SAND2018-10295J

MRS Advances

Functionalized Block-Copolymer Templates for Synthesis and Shape Control of Quantum Dots

Brian Billstrand[1], Kaifu Bian[1], Casey Karler[1] and Hongyou Fan[1,2,*]

[1]Sandia National Laboratories, Advanced Materials Laboratory, Albuquerque, New Mexico, 87106, United States;

[2]The University of New Mexico Center for Micro-Engineered Materials, Department of Chemical and Biological Engineering, Albuquerque, New Mexico 8713, United States

ABSTRACT

A new quantum dot synthesis method based on metallic-block copolymer precursors was developed. The synthesis produced CdS QDs assembled into chains. This method provides a new model for the study of 1D QD chains to determine its effect on charge transport and optoelectronic coupling. This synthesis method was readily extended to other semiconductor materials including PbS and perovskites producing QDs of various shapes. It evidenced further promise of this synthesis method to assist in the assembly, shape and size control of various nanomaterials

INTRODUCTION

Semiconductor quantum dots (QDs) have received a lot of attention in the past decades due to their band gap tunability due to quantum confinement and high photoluminescense quantum yields (PLQY).[1] The unique optical properties of QDs have led to their utilization in applications including solar cells, light emitting diodes, photocatalysis and biological labeling [2-4]. Previous research efforts have resulted in a wide variety of QD synthesis methods via a variety of routes such as micellular, solvothermal, hydrothermal and hot injection techniques. [5-8] Many of these syntheses relied upon oleate or trioctylphosphine based precursors.[9] Instead, in this work, a novel QD synthesis using carboxylate block copolymer precursor was developed. Additionally to build on the wide basis of isolated QDs there has been an emphasis on the self-

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

assembly of QDs into superstructures. Examples of these superstructures include the formation of quantum dot superlattices, chains, and necklace structures which exhibited unique optical properties due to changes in electronic state, electron injection, enhanced carrier diffusion length and plasmon coupling.[10-14] It is especially difficult to assemble spherical nanoparticles linearly due to their isotropic nature resulting in few examples. This work reports a novel synthesis for the one-dimensional assembly of CdS QDs using cadmium-polysyrene-b-polyacrylic acid (PS-PAA) block copolymer complex precursor. This method provides a new model for the study of 1D QD chains to determine its effect on charge transport and optoelectronic coupling. It was also shown that this synthesis method could be extended to other semiconductor materials including PbS and perovskites resulting into QDs of various shapes. It evidenced further promise of this synthesis method to assist in the assembly, shape and size control of various nanomaterials.

EXPERIMENT

CdS and PbS Quantum Dot Synthesis

In a typical synthesis, Cd precursor was first prepared by mixing 80 mg CdO powder, 300 mg PS-PAA block copolymer (molecular weight 20k-0.9k) and 10 mL of dimethylformamide (DMF) were mixed in a 50 mL flask which was connected to a Schlenk line. The mixture was degassed under vacuum for 10 min then heated to 140°C in argon environment to dissolve CdO with PS-PAA. After a clear solution was obtained it was cooled down in an ice-water bath and degassed for another 30 min to remove the generated water. For the hot injection synthesis, the Cd precursor was heated to 140°C again. In a Ar glove box, as sulphur precursor, 200 μL bis(trimethylsilyl) sulfide (TMS) was dissolved in 2 mL DMF and then quickly injected into the Cd-polymer solution. The mixture became yellow/green in color indicting QD formation. The reaction was stopped after 1 min by rapid cooling in a cold water bath. The QDs were extracted and purified by two cycles of precipitation using ethanol and toluene. The final product was a yellow and clear toluene solution. The synthesis of PbS nanocubes followed very similar procedure except for replacing CdO with PbO powder.

$CsPbX_3$ Perovskites Quantum Dot Synthesis

In a typical synthesis 10 mL octadecene (ODE), 0.5 mL of oleylamine (OLA), 210 mg PS-PAA (20k-0.9k), 0.1 mmol cesium carbonate and 0.1 mmol lead bromide or iodide were added to a 20 mL flask and sonicated at 60% amplitude for 20 minutes (QSonica sonicator 20kHz 120W). Iodide and bromide structures were obtained using an equimolar amount of lead iodide or lead bromide respectively. After synthesis the QDs were separated using centrifugation and re-dispersed in toluene.

Characterization Methods

TEM images were captured by a JEOL 2010 TEM operated at 200 kV. The average size was determined by statistics of QDs from multiple images. Powder X-ray diffraction (PXRD) was performed using a PANalytical X'Pert PRO operating at 45 kv and 40 mA. The standard diffraction pattern was generated by the commercial software CrystalMaker, version 9.2.2. Photoluminescence measurements were performed with a Horiba Fluoromax-4 fluorometer with monochromatic excitation at wavelength of 380 nm. Optical absorption spectrum was collected using a Perkin Elmer Lambda 950 UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

To synthesize the CdS QD chains shown in Figure 1a first PS-PAA block copolymer was used to disolve CdO powder. The acrylic part of the polymer served as active sites binding to Cd^{2+} ions while the hydrophobic polystrene provided solubility in non-polar solvents. The surfactant role of PS-PAA is similar to that of traditional ligands such as oleic acid and alkanethiols in nanoparticle synthesis. As sulphur precursor TMS was injected into the metal-polymer solution at elevated temperture of 140 °C. Immediate color change from a red brown to a yellow solution signaled the formation of the CdS QDs. Additional experiments were conducted with PS-PAA of different molecular weights produced similar results indicating a tolorence in the specification of block copolymers. Interestingly the colloidal stability of the nanoparticle solutions in different solvents could be adjusted by the usage of different PS-PAA block copolymers. As the size of the PS section increased the colloidal stability in toluene was noticibly improved and produced a homogenous solution. The concentration of block copolymer was also explored to show the effect on particle size and assembly mophology. It was shown that diluted PS-PAA reduced particle size and synthesized chains containing multiple layers of nanoparticles shown in Figure 1b. It is also important to mention that excess reaction times of over a few minutes deteriorited uniformity of the products QDs. It is thought that the chain structure is achieved via PAA chains which linearly connected the outside of particles. Previous research on the synthesis of CdS QD chains required more complicated surface deposition based reactions involving DNA templates or post synthesis modification.[13, 15] In contrast the PS-PAA template synthesis in this work enabled a facile in-situ assembly of CdS QDs. Importantly, this synthesis method can be easily modified using different block copolymer chain lengths, precursor concentrations and a variety of different metallic precursors to achieve a library of QDs.

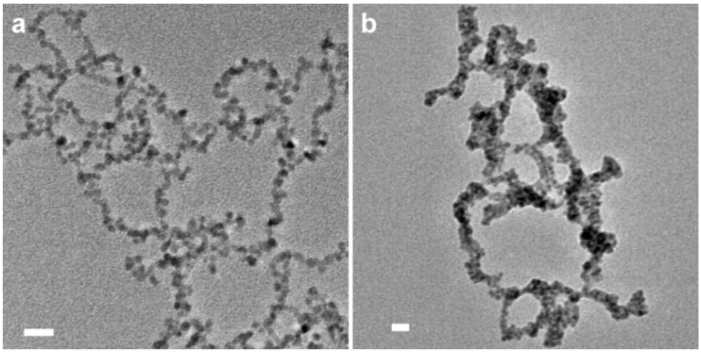

Figure 1. TEM images of synthesized CdS QDs. (a) Multiple particles. (b) QDs synthesied from reduced PS-PAA concentration. Scale bars are 20 nm.

XRD characterization (Figure 2a) revealed the synthesized CdS QDs contained cubic zinc-blende structure (space group F-43m) with lattice paramter of a = 5.8 Å. The broadening of peaks was attributed to Scherrer broadening effect due to the small particle size. The zinc-blende phase is common for CdS QDs synthesized at relatively low temperatures below 300°C since zinc-blende is a metastable phase at room temperature.[16] Based on this crystal structure and particle size, a photoluminescence peak at a wavelength around 500-600 nm was expected according to the work by Celebi et al. on polyacrylic acid stabilized cadmium sulfide nanocrystals.[17] Figure 2b presents optical absorption and photoluminescenc (peaks at 550 nm) spctra of the product CdS QDs in this work which are consistent with literature profiles. Both XRD and optical characterizations confirmed the sucessful synthesis of high quality CdS QDs passivated by block copolymers.

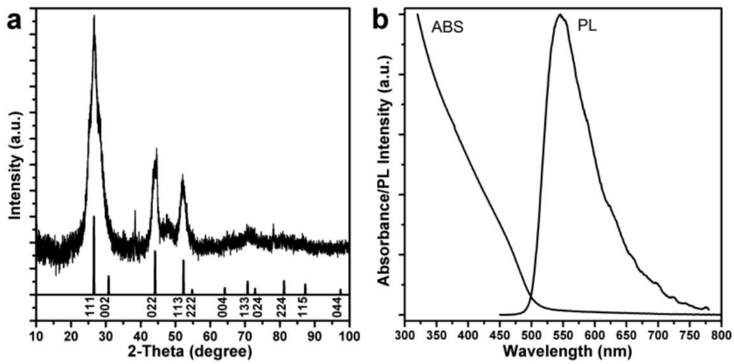

Figure 2. Characterization of the CdS-PS-PAA QDs. (a) XRD pattern with simulated standard peaks as reference are (b) Optical spectra including absorption and photoluminescence (PL).

To demonstrate the potential of this new synthesis method, it was extended to other semiconductor materials including PbS and perovskites. The use of a lead-polymer precursor resulted in large uniform PbS nanocubes (Figure 3a) consistent with the best uniformity achieved with other syntheses.[18] The large difference in size and assembly morphology compared to the CdS QDs is believed to be a result of difference in the reactivity of the precursors. Traditional hot injection method for PbS and CdS QDs of similar size requires injection temperature around 150°C and 300°C respectively. Lower injection temperature would result in smaller QDs. However the boiling point of DMF (153°C) limited the possible size of CdS QDs. To overcome the limitation, CsPbX3 perovskite nanostructures were synthesized using ultra sonication in a high-boiling point solvent octadecene. As presented by Figure 3b and 3c bundles of nanorods of both the bromide and iodide perovskites were obtained. It is important to note that in order to dissolve the metal-PS-PAA precursor in the non-polar octadecene the size of the PS section must significantly exceed the PAA section. These two additional successful syntheses of interesting nanoparticles evidenced the potential of this polymer-based method for a wide variety of nanomaterials including metallic, magnetic and other QDs.

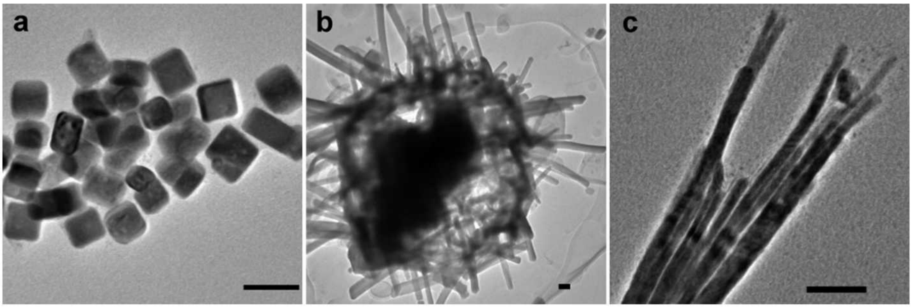

Figure 3. TEM images of semiconductor nanostructures synthisized by the block copolymer based method. (a) PbS nanocubes, (b) $CsPbBr_3$ perovskite nanorods and (c) $CsPbI_3$ perovskite nanorods. Scale bars are 50 nm.

CONCLUSIONS

In conclusion, a new synthesis method for semiconductor nanostructures using block copolymers as ligands was successfully developed. The as synthezied CdS QDs existed in chained 1D assemblie. This method overcame the complexity of previous methods involving nanoclusters or DNA templates. This synthesis can easily be substituted in place of other common oleate based nanoparticle syntheses to achieve new nanomaterial shapes and assembly morphology. For future impromens, more parametres have been panned to be explored including solvent type, polymer strcuture, precursor concentraton and reaction temeperature as well as their relationship to the optoelectronic, plasmonic and magnetic properties.

ACKNOWLEDGMENTS

This work was supported by Sandia's Laboratory Directed Research & Development (LDRD) program. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

REFERENCES

1. H. Wang, L. Xu, N. Liu, R. Zhang, J. Xu, W. Su and K. Chen, *Can. J. Phys.*, **92**, 802 (2014).
2. D. Zhao and C. Yang, *Renew. Sust. Energ. Rev.*, **54**, 1048 (2016).
3. R. Upadhyay, M. Sharma, D. Singh, S. Amritphale and N. Chandra, *Sep. Purif. Technol.*, **88**,39 (2012).
4. H. Zhang, S. Chen and X. Sun, *ACS Nano*, **12**, 697 (2018).
5. M. Hosseini and M. Kamali, *J. Lumin.*, **167**, 51 (2015).
6. I. Arellano, I. Arellano, J. Mangadlao, I. Ramiro, and K. Suazo, *Mater. Lett.*, **64**, 785 (2010).
7. S. Parani, N. Tsolekile, K. Pandian and O. Oluwafemi, J. Mater. *Sci. -Mater. Electron.*, **28**, 11151 (2017).
8. L. Zhang, X. Shen, H. Liang and J. Yao, *J. Phys. Chem. C*, **114**, 21921 (2010).
9. M. Hu and T. Zhu, *Nanoscale Res. Lett.*, **10**, 1 (2015).
10. M. Eita, A. Usman, A. El-Ballouli, E. Alarousu, O. Bakr and O. Mohammed, *Small*, **11**, 112 (2015).
11. L. Yi, D. Lacie, Z. Yadong, Z. Shengli and Z. Jing, *Prog. Nat. Sci. Mat Int*, **26**, 449 (2016).
12. A. Baranov, A. Litvin, A. Fedorov, E. Ushakova, S. Cherevkov and I. Kasatkin, *J. Phys. Chem. C*, **120**, 25061 (2016).
13. X. Zhang, L. Lv, L. Ji, G. Guo, L. Liu, D. Han and D. Yang, *J. Am. Chem. Soc.*, **138**, 3290 (2016).
14. N. Tavakoli, M. Adeli and M. Vossoughi, *Eur. Polym. J.*, **46**, 165 (2010).
15. L. Dong, T. Hollis, B. Connolly, N. Wright, B. Horrocks and A. Houlton, *Adv. Mat.*, **19**, 1748 (2007).
16. G. Tai, J. Zhou, W. Guo, J., *Nanotech.*, **21**, 175601 (2010).

17. S. Celebi, A. Erdamar, A. Sennaroglu, A. Kurt and H. Acar, *J. Phys. Chem. B*, **111**. 12668 (2007).

18. Y. Li, Q. Li, H. Wu, C. Huang, H. Lin and L. Qin, *J. Nanopart. Res.*, 17, 362 (2015).