]. The peak intensity and wavelength in the absorption spectrum of the Au–Ag–Au three-layered nanoshells could be fine tuned by changing the thickness and radius of the separate Ag layer.

These previous reports about three-layered metal nanoshells indicate that the LSPR properties are sensitive to multiple geometric factors such as inner core size, separate layer width and outer shell thickness. So, we believe the fluorescence quenching efficiency of these three-layered metal nanoshells has better tunability. In this paper, fluorescence quenching efficiency of Ag–dielectric–Au three-layered nanoshells has been studied. In order to guarantee the biological compatibility and take advantage of the silver's quenching ability, the three-layered nanoshells in this study has a gold outer shell and a silver inner core. The experimental results show that the synthesized Ag–dielectric–Au three-layered nanoshells have good fluorescence quenching ability. What's more, the fluorescence quenching efficiency could be further improved by choosing the initial Ag nanosphere size or tuning the gap thickness between the inner Ag core and outer Au shell.

## 2. Experimental

### 2.1. Materials and Chemicals

The following reagents are used in this study. We obtained ascorbic acid ( $C_6H_8O_6$ ), trisodium citrate ( $Na_3C_6H_5O_7$ ) and sodium hydroxide (NaOH) from Aladdin. Chloroauric acid tetrahydrate ( $HAuCl_4 \cdot 4H_2O$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Citric acid ( $H_3C_6H_5O_7$ ) was obtained from Tianli chemical Reagent Co., Ltd., China. Silver nitrate ( $AgNO_3$ ) was purchased from Xi'an Hairmer Co., Ltd., China. All reagents were used without further purification and the ultrapure water at resistivity of 18.2 M $\Omega$  cm was used throughout all experiments.

### 2.2. The Preparation of Ag Nanospheres

Ag nanospheres are prepared using previously reported method with slight modification [29]. Briefly, ascorbic acid ( $6.0 \times 10^{-4}$  M) and trisodium citrate ( $3.0 \times 10^{-3}$  M) were added into aqueous solution to a volume of 80 mL, and AA was served as a reduction agent. Then 0.2 mol/L citrate acid or 0.1 mol/L NaOH solution was used to adjust the pH value. In order to obtain the solution with pH = 8.0, 0.1 mol/L NaOH solution was added firstly to increase the pH value. If the PH value exceeded 8.0, 0.2 mol/L citrate acid was added to decrease the

pH value. As a result, the solution with pH = 8.0 was obtained for the following experiment. Finally, aqueous solution of 0.1 M  $AgNO_3$  with different amounts (0.6 mL, 0.8 mL, 1.4 mL, 1.6 mL, 3.0 mL) were added (the titration speed was 0.15 mL/min) in a 30 °C water bath under a stirring speed of 900 rpm. When the titration was finished after 10, 9, 6, 5 and 2 min respectively (the corresponding  $AgNO_3$  amount is 0.6, 0.8, 1.4, 1.6 and 3.0 mL), there is no further color change. In order to guarantee that the reaction finished completely, the subsequent experiment was carried out after 12 min for all samples.

### 2.3. The Preparation of Ag–Dielectric–Au three-Layered Nanoshells

The principle of preparing Ag–dielectric–Au three-layered nanoshells is similar to the previous reported method of Sun [30] with slight modification. Typically, the prepared colloidal Ag nanospheres with a diameter of 42, 60 and 79 nm were centrifuged at 9000, 8500, 8000 rpm/min for 15 min, respectively. Then the samples were dispersed in the solution using ultrapure water, and this process should be operated twice. After that, the Ag nanospheres were served as template to product Ag–dielectric–Au three-layered nanoshells under the stirring with a speed of 600 rpm/min in the 80 °C water bath. By controlling the amount of dropped  $HAuCl_4$  (1 mM), we could acquire Ag–dielectric–Au three-layered nanoshells with different sizes of inner Ag nanospheres.

### 2.4. Equipment and Characterization

The fluorescence spectra were acquired by FluoroMax-4P spectrofluorometer (HORIBA JOBIN YVON). Transmission electron microscopy (TEM) images were obtained by using a H-600 instrument (Hitachi, Japan) operated at an acceleration voltage of 75 kV. The observation of high resolution transmission electron microscopy (HRTEM) was carried out with the JEM-F200 instrument (JEOL, Japan). Shimadzu UV-3600 spectrometer (Shimadzu, Japan) was used to record all the absorption spectra. Millipore water purification system (Milli-Q, Millipore, USA) provided all the ultrapure water that we used. Centrifugation was carried out by using a 5810R centrifuge (Eppendorf, Japan) in this experiment.

## 3. Results and Discussions

### 3.1. Plasmonic Absorption Spectrum Properties of Ag Nanoparticles and Ag–Dielectric–Au three-Layered Nanoshells

Fig. 1 shows the absorption spectra of colloidal Ag nanospheres with five different sizes. As the amount of  $AgNO_3$  is increased from 0.6 to

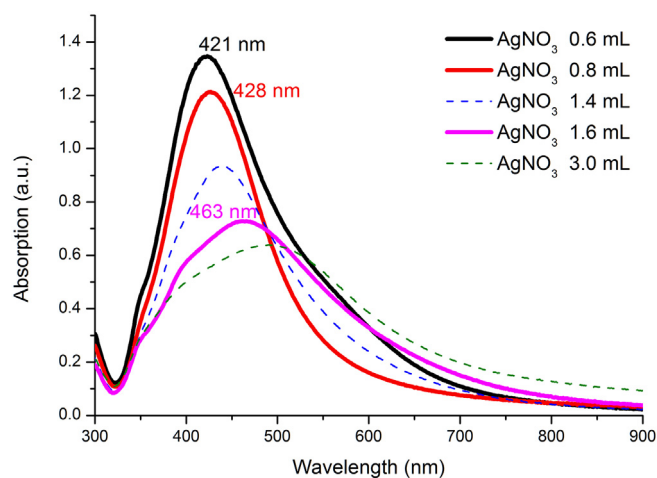


Fig. 1. Absorption spectra of Ag nanospheres with different addition of  $AgNO_3$ . The concentration of  $AgNO_3$  solution is 0.1 M, the pH value of the mixed solution is 8.0.

Download English Version:

<https://daneshyari.com/en/article/7668642>

Download Persian Version:

<https://daneshyari.com/article/7668642>

[Daneshyari.com](https://daneshyari.com)