

Measuring photoluminescence spectra of self-assembly array nanowire of colloidal CdSe quantum dots using scanning near-field optics microscopy

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A novel periodic array CdSe nanowire is prepared on a substrate of the porous titanium dioxide by using a self-assembly method of the colloidal CdSe quantum dots (QDs). The experimental results show that the colloidal CdSe QDs have renewedly assembled on its space scale and direction in process of losing background solvent and form the periodic array nanowire. The main peak wavelength of Photoluminescence (PL) spectra, which is measured by using a 100-nm aperture laser beam spot on a scanning near-field optics microscopy, has shifted 60 nm with compared to the colloidal CdSe QDs. Furthermore, we have measured smaller ordered nanometer structure in thin QDs area as well, a 343-nm periodic nanowire in thick QDs area and the colloidal QDs in edge of well-ordered nanowire.

Keywords: Photoluminescence (PL); CdSe nanowire; self-assembly method; quantum dots; porous titanium dioxide (porous TiO₂).

Optical properties of nanowire and quantum dots (QDs) based on CdSe material continue to attract attention from an applied point of view, such as photoelectric detector,¹ solar cell,² high sensitivity sensor,³ semiconductor laser,⁴ LED.⁵ With the development of micro and nanomachining technology, it has been made possible to prepare a high length-width ratio nanowire,⁶ including molecular beam epitaxy technology,⁷ template method,⁸ chemical synthesis method,⁹ laser gas deposition method,¹⁰ chemical vapor deposition method,¹¹ self-assembly method.¹² Chemical synthesis method have many advantages such as a low cost, easy transplant, well antioxidant products, which had been widely focused in nanoscience.^{13,14} However, it is still difficult to control its aggregation in transplant process. More larger the density of nanocrystallines will result in more serious aggregation. In addition, the self-assembly aggregation effects of colloidal CdSe QDs provides a novel method for preparing complex nanostructures,^{15–17} for example nanowire, nanoscale integrated circuits.

Photoluminescence (PL) spectra is a widely used tool to identify energy band structures of the material,^{18,19} especially in nanomaterial such as QDs and quantum wire. Owing to the restriction of diffraction limit, the fluorescent light of

nanomaterial is generally stimulated by using more 1 μm laser beam spot.^{20,21} Thus, it is very difficult to measure single nanoobject spectra including QD and quantum wire in nanoscale.²⁰ Owing to the advance of the near-filed optics technology, a sub-micrometer/nanometer laser beam spot has been applied for the study of micro/nano optical spectroscopy technology.^{22–25} Further, under a low background condition, it has been made possible that PL spectra of nanomaterial would be accurately measured at room temperature in nanoscale.

In this paper, a periodic array CdSe nanowire on the substrate of a porous TiO₂ is prepared by using a self-assembly method of the colloidal CdSe QDs at 80°C temperature in vacuum oven. In order to get the emissive spectra of a nanoscale, an aperture tip exciting mode (100 nm aperture) of scanning near-field optics microscopy (SNOM) is employed to measure PL spectra.

We use precursor method to prepare the stable optical spectra colloidal CdSe QDs in oleic acid-paraffin system.^{26,27} Detailed information of the CdSe QD is represented in Supplemental materials. The colloidal CdSe QDs solution is prepared with 1 mL colloidal CdSe QDs dispersing into 5 mL n-hexane. It is noticed that CdSe QDs with a colloidal cluster of forms is dispersed into n-hexane and kept in a

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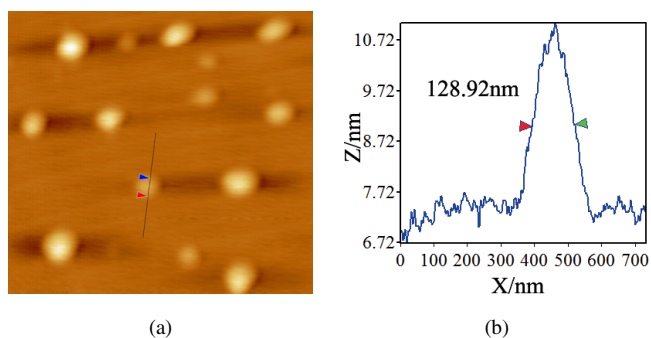


Fig. 1. AFM topographic map of colloidal CdSe QDs clusters on mica substrate. (a) AFM and (b) scale, lateral scale is 128.92 nm and its longitudinal scale is 3.8 nm.

stable existence unless the oleic acid and paraffin removed (see Supplemental materials). To obtain in situ the information of colloidal CdSe QDs clusters, we take a drop of colloidal CdSe QDs solution to disperse on a mica. The QDs is fixed on mica due to the losing background solvent. Atomic force microscopy (AFM, Benyuan Inc., CSPM 5500) is used for measuring its lateral scale on mica substrate. The morphology graphics is shown in Fig. 1(a). AFM results have showed that its lateral and longitudinal scale is respectively 128.92 nm and 3.8 nm in Fig. 1(b) corresponding to Fig. 1(a).

The substrate, the porous TiO₂ on aluminum base (pore size is 70 nm, pore deep is 5 μm), is tailored to 1 cm square and 1 mm thickness and is cleaned three times by ethyl alcohol. Then the substrate is dried under nitrogen. A drop of the colloidal CdSe QDs solution is dispersed onto the substrate surface, which is put into vacuum oven for standing 2 h under vacuum. After vacuum oven is rapidly heated up to 80°C temperature and kept for 24 h, vacuum oven is closed and vacuum annealed to the room temperature. Next, the nanowire sample is taken out and is prepared for measurement.

In order to decrease background noise and reduce CdSe QDs quantity on measuring area, we introduce a 100 nm aperture fiber tip (coated metal chromium on the tip surface) as a nanometer laser beam spot source for exciting the nanowire sample. The experiments are performed on sample scan mode of a scanning near-field optics microscopy (Nanonics, MV4000). The nanowire sample is held at room temperature and is excited at fiber tip incidence with linear polarized Gaussian pulses, derived though a single mode UV-VIS fiber and pulse shaping of the output from a wavelength 360 nm continuous laser with a repetition rate of 70 MHz and an energy of 50 mw. Here the energy from the laser to the fiber tip was decreased 10⁻⁴ order. PL spectra is received by long focus objective lens on measuring area at point by point scan mode.

Figure 2(e) depicts 25 points fluorescence spectrum corresponding to AFM graphics in Fig. 2(a) on a straight line, which is measured by 4 s integral time with an optical fiber spectrometer (Ocean optics, QE6500). Comparing the fourth

point (4 point) spectrum (black line) with the colloidal CdSe QDs clusters (red line), PL spectra has been changed in Fig. 2(b). The PL spectra main peak of the nanowire sample had shifted 60 nm to short wavelength and has increased fluorescence intensity as well. The results is considered that the CdSe QDs on porous substrate had aggregated to form more tiny nanocomposites at 80°C temperature under vacuum drying, which resulted in more stronger quantum confine effect. Meanwhile, under vacuum drying background solvent evaporated at 80°C temperature, the colloidal CdSe QDs clusters go together and increased their density.

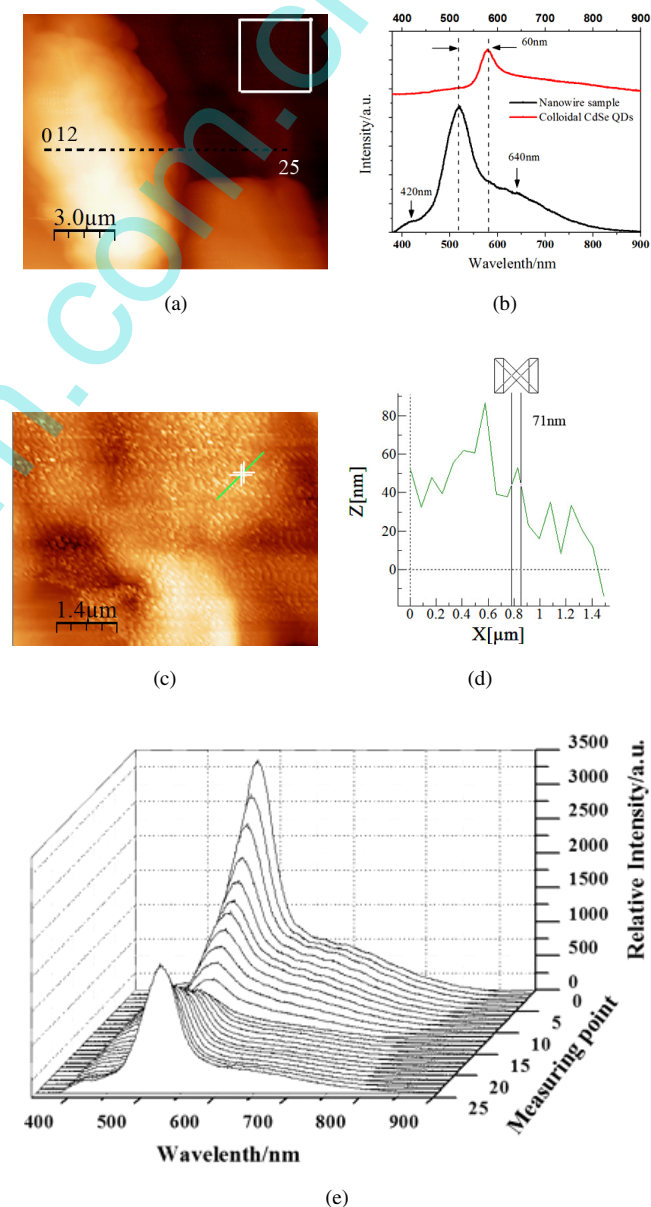


Fig. 2. AFM graphics and PL spectra of the nanowire sample. (a) AFM of the nanowire sample surface, (b) PL spectra of the colloidal CdSe QDs (red line) and the fourth point on straight line (black line). (c) Scale picture in black area of (a). (d) The more smaller lateral scale to the colloidal CdSe QDs in (c). (e) 25 measuring points PL spectra on a straight line of (a).

We observe a new PL spectra peak value (420 nm) on left-hand of the main peak. This is because of the vent of a more tiny nanostructure in self-assembly process. Figure 2(c) shows more little nanopattern from white box area in Fig. 2(a) than the colloidal CdSe QDs in Fig. 1(a). Another fluorescence peak (640 nm) is found on right hand of main peak due to the appearance of the larger nanostructure comparing with the colloidal CdSe QDs.

To investigate the distribution of differential nanostructure on the nanowire sample, we plot the distribution of the optical spectrum in Fig. 2(e). By comparison the differential height of AFM graphics on a straight line and its optical spectrum, the spectra sharp is basically same in different points. Moreover, with the varying of the different height in Fig. 2(a) on measurement points, the main peak intensity has kept consistency with Fig. 2(e). The results has verified the stability emissive fluorescence and the similar nanostructure on different points of the nanowire sample.

Owing to limit of the resolution of AFM tip, the real topographic map is unable to get on poor roughness surface. In order to observe precisely the fluorescence on nanowire sample, we keep contact with the sample and the tip, which change the fluorescence received mode by using a 514.5-nm long pass filter and PMT instead of optics spectrometer. Figure 3 showed distinctly the periodic nanowire fluorescence image corresponding to Fig. 2(a). Contrast to AFM topographic map, fluorescence image of SNOM has more distinct a results in resolution.

To demonstrate the scale of nanowire in Fig. 3, we locate on the nanowire area by setting $256 \text{ pixel} \times 256 \text{ pixel}$ scan points and 8ms sub-point count time in SNOM mode. The periodic wire fluorescence graphics in Fig. 4(b) shows the colloidal CdSe QDs to form a whole nanowire structure by self-assembly method. Fluorescence image is consistent with AFM graphics in Fig. 4(a). When the colloidal CdSe QDs clusters gather together because of background solution evaporated at certain temperature to form other

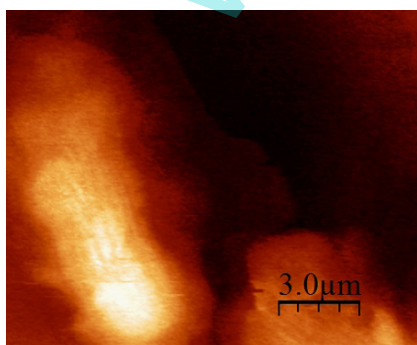


Fig. 3. Fluorescence image (PL intensity integration) with a 514.5-nm long pass filter.

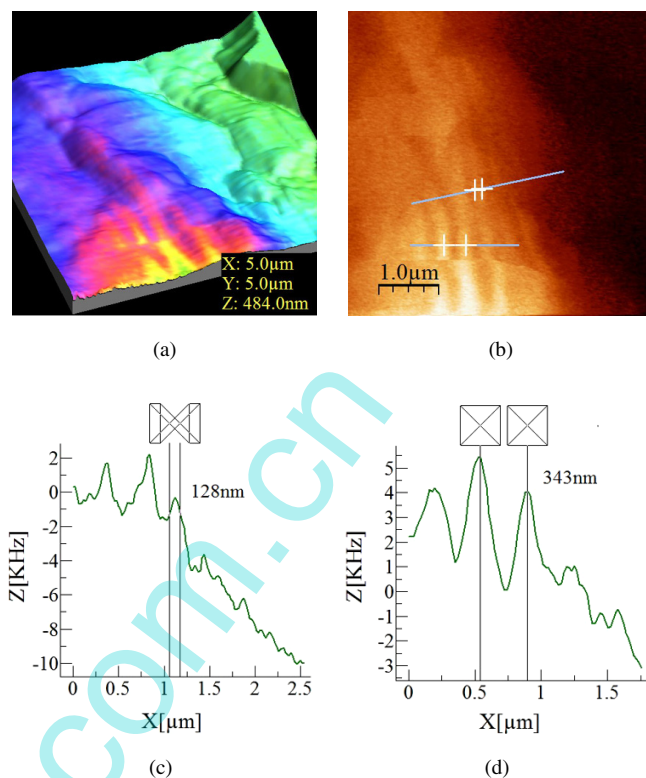


Fig. 4. Measuring a pitch of the periodic array CdSe nanowire with SNOM mode. (a) AFM graphics. (b) Fluorescence image of the nanowire. (c) Profile of the colloidal CdSe QDs cluster is 128 nm. (d) Measuring profile of a pitch is 343 nm in periodic array CdSe nanowire.

nanostructure, it is possible to exist the colloidal CdSe QDs on the edge of self-assembly nanostructure. We measured the fluorescence profile in margin of nanowire, single CdSe QDs in Fig. 4(c) is found. Its diameter by SNOM is agreed with AFM in Fig. 1.

The profile of the CdSe nanowire fluorescence in Fig. 4(d) shows a periodic array with 343 nm pitch and similar with a pitch of AFM graphics in Fig. 4(a). We consider that a different evaporation rate from background solvent result in an ordered gathering direction of the colloidal CdSe QDs. At 80°C temperature, the assembled QDs renews its self-assembly and surface texture with surface tension. However self-assembly direction is decided by surface evaporation rate of background solution. We use a 100 nm aperture laser beam spot to excite point by point the nanowire for emission fluorescence. This method not only reduce background noise but also improve the resolution of fluorescence image. So the periodic array nanowire is recognized in our experiment.

We have studied the periodic array nanowire prepared by the colloidal CdSe QDs with self-assembly method on porous titanium dioxide substrate. AFM graphics and PL spectra are simultaneously observed in SNOM with fiber tip exciting mode of a 100 nm aperture laser beam spot from

360 nm laser coupled to single mode optical fiber. The resolution of fluorescence from the nanowire is improved substantially to get a distinct periodic array nanowire topographic map comparing with non-uniform surface height of AFM graphics. The experiment results have indicated that the periodic array nanowire is prepared on porous titanium dioxide substrate by renewed organizing direction of the colloidal CdSe QDs due to background solution evaporated at 80°C temperature. Smaller nanopattern and the periodic array nanowire were both grown in the processing of self-assembly. Moreover the colloidal CdSe QDs was observed on edge of the nanowire in experiment. The novel preparing nanowire methods in this paper has important potential in the fields of high precision photoelectric detector, molecular sensor, solar cell, LED and quantum display.

Acknowledgments

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References

1. Y. S. Zhou et al., *ACS Nano* **6**, 6478 (2012).
2. Y. Y. Zhou et al., *Adv. Func. Mat.* **20**, 1464 (2010).
3. A. Khandelwal et al., *J. Elec. Mat.* **35**, 170 (2006).
4. J. Li et al., *Adv. Mat.* **25**, 833 (2013).

5. Z. Fan et al., *Proceedings of the National Academy of Sciences* **105**, 11066 (2008).
6. S. Banerjee et al., *J. Mat. Sci.* **37**, 4261 (2002).
7. P. Krogstrup et al., *Nat. Mat.* **44**, 400 (2015).
8. D. J. Pena et al., *J. Phys. Chem. B* **106**, 7458 (2002).
9. Z. Li et al., *Euro. J. Ino. Chem.* **2010**, 4325 (2010).
10. J. R. Morber et al., *J. Phys. Chem. B* **110**, 21672 (2006).
11. B. B. Xiao and Y. B. Xu, *Physica E: Low-Dimensional Systems and Nanostructures* **44**, 696 (2011).
12. R. Solanki et al., *Appl. Phys. Lett.* **81**, 3864 (2002).
13. F. Shieh et al., *J. Phys. Chem. B* **109**, 8538 (2005).
14. S. Zhang et al., *Nano Lett.* **15**, 1152 (2015).
15. Z. Nie, A. Petukhova and E. Kumacheva, *Nat. Nano.* **5**, 15 (2010).
16. W. Jin et al., *ACS Appl. Mat. & Int.* **7**, 13131 (2015).
17. S. Liu, W. H. Zhang and C. Li, *J. Cryst. Growth* **336**, 94 (2011).
18. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd edn. (Springer Science & Business Media, USA, 2013).
19. B. Valeur and M. N. Berberan-Santos, *Molecular Fluorescence: Principles and Applications* (John Wiley & Sons, USA, 2012).
20. L. Novotny and B. Hecht, *Principles of Nano-Optics* (Cambridge University Press, UK, 2012).
21. P. Anger, P. Bharadwaj and L. Novotny, *Phys. Rev. Lett.* **96**, 113002 (2006).
22. A. Singh et al., *J. App. Phys.* **117**, 033104 (2015).
23. A. Horneber et al., *Phys. Chem. Chem. Phys.* **7**(33), 21288 (2015).
24. A. Kuhlicke, A. Rylke and O. Benson, *Nano Lett.* **15**, 1993 (2000).
25. T. W. Larsen et al., arXiv preprint, arXiv:1503.08339 (2015).
26. Z. Deng, L. Cao, F. Tang and B. Zou, *J. Phys. Chem. B* **109**, 16671 (2005).
27. C. Cheng and X. Y. Cheng, *Nanophotonics and Devices* (Science Press, China, 2013).