Synthesis and optical properties of CdS quantum dots via paraffin liquid and oleic acid

Baha T. Chiad, Zainab S. Sadeq, Dunia K. Mehdi, Mohammed A. Jadaa

Physics Department, College of Science, University of Baghdad, Baghdad, Iraq

E-mail: zainab_ss2004@yahoo.com

Abstract

In this study, an easy, low-cost, green, and environmentally friendlier reagents have been used to prepare CdS QDs, in chemical reaction method by mixed different ratio of CdO and sulfur in paraffin liquid as solvent and oleic acid as the reacting media in different concentration to get the optimum condition of the reaction to formation CdS QDs. The results give an indication that the behavior is at small concentration of 4ml of the oleic acid is best concentration which give CdS QDs of small about to 9.23 nm with nano fiber configuration.

Key words

Quantum dots, Cd;S ratio, oleic acid concentration.

Article info.

Received: Mar. 2015
Accepted: Dec. 2015
Published: Apr. 2016

تحضير الخصائص البصرية ل CdS QDs عن طريق سائل البارافين وحامض الاوليك

بهاء طعمة جياد، زينب صبيح صادق، دنيا كامل مهدي، محمد عزيز جداع

قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

في الدراسة الحالية، استخدمت طريقة سهلة وقليلة التكاليف وصديقة للبيئة لتحضير مادة كبريتيد الكادميوم النانوية باستخدام طريقة التفاعل الكيمائي، حضرت العينات باستخدام نسب مختلفة من أوكسيد الكادميوم والكبريت في خليط مذيب البارافين وحامض الاوليك كعامل مساعد وبتراكيز مختلفة للوصول الى شروط التفاعل لتكوين CdS QDs. أظهرت النتائج انه عند التراكيز القليلة 4ml من حامض الاوليك يتم الحصول على افضل تركيز ممكن للحصول على حجم من CdS QDs صغير بحدود 9.24 nm بتشكيل نانوفايبر.

Introduction

Nanocrystalline structures (NCs) have attracted great interest over the past years because their properties are remarkably different from those of bulk materials and can be controlled by the particles composition, size, and surface [1-3]. Nanoparticles (NPs) possess these interesting characteristics due to several phenomena (quantum confinement of charge carriers, surface effects, and geometrical confinement of phonons, etc.) that turned them into promising materials for many applications, such as light-emitting diodes[4], photovoltaic devices [5], lasers [6], optical memories [7], miniaturized devices, and fluorescent probes in biological labeling [8,9].

In recent decades, due to the unique electronic and luminescent properties and the applications in biological labeling, light emitting diodes and solar cells. QDs became the focus of research attentions. QDs are a type of semiconductor NCs with a size range from one to tens nanometers, consisting of several hundreds to a few thousands of atoms. QDs can be synthesized by chemical methods, also known as colloidal QDs, which are coated by a layer of organic surfactant

molecules, also termed 'ligands' on the surface. [10].

QDs can be synthesized through many different methods, including molecular beam epitaxy (MBE), electron beam lithography (EBL), metal organic chemical vapor deposition (MOCVD) and colloidal synthesis. Each method has advantages and different types of applications. All of the synthetic techniques can be categorized into two main categories: either *top-down* or *bottom-up* techniques [11].

An alternative approach is to produce quantum dot in solutions, called colloidal synthesis, which deals with chemical reactions in solution on a nanometer scale. Colloidal synthesis has been conducted to make semiconductor nanostructures of different composition, size and shapes. This method involves growing nanoparticles of inorganic materials through chemical reaction of their precursors and, sometimes, controlled precipitation of the reaction product in certain solvents. Generally, the growth process starts with the fast formation of a huge number of nuclei. Then more and more of the solid product deposits onto the nuclei, so the sizes of the crystallites grow slowly till the desired size is reached, at which time the reaction must be quenched. Otherwise, the dots could keep growing under a process, known as Ostwald ripening, which is the growth of larger dots through the transfer of material from smaller ones, which have a higher solubility [11, 12].

The principle for colloidal synthesis of semiconductor nanocrystals is based on a study by Le Mur and Dinegar, which showed that a temporally short cluster nucleation event followed by controlled slow growth on the existing nuclei results in the formation of monodisperse colloids. A second approach to nanocrystals synthesis involves the mixing of the precursor in a coordinating solvent below the temperature of reaction. The reaction then undergoes a controlled increase in temperature that accelerates the reaction to the point of super saturation. Super saturation is again relieved by a discrete nucleation burst. The temperature is then strictly controlled to ensure the rate of reaction of the precursors is less than or equal to the rate of addition of material to the surface of the nanocrystals, thus avoiding a second super saturation state[13].

In this work a novel, cheaper and safer route to synthesize CdS QDs directly from sulfur and CdO powder using the paraffin liquid as solvent and the oleic acid as the reacting media was developed.

Experimental sections

1. Chemical materials

CdO and sulfur (99.5%) were purchased from Tianjin Guangfu Fine Chemical Research Institute. Paraffin liquid (99.9%) was purchased from Labort India BP. USP, oleic acid (98%) and cyclohexane (>99.5%) were purchased from BDH Chemicals Ltd Poole England, ethanol absolute (99.9%) and methanol anhydrous (99.5%) were purchased from Sigma Aldrch, chloroform (99.9%) was purchased from Tianjin Benchmark Chemical Reagent Co., Ltd. All chemicals were used without additional purification. All chemicals were of analytical grade.

2. Procedure

The typical synthesis procedures were described as follows:
1.0 mmol sulfur element was added into 10mL paraffin liquid in a round bottom flask and heated to 120C to form a light yellow solution (sulfur precursor).

1 mmol CdO, 1.92 mL oleic acid and 38mL paraffin liquid were injected into a round bottom flask. When the temperature slowly went up to 180 C, a transparent nigger-brown solution (Cd precursor) was formed. Then sulfur(S) precursor was added into Cd precursor quickly and maintained at 180 C.

The products were cooled to room temperature. Methanol anhydrous was added to precipitate CdS QDs.

The precipitated CdS QDs were separated by using centrifuge at 8000 rpm for 20 min, then washed with ethanol absolute and cyclohexane more than three times, respectively; then re-dispersed in ethanol absolute for reservation. All the products obtained were deposited on glass slides by drop casted method then tested by field emission scanning electron microscopes (SEM) type ULTRA 55 and SUPRA 55 with different magnification powers and detectors at the Sharifi University.

Results and discussion

1. Structure properties for different Cd:S ratio.

The effect of the synthesis conditions, Cd:S ratio and reaction time on CdS growth shape have studied by SEM.

The reaction temperature and growth time were fixed at 180 C, 6 minutes and 4ml oleic acid concentration. The effect of Cd:S ratio (1:1, 1:1.5, 1:2 , 1.5:1 and 2:1) on SEM measurements are shown in Figs. 1-3.

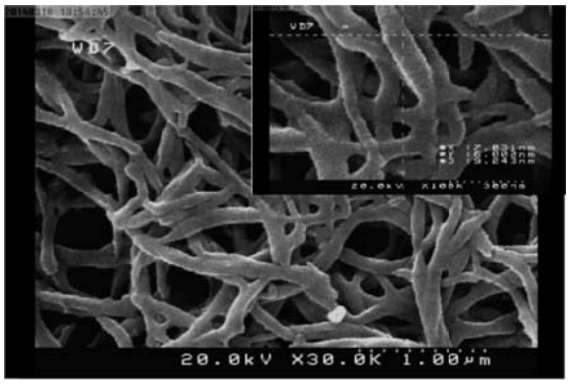

Fig. 1: SEM image of CdS NC with ratio of 1:1 for Cd:S.

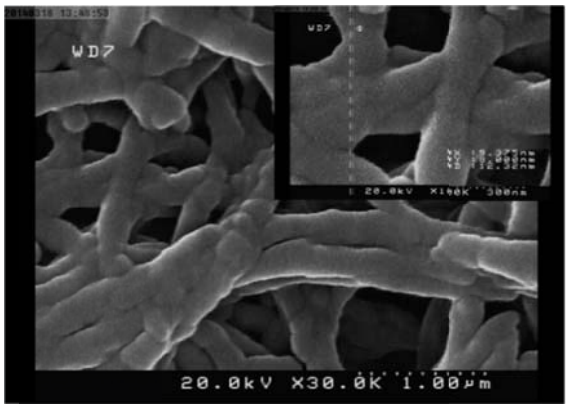

Fig. 2: SEM image of CdS NC with ratio of 1:1.5 for Cd:S.

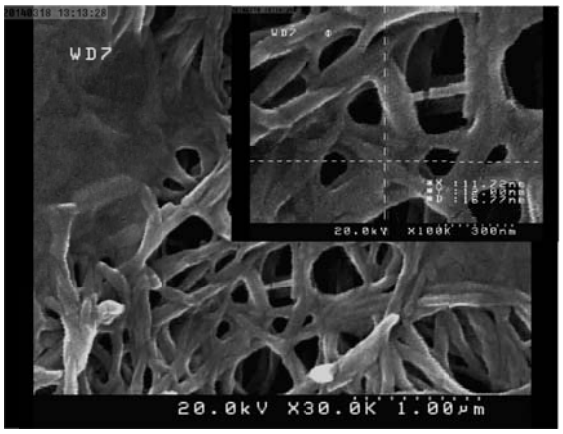

Fig. 3: SEM image of CdS NC with ratio of 1:2 for Cd:S.

It is clear that, an increase of the concentration of cadmium leads to the appearance of more cationic monomers so the nucleation process will quickly finish. as shown in the Figs. 4 and 5 of SEM measurements.

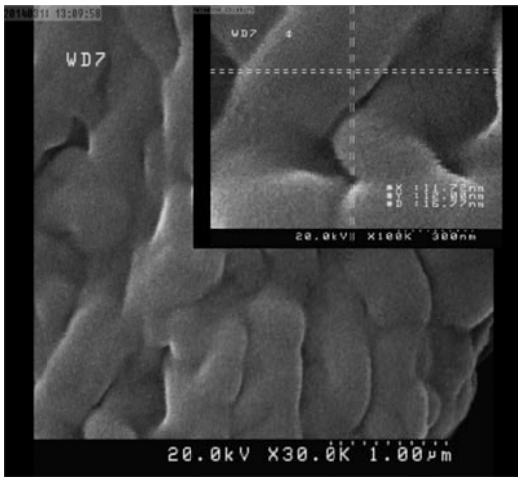

Fig. 4: SEM image with of CdS NC with ratio of 1.5:1 for Cd:S.

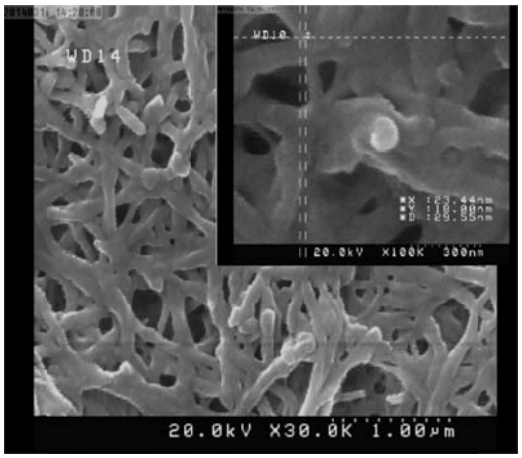

Fig. 5: SEM image of CdS NC with ratio of 2:1 for Cd:S.

One can notice, that the appropriate ratio of CdO and sulfur is important for the formation of CdS QDs and we found that the optimal ratio of CdO and sulfur was 1:1 from the above results which give a small diameter equal to 9.24 nm with nano fiber configuration.

2. Optical properties for different Cd:S ratio.

UV-VIS spectroscopy measurements were carried out by using UV/160 Shimadzu spectrophotometer and SL 174 spectrofluorometer from optimize company (Japan) were used to test the fluorescence spectra of CdS QDs. in order to characterize the optical properties of QDs.

The effect of Cd:S ratio (1:1, 1:1.5, 1:2, 1.5:1 and 2:1) on absorption and emission intensities are shown in Figs. 6 and 7.

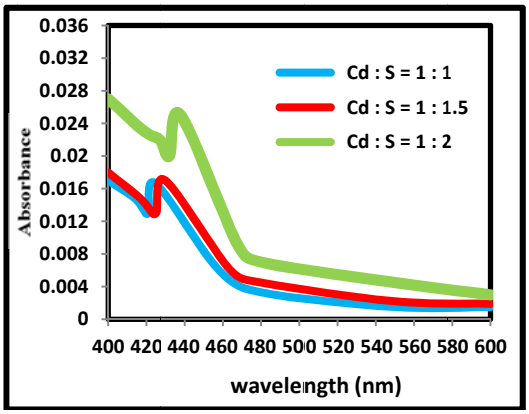

Fig. 6: UV- VIS absorbance spectra of CdS QDs prepared at different ratio of Cd:S.

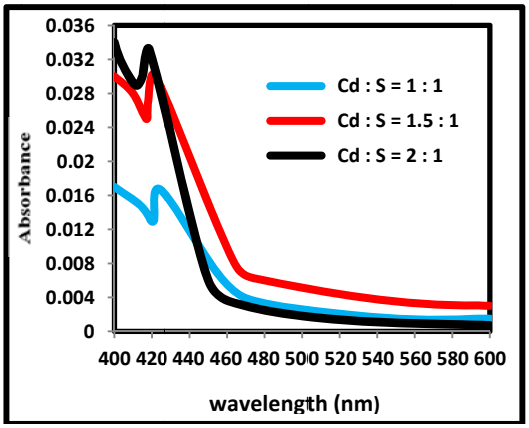

Fig. 7: UV- VIS absorbance spectra of CdS QDs prepared at different ratio of Cd:S.

It is clear that, as we seen in Figs. 7 and 9, excessive cadmium will be clung on the surfaces of particles, and this causes increases in the emission intensity of the quantum dots with blue shift in wavelength in both the absorption and emission spectra associated increases in the particle size.

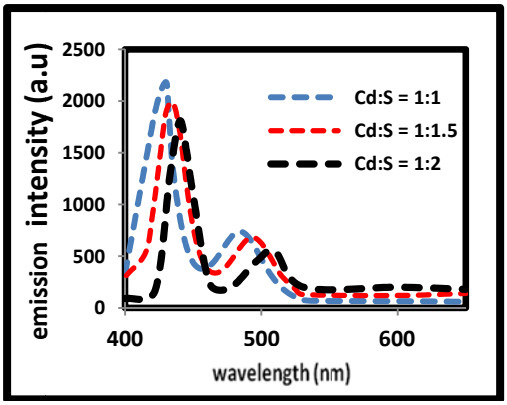

Fig. 8: Emission spectra of CdS QDs prepared at different ratio of Cd:S.

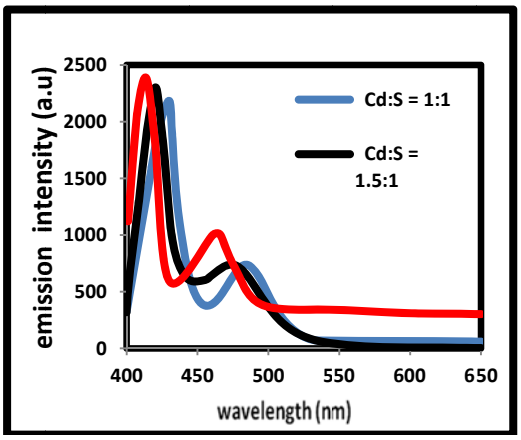

Fig. 9: Emission spectra of CdS QDs prepared at different ratio of Cd:S.

The energy gap was obtained from the relation between $(\alpha h\upsilon)^2$ versus $(h\upsilon)$. The result shows that the energy gap was increased with the increasing of sulfate ratio because the S was non metallic material. As shown in the Fig.10 and Table 1.

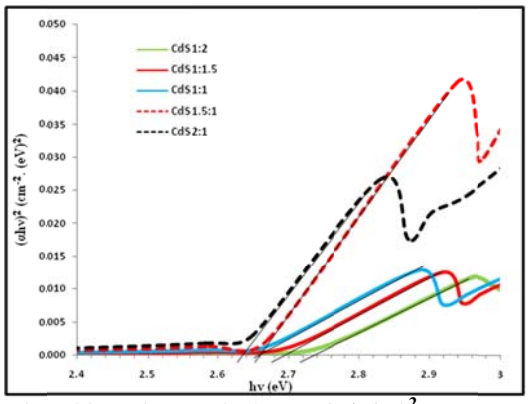

Fig. 10: The variation of $(\alpha h\upsilon)^2$ versus photon energy $(h\upsilon)$ of CdS QDs prepared at different ratios of Cd:S with 4ml oleic acid concentration, reaction temperature of 180 C^o and growth time of 6 minutes.

Table 1: Comparison between Eg calculated from Absorption of Cd:S with 4ml oleic acid concentration, reaction temperature 180 C and growth time of 6 minutes.

Cd:S	λ (nm)	Eg (eV) from Emission	Eg (eV) from absorption
1:2	414	2.9952	2.74
1:1.5	420	2.9524	2.69
1:1	425	2.9176	2.66
1.5:1	435	2.8506	2.66
2:1	440	2.8182	2.63

The estimated band gap energy (2.66eV) of the optimal ratio of Cd:SQDs was on a higher side than that reported (2.4eV) for the bulk material. Our results are in good agreement with the result of Kumar et. al [14].

This result revealed that the absorption and emission intensity strongly depends on the Cd:S ratio. The maximum wavelengths of the peaks are shifted to the higher wavelengths (red shift) when the Cd:S ratio increases, i.e., an excess of sulfite increasing the absorption intensity and decreases the emission intensity of the QDs.

It is generally believed that the QDs with larger average size have both UV-Vis absorption and emission peaks at longer wavelength than the smaller ones.

From Figs. 8 and 9, the increase of concentration of S powder from 1 mmol, 1.5 mmol to 2 mmol, we can clearly see that a fairly sharp emission feature and also red shifted from 430 nm to 440 nm. The sharp emission feature corresponding to the radiative recombination inside the CdS nanocrystals.

The red shift in absorption and emission spectra, is attributed to the increasing in the diameter of the Cd:S ratio.

Conclusions

In summary, CdS QDs have been obtained using paraffin liquid as non coordinating solvent and oleic acid as the reacting media.

The used quantity of the sulfur powder plays an important role for the size control of the final product. The UV-Vis absorption and emission spectra indicates that the CdS QDs are homogeneous and high fluorescence. The optimum reaction condition for Cd:S ratio is 1:1, 4 ml oleic acid concentration, reacting time at 6 minutes and high temperature in 180C. The size distribution for the above optimum conditions of CdS QDs prepared equal to 9.24 nm with nano fiber configuration.

References

[1] A. P. Alivisatos, J. Phys. Chem. 100 (1996) 13226-13239.

[2] S. V. Gaponenko, "Optical Properties of Semiconductor Nanocrystals, Cambridge University Press, Cambridge, U.K., 2005.

[3] H. Weller, Adv. Mater.5 (1993) 88-9.

[4] M. Gao, C. Lesser, S. Kirstein, H. Mohwald, A. L. Rogach, H. Weller, J. Appl. Phys., 87 (2000) 2297-2302.

[5] W. U. Huynh, J. J. Dittmer, W. C. Libby, G. L. Whiting, A. P. Alivisatos, Adv. Funct. Mater 13, (2003) 73-79.

[6] V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, H.-J. Eisler, M. G. Bawendi, Adv. Mater., 290 (2000) 314-317.

[7] R. J. Walters, P. G. Kik, J. D. Casperson, H. A. Atwater, R. Lindstedt, M. Giorgi, G. Bourianoff, Appl. Phys. Lett., 85 (2004) 2622-2624.

[8] M. Han, X. Gao, J. Z. Su, S. O. Nie., Nat. Biotechnol, 19 (2001) 631-635,.

[9] M. Green, Angew. Chem. Int. Ed., 43 (2004) 4129-4131.

[10] C. Yuan, Licentiate Thesis in Theoretical Chemistry and Biology School of Biotechnology Royal Institute of Technology Stockholm, Sweden, "The Study of II-VI Semiconductor Nanocrystal Sensitized Solar Cells ", 2012.

[11] F. K. Kanodarwala, Ph.D Thesis; "Synthesis, Characterisation and Functionalisation of CdSe Quantum Dots", University of New South Wales, 2012.

[12] Yang Xu; Ph.D Thesis; "Synthesis and Characterization of Silica Coated CdSe/CdSCore/Shell Quantum Dots"; Virginia Polytechnic Institute and State University, Electrical Engineering, 2005.

[13] M. D. Ventra, S. Evoy, J. R. Heflin, Jr., "Introduction to Nanoscale Science and Technology", Kluwer Academic Publishers, USA, 2004.

[14] P. Kumar, D. Kukkar, A. Deep, S. C. Sharma, L. M. Bharadwaj, Adv. Mat. Lett., 3 (2012) 471-475.