ChemComm

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c5cc03587b

Received 30th April 2015,
Accepted 10th June 2015

DOI: 10.1039/c5cc03587b

www.rsc.org/chemcomm

Sulfur copolymer for the direct synthesis of ligand-free CdS nanoparticles†

Trevor R. Martin,[abc] Katherine A. Mazzio,[ac] Hugh W. Hillhouse[bcd] and Christine K. Luscombe*[abce]

Organic coordinating ligands are ubiquitously used to solubilize, stabilize and functionalize colloidal nanoparticles. Aliphatic organic ligands are typically used to control size during the nanoparticle growth period and are used as a high boiling point solvent for solution-based synthesis procedures. However, these aliphatic ligands are typically not well suited for the end use of the nanoparticles, so additional ligand exchange or ligand stripping procedures must be implemented after the nanoparticle synthesis. Herein we present a ligand-free CdS nanoparticle synthesis procedure using a unique sulfur copolymer. The sulfur copolymer is derived from elemental sulfur, which is a cheap and abundant material. This copolymer is used as a sulfur source and high boiling point solvent, which produces stabilized metal-sulfide nanoparticles that are suspended within a sulfur copolymer matrix. The copolymer can then be removed, thereby yielding ligand-free metal-sulfide nanoparticles.

Aliphatic ligands that coordinate to the nanoparticle surface during a typical synthesis procedure are usually hydrophobic, highly insulating and create a significant barrier to ion or charge transport applications.[1] Therefore, ligand stripping or ligand exchange procedures must be implemented for many nanoparticle applications.[1–3] In this work, we use a sulfur copolymer to directly synthesize ligand-free CdS nanoparticles, thereby circumventing this issue. Polymers and nanoparticles synthesized using elemental sulfur offer a promising new paradigm for the development of new materials and processes. However, the range of nanomaterials that can be produced using elemental sulfur has not been widely studied. Despite a demand for elemental sulfur for use in various industrial processes, it is cheap and abundant since a significant excess of sulfur is produced as a by-product of petroleum refining.[4]

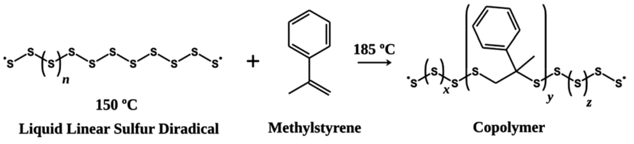
A previous study by Chung *et al.* showed that sulfur copolymers can be produced from elemental sulfur and a divinylic cross-linking monomer such as 1,3-diisopropenylbenzene (DIB) to produce high molecular weight copolymers.[4] The addition of the divinylic monomer causes the linear sulfur chains to react with DIB, which forms a stable network copolymer. This copolymer can be used to produce microstructured materials as well as electrochemical devices.[4,5] A separate study by Chung *et al.* showed that elemental sulfur can be heated and combined with a metal precursor to produce gold nanoparticles. After the nanoparticle synthesis, they added a similar cross-linking organic monomer, 1,4-divinylbenzene (DVB), to produce a polymeric sulfur and gold nanoparticle composite.[6] Char *et al.* examined how oleylamine (OLA), a conventional high boiling point solvent and nanocrystal coordinating ligand, will undergo a cross-linking reaction with elemental sulfur to produce a copolymer and PbS nanoparticle composite material.[7] However, this study is based upon conventional nanoparticle synthesis methods that use organic coordinating ligands and organic solvents. Related studies have examined polymeric sulfur as a high refractive index material and potential nanostructured photocatalyst.[8,9] Although these studies have provided a promising foundation for using elemental sulfur to produce polymeric and nanostructured materials, to our knowledge, sulfur copolymers have not been used to directly synthesize semiconductor nanoparticles, nor have the photonic properties of these materials been widely studied. Our goal was to use a sulfur copolymer as the sulfur source and high boiling point solvent in a CdS nanoparticle synthesis.

Herein we present a sulfur copolymer that is based on the DIB sulfur copolymer synthesis described by Chung *et al.*, but implements a different vinylic monomer.[4] Specifically, instead of using a divinyl monomer, a monovinyl monomer was used to limit cross-linking so that a liquid could be obtained at high temperatures for a nanoparticle synthesis. Using a liquid solvent is crucial for the diffusion mediated nanoparticle nucleation and growth

---

[a] *Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195-2120, USA. E-mail: luscombe@uw.edu*
[b] *Clean Energy Institute, University of Washington, Seattle, WA 98195-1653, USA*
[c] *Molecular Engineering and Sciences Institute, University of Washington, Seattle, WA 98195-1652, USA*
[d] *Department of Chemical Engineering, University of Washington, Seattle, WA 98195-1750, USA*
[e] *Department of Chemistry, University of Washington, Seattle, WA 98195-1700, USA*

† Electronic supplementary information (ESI) available: Includes detailed synthesis procedures, characterization techniques and spectroscopy data. See DOI: 10.1039/c5cc03587b



Scheme 1 Synthetic scheme for the sulfur copolymer.

process.[10] This sulfur copolymer is simple to synthesize, easy to process, and is a liquid at elevated temperatures. The reaction scheme for producing this sulfur copolymer is presented in Scheme 1. Elemental sulfur is heated to 150 °C, causing the S_8 rings to transition into a linearly structured liquid sulfur diradical.[4] At this stage, methylstyrene is injected into the liquid sulfur in a 1 : 50 molar ratio of methylstyrene molecules to sulfur atoms. The mixture is then heated to 185 °C and the reaction is allowed to proceed for 10 min prior to cooling. Upon cooling, the sulfur copolymer becomes an orange solid as depicted in Fig. 1a. The copolymer can then be reheated to form a liquid. The details of this synthesis are presented in the ESI.† Unlike the sulfur copolymers that are produced using the DIB and DVB cross-linking monomers, which are physically hard and difficult to process once cooled, this sulfur copolymer powder can be produced in bulk and then can be easily divided into smaller quantities and used as required.

CdS nanoparticles were produced by combining 3.0 mmol of cadmium acetylacetonate and 120 mmol of sulfur copolymer in a flask. The flask was placed under vacuum and purged with nitrogen several times to create an inert atmosphere for the synthesis. The mixture was heated to 200 °C for 30 min, resulting in the formation of a black liquid. In order to examine the growth of the nanoparticles over time and to determine the extent to which nanoparticle size can be tuned by changing the reaction time, aliquots of the reaction solution were examined using transmission electron microscopy (TEM) and absorbance spectroscopy (UV-Vis) (Fig. S3 and S4, ESI†). Once cooled, the liquid solidified into a black nanocomposite powder that is easily processed, as depicted in Fig. 1b. Since only some of the sulfur is consumed by the cadmium precursor, this synthesis produces CdS nanoparticles that are suspended within a sulfur polymer matrix. Next, the CdS nanoparticles were separated from the sulfur copolymer by ultrasonicating and centrifuging in chloroform, as depicted in Fig. 1c. The details of this synthesis are presented in the ESI.†

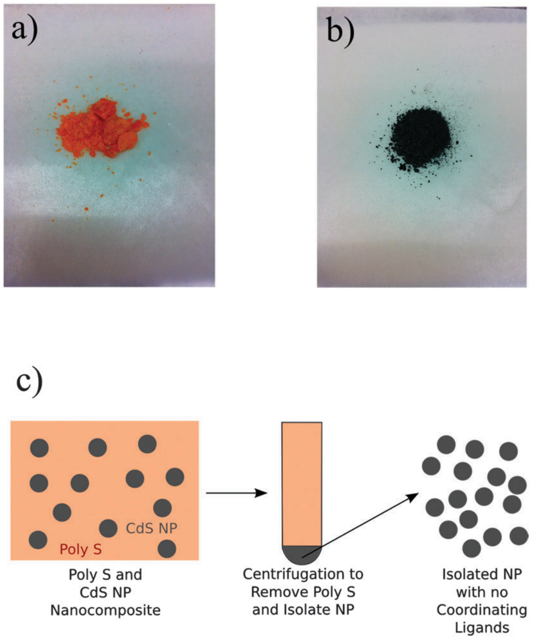


Fig. 1 (a) Image of sulfur copolymer. (b) Image of sulfur copolymer and CdS nanoparticle composite powder. (c) Procedure for separating CdS nanoparticles (CdS NP) from the sulfur copolymer (poly S) matrix.

In a manner consistent with that reported by Chung *et al.*,[6] a procedure was attempted with elemental sulfur instead of our sulfur copolymer to check if the polymeric material was indeed required for a nanoparticle synthesis. The elemental sulfur procedure resulted in the production of a viscous paste, that once cooled became a very hard brown material that cannot be easily processed and we were unable to synthesize viable CdS nanoparticles using this technique. Moreover, a metal-sulfide nanoparticle synthesis cannot be easily completed with a divinylic cross-linking monomer such as DIB in the sulfur source, since this monomer produces a highly viscous material due to the high molecular weight polymers produced and the cross-linking reactions taking place.[4] In contrast, once heated, the single vinylic group of the methylstyrene based sulfur copolymer promotes depolymerization and the formation of oligomeric radicals that cause the solution to remain a liquid at elevated temperatures and can subsequently react with the metal precursors.

TEM was used to image the resulting CdS nanoparticles in Fig. 2a and b, which show nanocrystals with a diameter of 7–10 nm that aggregate together once the copolymer is removed and the solvent has evaporated. The TEM image in Fig. 2b shows a clear crystal plane spacing of 3.3 Å, which is consistent with the (111) plane of zincblende CdS or the (002) plane of wurtzite CdS. The inset in Fig. 2a shows the energy dispersive X-ray spectroscopy (EDS) data for the CdS nanoparticles, where a nearly 1 to 1 ratio of Cd to S atoms is seen, which indicates that the sulfur copolymer has been effectively removed and further confirms the formation of CdS nanoparticles. The inset

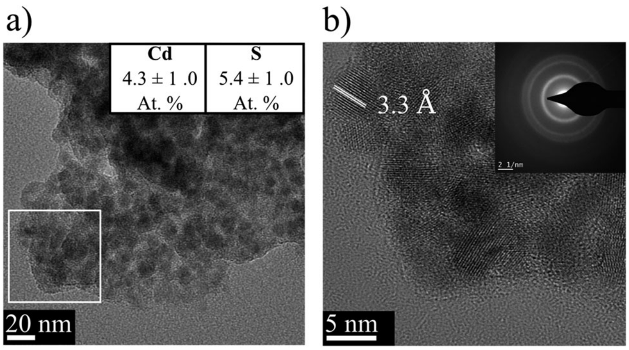


Fig. 2 (a) TEM image showing CdS nanoparticles with a diameter of 7–10 nm with inset showing EDS data (b) higher resolution TEM image of selected area from (a) with inset showing SAED pattern and a clear crystal plane spacing of 3.3 Å.

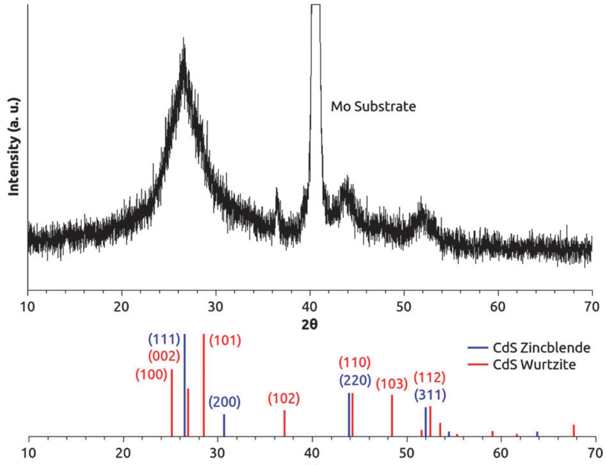


Fig. 3 XRD pattern for CdS nanoparticles drop-cast onto a molybdenum coated soda lime glass substrate.

in Fig. 2b shows the selected area electron diffraction pattern (SAED) for the CdS nanoparticles, which shows the presence of polycrystalline aggregates. X-ray diffraction (XRD) was performed to examine the crystal structure of the resulting nanoparticles. The diffraction pattern is consistent with the formation of wurtzite and zincblende structured CdS, as presented in Fig. 3 and confirms the TEM data, EDS data and is consistent with the diffraction rings seen in the SAED data.[11]

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) was used to examine the nanoparticles for the presence of coordinating ligands (Fig. 4). The ligand-free CdS nanoparticles were examined along with conventional CdS nanoparticles (synthesized using oleic acid and octadecylamine ligands, see ESI†), the cadmium acetylacetonate precursor and the sulfur copolymer. The top spectrum in Fig. 4 shows peaks for residual chloroform (7.26 ppm) and water (1.56 ppm) within the deuterated chloroform solvent.[12] The NMR spectrum does not show any prominent peaks in the aromatic region around 7–8 ppm (which are seen in the sulfur copolymer), in the vinylic region around 5–6 ppm (which are seen in the standard CdS nanoparticles and in cadmium acetylacetonate), or in the alkane region around 1–2 ppm (which are seen in all other spectra). Therefore, the sulfur copolymer and acetylacetonate have been effectively removed and the CdS nanoparticles do not have coordinating ligands. It is also important to note that the ligand-free CdS NP suspension is quite concentrated (1 mg ml^{-1}). Still, no NMR signals are seen from aromatic, vinylic, or alkane components. Fourier transform infrared (FTIR) spectroscopy was also conducted to confirm the absence of coordinating organic ligands (Fig. S5, ESI†). In addition, the sulfur copolymer NMR does not show any protons coordinating at the methylstyrene vinyl functional group at 5–6 ppm, which supports the sulfur copolymer structure presented in Scheme 1.

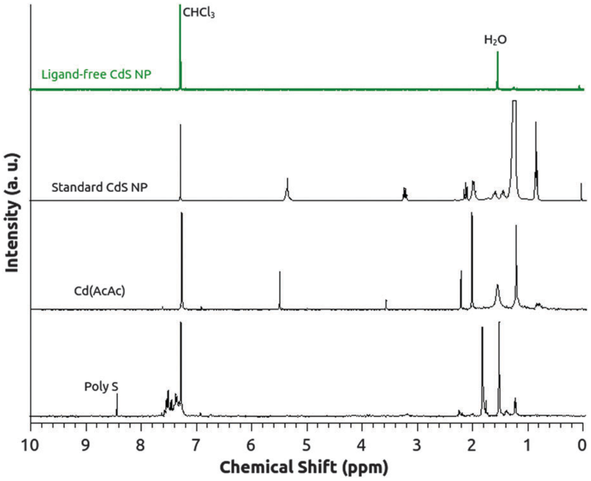


Fig. 4 ^{1}H NMR spectrum for the ligand-free CdS nanoparticles. Reference spectra for conventional CdS nanoparticles with oleic acid and octadecylamine ligands (standard CdS NP), the cadmium acetylacetonate precursor (Cd(AcAc)) and the sulfur copolymer (poly S) are also presented for comparison.

The nanoparticles were also examined using absorbance (UV-Vis-NIR) and photoluminescence (PL) spectroscopy. The UV-Vis-NIR spectrum (Fig. S3, ESI†) shows a broad absorption with a shoulder at approximately 510 nm (2.4 eV), which is consistent with the bulk bandgap of CdS. The PL spectrum (Fig. S4, ESI†) shows a broad peak centered at approximately 510 nm, which is also consistent with the CdS bandgap and with the absorption data. The broad nature of the absorption and PL spectra is likely due to quantum confinement effects coupled with a relatively high level of nanoparticle size dispersity as seen in the TEM images, as well as the presence of surface-mediated sub-bandgap energy states.[13–16]

We have demonstrated a unique method for utilizing elemental sulfur and have presented a novel technique for synthesizing ligand-free nanoparticles. Specifically, we have developed a sulfur copolymer that is simple to synthesize, easily processable and is a liquid at elevated temperatures. This sulfur copolymer can be used as a high boiling point solvent and as a sulfur precursor to synthesize stabilized metal-sulfide nanoparticles that are suspended within a sulfur copolymer matrix. Once the ligand-free nanoparticles are ready to be used, they can be separated from the sulfur copolymer. We believe that this nascent ligand-free nanoparticle synthesis method can potentially be useful in a range of situations including future biomedical and photonic materials applications, where the presence of aliphatic coordinating ligands is otherwise detrimental.

This work was supported by the State of Washington through the University of Washington Clean Energy Institute exploratory fellowship program.

Notes and references

1 E. Rosen and R. Buonsanti, *Angew. Chem.*, 2012, **51**, 684–689.
2 N. C. Anderson, M. P. Hendricks, J. J. Choi and J. S. Owen, *J. Am. Chem. Soc.*, 2013, **135**, 18536–18548.
3 J. S. Owen, J. Park, P. E. Trudeau and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2008, **130**, 1227912281.
4 W. J. Chung, J. J. Gribel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Guralnick, J. Park, A. Somogyi, P. Theato, M. E. Mackay, Y.-E. Sung, K. Char and J. Pyun, *Nat. Chem.*, 2013, **5**, 518–524.

5 A. G. Simmonds, J. J. Griebel, J. Park, K. R. Kim, W. J. Chung, V. P. Oleshko, J. Kim, E. T. Kim, R. S. Glass, C. L. Soles, Y.-E. Sung, K. Char and J. Pyun, *ACS Macro Lett.*, 2014, **3**, 229–232.

6 W. J. Chung, A. G. Simmonds, J. J. Griebel, E. T. Kim, H. S. Suh, I.-B. Shim, R. S. Glass, D. A. Loy, P. Theato, Y.-E. Sung, K. Char and J. Pyun, *Angew. Chem., Int. Ed. Engl.*, 2011, **50**, 11409–11412.

7 E. T. Kim, W. J. Chung, J. Lim, P. Johe, R. S. Glass, J. Pyun and K. Char, *Polym. Chem.*, 2014, **5**, 3617–3623.

8 J. J. Griebel, S. Namnabat, E. T. Kim, R. Himmelhuber, D. H. Moronta, W. J. Chung, A. G. Simmonds, K.-J. Kim, J. van der Laan, N. A. Nguyen, E. L. Dereniak, M. E. Mackay, K. Char, R. S. Glass, R. A. Norwood and J. Pyun, *Adv. Mater.*, 2014, **26**, 3014–3018.

9 S. Zhuo, Y. Huang, C. Liu, H. Wang and B. Zhang, *Chem. Commun.*, 2014, **50**, 11208–11210.

10 Y. Yin and A. P. Alivisatos, *Nature*, 2005, **437**, 664–670.

11 K.-T. Yong, Y. Sahoo, M. T. Swihart and P. N. Prasad, *J. Phys. Chem. C*, 2007, **111**, 2447–2458.

12 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

13 Q. Xiao and C. Xiao, *Appl. Surf. Sci.*, 2009, **255**, 7111–7114.

14 J. Z. Zhang, *J. Phys. Chem. B*, 2000, **104**, 7239–7253.

15 J.-O. Joswig, M. Springborg and G. Seifert, *J. Phys. Chem. B*, 2000, **104**, 2617–2622.

16 A. P. Alivisatos, *Science*, 1996, **271**, 933–937.