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Annealing structured Au nanoparticles enhanced light emission from CdSe quantum dots

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ABSTRACT

Enhancement of the light emission of CdSe quantum dots was observed by coupling through localized surface plasmons from Au nanoparticles. The enhancement was found to be relative to the shapes and sizes of Au nanoparticles. Au nanoparticles of different sizes were synthesized by a citrate-seeded method. By varying the annealing temperature, worm-like Au nanoparticles of different aspect ratios from 1 to 5 were obtained. Samples of the CdSe coupled with Au with an aspect ratio of 2 and annealed at 500 °C exhibited the best photoluminescence emission efficiency. Furthermore, a stronger photoluminescence enhancement was observed with increasing the size of Au nanoparticles. It was also found that when the localized surface plasmons resonance absorption wavelength of Au nanopartiles was just a little smaller than the emission peak of CdSe, the CdSe quantum dots exhibited the strongest photoluminescence intensity, with an enhancement of 6 times.

1. Introduction

Noble metal nanoparticles (NPs) and nanostructured metal films have attracted considerable attention because of their localized surface plasmons (LSPs). LSPs are charge density oscillations that confined to the metal nanoparticles and metallic nanostructures. The resonant excitation of LSPs on the surface of nanostructured metallic particles by an electromagnetic field causes strong light absorption and scattering; and simultaneously the local electromagnetic fields in regions near the metal particles are significantly enhanced. LSPs are expected to have a significant impact on a wide scope of science, ranging from physics, chemistry and materials engineering to biology. LSPs have been studied for a wide variety of potential applications, such as surface plasmon enhanced Raman scattering [1], fluorescence [2–8], LSPs enhanced light-emitting diodes [9,10], silicon solar cells [11], etc. Among those studies, LSPs enhanced light emission from semiconductor nanocrystals (NCs), such as CdSe quantum dots (QDs) [4–8] have been extensively studied because of their high photoluminescence (PL) efficiencies and size-dependent PL wavelengths.

These localized field enhancement effects are expected to be extremely sensitive to the size and shape of the metal particle, the orientation of the emitters, and the distance between the emitters and the metal. Many research groups have studied the variation in the fluorescence intensity as a function of the size of metal particles [3] and the distance between the fluorophore and the metal [12]. In addition, various shapes of Au or Ag NPs, including spheres, rods, triangles and prisms, have been synthesized by the improved fabrication approaches. Such shaped metal NPs are able to produce strongly confined and enhanced electromagnetic fields in special regions usually called hot spots. Zhang et al. [13] and Hao et al. [14] have used the discrete dipole approximation method to investigate the electromagnetic field induced by the localized surface plasmon resonances of silver nanoparticles of different topologic shapes. Atay et al. [15] have investigated the coupling between pairs of Au nanoparticles fabricated by high-resolution electron-beam lithography in experiments. A very large enhancement of the electromagnetic energy occurs in the immediate vicinity of the point contact between pairs of Au nanoparticles. However, because of the high cost of electron-beam lithography method, it is not adequate to be used in industry.

In this paper, Au NPs were synthesized by a simple citrate-seeded method, and worm-like Au NPs were formed by annealing at different temperatures. The optical properties of Au NPs with different shapes (formed by annealing) and sizes were investigated, and the mechanism of the PL enhancement of CdSe QDs on the Au NPs surface was also studied. It was found that Au NPs annealed at 500 °C possess the largest PL enhancement factor. For further understanding of the coupling between the emitter and the LSP modes, the PL enhancement effect of Au NPs with different sizes was also studied.

2. Experimental details

2.1. Self-assemble of Au NPs surface

Au colloids were synthesized by a citrate-seeded method, similar to Brown's [16] method. In short, a solution of 2.6 nm-diameter Au

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seed colloids was synthesized firstly [16], followed by larger Au colloids prepared by a citrate-seeded method. 200 mL of 0.01% $HAuCl_4$ was brought to boiling in a microwave oven. Then 0.8 mL of 1% sodium citrate and 0.4 mL of as-prepared Au seed colloids were rapidly injected to the boiled solution. The resulting solution was boiled for another 8 min and then stored at 4 °C, named S1. We have also obtained different sized Au colloids by varying the injected volume of Au seed colloids, as 0.2, 0.1 and 0.05 mL, the resulting solutions of which were named S2, S3and S4, respectively. Then the Au NPs were self-assembled on 3-Aminopropyltriethoxysilane (APS)-modified glasses [17] by perpendicularly immersing the slides into the as-prepared Au colloids solution for 12 h. After being dried at room temperature, the obtained Au colloid films were annealed in a rapid thermal annealing oven at 300, 500, and 700 °C for 10 min in N_2 atmosphere, respectively.

2.2. Coupling of CdSe QDs and Au NPs

The as-prepared Au NPs films were coupled with CdSe QDs by the following method. 0.1 mmol CdSe QDs fabricated by an organometallic synthetic approach [18] were dispersed in 10 mL of a 4% poly (methyl methacrylate) (PMMA) solution in chloroform. The prepared CdSe/PMMA was subsequently coated on the surface of glass substrates with and without Au NPs films by dipping the glass substrate into the CdSe/PMMA sol at a fixed speed of 1.5 cm/min. After standing 1 min, the slides were withdrawn from the solution at the same speed. For comparison, Au NPs films coated with a layer of PMMA chloroform sol without CdSe QDs were also prepared under the same conditions.

2.3. Measurements

The UV–visible absorption spectra were measured using a Shimadzu UV-2401 spectrophotometer. Photoluminescence (PL) spectra of CdSe QDs with and without Au NPs films were measured using a HITACHI F-2500 fluorescence spectrophotometer. All the spectra were recorded at room temperature. The morphologies of Au colloid films were investigated by field emission scanning electron microscopy (FESEM) with a Sirion200 microscope under 5.00 kV.

3. Results and discussion

3.1. Morphology property of Au NPs films

Figs. 1(a), (b), (c), and (d) show the morphologies of Au NPs films self-assembled in solution S1 as-prepared and annealed at 300, 500, and 700 °C, respectively. Worm-like Au clusters consisting of several 43 nm Au NPs were formed in the as-prepared film without annealing, as shown in Fig. 1(a). However, the adjacent Au NPs aggregated together at high temperature, and combined with the increasing of the annealing temperature. Finally several adjacent Au NPs combined to form a bigger spherical particle at 700 °C. The aspect ratios of the NPs were for the most part 3–5, 2, and 1 for samples with 10 minutes rapid thermal processing (RTP) at 300, 500, and 700 °C, respectively. Those Au NPs annealed at 300 and 500 °C exhibit similar worm-like shapes and mainly aggregated from 3–5 and 2 Au NPs, although there were a few spherical Au NPs existed. While the sample annealed at 700 °C was mainly spherical particles, due to the higher diffusion rate at high temperature. The FESEM images of the samples Au S2, S3, S4 (annealed at 500 °C) are also shown in Fig. 1(e), (f) and (g), respectively, and these samples exhibit similar shapes to the Au S1 annealed at 500 °C (Fig. 1(c)). The transverse diameter of those Au NPs increased from 50 nm to 65, 85 and 120 nm with the decrease of Au seed colloids volume, as given in Fig. 1(h).

3.2. Optical properties of Au NPs films

Fig. 2 shows the optical absorption spectra of Au NPs films with different shapes and sizes. Interestingly, the Au NPs films (self-assembled in solution S1) without annealing and annealed at lower temperatures such as 300 °C and 500 °C exhibited two surface plasmon resonance (SPR) modes: a longitudinal and a transverse plasmon resonance along and perpendicular to the chain axis, respectively. Meanwhile, the second absorption band blue-shifted with the increasing of the annealing temperature. When the annealing temperature was increased to 700 °C, the SPR modes were located around the SPR position of a single-particle dipole mode (530 nm). It should be noted that the transverse diameters of the Au NPs annealed at different temperatures changed slightly. Therefore, the transverse plasmon resonance bands are near 525 nm with a slight red-shift when increasing the annealing temperature. However, the axis lengths of the Au NPs rapidly decrease with the increase of the annealing temperature, leading to the blue-shift of the second plasmon resonance band. These performances are consistent with the FESEM of the Au NPs films. By varying the volume of the Au seed colloids, much larger Au NPs were obtained, resulting in the red-shift of the absorption band, as shown in Fig. 2(c), the samples of which were all annealed at 500 °C. The absorption band increased from 536 nm to 540 nm, 548 nm, and 595 nm, with the decrease of Au seed colloids volume, suggesting the increase of Au NPs size [19]. As the LSPs resonant frequency is not only determined by the size and shape of the metal NPs, but also relative to the dielectric constant of the surrounding medium [19]. The absorption properties of Au films coated with a layer of PMMA were also investigated. As shown in Fig. 2(b) and (d), the absorption bands red-shift from 536 nm to 555 nm, and from 548 nm to 570 nm, corresponding to samples self-assembled in S1 and S3 (annealed at 500 °C), respectively.

3.3. PL enhancement of CdSe QDs by Au LSP

In general, the PL enhancement effects near nanostructured metal can be understood as arising from two contributions: first, the resonant excitation of LSPs on the surface of nanostructured metallic particles by an incident electromagnetic field causes strongly enhanced local fields, which can lead to a considerable increase of the absorption rate and the excitation rate; and second, the recombination rate in the semiconductor can be significantly enhanced by the LSP resonant coupling of the metal nanoparticles. As the LSPs resonant frequency is extremely sensitive to the size and shape of the metal particle, and which accordingly influences the enhancement effect, we mainly investigated the shape and size effect of Au NPs for PL enhancement.

Fig. 3 shows the PL spectra of CdSe QDs coupled with and without Au, excited at 470 nm. The Au NPs films were self-assembled in solution S1, and annealed at 300, 500, and 700 °C, respectively. Without Au NPs, the CdSe QDs were peaked at 581 nm. The PL intensity of CdSe QDs was significantly enhanced by Au NPs, due to the coupling between LSP of Au NPs and the emission of CdSe. The radiative rates of CdSe QDs can be dramatically enhanced by the nearby noble metal NPs. It can be seen that, by increasing the annealing temperature, the PL enhancement factor first increases, from 1.3 to 1.9 times by increasing the temperature from 300 °C to 500 °C. However, the effect of higher annealing temperature is not always to increase the PL enhancement factor. By increasing the annealing temperature for Au up to 700 °C, the PL enhancement factor decreased to 1.7 times. These performances were expected to be attributed to the shape effect of Au NPs. As indicated by Lakowicz [20], for a spheroid, the most remarkable enhancement effect of radiative rates is for an emitter perpendicular to the surface of a metal spheroid with an aspect ratio of 1.75. However, the effect is smaller for a spherical shaped particles, and much smaller for a more elongated