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Fluorescence spectra of colloidal self-assembled CdSe nano-wire on substrate of porous Al_2O_3/Au nanoparticles*

Xin Zhang(张欣)[1,3], Li-Ping Shao(邵丽萍)[1,3], Man Peng(彭嫚)[1,3], Zhong-Chen Bai(白忠臣)[2,3,†], Zheng-Ping Zhang(张正平)[1,3], and Shui-Jie Qin(秦水介)[1,3]

[1] *College of Big Data and Information Engineering, Guizhou University,, Guiyang* 550025, *China*
[2] *College of Medicine, Guizhou University, Guiyang* 550025, *China*
[3] *Guizhou Province Key Laboratory for Photoelectric Technology and Application, Guizhou University, Guiyang* 550025, *China*

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We present a self-assembly method to prepare array nano-wires of colloidal CdSe quantum dots on a substrate of porous Al_2O_3 film modified by gold nanoparticles. The photoluminescence (PL) spectra of nanowires are in situ measured by using a scanning near-field optical microscopy (SNOM) probe tip with 100-nm aperture on the scanning near-field optical microscope. The results show that the binding sites from the edge of porous Al_2O_3 nanopores are combined with the carboxyl of CdSe quantum dots' surface to form an array of CdSe nanowires in the process of losing background solvent because of the gold nanoparticles filling the nano-holes of porous Al_2O_3 film. Compared with the area of non-self-assembled nano-wire, the fluorescence on the Al_2O_3/Au/CdSe interface is significantly enhanced in the self-assembly nano-wire regions due to the electron transfer conductor effect of the gold nanoparticles' surface. In addition, its full width at half maximum (FWHM) is also obviously widened. The method of enhancing fluorescence and energy transfer can widely be applied to photodetector, photocatalysis, optical display, optical sensing, and biomedical imaging, and so on.

Keywords: enhanced photoluminescence, CdSe nano-wire, colloidal self-assembled method, porous Al_2O_3 film

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1. Introduction

Semiconductor nanostructures are widely applied in photovoltaic devices,[1–4] heterojunction laser,[5–7] light-emitting diode (LED)[8,9] photoelectric converter,[10] and other fields[11,12] due to their special photoelectric characteristics, which differ from those of bulk materials. For example, CdSe quantum dots (QDs) can be applied to solar cells, black phosphorus QDs have the potential as an efficient agent for photoacoustic imaging,[13] and Antimonene QDs can be used as near-infrared photothermal agents for effective cancer therapy.[14] The main methods of preparing semiconductor nano-wires are the molecular beam epitaxy (MBE) method,[15] template method,[16] colloidal chemistry method,[17] chemical deposition method,[18] laser vapor deposition method, and so on. Of these, the colloidal chemistry has the simplest process and needs the mildest reaction condition. In addition, its product is antioxidant, which is easy to transport and convenient to transplant. However, its disadvantages lie in the difficulty of purification, monodisperse, and easy aggregation. In addition, the aggregation and non-mondisperse features also provide a new pathway to broadening its optical spectra and preparing new nanostructures applied to the wide spectral detection devices.

Owing to the fact that the surface of porous Al_2O_3 film has many defects,[19–21] such as oxygen vacancy and aluminum interstitials, its defect energy levels are formed inside its band gap, which makes it a semiconductor. Meanwhile, the positive surface charges are rooted in oxygen vacancies and can absorb the negative ions, thus dyeing the surface of porous Al_2O_3 film.[22,23] Moreover, the arrangement direction of the nanopore is also convenient when preparing nanostructures with the different morphologies. It can enhance the carrier number by regulating the defect concentration of porous Al_2O_3 film. Consequently, it is an important nanomaterial in fields of energy band engineering that has great potential applications in the researches of heterogeneous materials, photovoltaic,[24] optical detection,[25] and photocatalysis.[26] However, its surface detection increases the probability of carriers being captured, which restricts the practical applications of the porous Al_2O_3 film.

We use the electronic conductor effect of gold nanoparticles (NPs) to transfer the photo-generated carriers of CdSe QDs on the interface of CdSe QDs and porous Al_2O_3 film, thereby reducing the probability of carriers being captured

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†Corresponding author. E-mail: zcbai@gzu.edu.cn

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in the transport process and stabilizing the fluorescence of porous Al_2O_3 film.Thus, we prepare the array nano-wires on the porous Al_2O_3 surface by using the colloidal self-assembly method to form an Au/Al_2O_3/CdSe heterojunction and measure the photoluminescence (PL) spectra of heterojunction.

2. Experiments

The pore size and depth of cellular porous Al_2O_3 film of aluminum substrate, which was a commercialized porous nano-film material (available from the SHNTI Co., Ltd., China), were, respectively, about 90 nm and 5 μm. The size of monodisperse gold NPs (available from the Commercialized nanomaterials, Cytodiagnostics Inc., China) was about 15 nm, and its surface was packaged with the citric acid molecules. The colloidal CdSe quantum dots were prepared by our previous methods.[27,28] The size of single QD was about 3.5 nm, and its surface was packaged with the oleic acid molecules. The number density of gold NPs and CdSe QDs in raw solution were, respectively, about 2.0×10^{17} ml^{-1} and 2.0×10^{18} ml^{-1}. Both n-hexane and ethanol were analytically pure reagents, which were purchased from the Tianjin kermel reagent Co., LTD, China. The mica substrate (available from the SHNTI Co., Ltd., China) was used to measure the PL spectrum of CdSe QDs raw solution.

Before using the mica and porous Al_2O_3 film substrates, they were washed three times by using absolution ethyl alcohol to wipe off its surface dust. The raw solution of gold NPs and CdSe QDs were, respectively, dispersed into absolution ethyl alcohol and n-hexane in proportion of 1:10 volume for preparing the gold NPs solution and the CdSe QDs solution.

To measure the fluorescent spectrum of CdSe QDs, 1-μl CdSe QDs solution was fully coated on the surface of the mica substrate. It was then placed into the vacuum drying oven at 80 °C for drying and to solidify it. The preparing processes of self-assembly substrate of CdSe QDs was as follows: (i)the rear of porous Al_2O_3 film substrate was fixed on a glass sheet surface, then it was totally submerged in the gold NPs solution; and (ii) when the liquid level of gold NPs' solution was lowered to the bottom edge of porous Al_2O_3 film, the porous Al_2O_3 film was taken out and removed from the glass sheet surface, and then it was dried for preparing the substrate of porous Al_2O_3 film modified with the gold NPs in the vacuum drying at 80 °C. The CdSe QDs' solution was loaded into a medical injection syringe until it attained to a 100-μm tip of hollow fiber fixed on the three-dimensional (3D) position controlling holder. The CdSe QDs solution was dropped on the surface of porous Al_2O_3 film modified with the gold NPs by controlling the position of array sample points. And then, the self-assembly nanostructures of CdSe QDs was formed on the edge of sample points due to the loss of background solvent evaporating.

An ultraviolet (UV) laser of central wavelength at 360 nm (Changchun new industries Ltd., CNI-360) was coupled to a multimode fiber to attain a probe tip of SNOM (Nanonics, 100-nm aperture). A 100-nm laser spot was stimulated on the sample in an atomic force microscope (AFM) tapping mode on the scanning near-field optical microscope (Nanonics, Mv4000). The fluorescence was collected by an objective lens to a fiber optical spectrometer (Ocean optics, QE6500) to measure the PL spectrum. The PL spectra and surface topography map were *in situ* obtained in the process of scanning.

3. Results and discussion

Figure 1 shows the PL spectrum of the CdSe QDs, porous Al_2O_3 film modified by gold NPs, non-nanowire and nanowire of self-assembly CdSe QDs. A comparison between PL spectra shows that the peak of partial overlapping of CdSe QDs is far from that of the porous Al_2O_3 film modified by the gold NPs. Owing to the absorption of CdSe QDs from the fluorescence of porous Al_2O_3 film modified by gold NPs, the interface fluorescence of CdSe QDs could be increased via the energy transfer of porous Al_2O_3 film.

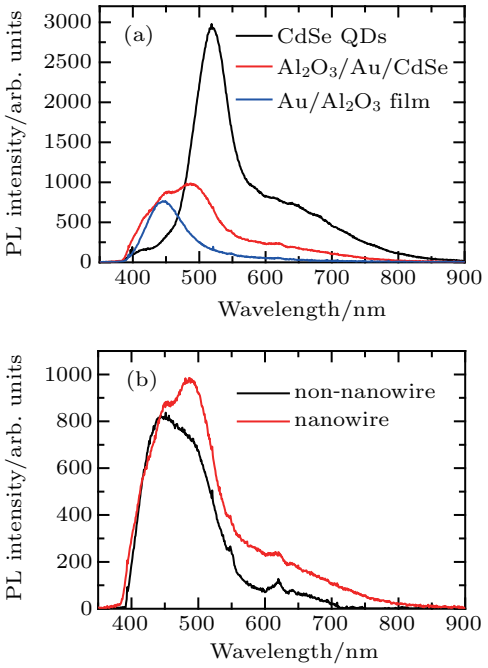


Fig. 1. PL spectrum of CdSe QDs, porous Al_2O_3 film modified with the gold NPs, self-assembly CdSe QDs, and non-self-assembly CdSe QDs.

The spectrum of Al_2O_3/Au/CdSe has two obvious peaks in comparison with that of the porous Au/Al_2O_3 film and the CdSe QDs. They originate from the interfacial fluorescence of porous Al_2O_3 film and CdSe QD. Here, the gold NPs act as an electron transfer conductor that transfers the interfacial photo-generated carries of porous Al_2O_3 film and CdSe QDs, which balances the quantity of electrons between the porous Al_2O_3 film surface and the CdSe QDs surface by their electric potentials. In addition, compared with the PL intensity of

non-nanowire structure, the PL intensity of nanowire structure is obviously enhanced, as shown in Fig. 1(b). This implies that the nanowire structure can promote the absorption of incident light, thereby enhancing the fluorescence on the surface of CdSe/Au/Al_2O_3.

To observe the self-assembly nano-wire structure of CdSe QDs on the porous Al_2O_3 film modified by the gold NPs, we measure in situ the AFM topographic map and spectrum of sample surface on the edge of CdSe QDs. The periodic array nano-wires of CdSe QDs are distinctly observed in Fig. 2(a). The period of array nano-wire structure and the thickness are about 2.2 μm and 50 nm, respectively, as shown in Fig. 2(b).

The physical process of generating the periodic array nano-wire can be explained as follows. First, the monodisperse gold NPs are self-assembled on the surface of porous Al_2O_3 film. The gold NPs packaged with the citric acid can enter into the hole of porous Al_2O_3 film by diffusion effect. This is combined with the surface of porous Al_2O_3 via the electrostatic interaction of carboxyl of gold NP surface with the positive charges on the surface of the porous Al_2O_3. The gold NPs are then increasingly accumulated in the pore. After losing background solvent in the process of vacuum drying, the gold NPs are further aggregated and therefore lots of gaps occur at the edge of pores, which can combine with other negatively charged ionic groups. These sites determine the nanostructures of self-assembly CdSe QDs. Second, after the CdSe QDs are pointed the sample at the surface of porous Al_2O_3 film modified by the gold NPs, the carboxyl groups of oleic acid from the CdSe QDs can combine with the positive charge site on the edge of pore. Third, the CdSe QDs in the hexane, which are aggregated toward the CdSe QDs, are combined with the edge of pore in the process of background solvent evaporated. The CdSe QDs then gradually cover the whole nano pores and are connected together to form a wire-like structure in the direction of vertical background solvent shrinking. As seen in Fig. 2(a), there is a lot of relatively high protuberance on the nano-wire, and in the middle the point sample area is relatively low. This further confirms the previous explanation.

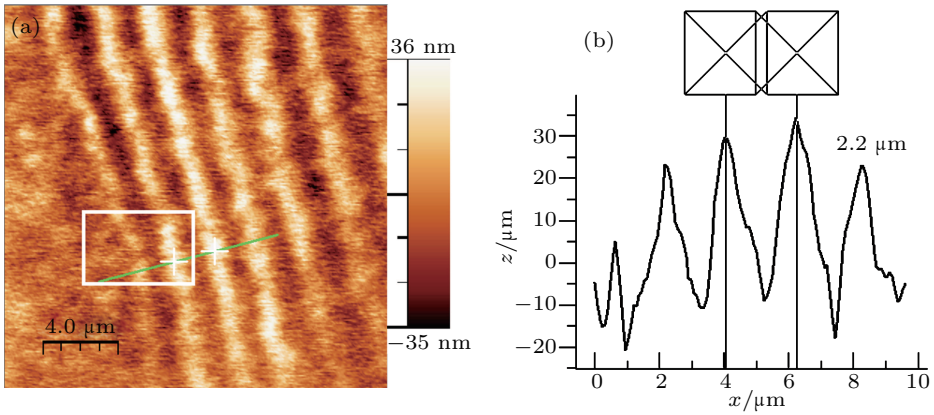


Fig. 2. AFM morphology and size of self-assembly nano-wires of CdSe QDs on the substrate of porous Al_2O_3 film modified by gold NPs.

To compare the fluorescent spectra of nano-wire structure and non-nanowire, we measure PL spectra of 20 sampling points on a measuring line from left to right in Fig. 2(a). The PL spectrum has only one peak located near 455 nm far from the PL peak of nano-wire structure, while there are two distinct peaks on the nano-wire structure that are located near 455 nm and 490 nm, respectively. Moreover, the peak at 490 nm becomes increasingly higher. This is the reason why the CdSe QDs are relatively rare or non-existent at the position far from the nano-wire structure to result in its PL spectra dominated by the porous Al_2O_3 film interface modified by the gold NPs. Because the structure of CdSe QDs is close to the nano-wire structure, the quantity of CdSe QDs increases to enhance the quantity of photo-generated carriers and facilitate the interface radiation of CdSe QDs and gold NPs. The quantity of CdSe QDs further increases on the surface of nano-wire to enhance the interfacial fluorescence of CdSe QDs. In other words, the gold NPs play an important role in transferring photo-generated carriers of porous Al_2O_3 film and CdSe QDs. This is a bridge that transfers photo-generated carriers between the interface of CdSe QDs and the porous Al_2O_3 film by their chemical differential potential.

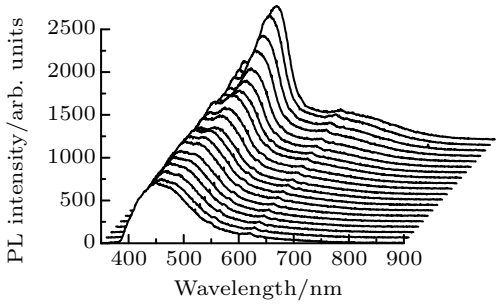


Fig. 3. PL spectra of the sampling points on the measuring line in Fig. 2(a).

The gold nanoparticles transfer the photo-generated carriers from the CdSe QDs. However, it also balances the number quantity of photo-generated carriers between the CdSe QDs and porous Al_2O_3 film via the electron conductor effect. The enhanced absorption of the nano-wire structure is also an important reason to explain why the florescence is enhanced. Thus, two main effects determine the enhanced PL effect: the first is the enhanced absorption from the nano-wire structure to

facilitate the increase of heterojunction fluorescence, the second is that the gold nanoparticles transfer and thus balance the photo-generated carriers between the porous Al_2O_3 film and the CdSe QDs as an electron conductor by their differential potential.

To further observe the peak distribution of PL spectra, we select a measurement region to measure the PL spectra at the edge of self-assembly nano-wire structure in the frame of Fig. 2(a); the optical spectral topographic map is shown in Fig. 4. In Fig. 4(a), the peak distribution of PL spectra is obvious and it clearly has a boundary of maximum optical spectrum peaks. Namely, the fluorescence is from the interface between porous Al_2O_3 film and gold NPs in the area of non-nanowire, while the fluorescence is from the interface between CdSe QDs and gold NPs. In Fig. 4(b), the nano-wire of CdSe QDs self-assembly is also observed, which indicates the coherence of optical spectral peak distribution on the nano-wire structure.

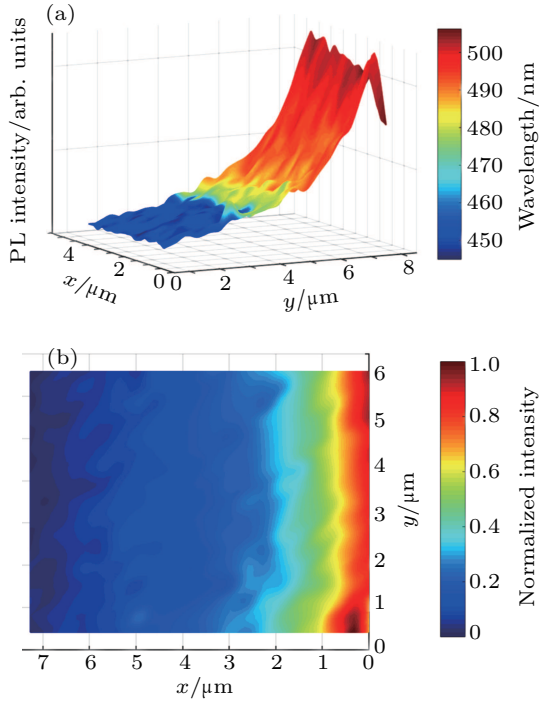


Fig. 4. Spectral topographic maps at the edge of self-assembly nano-wire structure, showing (a) peak fluorescence morphology map and distribution of peak fluorescence of measuring area of Fig. 2(a) and (b) distribution of peak fluorescence in panel (a).

4. Conclusions

In this work, we demonstrate the self-assembly preparation method of array nano-wire structure by using colloidal CdSe quantum dots on the substrate of porous Al_2O_3 film modified by the gold nano-particles. Moreover, their PL spectra are measured point by point on a scanning near-field optical microscope via an SNOM probe tip of 100-nm aperture. Our results indicate that the nano-pore of porous Al_2O_3 film filled with the gold NPs has many sites on the edge of the pore that can further combine with the CdSe QDs to self-assemble the periodic array nano-wires. Here, the sites on the edge of pore have an important role in self-assembling the nanostructure. Compared with the area of non-self-assembled nano-wire, the fluorescence on the Al_2O_3/Au/CdSe interface is significantly enhanced in the self-assembly nano-wire regions due to the electron transfer conductor effect of gold NPs' surface and its FWHW is obviously widened. The method of enhancing fluorescence and energy transfer can be widely applied to control photodetectors, photocatalysis, optical displays, optical sensing, biomedical imaging, and so on.

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