Materials Science in Semiconductor Processing 16 (2013) 263–268

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Lead chalcogenides stabilized by anacardic acid

S. Mlowe [a,b], A.A. Nejo [a], V.S.R. Rajasekhar Pullabhotla [a], E.B. Mubofu [b], F.N. Ngassapa [b], P. O'Brien [c], N. Revaprasadu [a,*]

[a] Department of Chemistry, University of Zululand, Private Bag X1001, Kwa-Dlangezwa 3886, South Africa
[b] Department of Chemistry, University of Dar es Salaam, P.O. Box 35061, Dar Es Salaam, Tanzania
[c] The School of Chemistry and the School of Materials, The University of Manchester Oxford Road, Manchester, M13 9PL, UK

ARTICLE INFO

Available online 26 November 2012

Keywords:
PbE nanoparticles
Pb source
TEM
Anacardic acid

ABSTRACT

PbE (E=S, Se and Te) nanoparticles stabilized by anacardic acid in the shape of spheres and cubes have been synthesized employing a simple solution based thermolysis route at moderate reaction temperatures. The route adheres to some of the principles of 'green' chemistry since a naturally occurring capping ligand, anacardic acid, is employed at a relatively low temperature. The lead sources were varied to study their effect on the morphology of the lead chalcogenide particles.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Lead chalcogenide nanoparticles have attracted interest because of their use in applications such as lasers, thermoelectric devices, light emitting diodes, biological imaging and solar cells [1–6]. The large Bohr radii of PbE (where E=S, Se, and Te) ensures that these materials exhibit large strong quantum confinement. Synthesis methodologies employing surface passivating agents such as amines or thiols are commonly used to control the particle sizes at the order of nanometers to achieve this quantum confinement. Various routes have been developed for the synthesis of lead chalcogenide nanoparticles; these include microwave irradiation [7], solvothermal [8,9], chemical bath deposition [10] and hot injection precursor route [11–17]. The latter route involves the rapid injection of a lead salt and chalcogenide source into co-ordinating solvents. Early work by the Scholes and the Ozin groups demonstrated the use of capping groups such as oleic acid and oleylamine, respectively [11,12] and prepared PbS nanoparticles with diverse shapes by using a combination of surfactants. A related method employing the use of single molecule precursors by the Cheon group [18] and the O'Brien group [19–22] also showed that good quality lead chalcogenide nanoparticles can be synthesized by preparing precursors that incorporate all the elemental constituents.

There have been recent reports of the use of green solvents such as olive oil as a capping group for nanomaterials [22]. Ancardic acid is naturally occurring oil, which can be extracted directly from crushed cashew nut shell. The use of this acid as a solvent will lead to a more environmentally benign method of synthesis. Our group has recently developed a new hybrid solution based thermolysis route to lead chalcogenide nanoparticles [23–25]. The synthesis method involves the reduction of sulfur, selenium or tellurium powder with sodium borohydride ($NaBH_4$) to produce sulfide, selenide or telluride ions, followed by the reaction with a lead salt. The as-formed lead chalcogenide is then thermolysed in an alkylamine to form the nanocrystalline material. Considerable control of the reaction is possible when lead carbonate is used as the salt and various shapes of nanoparticles are obtained at different temperatures and time. In this work, we have replaced the alkylamine with anacardic acid, a major component of solvent extracted from cashew nut shell liquid (CNSL). The thermolysis was

* Corresponding author. Tel.: +27 35 902 6152; fax: +27 35 902 6568.
E-mail address: nrevapra@pan.uzulu.ac.za (N. Revaprasadu).

1369-8001/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mssp.2012.10.017

carried out at 140–160 °C. To our knowledge this is the first report of the use of anacardic acid as a capping group for nanomaterials.

2. Experimental

2.1. Materials

All chemicals used were of analytical grade and of highest purity available. Selenium powder, tellurium powder, sulfur powder, sodium borohydride ($NaBH_4$), lead carbonate, lead chloride, deionized water, methanol, toluene and tri-*n*-octylphosphine (TOP) were purchased from Sigma-Aldrich. Cashew nut shells were collected from Mtwara/Coastal region cashew nut processing factory, in Tanzania. The anacardic acid was isolated from cashew nut shell liquid (CNSL) using the method described by Paramashivappa et al. [26].

2.2. Solvent extraction of CNSL from cashew nut shells

Pre-treatment processes were carried out on the cashew nut samples (Anacardium occidentale) prior to extraction process to ensure a high degree of purity. The processes include washing, drying and de-shelling as well as pulverizing in order to create a better surface area for the shell and solvent for easy removal of the CNSL. In this method, solvents were used to extract the CNSL from the shells of the cashew nuts [26]. The shells were soaked in petroleum ether for 3 days. A brown oily product (CNSL) was obtained when the solvent was removed from the colored liquid under reduced pressure using a rotary evaporator at about 40 °C.

2.3. Isolation of anacardic acid from CNSL

The isolation of anacardic acid from CNSL was carried out using a procedure reported by Paramashivappa et al. [26] with slight modifications reported by Lucio et al. [27]. Anacardic acid was selectively isolated as calcium anacardate. The isolation was carried out by dissolving the extracted CNSL (50 g) in 5% aqueous methanol (300 mL) followed by addition of calcium hydroxide (25 g) with stirring. Then the reaction was left at room temperature for 24 h. Thereafter, the calcium anacardate precipitates were vacuum-filtered and washed thoroughly with 5% aqueous methanol (200 mL). The calcium anacardate cake was carefully transferred into a flask containing a stirred mixture of 6.0 M HCl (200 mL) and 300 mL of ethyl acetate. The mixture was stirred for 1 h. The organic layer was washed twice with distilled water (100 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure using a rotary evaporator to yield anacardic acid (heterogeneous mixture of monoene, diene, and triene).

2.4. Synthesis of PbE nanoparticles

In a typical room temperature reaction, selenium/tellurium/sulfur powder was reduced to selenide/telluride/sulfide ion by adding 0.32 mmol of selenium/tellurium/sulfur powder to 20.0 mL of HPLC grade water in a three neck flask. A 0.79 mmol solution of sodium borohydride ($NaBH_4$) was added to the flask contents and the flask was purged with nitrogen flow to create an inert atmosphere. The reduction reaction was carried out for 2 h with continuous stirring and with the flow of N_2 gas. A 0.32 mmol solution of the lead salt was added to the reduced selenide/telluride/sulfide ion solution and stirred for 5 min, followed by the addition of excess methanol to form the bulk PbE (E=Se, Te and S). The preformed bulk PbE was isolated by centrifugation and dispersed in 6.0 mL of TOP. The resultant PbE–TOP mixture was then injected into 6.0 g of anacardic acid pre-heated to 140 °C or 160 °C. After injection a drop (20–30 °C) in the temperature was observed. The temperature was then stabilized at the injection temperature and the reaction was allowed to proceed for 2 h. After cooling, excess methanol was added to flocculate the nanoparticles. The flocculate was separated from the supernatant by centrifugation and the excess methanol was removed under vacuum to give anacardic acid capped PbE nanoparticles. The resultant particles were dissolved in toluene for further characterization. The reaction scheme is shown in Fig. 1. The as-synthesized particles were characterized by X-ray diffraction, TEM and HRTEM techniques.

2.5. Characterization

The crystalline phase was identified by X-ray diffraction (XRD), employing a scanning rate of 0.05° min^{-1} in a 2θ range from 20° to 80°, using a Bruker AXS D8 diffractometer equipped with nickel filtered Co Kα radiation (λ=1.5418 Å) at 40 kV, 40 mA and room temperature. The morphologies and particle sizes of the samples were characterized by a JEOL 1010 TEM with an accelerating voltage of 100 kV, Megaview III camera, and Soft Imaging Systems iTEM software. The detail morphological and structural features were investigated using HRTEM images with a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV.

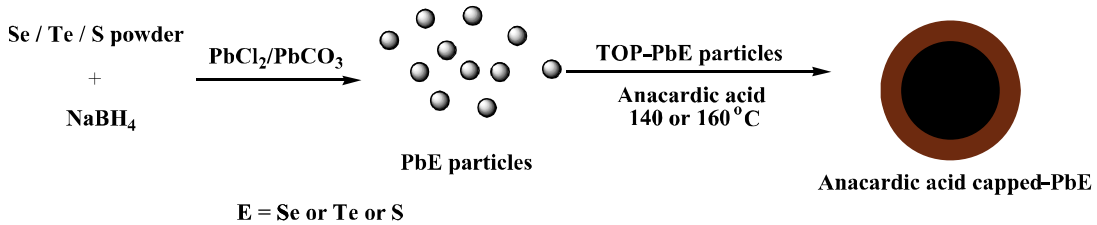


Fig. 1. Reaction scheme for the synthesis of anacardic acid capped PbE (E=S, Se or Te) nanoparticles.

3. Results and discussion

Cashew nut shell liquid (CNSL),is an amber-colored viscous oil obtained from the by-product of the cashew nut shells by extraction process [26]. It is often considered as a good, cheaper source of unsaturated phenols. The anacardic acid has C_{15} side chain (R), which can be either a saturated or unsaturated (monoene, diene or triene) alkyl group (Fig. 2) [28]. The sodium salts of CNSL and anacardic acid have been reported to possess anti vectorial activity [29]. Anacardic acids are also efficient enzyme inhibitors [30]. Anacardic acid is cheap, relatively abundant and chemically reactive, making it useful in many industrial applications, and also acts as a good passivating agent.

Anacardic acid capped PbS nanoparticles were synthesized by reacting reduced sulfur with lead chloride to form the bulk PbS. The isolated product was then dispersed in tri-octyphosphine and thermolysed in anarcardic acid at 140 °C. After cooling the particles were precipitated by the addition of methanol, isolated and redispersed in toluene. Fig. 3 shows the TEM image of anarcardic acid capped PbS synthesized at 140 °C. The particles are evenly distributed on the grid and have a faceted shape with an average size of 9.85 ± 2.70 nm. The shape of the particles is very similar to the olive oil capped PbS nanoparticles reported by O'Brien's group [22].

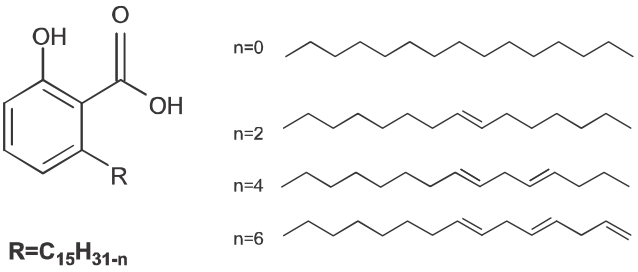


Fig. 2. Structure of anacardic acids [29].

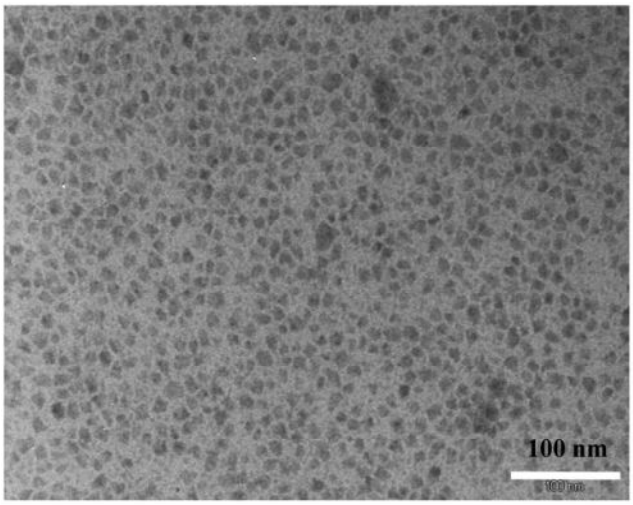


Fig. 3. TEM image of anacardic acid capped PbS nanoparticles synthesized at 140 °C.

The X-ray diffraction pattern shows broad peaks that can be assigned to the (111), (200) and (220) planes of cubic PbS (Fig. 6a). The estimated particle size using the Scherrer

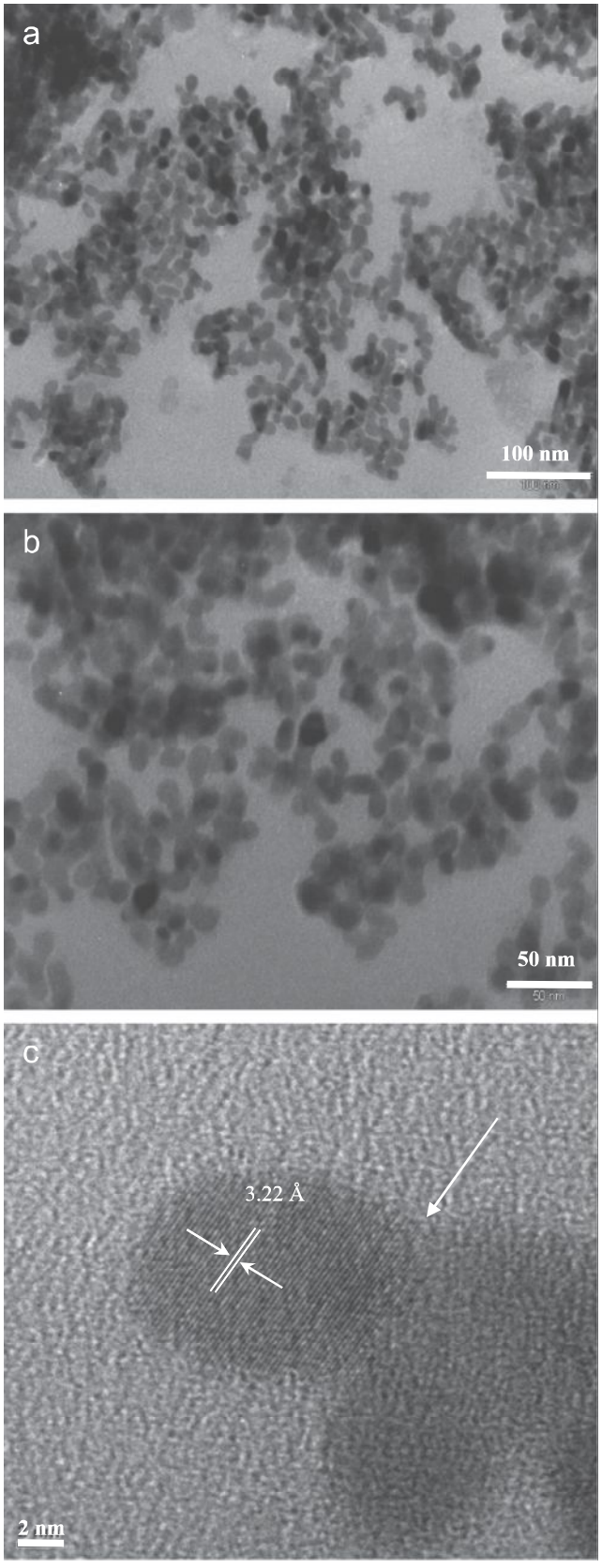


Fig. 4. (a, b) TEM and (c) HRTEM images of anacardic acid capped PbSe nanoparticles synthesized at 140 °C.

equation is 11.67 nm [31]. This is in good agreement with the TEM size measurements.

Anacardic acid capped PbSe nanoparticles were synthesized by a similar method to that used for PbS nanoparticles. An aqueous suspension of the lead salt was added to the reduced selenide ion. The resultant bulk PbSe was then thermolysed in anacardic acid at 140 °C. The anacardic acid capped PbSe nanoparticles formed were regular in shape. Predominantly spherical shaped particles were formed and some of the particles were joined together to form chain-like aggregate particles which are visible in the TEM images (Fig. 4a and b). The average particle size of the spheres was 13.25 ± 3.35 nm. The corresponding HRTEM image shows that the particles are single crystals with observable distinct lattice fringes (Fig. 4c). The lattice spacing of 3.22 Å was estimated from the HRTEM image which is assigned to the [200] plane of PbSe. The HRTEM images also provide further evidence for the fusion of particles. There are discontinuities in the lattice fringes as shown by the arrows which suggest that growth occurs via an oriented attachment mechanism. There have been previous reports of PbSe nanowires formed through the oriented attachment of nanocrystal building blocks [32]. The X-ray diffraction pattern shows peaks corresponding to the (111), (200) and (220) reflections of cubic PbSe (Fig. 6b). The estimated particle size from the XRD analysis is 12.49 nm.

The reaction conditions for the synthesis of the anacardic acid capped PbTe nanoparticles were similar to that for PbSe, with selenium being replaced by tellurium. The anacardic acid capped PbTe nanoparticles are regular cubes shaped with an average size of 24.4 ± 4.10 nm as shown in Fig. 5a–c. It has been previously reported that lead chalcogenide nanoparticles undergo a shape evolution from spherical to cubic with increasing particle size [18]. Our previous work on hexadecylamine (HDA) capped PbTe yielded close to spherical and rod shaped particles at reaction temperatures between 190 and 270 °C [23]. The growth rate on different facets of the particles is dominated by the surface energy. The cubic rock salt structure of PbTe possesses different surface energies, allowing for particle growth to occur along different facets. In this work the anacardic acid capping group allows the [111] facet to grow faster than the lower surface energy [100] face, favouring the formation of cubes [33]. The cubic morphology is confirmed by the HRTEM image (Fig. 5d) which shows a cube shaped particle with distinct lattice fringes. The lattice spacing of 3.23 Å is assigned to the (200) cubic PbTe. The (111), (200), (220) and (222) planes of cubic PbTe are visible in the X-ray diffraction pattern (Fig. 6c). There additional peaks could be due to the unreacted lead carbonate. The estimated particle size from the XRD analysis using the Scherrer equation is 23.24 nm.

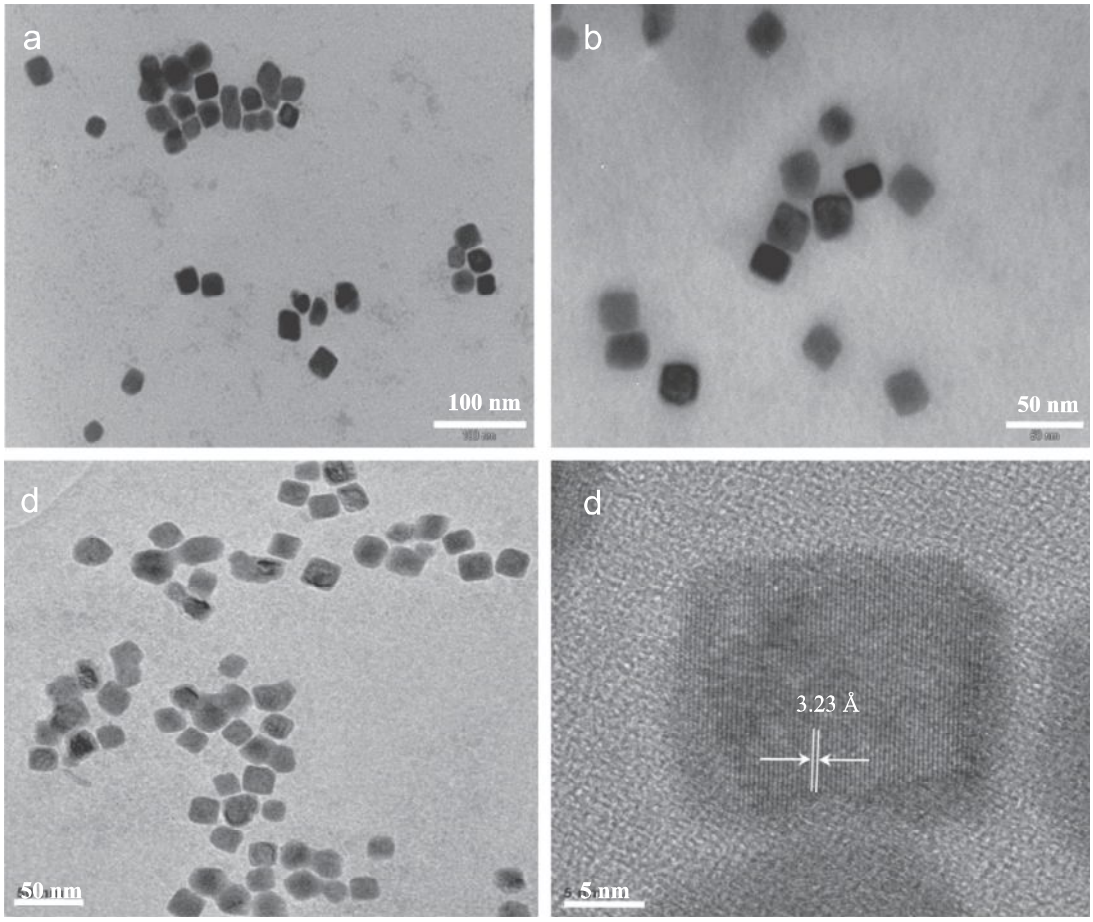


Fig. 5. (a–b–c) TEM and (d) HRTEM images of anacardic acid capped PbTe nanoparticles synthesized at 160 °C.

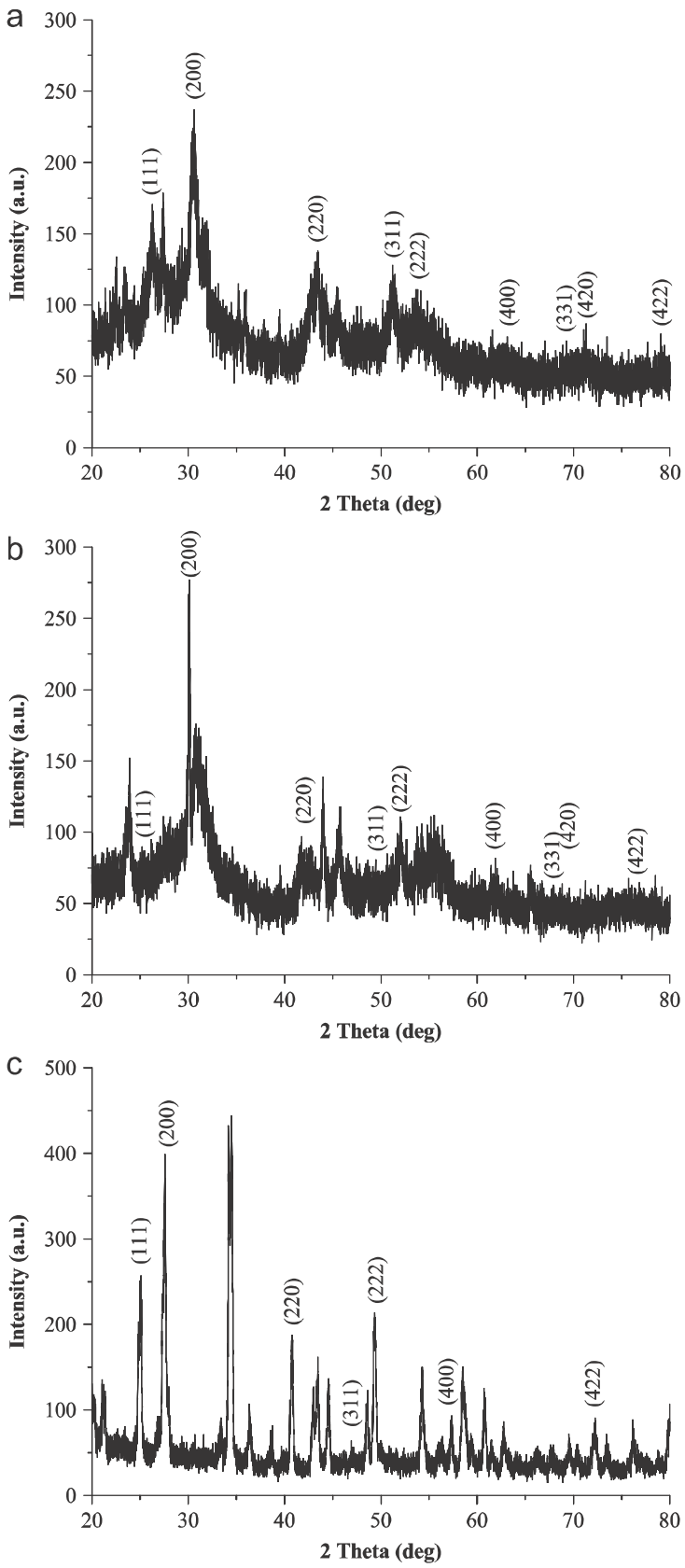


Fig. 6. Powder X-ray diffraction spectra of anacardic acid capped (a) PbS, (b) PbSe and (c) PbTe nanoparticles.

4. Conclusions

We have synthesized anacardic acid capped lead chalcogenide (PbS, PbSe and PbTe) nanoparticles using a simple route at a moderate temperature. The PbS and PbSe particles are close to spherical whereas the PbTe particles are cubes. The X-ray diffraction and high resolution studies of the materials show them to be crystalline.

The naturally obtained anacardic acid seems to be an effective capping group for nanomaterials synthesized at low reaction temperatures.

Acknowledgments

The authors are grateful to the National Research Foundation (NRF), Department of Science and Technology (DST) South Africa and Royal Society Leverhulme Africa Award for funding. The authors also thank Dr. James Wesley-Smith from the Electron Microscopy Unit, University of Kwa-Zulu Natal for electron microscopy (TEM) measurements and CSIR, Pretoria, for HRTEM facility.

References

[1] T. Mokari, M. Zhang, P. Yang, Journal of the American Chemical Society 129 (2007) 9864–9865.
[2] H. Du, R. Chen, T. Krishnan, T.D. Krauss, J.M. Harbold, F.W. Wise, M.G. Thomas, J. Silcox, Nano Letters 2 (2002) 1321–1324.
[3] R. Ellington, M. Beard, J.C. Johnson, P. Yu, O. Micic, A. Nozik, A. Shabaev, A. Efros, Nano Letters 5 (2005) 865–871.
[4] S.A. McDonald, P.W. Cyr, L. Levina, E.H. Sargent, Applied Physics Letters 85 (2004) 2089–2091.
[5] S.A. McDonald, G. Konstantatos, S. Zhang, P.W. Cyr, E.J.D. Klem, L. Levina, E.H. Sargent, Nature Materials 4 (2005) 138–142.
[6] A.A.R. Watt, D. Blake, J.H. Warner, E.A. Thomsen, E.L. Tavenner, H. Rubinsztein-Dunlop, P. Meredith, Journal of Physics D: Applied Physics 38 (2005) 2006.
[7] J.J. Zhu, O. Palchick, S.G. Chen, A. Gedanken, Journal of Physical Chemistry B 104 (2000) 7344–7347.
[8] U.K. Gautam, R. Seshadri, Materials Research Bulletin 39 (2004) 669–676.
[9] Y. Xie, H.L. Su, B. Li, Y.T. Qian, Materials Research Bulletin 35 (2000) 459–464.
[10] L. Raniero, C.L. Fereira, L.R. Cruz, A.L. Pinto, R.M.P. Alves, Physica B: Condensed Matter 405 (2010) 1283–1286.
[11] M.A. Hines, G.D. Scholes, Advanced Materials 15 (2003) 1844–1849.
[12] L. Cademartiri, J. Bertolotti, R. Sapienza, D.S. Wiersma, G.V. Freymann, G.A. Ozin, Journal of Physical Chemistry B 110 (2006) 671–673.
[13] J.H. Warner, E. Thomson, A.R. Watt, N.R. Heckenberg, H. Rubinsztein-Dunlop, Nanotechnology 16 (2005) 175.
[14] J.H. Warner, H. Cao, Nanotechnology 19 (2008) 305605.
[15] K.A. Abel, J. Shan, J.C. Boyer, F. Harris, F.C.J.M. van Veggel, Chemistry of Materials 20 (2008) 3794–3796.
[16] J. Liu, H. Yu, Z. Wu, W. Wang, J. Peng, Y. Cao, Nanotechnology 19 (2008). 345602–3456.
[17] J. Joo, H.B. Na, T.Y. Yu, J.H. Yu, Y.W. Kim, F. Wu, J.Z. Zhang, T. Hyeon, Journal of the American Chemical Society 125 (2003) 11100–11105.
[18] Y.W. Lee, S.N. Jun, Cho, J.W. Cheon, Journal of the American Chemical Society 124 (2002) 11244–11245.
[19] T. Trindade, P. O' Brien, X. Zhang, M. Motevalli, Journal of Materials Chemistry 7 (1997) 1011–1016.
[20] J. Akhtar, M.A. Malik, P. O'Brien, M. Helliwell, Journal of Materials Chemistry 20 (2010) 6116.
[21] M.J. Moloto, N. Revaprasadu, G.A. Kolawole, P. O'Brien, M.A. Malik, **South African Journal** of **Science** 101 (2005) 463–465.
[22] J. Akhtar, M.A. Malik, P. O'Brien, K.G.U. Wijayantha, R. Dharmadasa, S.J.O. Hardman, D.M. Graham, B.F. Spencer, S.K. Stubbs, W.R. Flavell, D.J. Binks, F. Sirotti, M. El Kazzi, M. Silly, Journal of Materials Chemistry 20 (2010) 2336.
[23] N. Ziqubu, K. Ramasamy, V.S.R.R. Pullabhotla, N. Revaprasadu, P. O'Brien, Chemistry of Materials 22 (2010) 3817–3819.
[24] K. Ramasamy, A.O. Nejo, N. Ziqubu, V.S.R.R. Pullabhotla, A.A. Nejo, N. Revaprasadu, P. O' Brien, European Journal of Inorganic Chemistry (2011) 5196–5201.
[25] A.O. Nejo, A.A. Nejo, V.S.R.R. Pullabhotla, N. Revaprasadu, Journal of **Alloys** and **Compounds** 537 (2012) 19–23.
[26] R. Paramashivappa, P.P. Kumar, P.J. Vithayathil, A.S. Rao, Journal of Agricultural and Food Chemistry 49 (2001) 2548–2551.
[27] P.L.L. Lucio, C.O. Santos, L.A.S. Romeiro, A.M. Costa, J.R.O. Ferreira, B.C. Cavalcanti, O.M. Moraes, L.V. Costa-Lotufo, C. Pessoa, M.L. Santos, European Journal of **Medicinal Chemistry** 45 (2010) 3480–3489.
[28] J.H.P. Tyman, Journal of **Chromatography** 111 (1975) 285–292.
[29] A. Laurens, C. Fourneau, R. Hocquemiller, A. Cave, C. Bories, P.M. Loiseau, **Phytotherapy** Research 11 (1997) 145–146.
[30] M. Toyomizu, S. Sugiyama, R.L. Jin, T. Nakatsu, **Phytotherapy** Research 7 (1993) 252–254.
[31] A.L. Patterson, Physical Review 56 (1939) 978.
[32] K.S. Cho, D.V. Talapin, W. Gaschler, C.B. Murray, Journal of the American Chemical Society 127 (2005) 7140–7147.
[33] E. Dowty, American Mineralogist 61 (1976) 448–459.