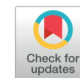
Journal of Alloys and Compounds 741 (2018) 141–147

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Ag nanobox/silica/CdTeS quantum dot nanoprobe with photoluminescence emission enhancement for labeling cancer cells



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ARTICLE INFO

Article history:
Received 29 November 2017
Received in revised form
9 January 2018
Accepted 10 January 2018
Available online 11 January 2018

Keywords:
Coating materials
Optical materials
Chemical synthesis
Computer simulations

ABSTRACT

Ag nanobox/silica/quantum dot (QD) nanoprobe was synthesized by using a hydrothermal method to investigate the interaction between Ag nanobox and CdTeS QDs for the first time. Finite-difference time domain method was used to compare the optical behavior of Ag nanobox with Ag nanosquare. The comparison demonstrated that the Ag nanobox had excellent optical characteristics. In the nanoprobe, the silica shell was used to adjust the distance between the Ag nanobox and CdTeS QDs. A 4.5-fold increase in the fluorescence intensity of CdTeS QDs was achieved based on the local surface plasmon resonance (LSPR) of Ag nanobox. The Ag nanobox/silica/CdTeS QD nanoprobe was used to label cancer cells, thereby indicating that the nanoprobe was a suitable and excellent fluorescence probe.

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1. Introduction

In the past few years, the development of nanotechnology has greatly promoted the progress of technological innovation [1–5]. For example, metallic nanoparticles have received much attention due to their LSPR [6,7], a collective resonance phenomenon of free conduction-band electrons, that could boost the absorption coefficient and quantum yield of adjacent chromophores. Metallic nanoparticles are widely researched in various fields, such as photothermal therapy [8,9], fluorescent labeling [10–12] based on the LSPR. Xia et al. reported the gold nanocage with intense absorption coefficient as a photothermal nanoprobe [13] to realize its function of destroying targeted cancer cells. Li et al. studied metal-enhanced fluorescence in gold core/porous silica shell encapsulated with Y_2O_3:Eu [14]. Recently, our group obtained the structure of Ag core/silica shell implanted with dye molecule, realizing an enhancement factor up to three times higher than the bare dye molecule [15]. These results show that metallic nanoparticles have an excellent LSPR effect.

Fluorescent technology has become an important detection tool in medicine, biology and electronics [16,17]. In the area of biomedicine, organic dye was used as a traditional fluorescent probe due to its high fluorescent intensity and narrow spectra. However, the fluorescent lifetimes of organic dye were relatively lower, thereby limiting its widespread application in various fields [18]. In recent years, QDs, as a new generation of fluorescent probes, received increasing attention by science researchers. The advantages of QDs over organic dye were their large Stokes shift, long lifetime and good stability [19,20]. However, the fluorescent intensity of QDs was limited, thus seriously restricting their further applications. A range of metallic sphere core/QDs-doped silica shell nanoprobes were synthesized [21,22] to improve fluorescent intensity. The fluorescent intensity of QDs was enhanced based on the LSPR effect of metallic sphere. For example, Li et al. reported that a more than fourfold increase in the fluorescence intensity of QDs was obtained in their Ag sphere core/QDs-doped silica nanoprobe [14].

Recently, several studies verified that the LSPR effect of metallic materials was related to the size, shape and composition of the materials. Liu et al. studied the enhancement effect of Ag nanoparticle on CdSe QDs and found that worm-like Ag nanoparticles had a higher enhancement effect than the Ag sphere [23]. Here, a designed an Ag nanobox/silica/CdTeS QD nanoprobe was designed and the LSPR effect of Ag nanobox on the CdTeS QDs was investigated. With the use of theoretical calculation, the advantage of Ag nanobox was emphasized through the finite difference time domain (FDTD) method. The thickness of the silica shell was

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https://doi.org/10.1016/j.jallcom.2018.01.149
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adjusted to the distance of metal-QDs to obtain the largest fluorescence enhancement effect of the Ag nanobox. Finally, the Ag nanobox/QDs nanoprobe was used to target cancer cells.

2. Experiment

2.1. Material

Deionized water (18.25 MΩ cm^{-1}), absolute ethanol (99.7%, AR), silver trifluoroacetate (CF_3COOAg, AR), ethylene glycol (EG, AR), hydrochloric acid (36% HCl), sodium hydrosulfide (NaHS, AR), polyvinylpyrrolidone (PVP, MW = 55000), cadmium chloride (99.0%), tellurium powder (99.5%), 3-Mercaptopropionic acid (MPA, 99+%, Sigma-Aldrich), ascorbic acid (99.7%, AR), ammonia (25%–28% NH_3), sodium borohydride ($NaBH_4$, 99%), tetraethyl orthosilicate (28.4% SiO_2), 3-aminopropyltrimethoxysilane (APS, 98%, Sigma-Aldrich), phosphate buffered saline (PBS, AR), 4′,6-diamidino-2-phenylindole (DAPI), high glucose Dulbecco's modified Eagle medium (DMEM), breast cancer cells (MDA-MB-231, Anhui Medical University). The other reagents were of analytical grade and used without further purification. All cell culture media and supplements were obtained from Anhui Medical University. CdTeS QDs were synthesized by our group.

2.2. Synthesis of Ag nanobox

The preparation progress of the Ag nanobox was consistent with that in our previous report with minor modification [24]. Liquid-phase reduction method was used to synthesize the Ag nanobox with CF_3COOAg and EG as the precursor and the reducing agent, respectively. After refluxing 10 mL EG solution was refluxed at 140 °C for 20 min in a magnetron oil bath pan, 200 μL of 2 mM NaHS solution was dropped into the reaction solution through rapid magnetic stirring. As the mixing was completed, 2.5 mL of 0.167 M PVP solution was titrated into the mixture, followed by the addition of 0.8 mL of 0.3 M CF_3COOAg solution. Subsequently, the mixture was refluxed at 130 °C under vigorous stirring. The size and shape of the Ag nanobox can be controlled by the reaction time. Finally, the Ag nanobox was collected from the reaction solution through multiple centrifugations and dispersed in 10 mL deionized water for next usage.

2.3. Preparation of Ag nanobox/CdTeS QD nanoprobe

First, a modified Stöber method was used to prepare the core-shell Ag nanobox/SiO_2 shell composite [25]. Then, 1 mL Ag nanobox solution was mixed with 10 mL absolute ethanol under vigorous stirring, followed by the addition of 0.5 mL ammonium hydroxide. As the mixture became homogenous solution, TEOS solution was added to the reaction mixture under low-speed stirring and the reaction lasted for 12 h at room temperature. The dosage of TEOS solution can be used to tune the thinness of the SiO_2 shell, which can control the distance between Ag box and QDs. Subsequently, the Ag nanobox/SiO_2 nanoparticle was washed with a large amount of ethanol solution and was re-dispersed in 10 mL ethanol solution. Second, APS (a silane coupling agent with -NH_2 groups) was used to function onto the surface of Ag nanobox/SiO_2 nanoparticle, which was suitable for the interlinkage between the nanobox/SiO_2 nanoparticle and QDs. A total of 50 μL APS was pipetted into the Ag nanobox/SiO_2 solution under moderate stirring. As the mixture reacted for 6 h at room temperature, the mixture was washed and re-dispersed in 10 mL ethanol solution. Third, highly fluorescent CdTeS QDs were linked onto the Ag nanobox/SiO_2 nanoparticle on the basis of the strong bonds between carboxyl and -NH_2 groups. A total of 50 μL of carboxyl-modified CdTeS QDs and 5 mL Ag nanobox/SiO_2 nanoparticle were mixed under vigorous stirring for 6 h. Finally, 1 mL of folic acid was used to function onto the surface of Ag nanobox/SiO_2 to improve the uptake capability of cancer cell for Ag nanobox/CdTeS QD nanoprobe. Similar to this progress, bare CdTeS QDs was also been functioned with folic acid.

2.4. Cytotoxicity

The cytotoxicity of the Ag nanobox/CdTeS QD nanoprobe on the breast cancer cells (MDA-MB-231) was evaluated by MTT assay. The nanoprobes with different concentrations ranging from 0 to 18 mg/mL were prepared. As cancer cells were treated by the nanoprobes for 24 h, MTT method was used to assess the cell viability, which was expressed in the form of percentage of surviving cells. Six wells of cancer cells were set as the zero group only with fresh DMEM, while another 12 wells were set as the control group with any addition of different concentrations of the nanoprobes. The cell viability was calculated using $A_{control}/A_{zero} \times 100\%$. All the dates were measured for five times and calculate the mean values.

2.5. Cancer cell labeling

MDA-MB-231 cancer cells were seeded on a glass coverslip in a 12-well culture plate and cultured for 24 h at 37 °C in 5% CO_2 (v/v). As the coverage of cancer cells on the glass coverslip reached approximately 60%–80%, the coverslip was washed with a large amount of PBS solution. Subsequently, 50 μL Ag nanobox/QD nanoprobes were titrated onto the glass coverslip and incubated for another 1 h at 37 °C. Finally, the cancer cells were washed again with PBS solution and allowed to dry overnight.

2.6. Characterization

Microstructure of the nanoparticle and nanoprobe was recorded with a JEM-1400 transmission electron microscope (TEM, JEOL Co., Ltd., Japan) at an acceleration voltage of 120 kV. The UV–visible absorption spectra and emission spectra were obtained with a Shimadzu UV-2401 spectrophotometer and Shimadzu RF-5301 fluorescence spectrophotometer. The image of cancer cells were obtained by Olympus Bx53 Mons fluorescence microscope. The absorption spectrum and electromagnetic field distribution of nanoparticle were simulated by the three-dimensional FDTD solution method.

3. Results and discussion

Through the FDTD solution method, Ag nanosphere model (radius: 30 nm) and Ag nanobox model (side length: 60 nm) were computed, whose centers were set on the origin of coordinates of the simulation system. The direction of the incident light was along the Y-axis, whereas that of the polarization was along the X-axis. Fig. 1 shows the electric field (e-field) distribution of the Ag nanosphere and nanobox with their corresponding best excitation wavelength. Fig. 1a (x-z plane with y = 0) shows an intensive e-field around the Ag nanosphere, which was consistent with previous report. The x–z plane with y = 0 and $y = 3 \times 10^{-8}$ m are shown in Fig. 1b and c to display the e-field distribution of the Ag nanobox, respectively. Compared with the Ag nanosphere, the Ag nanobox generated a larger enhancement factor, which reached up to four orders of magnitude, especially in the corner and edge. The Ag nanobox was used to enhance the fluorescence intensity of QDs in the Ag nanobox/CdTeS QD nanoparticle based on the principle.

Fig. 2 shows the preparation progress of the Ag nanobox/CdTeS QD nanoparticle. The Ag nanobox was synthesized through

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