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Localized surface plasmon resonance enhanced photoluminescence of CdSe QDs in PMMA matrix on silver colloids with different shapes

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ABSTRACT

Localized surface plasmon resonance (LSPR) enhanced photoluminescences (PL) from CdSe quantum dots (QDs) on worm-like or quasi-spherical silver colloids have been investigated. The shape of silver colloid film is controlled by annealing temperature (200 °C~350 °C). Strong PL enhancements of CdSe QDs on both as-grown and annealed silver colloid films are observed. The results show that the PL enhancement factor of CdSe QDs on worm-like silver colloid film reaches as high as 15-fold. Moreover, the enhancement factor is 5 times larger than that obtained from the quasi-spherical silver colloids. The superiority of worm-like silver nanostructure on LSPR enhanced photoluminescence is attributed to its larger size, hot spots and multiple dipole resonance modes coupling, which are induced by aggregation effect.

1. Introduction

Recently, the modification of photoluminescence (PL) from quantum dots (QDs) near metallic nanostructure has been of great appeal for various applications, such as sensors [1], biolabeling [2], optoelectronic devices [3,4]. The enhanced PL of QDs near metallic nanostructure is attributed to the excitation of localized surface plasmon resonances (LSPR) in metal nanostructure [5]. As a characteristic property of metal nanoparticles (NPs), LSPR is induced by resonant excitation of the oscillating electric fields in metal NPs with the incident light, and known for giving rise to strong local electromagnetic (EM) field on the surface of metal NPs. The enormous enhancement of the local EM field makes Au or Ag NPs attractive for applications in transport and storage of energy [6], cellular localization and guiding [7], as well as surface-enhanced spectroscopy [8,9].

In recent years, various shapes of Ag NPs, including cubes [10], rods [11], wires [12] and prisms [13], have been synthesized through the improved fabrication approaches, such as the use of rigid and soft templates [12], seed-mediated growth [11], as well as surfactants and co-surfactants for NPs growth [10,13]. A series of surface plasmon absorption have been obtained in Ag NPs by varying the size, shape, composite and imbedding medium of Ag NPs [10–13]. Among all the factors mentioned above, the geometrical shape of Ag NPs plays a prominent role in determining their surface plasmon absorption. The shape of Ag NPs is usually controlled in the growth process, while a simple heat treatment of the as-grown Ag NPs can also alter their morphology by melting the Ag NPs [14–16]. For example, the snips of Ag prism were rounded by annealing at 200 °C for 20~30 min [14], coalescence of the Ag NPs was observed by sintering Ag nanopowders at 150 °C [15], and Ag NPs were formed in SiO_2 matrix due to the annealing-induced diffusion of Ag clusters [16]. Thus, anneal of Ag NPs can modify the surface of NPs, connect the adjacent NPs, and cause the diffusion of NPs in matrix. Moreover, it has also been found that the heat treatment of Ag NPs in H_2 or N_2 atmosphere could induce a strong LSPR absorption due to the decomposition of Ag_2O at 190 °C [17]. Though there are many reports about annealing of Ag NPs or Ag–SiO_2 composite [14–17], only a few concern the annealing of self-assembled silver colloid film at different temperatures in N_2 atmosphere. According to the molecular-dynamic theory, melting initiates at boundaries or surfaces of the silver NPs and propagates through the system with a velocity which increases with temperature [18,19]. So the morphology of the annealed silver colloid film is expected to be changed with the annealing temperature and the proximity of as-grown silver colloids.

Although a vast amount of information about the fabrication and optical properties of metal NPs with different shapes have been obtained, there are still many ongoing issues on the LSPR enhanced photoluminescence. (i) While metal NPs with various morphologies are synthesized, studies of LSPR enhanced photoluminescence dependent on morphology of metal NPs are limited. The metal NPs with irregular shape are supposed to be superior in LSPR enhanced photoluminescence because they can provide more hot spots of the

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local EM field, such as tips and corners of metal NPs [20]. The EM intensity of hot spots can be enhanced by several orders of magnitude compared to the average enhancement [20–22]. Recently, much effort have been made in creating hot sites for surface-enhanced Raman scattering (SERS), such as nanoparticle (NP) pairs, NP trimers, and NP chains [23,24]. Isolated NPs usually yield a weak SERS response compared to the above mentioned aggregates. This phenomenon is called aggregation effect. Analogously, aggregation of NPs is also expected to affect the LSPR enhanced photoluminescence. However, most of reports on surface plasmon enhanced PL used conventional metallic nanostructure with regular shape [5,25,26]. (ii) Quenching process including chemical bonding and non-radiative energy transfer were often observed from the fluorescent QDs near the metal NPs [27–29]. PL enhancement and quenching of fluorescent QDs were also simultaneously observed in the interface between metal NPs and QDs. This makes it difficult to realize the overall enhancement [5,29]. Understanding and controlling the balance of two processes are crucial for the development of LSPR enhanced photoluminescence. (iii) It is generally agreed that the PL enhancement owes to the local EM field enhancement around the surface of metal NPs. Nevertheless, a clear physical interpretation about the interaction among the incident light, the emission of QDs and the local EM field is still under construction.

In this paper, we report PL enhancements of CdSe QDs doped polymethyl methacrylate (PMMA) on Ag colloid films with different shapes. Our main goal is 2-fold: first we show the effects of annealing temperature in N_2 atmosphere on the morphology and surface plasmon absorption of silver colloid films, and second, we investigate how the different morphologies of silver colloid films affect the PL enhancement of CdSe QDs. Additionally, further attentions are paid for the changes of excitation spectrum of CdSe QDs before and after coupling with the silver colloids.

2. Experimental details

2.1. Preparation of silver colloids

The silver colloids were prepared by citrate reduction method in a microwave oven under the power of 700 W. 150 ml 0.017 wt.% $AgNO_3$ aqueous solution was heated to boiling through microwave. Upon boiling, 3 ml of 1 wt.% sodium citrate aqueous solution was injected. The resulting solution was refluxed for 3 min in a microwave oven.

2.2. Deposition of silver colloids onto glass substrate

The specially cleaned glass slides were placed in a dilute solution of 3-aminopropyltrimethoxysilane (APTMS) (5 g APTMS in 40 g CH_3OH) for 12 h and rinsed with copious amounts of CH_3OH upon removal. The APTMS-coated slides were subsequently immersed in silver colloidal solution for 12 h for assembling silver colloids, followed by rinsing with water.

2.3. Anneal of silver colloid films

The silver colloid films were annealed in a rapidly thermal annealing oven at various temperatures (200, 260, 300, and 350 °C) for 30 min under nitrogen atmosphere.

Coating of CdSe QDs doped PMMA onto as-prepared silver colloid films. 0.01 mmol CdSe QDs prepared by traditional method were dispersed in 15 ml chlorobenzene [30]. 0.1 g PMMA was added into chlorobenzene and dissolved by sonication. The prepared CdSe/PMMA sol was subsequently coated on bare glass and glass substrates covered with silver colloid films by dipping (and withdrawing) the glass substrate into (and out of) the CdSe/PMMA sol at a fixed speed. The bare glass coated with CdSe/PMMA was the reference sample. All samples (including the reference sample) were baked at 180 °C for 120 s to create uniform CdSe/PMMA thin films. The thicknesses of CdSe/PMMA films were almost 200 nm. The smoothness of CdSe/PMMA film was confirmed by confocal microscope.

2.4. Measurements

Absorption spectra were measured by an HP 8453 diode array spectrophotometer. PL spectra were measured using a HITACHI F-2500 fluorescence spectrophotometer at 472 nm excitation. All the spectra were recorded at room temperature. The morphologies of silver colloid films were characterized by field emission scanning electron microscope (FESEM, Sirion200, FEI) with an accelerating voltage 15 kV.

3. Results and discussion

Fig. 1 shows the FESEM images of the as-grown silver colloid film, as well as the silver colloid films annealed at different temperatures. In fact, the as-grown silver colloids are a mixture of nanospheres, nanorods and nanowires, showing disorder and aggregation. After annealed at 200 °C, the initial worm-like silver colloids are created as shown in Fig. 1(b). They have mixed morphologies, such as peanut-like NPs, silver triangles with three silver NPs coupled, and a few chain-like ("Y"and "L"shape) aggregations with several silver NPs linked. It is generally agreed that melting does not occur all at once throughout the NPs, but rather initiates via boundaries or surfaces of silver NPs [18]. For the annealing temperature around 200 °C, the surface melting dominates. In this case, it will cause two physical phenomena: the shrinkage of the boundary of silver colloids and the coalescence of the adjacent colloids. These phenomena would result in the formation of the worm-like silver nanostructure. Therefore, the morphology of worm-like silver colloids is affected by the annealing temperature and the proximity of the as-grown silver colloid film. As the annealing temperature increases to 260 °C, more silver colloids are involved in aggregation, which leads to the appearance of larger and more irregular colloids as shown in Fig. 1c. However, as the annealing temperature approaches 300 °C or 350 °C, the silver colloids become dispersed, ordered and quasi-spherical. In fact, surface melting of silver colloids occurs in a continuous manner over a broad temperature range. With the increasing temperature, the liquid layer caused by the surface melting would consume more and more adjacent solid colloids [31]. Then the shape of silver colloids would be greatly changed, as shown in Fig. 1(d). As the annealing temperature reaches the critical temperature, the homogeneous melting of the solid core of silver colloids would occur abruptly, which would result in the forming of liquid droplet [32]. Thus, the isolated and spherical silver colloids are formed (see Fig. 1(e)). The density of silver colloids on glass substrate becomes lower after 350 °C annealing for 30 min because of the diffusion of some silver colloids into the glass substrate [16]. It is worth to note that the as-grown silver colloid film exhibits a gray color, which gets yellow-green and yellow after annealing at 200 °C and 260 °C, respectively. The color finally becomes a little red after anneal above 300 °C, which may be related to the diffusion mentioned above.

Analogous to the FESEM images, the UV–Visible spectra can also be used to trace the morphological change of silver colloids. The absorption spectra of the as-grown and annealed silver colloids are shown in Fig. 2. The absorption spectrum of the as-grown silver colloid film shows broad around 402 nm. Actually, the peak at 402 nm contains several peaks because of the mixed morphologies and wide size distribution. After annealed at 200 °C for 30 min, the absorption spectrum of silver colloids shows multiple peaks at 358 nm, 404 nm and 487 nm respectively. As far as we know, when the inter-particle separation within NP pairs is varied from point contact to a widening of the interconnection "neck", the surface plasmon absorption peak would be split up into two peaks [33]. One of the two peaks is transverse quadrupole resonance, the other one is longitudinal dipole resonance. Analogous to the NP pairs, most of the silver colloids