



Synthesis and Characterization of Glucuronic Acid Capped CdO and CdS Nanoparticles

NOBATHEMBU FALENI¹, SWIKISANI NELWAMONDO¹, MAKWENA J. MOLOTO^{2,*} and NOSIPHO MOLOTO³

¹Applied Chemistry, Faculty of Science, University of Johannesburg, P.O. Box 17011, Doornfontein, Johannesburg-2028, South Africa

²Department of Chemistry, Faculty of Applied and Computer Science, Vaal University of Technology, P/Bag X021 Vanderbijlpark-1900, South Africa

³School of Chemistry, Faculty of Science, University of the Witwatersrand, P/Bag X 3, Johannesburg-2050, South Africa

*Corresponding author: E-mail: makwenam@vut.ac.za

Received: 26 July 2014;

Accepted: 19 November 2014;

Published online: 20 February 2015;

AJC-16921

Cadmium oxide and cadmium sulphide nanoparticles have been prepared with variety of stabilizers for different purposes and glucuronic acid is used for capping CdS and CdO nanoparticles. These nanoparticles were prepared by using cadmium acetate with thioacetamide for CdS and cadmium chloride and the strong base for CdO nanoparticles. The as obtained CdO and CdS nanoparticles were characterized by a combination of microscopy and spectroscopic techniques for their morphology, size and crystallinity. The glucuronic acid-capped CdS and CdO nanoparticles showed blue shifts in their absorption band edges and with emission maxima red shifted from the band edge. The particles were obtained with good crystallinity and spherical in shape with relatively narrow size distribution.

Keywords: Glucuronic acid, Cadmium oxide, Cadmium sulphide, Nanoparticles, Thioacetamide.

INTRODUCTION

Semiconductor nanocrystals have been of interest in research and technical applications, with respect of its size-dependent optical and electronic properties¹⁻³. Various synthetic techniques have been used to produce particles with change in optical properties due to the influence of the crystallite size on the electronic structure and quantum effects^{4,5}. Researchers have extensively been studying efficient synthetic routes to well-defined nanocrystals with controlled size and shape. Their methods include gas-phase synthesis utilizing vapour-liquid-solid^{6,7}, chemical vapour deposition^{8,9} and thermal evaporation¹⁰ methods, colloidal synthesis in aqueous media^{11,12} or non-hydrolytic media¹³. A lot of research has been done on metal sulphide nanoparticles, such as cadmium sulphide (CdS), with various compositions and shapes¹⁴. It is a challenge to synthesize anisotropic-shaped CdS nanocrystals with controllable shape and size in the quantum confinement range, because the preparation of high quality 1D CdS nanorods in this size range is still difficult to achieve through common methods (the diameters of the nanorods or nanowires prepared by common methods are usually beyond 10 nm)¹⁵. Among these materials metal oxide nanoparticles are of technological importance for solar cells, chemical sensors and liquid crystal displays¹⁶. Cadmium oxide (Eg 2.3 eV) is an n-type degenerate semiconductor with high electrical conductivity. Due to its

large linear refractive index ($n_0 = 2.49$) it is a promising candidate for optoelectronic applications and other applications including solar cells, photo transistors, photodiodes, transparent electrodes and gas sensors^{16,17}.

The ultimate goal of nanochemistry is to identify safer, more cost-effective, high-yielding and more controllable methods of nanoparticles synthesis¹⁵. Cadmium oxide nanoparticles have been synthesized by several different methods and in most of them CdO has been generated from Cd(OH)₂, for example, the generation of Cd(OH)₂ and CdO nanoparticles from dimethyl cadmium in THF¹⁸ have been reported. The synthesis of glucuronic acid capped CdS using thioacetamide as a precursor and molecules with thiol (-SH) groups are proven to be effective coatings for CdS and CdSe¹⁹. In this paper we report the synthesis of CdS and CdO nanoparticles using cadmium salt and sodium hydroxide and thioacetamide as a sulphide sources in an alcoholic medium.

EXPERIMENTAL

Cadmium chloride monohydrate, cadmium acetate, methanol, sodium hydroxide, glucuronic acid, thioacetamide, were purchased from Sigma Aldrich and used as obtained.

Several analytical techniques were used to characterize the as prepared materials. Powder X-ray diffractometry (XRD) (Phillips X'Pert materials research diffractometer using secondary graphite monochromated CuK α radiation ($\lambda = 1.54060 \text{ \AA}$) at

40 kV/50 mA), transmission electron microscopy (TEM) (JEM-2100 JEOL electron microscope), fourier-transform infrared spectra (FT-IR) (Perkin Elmer 100 spectrometer), UV-visible spectroscopy (UV) (Analytikjena Specord50) and photoluminescence (PL) (LS 45 Perkin-Elmer fluorimeter with a Xenon lamp).

Synthesis of glucuronic acid capped and CdO and CdS nanoparticles: The synthesis of CdO and CdS nanoparticles were prepared using different precursors. Cadmium oxide nanoparticles were prepared using $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, methanol, sodium hydroxide (0.10 M) and glucuronic acid. Equivalent moles of cadmium chloride monohydrate solution and sodium hydroxide solution were mixed in methanol and followed by addition of glucuronic acid (1 g) and the mixture was stirred and heated to about 70 °C and for 45 min. Upon cooling the solution was filtered and centrifuged to obtain white powder of CdO nanoparticles embedded in glucuronic acid.

Cadmium sulphide nanoparticles were prepared by sequential addition of cadmium acetate (0.5 g), thioacetamide (0.5 g) and few millimetres of NaOH solution (0.1 M in methanol). For this synthesis about 1 g of glucuronic acid, temperature of 70 °C and 45 min of stirring were used. The resulting product on cooling to room temperature was filtered and centrifuged.

RESULTS AND DISCUSSION

Semiconductor particles of similar dimensions to the de Broglie wavelength of an electron (or hole) contained within them have an absorption edge shifted from the bulk value to higher energy, a quantum size effect²⁰⁻²². In the synthesis of colloidal semiconductor nanoparticles, luminescent property plays a crucial role in determining uniform morphology and size in the synthesis of glucuronic acid capped CdO and CdS nanoparticles.

In order to follow the progress of CdO and CdS nanoparticles formation during ripening and the changing crystal size was monitored by recording UV-visible absorption and photoluminescence (PL) spectra. From the absorption spectrum in Fig. 1(i)(a), the excitonic absorption peak is well defined with a maximum about 411 nm. It is well known that the excitonic

absorption peak is associated with the lowest optical transition and it provides a simple way to determine the nanoparticles band edge. This is a blue shift in relation to the bulk CdO (2.3 eV). The photoluminescence emission maximum [Fig. 1(i)(b)] of 462 nm was observed red shifted from the excitonic feature of the absorption spectrum. The absorption band edge (475 nm) of CdS nanoparticles indicates a blue shift of about 40 nm from the bulk CdS (2.41 eV). The emission maximum appears at 517 nm with broad emission edge signifying larger particle size distribution of glucuronic acid capped CdS nanoparticles [Fig. 1(ii)b].

The size and morphology of glucuronic acid capped nanoparticles are depicted in Fig. 2. TEM images showed spherical shaped nanoparticles for both CdO and CdS with particle size distribution of 5-10 and 3-15 nm, respectively. Their crystallinity is also evident from their lattice fringes observed from the images. This conforms to the broader photoluminescence peak for CdS nanoparticles as compared to CdO nanoparticles. This shows similar trends to the CdS nanoparticles prepared using hexadecylamine capping molecule for cadmium alkylxanthates²³ and cadmium dithiobiurea complexes²⁴.

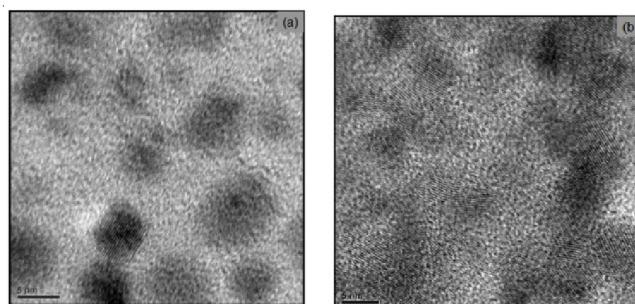


Fig. 2. HRTEM images of glucuronic acid capped CdO (a) and CdS (b) nanoparticles

The powder X-ray diffraction (Fig. 3) reveals that the obtained glucuronic acid capped CdO nanocrystals gave a mixture of cubic and hexagonal phases, while CdS nanoparticles is predominantly cubic. It has been reported that the crystallographic

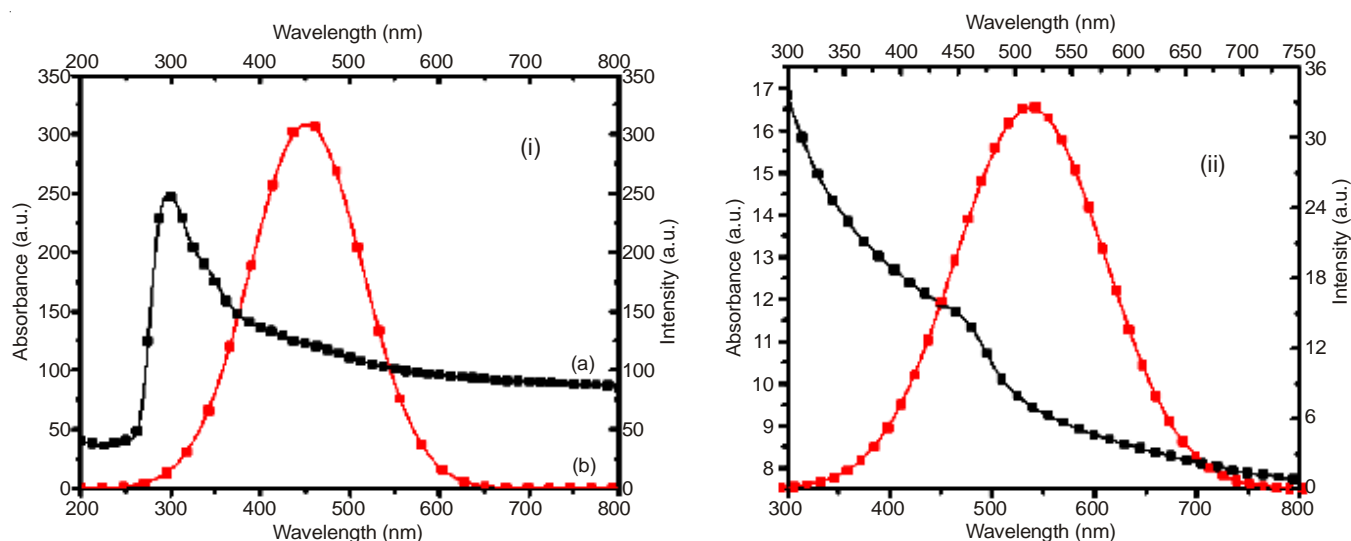


Fig. 1. Absorption (a) and emission (b) spectra of glucuronic acid capped CdO (i) and CdS (ii) nanoparticles

morphology $\text{Cd}(\text{OH})_2$ can be influenced by many experimental parameters, such as pH value of the reaction solution, precursor and temperature. Cadmium hydroxide is an important precursor that can be potentially converted into cadmium oxide through dehydration or into other functional materials (*e.g.* CdO , CdS , CdSe) by appropriate reaction with other elements or compounds. Cadmium oxide can be transformed from $\text{Cd}(\text{OH})_2$ through dehydration depending on the concentration of NaOH and synthesis temperature. In this work, the XRD shows no presence of the cadmium hydroxide intermediate indicate successfully converting the intermediate to cadmium oxide and sulphide.

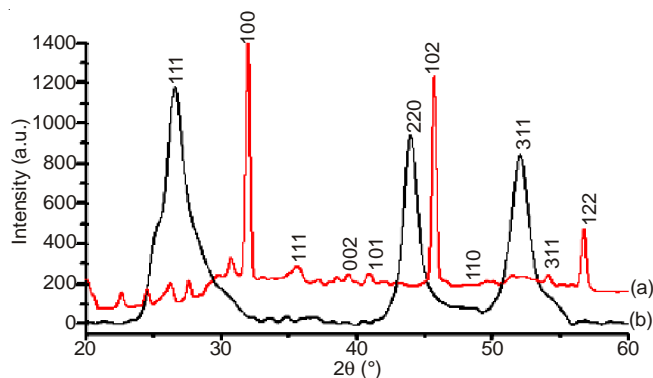


Fig. 3. X-ray diffraction patterns of glucuronic acid capped CdO (a) and CdS (b) nanoparticles

Fig. 4 shows the interaction between the nanoparticles and stabilizing agent glucuronic acid. Glucuronic acid shows three bands in 3100-3400 region, indicating the O-H stretching bonded to carbon inside the ring and bonded to carbonyl carbon. The spectra for both CdO and CdS nanoparticles show the broad band at 3290 cm^{-1} which is associated with the O-H stretching. The medium band of both CdO and CdS nanoparticles at 1587 cm^{-1} associated with $\text{C}=\text{O}$ stretching has shifted to lower wavelength showing the interaction of the glucuronic acid and the nanoparticles.

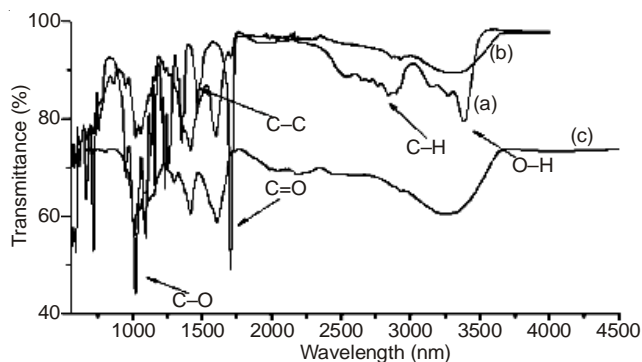


Fig. 4. FTIR spectra of free glucuronic acid (a), glucuronic acid capped CdO (b) and CdS nanoparticles (c)

Conclusion

Glucuronic acid-capped CdO and CdS nanoparticles were successfully obtained using a simple, mild and environmental friendly method. The obtained nanoparticles can be used for biological application due to the water soluble nature of glucuronic acid. The capping molecule provides binding and stability around the nanoparticles with similar particle size and shape. The use of the base normally encourages the formation of the intermediate hydroxide which XRD indicated its absence. FTIR spectra also indicates significant changes in the shifts of peaks due to bonding of glucuronic acid to the nanoparticles.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of South Africa, University of Johannesburg and Vaal University of Technology.

REFERENCES

1. A.P. Alivisatos, *Science*, **271**, 933 (1996).
2. S. Coe, W.K. Woo, M. Bawendi and V. Bulovic, *Nature*, **420**, 800 (2002).
3. M. Bruchez Jr., M. Moronne, P. Gin, S. Weiss and A.P. Alivisatos, *Science*, **281**, 1203 (1998).
4. A. Henglein, *Chem. Rev.*, **89**, 1861 (1989).
5. M.A. Malik, M.M. Zulu, P. O'Brien and G. Wakefield, *J. Mater. Chem.*, **8**, 1885 (1998).
6. J. Hu, T.W. Odom and C.M. Lieber, *Acc. Chem. Res.*, **32**, 435 (1999).
7. X. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Adv. Mater.*, **15**, 353 (2003).
8. X. Duan and C.M. Lieber, *Adv. Mater.*, **12**, 298 (2000).
9. J. Goldberger, R. He, Y. Zhang, S. Lee, H. Yan, H.-J. Choi and P. Yang, *Nature*, **422**, 599 (2003).
10. Z.W. Pan, Z.R. Dai, L. Xu, S.T. Lee and Z.L. Wang, *J. Phys. Chem. B*, **105**, 2507 (2001).
11. M.P. Pileni, *Catal. Today*, **58**, 151 (2000).
12. M.L. Steigerwald, A.P. Alivisatos, J.M. Gibson, T.D. Harris, R. Kortan, A.J. Muller, A.M. Thayer, T.M. Duncan, D.C. Douglass and L.E. Brus, *J. Am. Chem. Soc.*, **110**, 3046 (1988).
13. V.F. Puentes, K.M. Krishnan and A.P. Alivisatos, *Science*, **291**, 2115 (2001).
14. Y. Jun, Y. Jung and J. Cheon, *J. Am. Chem. Soc.*, **124**, 615 (2002).
15. Y. Li, X. Li, C. Yang and Y. Li, *J. Mater. Chem.*, **13**, 2641 (2003).
16. R. Jayakrishnan and G. Hodes, *Thin Solid Films*, **440**, 19 (2003).
17. M. Ristic, S. Popovic and S. Music, *Mater. Lett.*, **58**, 2494 (2004).
18. N. Singh, S. Charan, K.R. Patil, A.K. Viswanath and P.K. Khanna, *Mater. Lett.*, **60**, 3492 (2006).
19. S. Celebi, A.K. Erdamar, A. Sennaroglu, A. Kurt and H.Y. Acar, *J. Phys. Chem. B*, **111**, 12668 (2007).
20. L.E. Brus, *J. Phys. Chem.*, **90**, 2555 (1986).
21. U. Koch, A. Fojtik, H. Weller and A. Henglein, *Chem. Phys. Lett.*, **122**, 507 (1985).
22. D. Segets, L. Martinez Tomalino, J. Gradl and W. Peukert, *J. Phys. Chem. C*, **113**, 11995 (2009).
23. Y. Li, X. Li, C. Yang and Y. Li, *Chem. Mater.*, **13**, 2461 (2003).
24. P. Sreekumari Nair, N. Revaprasadu, T. Radhakrishnan and G.A. Kolawole, *J. Mater. Chem.*, **9**, 1555 (2001).