

Synthesis of SiO₂@CdSe nanoparticles: dispersion and optical properties

SHAOLIE CHEN, QIUYU ZHANG*, JUNPING ZHANG, JUNWEI GU, HEPENG ZHANG, QING LIU, JIAN ZHOU
Key Laboratory of Space Materials Science and Technology of Ministry of Education, Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Shaanxi Xi'an, 710129, China

Uniform SiO₂@CdSe nanoparticles were obtained by using electrostatic adsorption of CdSe onto the surface of the monodisperse silica. SiO₂@CdSe nanoparticles presented stronger fluorescence intensity compared to that of dispersant coated CdSe nanoparticles ascribe to naked CdSe. Its application as donor or acceptor in a FRET system was also investigated in this work, and the results showed that SiO₂@CdSe nanoparticles can act as donor or acceptor in the FRET system. Because of naked CdSe particles, the ability of electron donor or acceptance of SiO₂@CdSe nanoparticles was much better than that of dispersant coated CdSe nanoparticles. The mechanism of formation of SiO₂@CdSe nanoparticles was also discussed in this paper. The obtained SiO₂@CdSe nanoparticles can be dispersed well in ethanol or solid film, resulting in better optical properties compared to that of dispersant coated CdSe nanoparticles.

(Received March 10, 2011; accepted April 11, 2011)

Keywords: Monodisperse silica, SiO₂@CdSe nanoparticle, naked CdSe, dispersion, Optical properties

1. Introduction

The preparation and characterization of semiconductor nanomaterials have been attracted considerable attention in recent years due to their electronic, optical properties, and their potential applications in constructing nanoscale electronic and optoelectronic devices [1-7].

Cadmium selenide (CdSe) nanocrystal, one of the most important semiconductor in various promising optoelectronic applications owing to its excellent optical conductivity, such as nonlinear optical materials and quantum size effect semiconductors [8]. However, for the super high specific area of nanoparticles, they are easily aggregate. Thus, dispersion of nanoparticles becomes a critical problem for their application. There is basically one main approach that has been recognized, which dispersing in organic coatings. In most previous cases, CdSe nanoparticles were normally capped with an organic layer such as a mixture of trioctyl phosphine and trioctyl phosphine oxide (TOP/TOPO) [9]. Rogach research group [10] have developed a series of thiol-capped crystalline CdSe nanoparticles in a facile way by using mercapto-alcohols (2-mercaptoethanol, 1-thioglycerol), and mercapto acids (thioglycolic acid, thiolactic acid) as stabilizers. Yujun Yang [11] have synthesized nearly monodisperse CdSe nanoparticles with poly(vinylpyrrolidone)(PVP) as capping agent. However, all above mentioned approaches seriously impeded the

nano-semiconductor applications in optical devices ascribe to coating the surface of nano-semiconductor with a layer of organic reagents. Recently, there were several references have reported that using polystyrene (PS) spheres as the templates for deposition of naked CdSe [12, 13]. Hence, inspiration from these reports, monodisperse nano-silica was used as template in this paper, and then electrostatic adsorbed a layer of CdSe on the surface of nano-silica, this composite nanoparticles could be well dispersed in the liquid phase or solid film with naked CdSe, and its structure and optical properties were also investigated in this paper.

2. Experimental

2.1 Materials

Tetraethyl orthosilicate (TEOS, 99 wt %), CdCl₂·3/2H₂O (99.8 wt %), poly(vinylpyrrolidone)(PVP) and ammonia were purchased from Beijing Chemical Reagent Cooperation (China), Ethylene Diamine Tetraacetic Acid (EDTA), Se powder (99.8 wt %), triethanolamine (99.8 wt %), thioglycerol (TG) and sodium sulfite (99.9 wt %) were purchased from Shaanxi Reagent Cooperation (China). Trinitrotoluene (TNT) was afforded by the Xi'an Modern Chemical Research Institute and fluorescent polymer was synthesized according to the Ref [14].

2.2 Synthesis of monodisperse silica nanoparticles

The monodisperse silica nanoparticles were prepared according to the modified Stober method [15]. The reaction was carried on by hydrolyzing of TEOS in ethanol medium in the presence of ammonia. 57mL ammonia solution (25%) was added into the co-solvents of 20ml deionized water and 200ml anhydrous ethanol to prepare solution A. Then, 60g TEOS was dissolved completely in 150mL anhydrous ethanol to prepare solution B. Finally, solution A was added into solution B by dropwise in an hour with vigorous stirring at ambient temperature. The final solution was stirred for another 4 hours, and the formed precipitate was isolated by centrifugation to get monodisperse SiO₂ spherical colloids, dried under vacuum at 40°C for the next step using.

2.3 Preparation of Na₂SeSO₃ solution

Na₂SeSO₃ solution was prepared according to the published literature [16]. 12.6g Na₂SO₃ was dissolved in 100 mL deionized water in three-neck flask, the solution was heated to reflux, and then 3.95g Se powder was added into the solution with vigorous stirring for 1h under nitrogen atmosphere to get Na₂SeO₃ solution. This solution was kept in dark place for the next step using.

2.4 Synthesis of CdSe nanoparticles

1.55g CdCl₂·3/2H₂O and 1.86g EDTA were put into the autoclave and dissolved completely in 100 ml deionized water, adjusting the solution PH value between 9 to 11 by dropping triethanolamine. Then, 10mL Na₂SeSO₃ solution was added into the solution, and the final solution was put in oven under 180°C for 12h, the formed precipitate was isolated by centrifugation and washed with ethanol several times to get crimson nanoparticles.

2.5 Preparation of surface dispersant modified CdSe nanoparticles

1g PVP (Mw=30,000) was dissolved in 100 mL as-prepared 0.01 M Na₂SeSO₃ aqueous solution. White precipitate was observed upon the addition of 0.005 mol cadmium chloride into the solution. White precipitate dissolved immediately and transparent solution was obtained after the addition of 0.005 mol thioglycerol (TG) into the solution under stirring. The solution turned from colorless into yellow gradually. The formed precipitate was isolated by centrifugation and washed with water and ethanol for several times. The formed precipitate was dried in vacuum oven at room temperature for 2h.

2.6 Synthesis of SiO₂@ CdSe nanoparticles

1.55g CdCl₂·3/2H₂O and 1.86g EDTA were dissolved completely in 100 mL water, then 2.0g as-prepared monodisperse silica were added into the solution with vigorous stirring, adjusting the solution PH value between 9 and 11 by dropping triethanolamine. Finally, 10 mL Na₂SeSO₃ solution was added into the solution, and the final solution was stirred for 2 h under 60°C. The formed precipitate was isolated by centrifugation and washed with ethanol several times, dried in vacuum oven at ambient temperature for further research and analysis.

2.7 Characterization

Photoluminescence emission spectra were measured in a HITACHI F-4600 fluorescence spectrometer. FT-IR spectra were taken on a Bruker Tensor 27FT-IR spectrophotometer with KBr pellets. XRD experiments were performed in PHILIPS PW3040/60 powder diffractometer using nickel-filtered Cu K α radiation at 40KV and 40 mA in a 2 θ range from 20° to 80°. Scanning electron microscope (SEM) images were performed in SHIMADZU SSX-550. Metallurgical microscope images were recorded on DMM-300C.

3. Results and discussion

3.1 SEM and metallurgical microscope images studies

Fig. 1(a) presents the SEM image of SiO₂ nanoparticles. From the SEM image, the as-prepared sample is sphere-like with very smooth surface, of which the average diameter is about 600nm. Furthermore, the dispersion of the obtained products is very good. Figure 1(b) presents the SEM image of SiO₂@CdSe nanoparticles. It shows that a layer of CdSe nanoparticles were deposited on each silica nanoparticle which result in a very rough surface, and the distribution of CdSe particles on the surface of silica are not very homogeneous, this might be due to there exist a large number of Na⁺ in the solution during the reaction, which leading to an uneven Cd²⁺ concentration around the silica, resulting in uneven nucleation of CdSe. Thus, CdSe grew rapidly to form larger particles at the prior nucleated place. Figure 1(c) presents the SEM image of CdSe nanoparticles. It shows that the nanoparticles were aggregated very seriously ascribe to the super high specific area. Figure 1(d) presents the SEM image of dispersant coated CdSe nanoparticles, and the nanoparticles were well dispersed ascribe to coating a layer of dispersant on each CdSe surface.

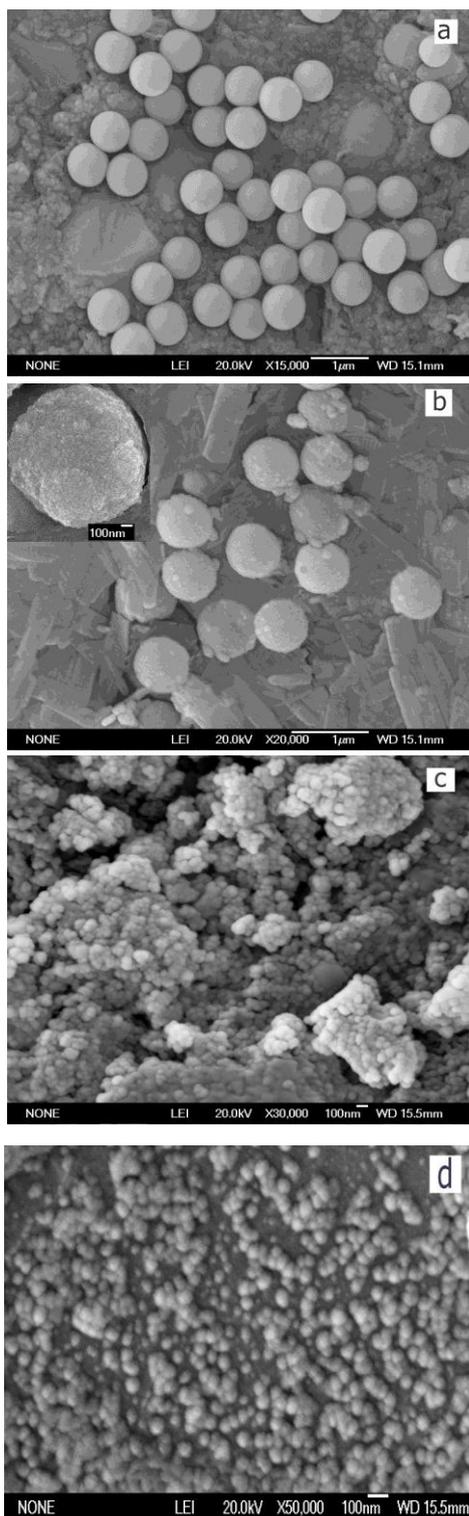


Fig.1. SEM images of (a) SiO₂ nanoparticles, (b) SiO₂@CdSe nanoparticles, (c) CdSe nanoparticles and (d) dispersant coated CdSe nanoparticles

Fig. 2 shows metallurgical microscope images of the dispersion of (a) CdSe nanoparticles and (b) SiO₂@CdSe nanoparticles in the ethanol solution. It seems that the dispersion of CdSe nanoparticles in the ethanol solution is

very bad compared to that of SiO₂@CdSe nanoparticles. Thus, we can conclude that the CdSe electrostatic adsorbed on the monodisperse silica can be dispersed well in ethanol.

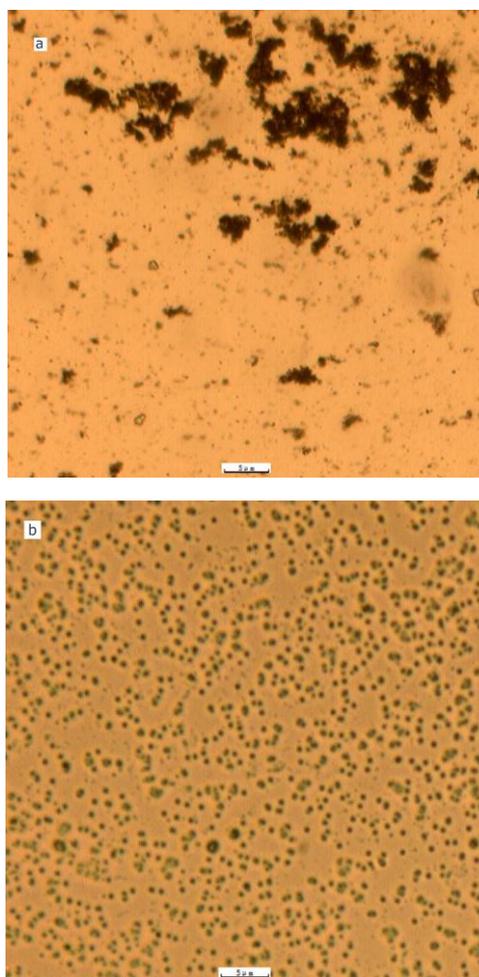


Fig. 2. Metallurgical microscope images of (a) CdSe nanoparticles and (b) SiO₂@CdSe nanoparticles in ethanol

3.2 FT-IR spectra of SiO₂ nanoparticles

Fig. 3 shows the FT-IR spectrum of SiO₂ nanoparticles. 1105, 813, 470 cm⁻¹ are the as-prepared silica characteristic absorption peaks, which are in good agreement with the standard spectra of silica [15]. 3437 cm⁻¹ is the asymmetric stretching vibration peak of O-H, which indicates that the as-prepared nanoparticles are amorphous SiO₂·H₂O. It's worthy to note that 955 cm⁻¹ is the stretching vibration peak of Si-OH, which indicates that there exists a large of Si-OH bond on the surface of silica.

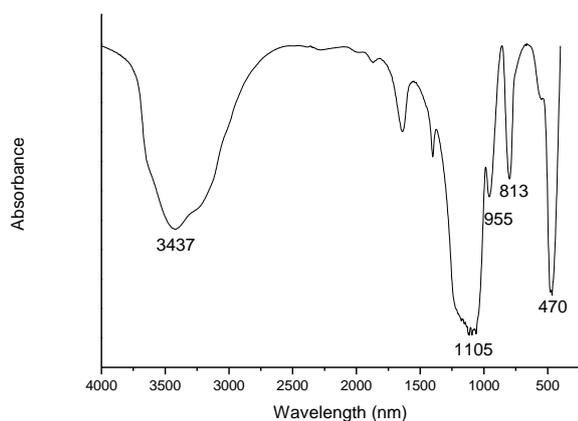


Fig. 3. FT-IR spectra of monodisperse silica nanoparticles

3.3 XRD of SiO₂@CdSe nanoparticles

Fig. 4 shows the XRD pattern of the as-prepared SiO₂@CdSe sample. The vertical bars represent the calculated reflections for CdSe 2 θ : 25.5° (111), 42.2° (220), 49.6° (311), 67.5° (331) and 76.5° (422). The observed peak positions were corresponding to the values expected for crystalline CdSe (JCPDS No. 08-0549). No other impurities, such as CdO, CdSeO₃ or Se, are detected in the samples. There is no silica diffraction peak due to the as-prepared silica is amorphous which have been proven in the IR spectra.

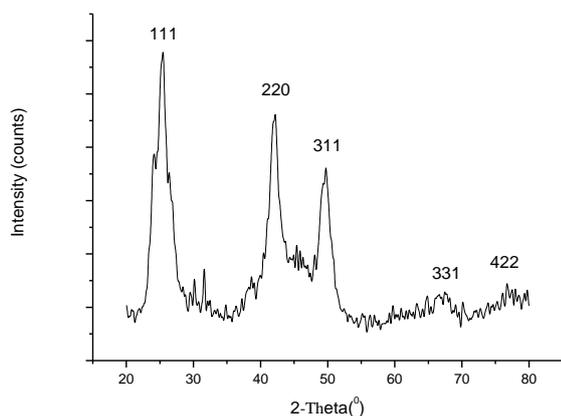


Fig. 4. X-ray diffraction spectrum of SiO₂@CdSe

3.4 PL spectra studies

The fluorescence spectra of the as-formed nanoparticles are shown in figure 5. Thin films were prepared by dropping on a quartz glass using dispersant coated CdSe or SiO₂@CdSe solution (100 mg nanoparticles were ultrasound dispersed in 10 ml chloroform), and placed under vacuum at 40°C for an

hour before testing. The samples were excited at 400nm. As can be seen from the figure, all the films showed strong fluorescence peaks, but the fluorescence peak of dispersant coated CdSe was much weaker compared to that of SiO₂@CdSe nanoparticles, and this is might be due to its surface was coated with a layer of organic agent which resulting in weak light absorption and emission.

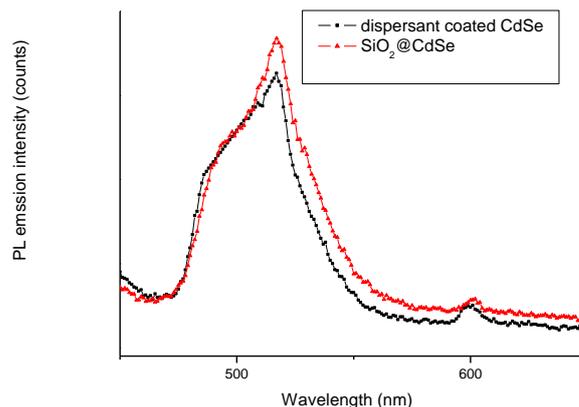


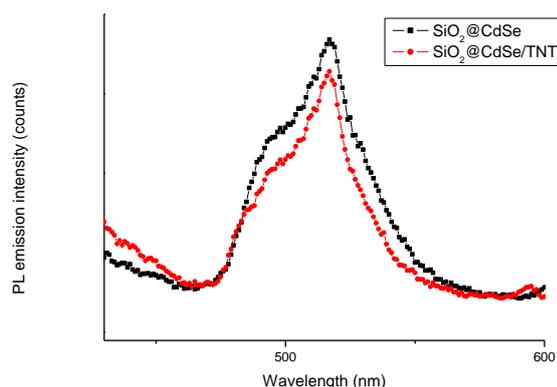
Fig. 5. The fluorescence spectra of dispersant coated CdSe nanoparticles (diamond) and SiO₂@CdSe nanoparticles (triangle)

3.5 Application in FRET system studies

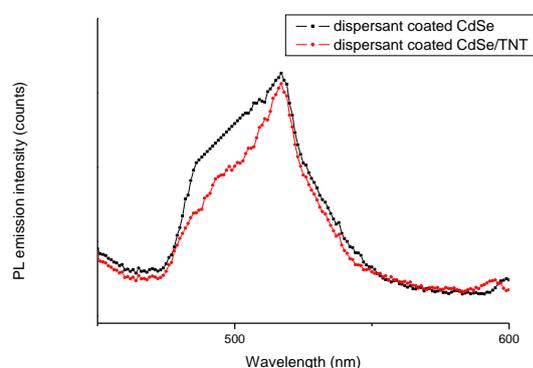
Fluorescence resonance energy transfer (FRET) is a phenomenon in which photo-excitation energy is transferred from a donor fluorophore to an acceptor molecule. Förster theory correlates the rate for this energy transfer to the spectral overlap of donor emission and acceptor absorption and the donor-acceptor spatial arrangement [17]. CdSe nanoparticle can act as both donor and acceptor in FRET system.

3.5.1 CdSe nanoparticles as FRET donors

Energy transfer between a donor SiO₂@CdSe nanoparticle or dispersant coated CdSe nanoparticle and an organic acceptor TNT in solid films were investigated in this work. Composite films were prepared by dropping on a quartz glass using SiO₂@CdSe or dispersant coated CdSe and TNT solution (100 mg SiO₂@CdSe or dispersant coated CdSe nanoparticles and 10 mg TNT were ultrasound dispersed in 10 ml chloroform), the composite films were dried under vacuum at 40°C for an hour then were recorded immediately by fluorescence spectra which are shown in figure 6 at excitation wavelengths of 400nm.



a



b

Fig. 6. Fluorescence spectra of SiO₂@CdSe/TNT composite film (a), CdSe/TNT composite film (b)

It appears that the intensity of the fluorescence was decreased when the nanoparticles was mixed with TNT in figure 6. This is due to the exciton of CdSe was destroyed upon interacting with TNT molecules. As we know, nitroaromatic is a good electron acceptor. This phenomenon proved that the SiO₂@CdSe nanoparticles can be act as donor, and according to the formula:

$$Q\% = \frac{F_A - F_B}{F_A} \times 100$$

, Where, Q% denotes quenching rate, F_A denotes fluorescence intensity when the quencher concentration is zero, F_B denotes the fluorescence intensity when a certain mass of quencher is added to the donor solution. Thus, we can attained the fluorescence quenching rates are 11.05%(left) and 4.47%(right), respectively, it revealed that the SiO₂@CdSe nanoparticle has a better electron transport ability in contrast to dispersant coated CdSe nanoparticle.

3.5.2 CdSe nanoparticles as FRET acceptors

Energy transfer between an organic donor fluorescent polymer and an acceptor SiO₂@CdSe nanoparticle in solid films were investigated in this work. Composite films were prepared by dropping on a quartz glass using fluorescent polymer and SiO₂@CdSe or dispersant coated CdSe solution (10 mg SiO₂@CdSe or dispersant coated CdSe and 100 mg fluorescent polymer in 10 ml chloroform), the composite films were dried under vacuum at 40°C for an hour then were recorded immediately by fluorescence spectra which are shown in Fig. 7 at excitation wavelengths of 400nm.

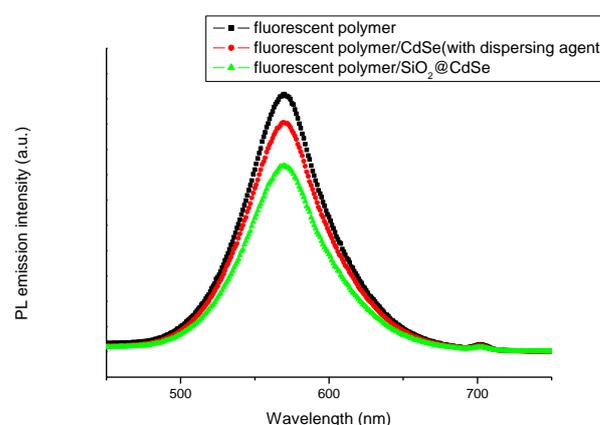


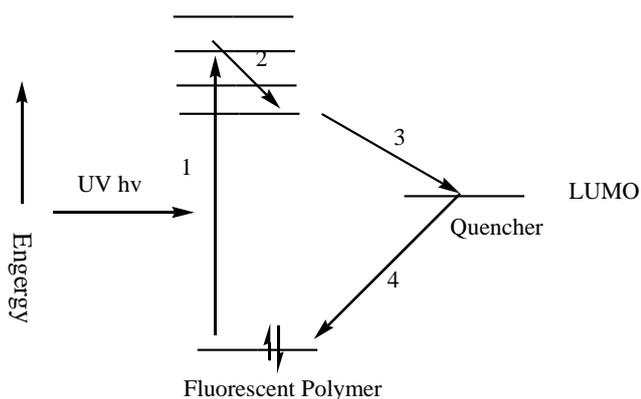
Fig. 7. Fluorescence spectra of fluorescent polymer film (diamond), fluorescent polymer /CdSe film (circle), and fluorescent polymer/SiO₂@CdSe film (triangle)

It appears that the intensity of the fluorescence was decreased when fluorescent polymer was mixed with SiO₂@CdSe or dispersant coated CdSe in figure 7. This is due to the conjugation of polymer was destroyed upon interacting with CdSe nanocrystals. Fluorescent polymers are electron donors. Donor ability is further enhanced in their delocalized π^* excited states. Excited state delocalization is important because exciton migration increases the frequency of interaction with a bound quencher. Fluorescence quenching is often achieved through an electron-transfer donor-acceptor mechanism, as depicted in figure 8. It proved that the SiO₂@CdSe nanoparticles can be act as acceptor, and according to the

formula: $Q\% = \frac{F_A - F_B}{F_A} \times 100$, the fluorescence quenching rates are 11.0% for fluorescent-polymer/CdSe

film and 19.6% for fluorescent-polymer/SiO₂@CdSe film, respectively. It revealed that the ability of electron acceptance of SiO₂@CdSe nanoparticle was much better than that of dispersant coated CdSe nanoparticle due to with naked CdSe.

Hereto, we can conclude that with naked CdSe, SiO₂@CdSe nanoparticles present much better optical properties than that of dispersant coated CdSe nanoparticles whether was act as acceptor or donor in the FRET system.



1. UV light excites an electron
2. Non-radiative decay
3. Electron-transfer quenching
4. Back electron transfer

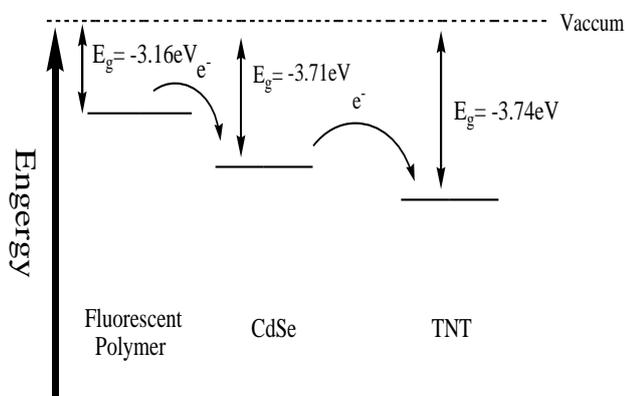


Fig. 8. Electron-transfer fluorescence quenching

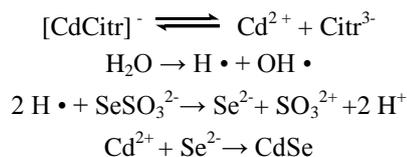
3.6 Mechanism of formation of SiO₂@CdSe nanoparticles

Growth mechanism of CdSe nanocrystals electrostatic adsorption on the SiO₂ surface, we can use the following theory to explain:

First, there exist a large number of negative Si-OH (-OH⁻) group on the surface of silica nanoparticles, which has been proven by the IR spectra of silica. When [CdCitr]⁻ solution released Cd²⁺, and the Cd²⁺ was adsorbed on the surface of silica by electrostatic

adsorption. Thus, it formed a higher Cd²⁺ concentration double-layer structure around the silica. The water produced H• during heating [18], and when H• meet SeSO₃²⁻ solution, it would react with SeSO₃²⁻ to generate Se²⁻. When the Se²⁻ concentration increased to a certain extent, CdSe nucleation was formed on the surface of silica. Cd²⁺, Se²⁻ were released continuously from the [CdCitr]⁻ solution and SeSO₃²⁻ solution, respectively. Finally, CdSe nanocrystals gradually grow up on the surface of silica.

The chemical reaction equations about the process of CdSe growth on the surface of silica are summarized as follows:



4. Conclusions

In summary, uniform SiO₂@CdSe nanoparticles were obtained using electrostatic adsorption CdSe on the surface of silica. SiO₂@CdSe nanoparticles presented stronger fluorescence intensity compared to that of dispersant coated CdSe nanoparticles ascribe to with naked CdSe. Its application as donor or acceptor in FRET system was also investigated, and the results indicated that its ability of electron donor or acceptance was better than that of dispersant modified CdSe nanoparticles ascribe to the latter is coated with a layer of organic reagent on surface, which resulting in impeding the electron transfer between donor and acceptor. Moreover, the mechanism of formation of SiO₂@CdSe nanoparticles was also discussed in this paper. In a word, electrostatic absorption CdSe on the surface of monodisperse silica can be dispersed well in ethanol or solid film, and with better optical properties compared to that of dispersant coated CdSe nanoparticles.

Acknowledgement

We would like to thank the 'Doctorate Foundation of Northwestern Polytechnical University (CX28111), National Program on Key Basic Research Project (973 Program) (2010CB635111)' for funding this work.

References

- [1] J. C. Ferrer, A. Salinas-Castillo, J. L. Alonoso, S. F. de Avila, R. Mallavia, Proceedings of the 2009 Spanish Conference on Electron Devices- Feb 11-13, 2009. Santiago de Compostela, Spain.
- [2] X. J. Hao; E-C. Cho; C. Flynn; Y.S. Shen; S.C.Park; G. Conibeer; M.A.Green. Solar Energy and Materials and Solar Cells, **2**(93), 273 (2009).

- [3] Xiaomin Li, Huaibin Shen, Sen Li, Jin Zhong Niu, Hongzhe Wang, Lin Song Li. *Journal of Material Chemistry*, , **20**, 923 (2010).
- [4] Shiding Miao, Stephen G. Hickey, Bernd Rellinghaus, Christian Waurisch, Alexander Eychmüller. *J. Am. Chem. Soc.* **132**(16), 5613 (2010).
- [5] Y. K. Du, Y. Qiao, C. E. Zou, J. T. Dai, P. Yang, *Colloid & Polymer Science*, , **285**, 553 (2007)
- [6] A. E. Saunders, I. Popov, U. Banin, *Journal of Physical Chemistry B*, **110**, 25421 (2006).
- [7] Y. K. Du, W. Zhang, X.M. Wang, P. Yang, *Catalysis Letter*, **107**, 177 (2006).
- [8] X. G. Peng, L. Manna, W. D. Yang, J. Wickhan, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, **404**,59 (2000).
- [9] C. B. Murray, D. J. Norris, M D. Bawendi *Journal of American Chemistry Society.*, **115**, 8706 (1993).
- [10] Andrey L. Rogach, Andreas Kornowski, Mingyuan Gao, Alexander Eychimuller, Horst Weller. *Journal of Physical Chemistry B*, **103**, 3065 (1999).
- [11] Y. J. Yang, B. J. Xiang, *Journal of Crystal Growth*, **284**, 453 (2005)
- [12] M. Q. Chu, Y. Sun, G. J. Liu, *Material Science and Technology* **22**, 1240 (2006).
- [13] M. Z. Xia, D.S. Li, D. R. Yang, D. L. Que, *Journal of inorganic materials* **20**,1306 (2005).
- [14] Li Zhang; Qy Zhang; Yy Gao; Jw Gu; Hp Zhang; Hl Yan, *Acta Chimica Sinica*, **67**, 2475 (2009).
- [15] W. Stober, A. M. Fink, E. Bohn, et al., *Colloid Interface Science* **26**, 62 (1968).
- [16] Wang Xiong, Zhang Zude, *Appllied Physics A*, **6**(1):134 (2004).
- [17] J. R. Lakowicz, Kluwer Academic Publishers, New York, 2nd edn, 1999
- [18] H. L. Xia, F. Q. Tang *Journal of Physical Chemistry B* **107**, 9175 (2003).

*Corresponding author: qyzhang@nwpu.edu.cn