

Synthesis of rice-like CdS nanoparticles through polyelectrolyte-modified microemulsions

K. Akhavan^{1,*}

¹ *Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran*

Received: 11 August 2021; Accepted: 14 October 2021

ABSTRACT: The paper is focused on the formation of Cadmium sulfide (CdS) nanoparticles in polyelectrolyte-modified microemulsions, in a microemulsion template phase consisting of cyclohexane, water, cationic surfactant and cosurfactant, in the presence of Na-polyacrylate (PAA) as an anionic polyelectrolyte. It is shown that PAA can be incorporated into the individual inverse microemulsion droplets. The PAA-filled microemulsion droplets can be successfully used as a template phase for the rice-like CdS nanoparticles formation. Formation of CdS at room temperature was confirmed by X-ray diffraction (XRD). Size and morphology of CdS samples were characterized using transmission electron microscopy (TEM).

Keywords: *Microemulsion, Na-polyacrylate, Polyelectrolyte–modified microemulsion, Rice-like nanoparticles.*

INTRODUCTION

Synthesis of semiconductor Nano sized particles has a topic of great attraction in the recent years due to their unique optical, electrical properties. The properties of Nano sized semiconductors strongly depend on their shape and size. The decrease of their size also leads to an increase of band gap energy that is known as a quantum size effect. Among the semiconductor nanocrystal, Cadmium Sulfide CdS is one of the most important II-VI group elements possessing size tunable optical transition in solar cell, optoelectronics and wider range of applications [1-7]. Various synthesis methods, including co-precipitation, hydrothermal reactions, sol-gel synthesis, pyrolysis of aerosols, and recently microemulsion, have been used for preparation of CdS. Among these methods, the microemulsion method is

one of the most flexible and convenient methods, being able to deliver a particle size and morphology in nanometer scale with minimum agglomeration [8-15]. Microemulsion, i.e. thermodynamically stable, optically clear isotropic dispersions of two immiscible liquids consisting of nano-sized droplets of one liquid in another, in such away the system is stabilized by added surfactant. Different types of microemulsion were known, such as water-in-oil (w/o), oil-in-water (o/w). In the case of a water-in-oil microemulsion, reverse micelles are formed when the aqueous phase is dispersed as microdroplets surrounded by a monolayer of surfactant in the continuous organic phase [16-23]. However, one problem is that the bending elasticity and stability of the surfactant film is often not strong enough to confine the growth of the particles to the interior of the microemulsion droplet. To overcome this problem, a com-

(*) Corresponding Author - e-mail: kobra.akhavan@gmail.com

ponent should be added which improve the surfactant film stability; control the particle growth processes and stabilize the particles against flocculation during the re- dispersion process. Recently different authors have shown that water-soluble polymers (polyelectrolytes) can be incorporated into inverse microemulsion droplets. On the other hand, the polyelectrolytes can control the size and shape of the nanoparticles during the formation process, polyelectrolyte-modified microemulsion can be successfully used as a new type of template for synthesis of nanoparticles with controlled size, shape, and morphology [24-26], Fig. 1. The aim of the present study is to use the cetyltrimethylammonium Bromide-based microemulsion in the presence of anionic polyelectrolyte, i.e. Na-Polyacrylate as a template phase for the formation of CdS nanoparticles.

MATERIALS AND METHODS

The starting materials used in this work included $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, cyclohexane, n-pentanol, cetyltrimethylammonium bromide, CTAB with 99% purity, Na-Polyacrylate (PAA), and deionized water. All chemicals were prepared with analytical grade and were used without further purification. Aqueous solutions were made by dissolving sufficient amounts of reagents in deionized water. The Na-polyacrylate was used as commercial product with low molar mass (MW = 8000 g/mol). After dissolving 1.82g CTAB in 60ml cyclohexane and 1.6ml n-pentanol, reverse micelle solution with 0.1M concentration was obtained and then 1 ml of 1M CdCl_2 in 4% (w/v) of polymeric aqueous solution was injected slowly into the reverse micelle solution. Transparent solution was obtained upon vigorous stirring the system for about 15 min. for formation of CdS, under vigorous stirring, 1ml of 1M Na_2S aqueous solution was directly added to the above reverse microemulsion system, Transparent solution was obtained upon vigorous stirring the system for about 30 min, then aged with continuous stirring at room temperature for one day. Finally, a small amount of ethanol was added into the transparent solution to afford the production of white slurry, which was centrifuged to collect the colloidal (CdS). The precipitates were washed with ethanol for three times and dried at

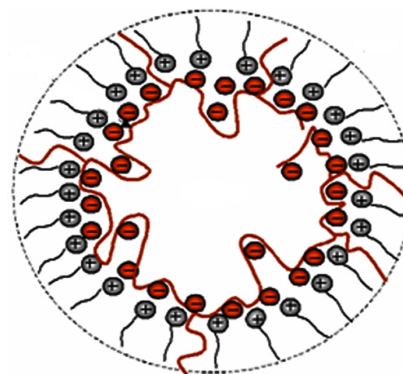


Fig. 1. Detail of polyelectrolyte modified microemulsion formed by CTAB as surfactant and Na-polyacrylate (PAA) as polyelectrolyte.

50°C for 24h. Dried products were characterized by XRD (Philips expert pro. with Cu K α radiation ($\lambda = 0.154$ nm)), scanning electron microscope (SEM; Philips XL30). Transmission electron microscope (TEM; Philips).

RESULTS AND DISCUSSION

Polyelectrolyte-modified microemulsions seem to be very interesting template phases for the nanoparticles formation due to the special features of the incorporated polyelectrolyte.

The “innovation effect” of polyelectrolytes in inverse microemulsions with regard to the nanoparticle formation process can lead to:

- Increase of the film stability of the microemulsion droplets due to polyelectrolyte-surfactant interactions,
- Control/inhibition of the nanoparticle growth process due to polyelectrolyte-nanoparticle interactions,

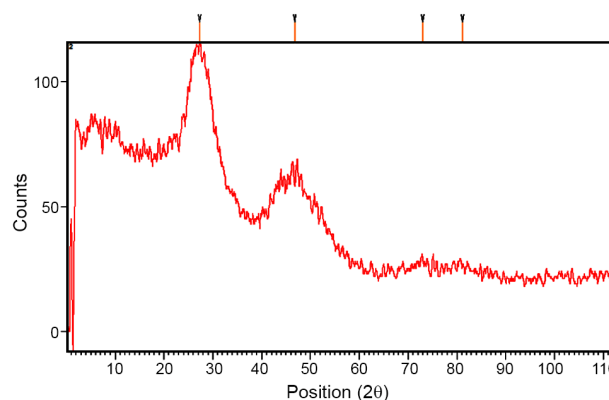


Fig. 2. XRD patterns of synthesized CdS in the polyelectrolyte-modified microemulsion system.

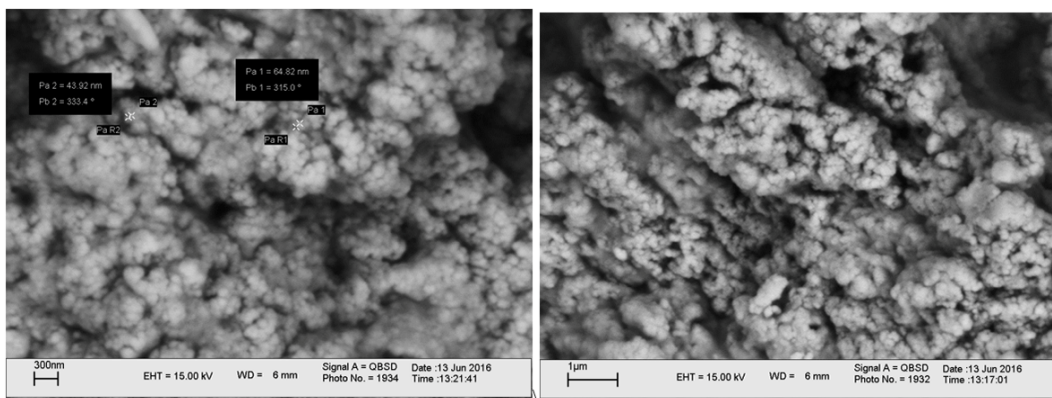


Fig. 3. SEM micrographs of synthesized CdS in the polyelectrolyte-modified microemulsion system.

- Stabilization of the nanoparticles (electrosteric stabilization) due to polyelectrolyte-nanoparticle interactions.

However, these effects have to be optimized with regard to the polyelectrolyte, the type of microemulsion as well as the type of used nanoparticles [27-33]. In the following study, our interest was focused on preparing of CdS nanoparticles by microemulsion method in presence of PAA [34]. Fig. 2 shows the XRD patterns of the obtained particles via Polyelectrolyte-modified microemulsion in the presence of PAA at room temperature. Using low temperature may be cause poor crystalline nature of the prepared CdS. Because of poor crystallinity of nanoparticles, the peaks of CdS/

PAA composite is broad. Through the XRD it proved that the synthesized crystals were all CdS [35].

Fig. 3 shows the SEM images of CdS obtained in the presence of polyelectrolyte. These images suggest that the presence of polyelectrolyte has a great influence distribution and morphology of the product due to polyelectrolyte-surfactant and polyelectrolyte-nanoparticle interaction in the polyelectrolyte-modified microemulsion droplets.

Fig. 4 shows the morphology of CdS products in Polyelectrolyte-modified microemulsion, in the form of a rice-like shape. The particle size is about 20nm in diameter. As result, only rice-like particles of CdS were obtained [34]. With incorporating of PAA in the

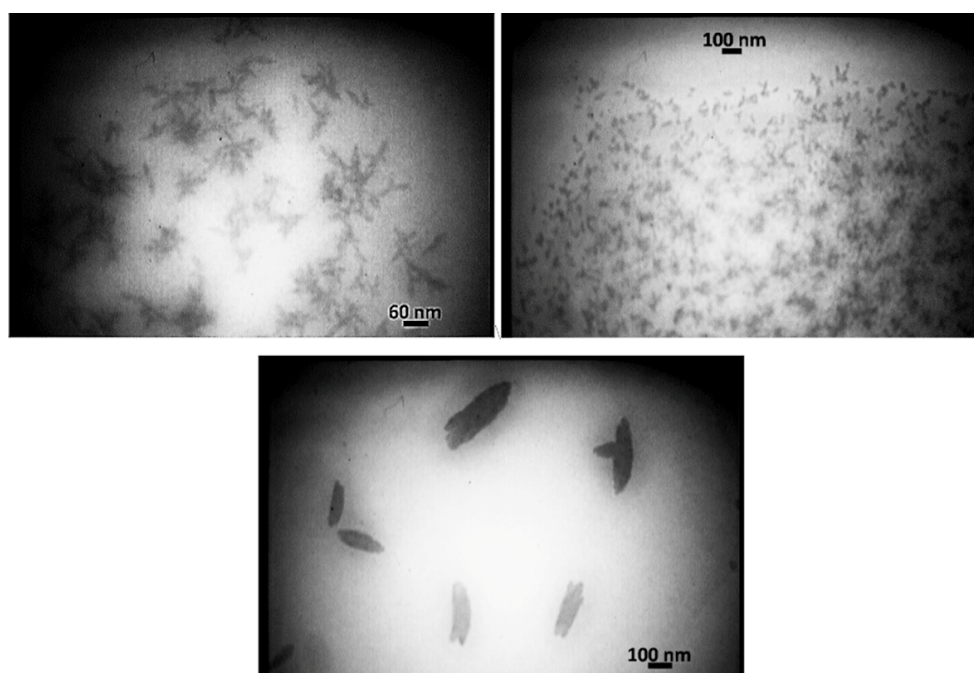


Fig. 4. TEM micrographs of synthesized CdS in the polyelectrolyte-modified microemulsion system.

reverse micelles, the droplet size increased up to dimension much larger and even deformed their shapes to cylindrical micelles. In fact, the reverse micelles changed their shapes from spherical to cylindrical. Crystal grew along a single crystal direction under the restriction of the water conduit of the microemulsion.

CONCLUSION

Incorporation of PAA into individual microemulsion droplets can increase the templating effect of the microemulsions and stabilize the formed nanoparticles during the solvent evaporation. In the presence of PAA, CdS nanoparticles were synthesized in rice-like shapes. They can be stored in the microemulsions for a long time. Therefore, the polymer fulfills indeed the requirements of a size-regulating and stabilizing component in the process of nanoparticle formation. It could offer a novel approach to the fabrication of new colloid materials for use in wide range of technological applications.

ACKNOWLEDGEMENTS

The financial and encouragement support provided by the research vice presidency of Department of Chemistry, Faculty of Science, Islamic Azad University, Rasht Branch, Rasht, Iran.

REFERENCES

- [1] Weller H., *Angew. Chem. Int. Ed. Engl.*, 32(1993), 41.
- [2] Alivisatos A.P., *Science.*, 271(1996), 933.
- [3] Romeo N., Bosio A., Tedeschi R., et al., *Sol. Energ. Sol..C.*, 58(1999), 209.
- [4] Othmani A., Plenet J. C., Bernstein E., et al., *Radiat. Eff. Defect S.*, 137(1995), 1335.
- [5] Salata O.V., Dohson P.J., Sabesan S., et al, *Thin Solid Films*, 288(1996), 235.
- [6] Petit C., Pileni M.P., *J. Phyc. Chem.*, 92(1988), 2282.
- [7] Agostiano A., Catalano M., Curri M.L., et al., *Micron*, 3(2000), 253.
- [8] Li Y.D., Liao H.W., Ding Y., et al., *Chem. Mater.*, 10(1998), 2301.
- [9] Rao C.N.R., Covindaraj A., Deepak F.L., et al., *Appl. Phys. Lett.*, 78(2001), 1853.
- [10] Burgues J.T., Boix J.T., Fraile J., *Cryst. Res. Technol.*, 36(2001), 1065-75.
- [11] Arensds J., Chistoffersen J., Chistoffersen M.R., Eckert H., *J. Cryst. Growth.*, 84 (1987), 515-32.
- [12] Pon-on W., Meejoo S., Tang IM. *Mater Chem. Phys.*, 112(2008), 453-60.
- [13] Barroug A., Glimcher M.J., *J. Orthop. Res.*, 20(2007), 1274-80.
- [14] Kakizawa Y., Miyata K., Furukawa S., *Adv. Mater.*, 16(2004) 699-702.
- [15] Husein M.M., Rodil E., Vera J.H., *J. Nano. Res.*, 9(2007), 787-96.
- [16] Wang Y.J., Lai C., Wei K., Tang S. *Mate. Lett.*, 59(2005), 1098-1104.
- [17] Singh S., Bhardwaj P., Singh V., Aggarwal S., *J. Colloid and Interface Sci.*, 319(2008), 322-9.
- [18] Li H., Zhu M.Y., Li L.H., Zhou CR., *J. Mater. Sci.*, 43(2008), 384-9.
- [19] Tojo C., Barroso F., *Materials.*, 4(2011), 55-72.
- [20] Sarkar D, Tikku S, Thapar V, Srinivasa RS, Khilar KC. *Colloids Surf, A: Physicochemical and Engineering Aspects* 381(2011), 123-9.
- [21] Kotez J., Bahnemann J., Lucase G., *Colloid Surf A Physicochem Eng Aspects.*, 250(2004), 423-30.
- [22] Kotez J., Baier J., Kosmella S., *Colloid Polym Sci.*, 333(2009), 741-8.
- [23] Sarkar D., Tikku S., Thapar V., Srinivasa R.S., Khilar K.C., *Colloids Surf., A: Physicochemical and Engineering Aspects.*, 381(2011), 123-129.
- [24] Meier W., *Langmuir.*, 12(1996), 1188-1192.
- [25] Bellocq A.M., Phase equilibria of polymer-containing microemulsions. *Langmuir*, 14(1998), 3730-3739.
- [26] Jakobs B., Sottmann T., Strey R., Allgaier J., Willner L., Richter D., *Langmuir.*, 15(1999), 6707-6711.
- [27] Kotez J., Bahnemann J., Lucase G., Tiersch B., Kosmella S., *Colloid Surface A: Physicochemical and Engineering Aspects.*, 250(2004), 423-430.
- [28] Kotez J., Baier J., Kosmella S. *Colloid Polymer Sci.*, 387(2009), 1233-1240.
- [29] Kotez J., Baier J., Kosmella S. *Colloid Polymer Sci.*, 387(2009), 1233-1240.

- Science., 285(2007), 1719-1726.
- [30] Lim G.K., Wang J., Gan L.M., *Material Letters.*, 28(1996), 431-436.
- [31] Mollazadeh S., Javadpour J., Khavandi A. *Ceramic International.*, 33(2007), 1579-1583.
- [32] Wang Y., Chen J., Wei K., Zhang S., Wang X., *Material Letters.*, 60(2006), 3227-3231.
- [33] Sinha A., Guha A., *Material Science Engineering C.*, 29(2008), 1330–1333.
- [34] Zhou H.C., Sheng X., *Chem. Res. Chinese U.*, 22(2006), 11-13.
- [35] Wang H., Yinong L., Junjie Z., *Inter. J. Nanoscience.*, 6(2002), 437.

AUTHORS BIOSKETCHES

Kobra Akhavan, Assistant professor, Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran, *Email: kobra.akhavan@gmail.com*