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Enhanced photoluminescence of CdSe quantum dots by the coupling of Ag nanocube and Ag film*

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The coupling of local surface plasmon (LSP) of nanoparticle and surface plasmon (SP) mode produced by metal film can lead to the enhanced electromagnetic field, which has an important application in enhancing the fluorescence of quantum dots (QDs). Herein, the Ag nanocube and Ag film are used to enhance the fluorescence of CdSe QDs. The enhancement is found to relate to the sizes of the Ag nanocube and the thickness of the Ag film. Moreover, we also present the fluorescence enhancement caused by only SP. The result shows that the coupling between metal nanoparticles and metal film can realize larger field enhancement. Numerical simulation verifies that a nanocube can localize a strong electric field around its corner. All the results indicate that the fluorescence of QDs can be efficiently improved by optimizing the parameters of Ag film and Ag cubes.

Keywords: Ag nanocube, local surface plasmon, Ag film, photoluminescence

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1. Introduction

Noble metal has been receiving considerable attention for many decades due to surface plasmons (SPs). SPs are quasi-particles formed at the interface of metal-dielectric because of the collective oscillation of conduction electrons,[1] of which, an electron oscillation propagating along the interface is known as a surface plasmon polariton (SPP). Surface plasmons highly localized at the surface of the metal nanoparticles are referred to as localized surface plasmons (LSPs).[2,3] Electromagnetic fields induce the resonance of LSPs on the surface of the metal nanoparticle, which causes strong light absorption, scattering, and enhanced local electromagnetic fields.[4] SPs phenomena have key applications, such as surface-enhanced Raman scattering (SERs),[5,6] metal-enhanced fluorescence (MEF),[7] surface-enhanced infrared absorption,[8] and enhanced Rayleigh scattering.[9] SPPs have an exciting application due to the unique properties of sub-wavelength optical confinement and significant field enhancement, such as near-field microscopy and biomedical sensing.[10]

Recently, MEF has attracted a lot of attention. Based on the enhancement of local fields associated with excitation of collective electron oscillations in metal, localized surface plasmon resonances (LSPRs) can be excited to improve the fluorescent substance radiation rate, which has a broad prospect in bio-labeling. Numerous medical and biological researches involve the detection of biomolecules with fluorescence. In the process, the interfering background and relatively small fluorescence signal make fluorescence detection more difficult.[7] Among the various metals, Ag or Au nanostructures are regarded as the best candidates for enhancing fluorescence due to their SP absorption bands in the visible and near-infrared spectral regions.[7] The position and intensity of the surface plasmon resonance peak of metal nanoparticles can be tuned by changing the size, shape, morphology, composition of the nanoparticle, the dielectric environment around the nanostructure, crystallinity, etc.[11,12] The Ag nanocube has eight corners. The special structure can exhibit simultaneous low extinction and high local field enhancement properties in the resonance mode. The strong local field enhancement is attributed to the polarized charge highly confined in a very limited volume around the corner of the nanocube.[13] Therefore, Ag nanocubes are promising candidates for fluorescence enhancement.

Many groups have used the LSP mode of metal nanostructure to enhance fluorescence. Li *et al.*[14] investigated the fluorescence enhancement mechanism of Er^{3+} in germanate glass containing silver particles. The fluorescence of Er^{3+} was enhanced 4.2 times in the 10-min-annealed sample with Ag particles. Deng and Goldys[7] reported a plasmonic approach to enhancing the fluorescence for applications in biotechnology and the life sciences. Hèléne *et al.*[15] prepared glass-deposited monolayers of polystyrene-coated gold nanoparti-

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cles with controlled inter-particle distance. Stuartand Hall[16] reported the enhanced dipole–dipole interaction between elementary radiators near a surface. Yean-Woei Kiang[17] numerically synthesized a two-dimensional metallic nanostructure consisting of a Au half space and two separate Ag elliptical cylinders by the simulated annealing (SA) method. The simulated nanostructure was so designed that the surface plasmon polariton (SPP) and the localized surface plasmon (LSP) are simultaneously excited to the enhancement of the emission of a nearby dipole source. This group proposed that this enhancement effect is more significant than that of the case where only one of the SPP and LSP is excited. Cesario[18] published a theoretical study on electromagnetic coupling between a metal nanoparticle grating and a metallic surface. Papanikolaou[19] studied theoretically the optical properties of metallic nanoparticle arrays on a thin metallic film. However, most reports related to the study of the SPP and LSP modes of metal structure and optimizing parameters to enhance fluorescence in theory, or the discussion of the LSP mode of metal nanostructure only. Very few researches have dealt with the superposition relationship between the SPP mode and the LSP mode to enhance quantum dots in experiment.

In this paper, we study the coupling effects of the LSP and SPP modes on the photoluminescence properties of CdSe QDs. The distance between Ag nanocube/Ag film and CdSe is controlled with polymethylmethacrylate (PMMA) film. Herein, three different sizes of Ag nanocubes and two different Ag film structures are combined to enhance the fluorescence of CdSe QDs, respectively. In addition, the electric field distributions of the Ag nanocube and the Ag film composite structure are computed using the three-dimensional finite-difference time-domain method.

2. Experiment

2.1. Materials

In our experiments, the following materials were used: ethylene glycol (EG, 99.0%), silver nitrate ($AgNO_3$, 99.8%), acetone (99.5%), ethanol (99.7%), CdO (99%, AR), Se powder, stearicacid (SA, AR), diethylene glycol (DEG, $\geq$ 99%), and silver filament (0.2 mm in diameter), which were directly used without further purification and obtained from Sinopharm Chemical Reagent Co., Ltd., Poly (vinyl pyrrolidone) (PVP, powder, Mw $\approx 5.5 \times 10^4$, Aldrich), sodium hydrosulfide hydrate (NaHS, Aldrich), deionized water (18.25 MΩ·cm), slides, poly (methyl methacrylate) (PMMA, Aldrich), tri-n-octylphosphine oxide (TOPO, 98%, Alfa Aesar), hexadecylamine (HDA, Fluka), octadecylamine (ODE, 90%, Alfa Aesar), and trioctylphsphine (TOP, 90%, Fluka).

2.2. Synthesis of CdSe QDs

CdSe QDs were synthesized as follows.[20] 0.1 mmol of CdO, 0.4 mmol of SA, and 2.5 mL of ODE were mixed and then heated to 150 °C until CdO was completely dissolved. Next, 0.5 g of TOPO and 1 g of HDA were added. The solution was kept at 120 °C for 30 min under a N_2 flow. This system was reheated to 280 °C . At this temperature, 1 mL of the Se precursor stock solution TOP-Se (0.5 mmol of Se powders dissolved in 2 mL of TOP) was swiftly injected into the flask. After 2 min, the solution was dissolved in 10 mL of toluene.

2.3. Synthesis of Ag nanocube and Ag film

The sulfide-mediated polyol method was used to prepare Ag nanocubes.[21,22] 6 mL of EG (or DEG) was pipetted into a reaction vial, and heated in an oil bath at 150 °C for 1 h with stirring. 100 μL of NaHS (3 mM in EG (or DEG)) was quickly injected into the vial. After 8 min, 1.5 mL of PVP (0.18 M in EG (or DEG)) was added. 2 min later, 0.5 mL of $AgNO_3$ (0.28 M in EG (or DEG)) was added into the vial. The vial was placed into water to suspend the reaction. Three different sizes of Ag nanocubes were synthesized by changing the reaction time and reducing agent. 35-nm, 68-nm Ag nanocubes were synthesized in an EG environment by reacting for 15 min, 30 min. A 27-nm Ag nanocube was synthesized in a DEG environment. The products were washed by acetone and ethanol, and then the Ag nanocube was dispersed in ethanol for further application.

In addition, two kinds of Ag thin films with different thickness values were sputtered onto the glass substrates with vacuum thermal deposition by changing the amount of the Ag source. Glass substrates had been cleaned by sequential baths of acetone, ethanol, and deionized water with sonication before use. The thicker Ag film and the thinner Ag film were named Ag F1 and Ag F2, respectively.

2.4. Preparation of samples

CdSe QDs-doped PMMA films/Ag film/Ag nanocube, CdSe QDs-doped PMMA films/Ag film, and CdSe QDs-doped PMMA films were prepared by the following process: each Ag film was cut into two pieces. One of them was coupled with the Ag nanocube, the other was kept as a reference sample. 100 μL of as-prepared ethanol solution of Ag nanocubes with different sizes were spin-coated on Ag F1 and Ag F2 at a speed of 3600 rpm for 30 s, respectively. The as-prepared CdSe QDs were dispersed in 10 mL of a 2% PMMA solution in chloroform. The CdSe QDs-doped PMMA films were obtained by dipping the substrate into CdSe/PMMA sol at a fixed speed of 2 cm/min. After standing for 150 s, the substrates were withdrawn from the solution at the same speed.

2.5. Characterization

The UV-visible absorption spectra were measured using a UV-3600 UV-VIS-NI spectrophotometer. Photoluminescence spectra were investigated by using an F-4600 fluorescence spectrophotometer. The morphology of the Ag nanocubes and

the structure of the Ag films were conducted by transmission electronic microscopy (TEM, JEOL, JEM-2010) and scanning electron microscopy (SEM, JSM-6700F). The electric field distribution was computed using the three-dimensional finite-difference time-domain method (FDTD).

3. Results and discussion

Figure 1 shows the sketches of CdSe QDs-doped PMMA films/Ag film/Ag nanocube, CdSe QDs-doped PMMA films/Ag film, and CdSe QDs-doped PMMA films, respectively.

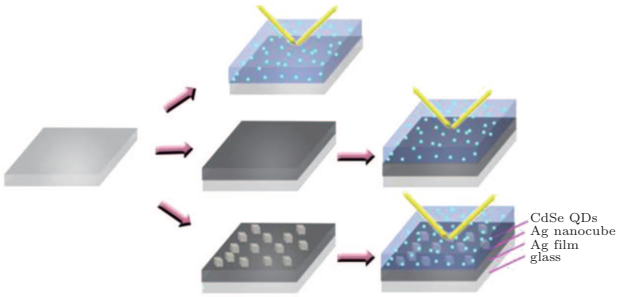


Fig. 1. (color online) Schematic representations of CdSe QDs-doped PMMA films/Ag film/Ag nanocube, CdSe QDs-doped PMMA films/Ag film, and CdSe QDs-doped PMMA films, respectively.

Table 1. Names of experiment products.

Ag f1	Ag f2	Ag C1	Ag C2	Ag C3
Ag film 1	Ag film 2	Ag nanocube of 27 nm	Ag nanocube of 35 nm	Ag nanocube of 68 nm

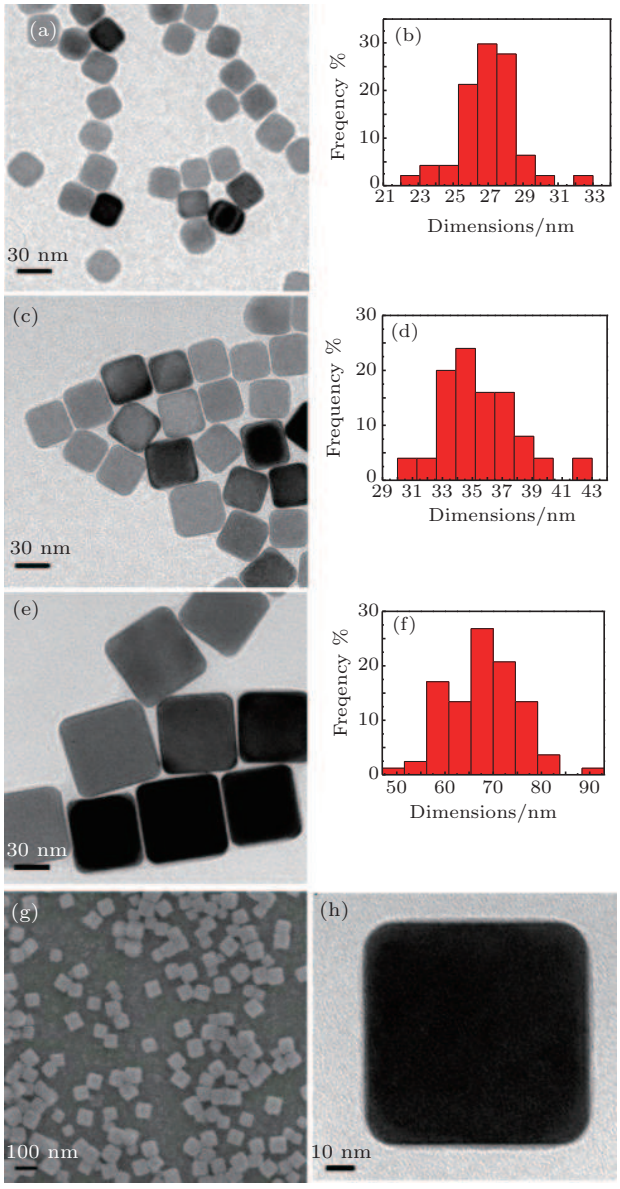


Fig. 2. (color online) TEM images of Ag nanocubes with (a) 27-nm, (b) 35-nm, (c) 68-nm edge lengths. (b), (d), and (f) Particle size statistics corresponding to panels (a), (b), and (c), respectively. (g) SEM and (h) TEM images of Ag nanocubes with a 68-nm edge length, respectively.

The TEM images of Ag nanocubes (Figs. 2(a), 2(c), and 2(e)) confirm that Ag nanocubes of different sizes (27-nm, 35-nm, and 68-nm edge lengths) are successfully synthesized. Figures 2(b), 2(d), and 2(f) show the corresponding particle size distributions of three kinds of Ag nanocubes, which clearly demonstrate that Ag nanocubes are highly uniform in particle size distribution. Figures 2(g) and 2(h) show the SEM and TEM images of Ag nanocubes with the 68-nm edge length, respectively.

As seen from Fig. 3(a), the distribution of Ag nanocubes is monodisperse on Ag F2. Figure 3(b) clearly demonstrates the SEM image of Ag F2, which is highly uniform in thickness distribution. Ag F2 was produced by an 8-cm silver filament, and its thickness is about 120 nm. Figures 3(c) and 3(d) show the SEM images of Ag film F1. Ag film F1 is a thinner island film, which was produced by a 4-cm silver filament. This structure is formed due to the surface tension.

The absorption spectrum of the Ag nanocube presents three main peaks, as shown in Fig. 4(a). The left peak is attributed to a hybrid resonant mode containing both dipole component and quadrupole component.[13] The middle peak corresponds to a quadrupole resonance mode. The right peak is attributed to a pure dipole mode. As the size of the Ag nanocube increases from 27 nm, 35 nm to 68 nm, the dipole resonance mode is red-shifted from 405 nm, 439 nm to 470 nm, and the quadrupole modes become more intense.[11] The surface plasmon resonance (SPR) peak wavelength is closely related to the local electric field distribution of the metallic nanostructure. The amplitude of the local field influences the energy of SPR. The SPR peak is blue-shifted as this energy increases, whereas it is red-shifted as the energy decreases.[23] With the increase of the size of the Ag nanocube, the restoring force of the oscillatory electrons decreases, which corresponds to the decrease of dipole mode energy. The SPR peak presents a redshift. In addition, the peak corresponding to the dipole mode broadens as the size of the

Ag nanocube increases. The broadening can be deemed to be resonance damping due to the radiation effects, that is, losing energy through scattering.[11]

Figures 4(b)–4(e) show the photoluminescence (PL) spectra of CdSe QDs-doped PMMA films/Ag film/Ag nanocube, CdSe QDs-doped PMMA films/Ag film, and CdSe QDs-doped PMMA films, excited at 340 nm. As seen from Fig. 4(b), the fluorescence intensity of CdSe on Ag F2 is stronger than that on Ag F1. The PL enhancement factor increases from 2.5 to 8.1 times, by changing Ag film. Ag films have a greater influence on fluorescence enhancement effect. For CdSe QDs on Ag film, the PL intensities are enhanced and the PL peaks have a slight redshift compared with CdSe QDs on a glass substrate.

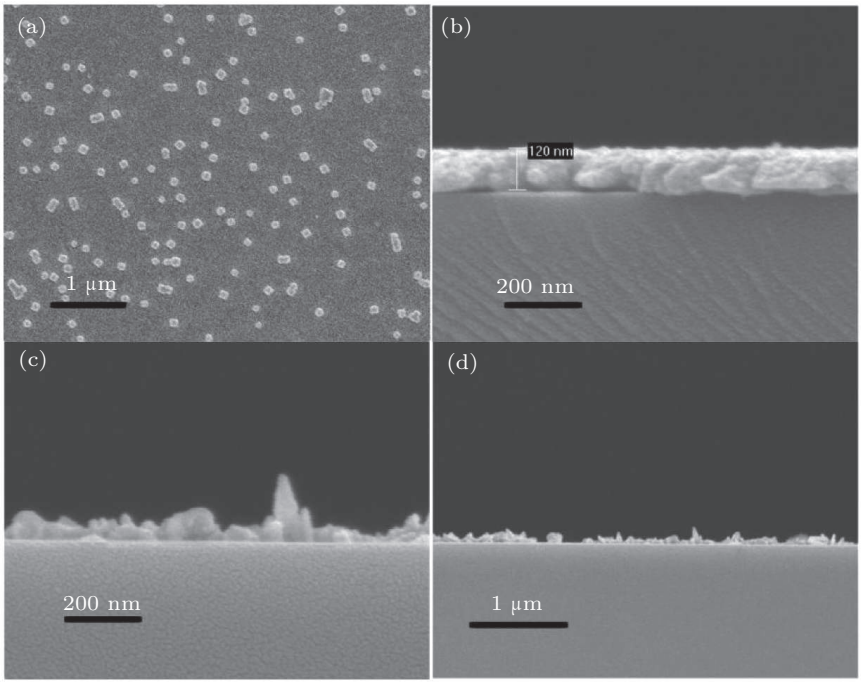


Fig. 3. SEM images of (a) Ag C3 on Ag F2, (b) Ag F1, ((c) and (d)) Ag F2.

In order to obtain the largest fluorescence enhancement, Ag nanocube and Ag film composite structures are built. In general, spectral overlap control of plasmon resonance of metal nanostructures with the absorption or emission bands of the fluorescent substance is understood as one of the crucial factors in the PL enhancement effects.[2] In addition, when the frequency of incident light couples with the inherent frequency of metal nanoparticles, the resonance phenomenon of LSPs will happen. The resonant excitation caused by the coupling of LSPs and the incident electromagnetic field can strongly enhance the local field, which can dramatically increase the absorption rate and the excitation rate. The LSP resonant frequency is extremely sensitive to the size of the metal particle, which greatly influences the enhancement effect. Therefore, the three different sizes of Ag nanocubes are investigated. From Figs. 4(c)–4(e) it follows that the enhancement factors of CdSe/Ag F2/Ag C1, CdSe/Ag F2/Ag C2, and CdSe/Ag F2 are 8, 8, and 8.1, respectively. The fluorescence intensities of CdSe/Ag F2/Ag C1, CdSe/Ag F2/Ag C2 have no obvious change compared with that of CdSe/Ag F2. The enhancement factors of CdSe/Ag F1/Ag C1, CdSe/Ag F1/Ag C2, and CdSe/Ag F1 are 3.5, 3.6, and 2.5, respectively. The fluorescence intensities of CdSe/Ag F1/Ag C1, CdSe/Ag F1/Ag C2 have a little improvement compared with that of CdSe/Ag F1. The reason should be that Ag nanocubes fill in the recession of Ag film F1, leading to the additional contribution from the reflected component of incident light. The PL intensities of CdSe/Ag F1/Ag C3 (the enhancement factor is 6.7) and CdSe/Ag F2/Ag C3 (the enhancement factor is 11.7) have both remarkable enhancements in comparison with those of CdSe/Ag F1 and CdSe/Ag F2. These results indicate that the fluorescent enhancement effect is extremely sensitive to the size of the Ag nanocube. In addition, it is found that the enhancement factors of CdSe/Ag F2/Ag C1, Ag C2, and Ag C3 are respectively greater than those of CdSe/Ag F1/Ag C1, Ag C2, and Ag C3, which reveal that the fluorescence enhancement effect is dependent on the Ag film substrate.

As shown in Fig. 4(f), the absorption peak of the Ag F2/Ag C3 composite structure (363 nm) is just between excitation (340 nm) and emission (580 nm) maxima of the CdSe QDs, which benefits the confinement of local fields around the metal nanocube for maximum excitation enhancement. In addition, the absorption spectrum of the composite structure has a certain spectral overlap with the emission spectra of

CdSe QDs, which are beneficial to the emission enhancement. As indicated by Zakharko *et al*.,[24] the fluorescence intensity of emitters nearby the metal nanoparticle is strongly dependent on the spectral overlap between the LSPR modes of the nanoparticles and emitter. The brightest fluorescence is observed when the emitter is attached to the metal nanoparticle with LSPR peaks at higher energy than the emission peak of the emitter.

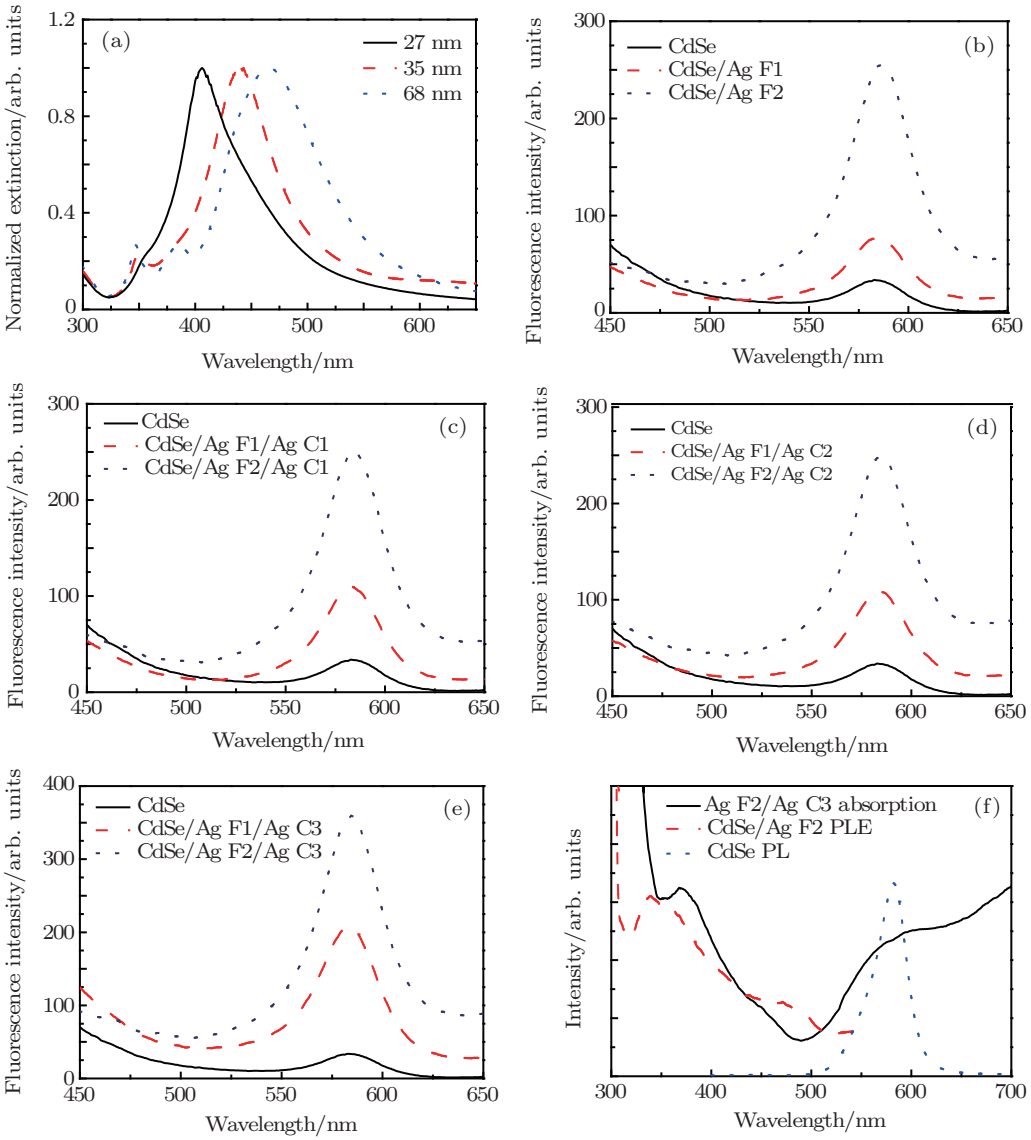


Fig. 4. (color online) (a) UV-visible absorption spectra of Ag nanocubes with different sizes. (b) PL spectra of CdSe QDs coupled with different Ag films. PL spectra of CdSe QDs coupled with different Ag films and (c) Ag C1, (d) Ag C2, (e) Ag C3 respectively. (f) The relationship among CdSe excitation spectrum, PL spectrum, the absorption spectrum of Ag F2 and Ag C3 composite structure.

By adding 68-nm Ag nanocubes, the PL enhancement factor of CdSe/Ag F1 increases from 2.5 to 6.7, and that of CdSe/Ag F2 increases from 8.1 to 11.7. As for the sample of CdSe QDs coupled with Ag film, CdSe QDs can be regarded as a radiating point dipole, which can help excite the SPP mode by wave vector compensation.[25,26] The high frequency components of the dipole radiation can allow the excitation of SPPs on the film. The fluorescence of CdSe QDs is further enhanced by constructing the composite structure of the Ag film and the Ag nanocube. When Ag nanocubes are placed on the Ag film, LSP scattering from the nanocube induces SPPs on the Ag film, which in turn couples with the LSPs. This coupled plasmonic interaction can modify the E-field distribution. Ag nanocubes provide hot spots of the local electric field in the immediate vicinity of eight corners. Localized electric fields are confined around hot spots, which is due to the suppression of scattering into the far-field via excitation of plasmon modes.[24] In the experiment, Ag nanocube surface coverage is low and the average center-to-center inter-particle distance is far, so the inter-particle interaction can be ignored. The enhancement effect is owed to the LSP from a single Ag nanocube. CdSe/Ag F2/Ag C3 achieves a high PL enhancement, which is due to the coupling effect between the localized plasmon of the nanoparticle and the surface plasmon

mode caused by the Ag film.

Figures 5(a) and 5(b) show the calculated E-field distributions of a single 68-nm Ag nanocube on the substrate with 120-nm Ag film in the y–z plane and x–z plane. The interactions among nanocubes are ignored in the computation due to the far space between them. The E-field distribution is located at the corners of the cube, forming hot spots. As a result, the fluorescence intensity of CdSe QDs will be enhanced, which is consistent with the experimental results. The SPs caused by the Ag nanocube and the Ag film interact with each other, which induce a strong E-field located at the upper corners of the cube. The corresponding Poynting vector image is shown in Fig. 5(c). It follows from the wave vector distribution of the Poynting vector image that the wave vectors at the corners of the nanocube are dense, which also testify that the corners of the Ag nanocube will localize the E-field around them.

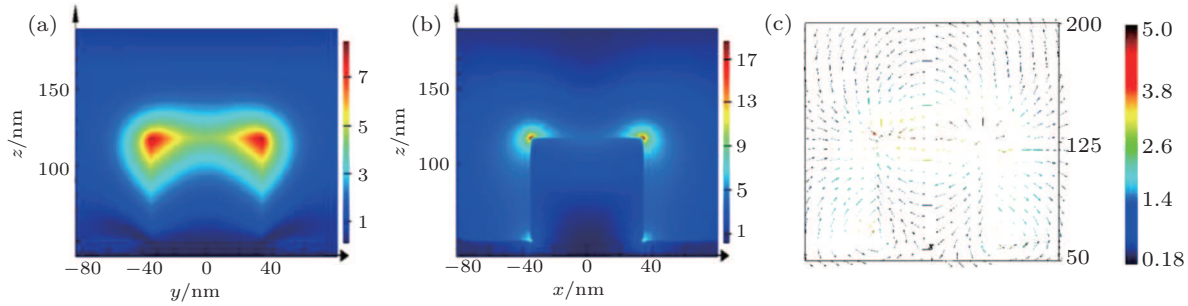


Fig. 5. (color online) Near-field intensity distribution of Ag nanocube on the substrate with Ag film, calculated with the FDTD method in (a) the y–z plane and (b) the x–z plane, respectively, (c) the corresponding Poynting vector image. The polarization of the incident laser is along the y axis.

4. Conclusion

In this paper, three sizes of Ag nanocubes and two kinds of Ag films are coupled to enhance the fluorescence of CdSe QDs. As contrast experiments, the two kinds of Ag films are also used to investigate the PL properties of CdSe QDs, respectively. Experimental results indicate that the fluorescence intensities can be more efficiently improved by introducing the Ag nanocube and the PL enhancement effect of CdSe QDs is sensitive to the structure of the Ag film and the sizes of Ag nanocubes. Herein, the coupling structure of Ag F2 and Ag C3 presents the best enhancement effect on QDs PL (up to an enhancement factor of 11.7). In addition, numerical simulation results exhibit that Ag nanocubes enhance the localized electric field around their corners, which is beneficial to improving the fluorescent efficiency of QDs. We believe that the composite structure of Ag film and Ag nanocubes will have a potential application in detecting the faint fluorescence signal.

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