PRAMANA — journal of physics

Vol. 84, No. 6
June 2015
pp. 1049–1054

Narrowing the size distribution of CdTe nanocrystals using digestive ripening

MONA MITTAL and SAMEER SAPRA*

Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110 016, India

*Corresponding author. E-mail: sapra@chemistry.iitd.ac.in

DOI: 10.1007/s12043-015-1007-7; ***e*Publication:** 2 June 2015

Abstract. Digestive ripening of polydispersed colloidal CdTe nanocrystals is performed which results in monodispersed nanocrystals (NCs) as studied by optical spectroscopy. Optimization of ligand and refluxing time is carried out. Monodispersed NCs are obtained using mercaptopropionic acid (MPA) as a digestive ripening agent at a refluxing time of 1–2 h. Digestive ripening of CdTe NCs, which are less polydispersed, is also executed and it leads to more monodispersed NCs. In all the cases, there is a shift of maximum emission wavelength of CdTe NCs after digestive ripening that may be due to Ostwald ripening along with digestive ripening.

Keywords. CdTe nanocrystals; digestive ripening; monodisperse.

PACS Nos 61.46.Hk; 81.07.Bc

1. Introduction

Semiconductor nanocrystals (NCs) have applications in the field of biotechnology [1,2], photovoltaics [3] and light emitting devices [4] because of their unique electronic and optical properties. They show size- and shape-dependent optical, electrical and magnetic properties [5–7]. Therefore, it is important to control the size and size distribution as well as the shape of these NCs. Several synthetic methods have been developed to get monodispersed nanoparticles by carefully controlling the amount of precursor, capping agent, rate of the reaction and the reaction temperature. Size-selective precipitation, a post-synthetic method, is used to achieve monodispersed nanoparticles but it leads to loss of material and hence is not the best suited method. Free flow electrophoresis [8] is also used for the separation of nanoparticles into monodispersed size group. Another post-synthetic method, i.e. digestive ripening is an efficient and convenient method that leads to nearly monodispersed nanoparticles from polydispersed ones without the loss of material. Digestive ripening involves the heating of a colloidal suspension at or near the boiling point of a solvent in the presence of surface-active ligands in an inert atmosphere [9]. Klabunde *et al* [10] were the first to use the digestive ripening process for synthesizing Au nanoparticles with narrow size distribution. A number of groups employed a combination of solvated metal atom dispersion (SMAD) and digestive ripening process for metal nanoparticles, semiconductor nanocrystals, core shell nanoparticles, nanocomposites and nanoalloys [11–14]. Various groups reported digestive ripening process for metal nanoparticles with different capping agents using as-prepared metal colloids having broad distribution [9,15–19]. Here, for the first time we report the digestive ripening of CdTe NCs using their colloidal solution. The size and size distribution of NCs are monitored using UV–Vis absorption spectroscopy (Perkin–Elmer UV–Vis–NIR Lambda 1050 spectrophotometer) and photoluminescence (PL) spectroscopy (Perkin–Elmer LS-55 spectrometer using constant 10 nm excitation and emission slit widths).

2. Experimentation and results

2.1 *Materials required*

Cadmium perchlorate hexahydrate ($CdClO_4 \cdot 6H_2O$), mercaptopropionic acid (MPA, 99%), thioglycolic acid (TGA, 98%) and zinc telluride (ZnTe, 100 mesh, 99.99%) were purchased from Sigma Aldrich and were used as-received. Sodium hydroxide pellets (NaOH) and hydrochloric acid (HCl) were purchased from Fisher Scientific. All the chemicals were used without further purification.

2.2 *Synthesis of CdTe NCs*

CdTe NCs were synthesized by previously reported methods with slight modification to get broad distribution of NCs [20]. A cadmium solution was prepared by dissolving $Cd(ClO_4)_2 \cdot 6H_2O$ (1.0 mmol) and MPA (1.3 mmol) in 50 ml Millipore water with continuous stirring and 1 M NaOH solution is added to adjust the pH at 12.0. Argon, an inert gas, was passed through the solution for about 20 min and then H_2Te was passed through the solution which was prepared by adding HCl solution to ZnTe, along with the inert gas for about 30 min. Thus, CdTe NC precursors were formed at this stage which was accompanied by a change in colour. The precursor solution became acidic and then its pH was maintained at 12.0 again. The solution was refluxed at 100°C under open air conditions with a water condenser. Then, these NCs were precipitated with acetone and dispersed in MilliQ water for further characterization.

Figure 1 displays the UV–Vis absorption and PL spectra of the as-prepared MPA-capped CdTe NCs at $\lambda_{ex} = 377$ nm. They show broad absorption at 550 nm and broad emission at 580 nm with full-width at half-maximum (FWHM) of 90 nm. The size of the MPA-capped CdTe NCs is 3.24 nm as calculated from the first excitonic band of UV–Vis absorption spectra [21]. The band edge luminescence depends strongly on the size and size distribution of NCs [22]. A large FWHM indicates the broad size distribution of NCs. Hence, the shape of luminescence spectra and FWHM are used as the criteria for studying the digestive ripening of CdTe NCs.

2.3 *Digestive ripening in the presence of different capping agents*

These as-prepared CdTe NCs were refluxed in the presence of excess of MPA or TGA at 100°C in MilliQ water for 90 min under an inert atmosphere [9]. The colloids were then

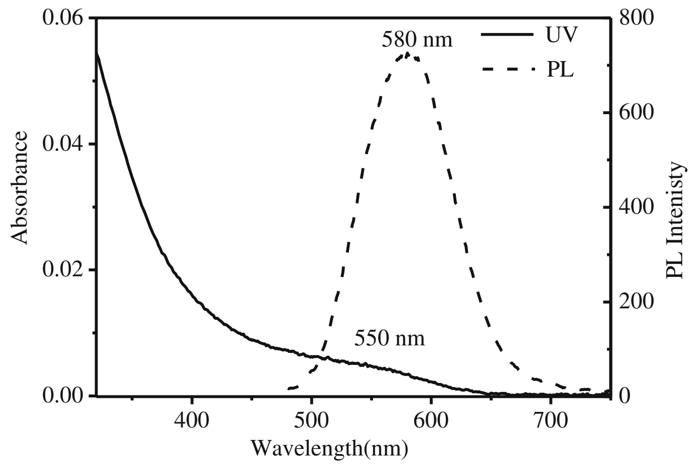

Figure 1. UV–Vis absorption (solid line) and PL spectra (dashed line) of the as-prepared MPA-capped CdTe NCs ($\lambda_{ex} = 377$ nm).

precipitated with acetone and redispersed in MilliQ water. Figure 2 shows the UV–Vis absorption and PL spectra of the as-prepared, MPA-capped and TGA-capped CdTe NCs. Table 1 represents the optical characteristics of these NCs. According to the data shown in the table, MPA acts as a better digestive ripening agent than TGA as it provides lower FWHM as well as symmetrical distribution of luminescence spectrum which is a strong indication of monodispersity of CdTe NCs. There is also a shift of λ_{em} and λ_{max}which may be due to the Ostwald ripening along with digestive ripening, as refluxing is carried out at 100°C that is also the reaction temperature employed for the synthesis of CdTe NCs [23].

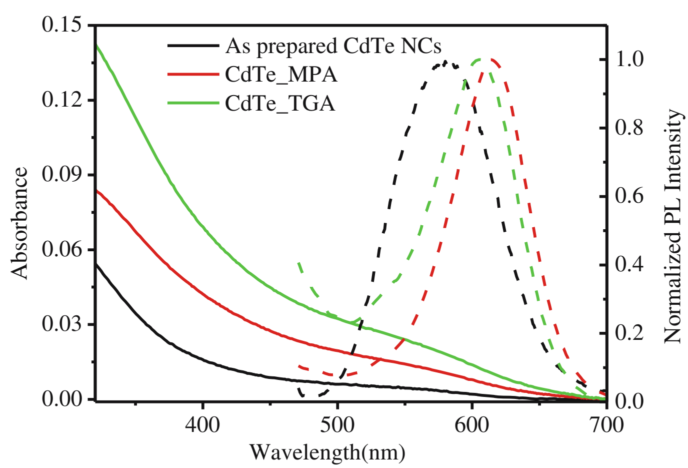

Figure 2. UV--Vis absorption (solid line) and PL spectra (dashed line) of the as-prepared CdTe NCs, MPA-capped CdTe NCs and TGA-capped CdTe NCs ($\lambda_{ex} = 377$ nm).

Table 1. Optical characteristics of CdTe NCs, MPA-capped CdTe NCs and TGA-capped CdTe NCs.

System	λ_{max} (nm)	Average size [21] (nm)	λ_{em} (nm)	FWHM (nm)	Distribution
CdTe	550	3.24	580	90	Symmetric
CdTe-MPA	570	3.42	614	66	Symmetric
CdTe-TGA	565	3.38	604	76	Asymmetric

2.4 *Effect of refluxing time on digestive ripening*

To get the control on NCs size and size distribution, digestive ripening is performed using the above-mentioned procedure by varying the refluxing time from 1 to 7 h. Figure 3 shows the PL spectra ($\lambda_{ex} = 377$ nm) of the as-prepared MPA-capped CdTe NCs and MPA-capped CdTe NCs under different refluxing time. Table 2 represents the corresponding optical characteristics of CdTe NCs. As refluxing time is increased beyond 2 h, distribution of luminescence spectrum become asymmetrical and FWHM increases which limits the refluxing time period for digestive ripening of CdTe NCs.

2.5 *Digestive ripening of CdTe NCs having small FWHM*

Digestive ripening of CdTe NCs having small FWHM is also performed which results in further narrowing of PL spectrum. Figure 4 displays the UV–Vis absorption and PL spectra of the as-prepared MPA-capped CdTe NCs, CdTe NCs digestive ripened with MPA and its corresponding characteristics is shown in table 3. It suggests that if the as-prepared, relatively monodispersed CdTe NCs, further undergo digestive ripening, it improves their monodispersity.

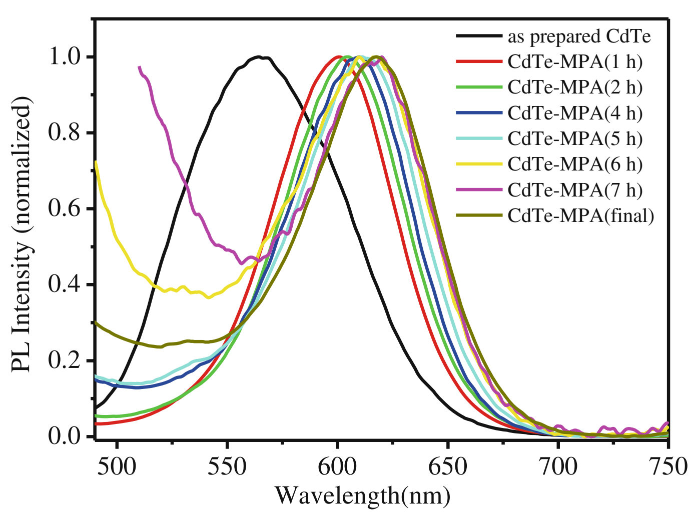

Figure 3. PL spectra of the as-prepared CdTe NCs and MPA-capped CdTe NCs under different refluxing time ($\lambda_{ex} = 377$ nm).

Table 2. Optical characteristics of CdTe NCs and MPA-capped CdTe NCs under different refluxing time.

System	λ_{max} (nm)	Average size [21] (nm)	λ_{em} (nm)	FWHM (nm)	Distribution
CdTe	540	3.12	565	90	Symmetric
CdTe-MPA (1 h)	563	3.37	600	65	Symmetric
CdTe-MPA (2 h)	565	3.38	604	65	Symmetric
CdTe-MPA (4 h)	567	3.40	608	66	Asymmetric
CdTe-MPA (5 h)	568	3.41	611	67	Asymmetric
CdTe-MPA (6 h)	570	3.43	614	82	Asymmetric
CdTe-MPA (7 h)	573	3.45	617	77	Asymmetric
CdTe-MPA (final)	573	3.45	617	71	Asymmetric

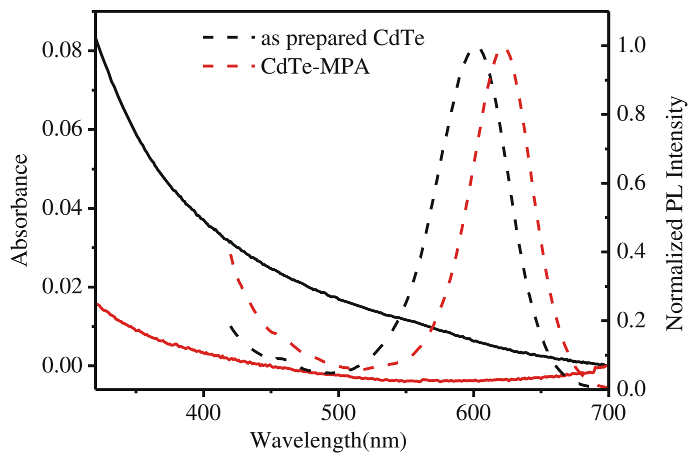

Figure 4. UV–Vis absorption and PL spectra of the as-prepared CdTe NCs and MPA-capped CdTe NCs ($\lambda_{ex} = 377$ nm).

Table 3. Optical characteristics of CdTe NCs and MPA-capped CdTe NCs.

System	λ_{max} (nm)	Average size [21] (nm)	λ_{em} (nm)	FWHM (nm)	Distribution
CdTe	565	3.38	602	64	Symmetric
CdTe-MPA	580	3.50	622	56	Symmetric

3. Conclusions

An efficient post-synthetic method of digestive ripening for the conversion of polydispersed CdTe NCs into monodispersed ones is presented. MPA is a better digestive ripening agent for CdTe NCs and refluxing time of 1–2 h is sufficient for digestive ripening in an inert atmosphere. Digestive ripening can be further carried out on NCs that have narrow size distributions in order to further increase their monodispersity.

References

[1] A Sharma, C M Pandey, Z Matharu, U Soni, S Sapra, G Sumana, M K Pandey, T Chatterjee and B D Malhotra, *Anal. Chem.* **84**, 3082 (2012)
[2] W C Chan, *Science* **281**, 2016 (1998)
[3] N Greenham, X Peng and A Alivisatos, *Phys. Rev. B* **54**, 17628 (1996)
[4] M C Schlamp, X Peng and A P Alivisatos, *J. Appl. Phys.* **82**, 5837 (1997)
[5] A P Alivisatos, *J. Phys. Chem.* **100**, 13226 (1996)
[6] C N R Rao, G U Kulkarni, P J Thomas and P P Edwards, *Chem. Eur. J.* **8**, 28 (2002)
[7] M A El-Sayed, *Acc. Chem. Res.* **37**, 326 (2004)
[8] S Ho, K Critchley, G D Lilly, B Shim and N A Kotov, *J. Mater. Chem.* **19**, 1390 (2009)
[9] B L V Prasad, S I Stoeva, C M Sorensen and K J Klabunde, *Langmuir* **18**, 7515 (2002)
[10] X M Lin, C M Sorensen and K J Klabunde, *Chem. Mater.* **11**, 198 (1999)
[11] S P Bhaskar and B R Jagirdar, *J. Chem. Sci.* **124**, 1175 (2012)
[12] S Stoeva, K J Klabunde, C M Sorensen and I Dragieva, *J. Am. Chem. Soc.* **124**, 2305 (2002)
[13] S Cingarapu, Z Yang, C M Sorensen and K J Klabunde, *J. Nanomater.* **2012**, 1 (2012)
[14] S B Kalidindi and B R Jagirdar, *J. Phys. Chem. C* **112**, 4042 (2008)
[15] X M Lin, C M Sorensen and K J Klabunde, *J. Nanopart. Res.* **2**, 157 (2000)
[16] B L V Prasad, S I Stoeva, C M Sorensen and K J Klabunde, *Chem. Mater.* **15**, 935 (2003)
[17] P Sahu and B L V Prasad, *Chem. Phys. Lett.* **525–526**, 101 (2012)
[18] D S Sidhaye and B L V Prasad, *New J. Chem.* **35**, 755 (2011)
[19] A B Smetana, K J Klabunde and C M Sorensen, *J. Colloid Interface Sci.* **284**, 521 (2005)
[20] N Gaponik, D V Talapin, A L Rogach, K Hoppe, E V Shevchenko, A Kornowski, A Eychmüller and H Weller, *J. Phys. Chem. B* **106**, 7177 (2002)
[21] W W Yu, L Qu, W Guo and X Peng, *Chem. Mater.* **15**, 2854 (2003)
[22] X Peng, J Wickham and A P Alivisatos, *J. Am. Chem. Soc.* **120**, 5343 (1998)
[23] A L Rogach, T Franzl, T A Klar, J Feldmann, N Gaponik, V Lesnyak, A Shavel, A Eychmuller, Y P Rakovich and J F Donegan, *J. Phys. Chem. C* **111**, 14628 (2007)