European Journal of Chemistry 9 (1) (2018) 39-43

European Journal of Chemistry

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Comparison of the observed size-dependent melting point of CdSe nanocrystals to theoretical predictions

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RESEARCH ARTICLE

10.5155/eurjchem.9.1.39-43.1676

Received: 28 November 2017
Received in revised form: 02 January 2018
Accepted: 07 January 2018
Published online: 31 March 2018
Printed: 31 March 2018

KEYWORDS

CdSe
Size effects
Nanocrystals
Phase transitions
Electron microscopy
Melting point depression

ABSTRACT

Cadmium selenide nanocrystals were observed to have a size-dependent melting point which was depressed relative to the bulk melting temperature. The observed size-dependent melting point ranged from 500-1478 K, while a model based on the surface area to volume ratio predicted that is should range between 774-1250 K. The nanocrystals were heated *in situ* in the electron microscope, and the melting point was almost immediately followed by the vaporization of the CdSe nanocrystals, allowing for straightforward determination of the melting temperature. The differences between the observed melting point of CdSe nanocrystals and the values predicted by the surface area to volume ratio model indicates that additional factors are involved in the melting point depression of nanocrystals.

Cite this: *Eur. J. Chem.* **2018**, *9(1)*, 39-43 **Journal website**: www.eurjchem.com

1. Introduction

Semiconductor nanocrystals have well documented size-dependent optical properties [1-5]. More recently, researchers have begun to investigate the size dependent physical properties of nanoscale systems [6-9]. The size-dependence of physical properties, such as the melting point, was predicted previously by Pawlow [10] and Turnball [11]. In the bulk material the melting point of a compound is well characterized, and does not depend on the size of the material in question. However, Pawlow's model predicts that as the volume of the material shrinks, the melting point of the pure compound becomes depressed, relative to the melting point of the bulk material. This is due to the material having a larger surface to volume ratio at sizes below the bulk value.

Previous researchers have published a model based to predict the size-dependent melting point of nanocrystals based on the surface area to volume ratio [12]. Gupta *et al.* have previously used this model to predict the melting point of nanocrystals that accounts for the ratio of surface atoms to interior atoms [13]. Their model is described in equation 1 [12,13].

$$T_{mnp} = T_{mb}\left(1-\frac{N}{2n}\right) \quad (1)$$

The melting point of the nanocrystal is T_{mnp}, and T_{mb} is the bulk melting point. The surface to volume ratio for the nanocrystals is accounted for by considering the number of atoms at the nanocrystal surface, N, and the total number of atoms in the nanocrystal, n. Thus, at sizes when the surface area to volume ratio is large, the melting point is predicted to be depressed relative to the bulk value. This prediction is consistent with observations that other researchers have made on the melting point of nanoscale systems [6,14,15]. It remains unclear how accurately a model of melting point depression based strictly on the size and shape of the given nanocrystal predicts the materials' melting point. In order to test the accuracy of the predictions made by Gupta *et al.* we have synthesized CdSe nanocrystals of varying sizes with an approximately spherical morphology and measured the melting point of these nanocrystals *in situ* in an electron microscope.

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http://dx.doi.org/10.5155/eurjchem.9.1.39-43.1676

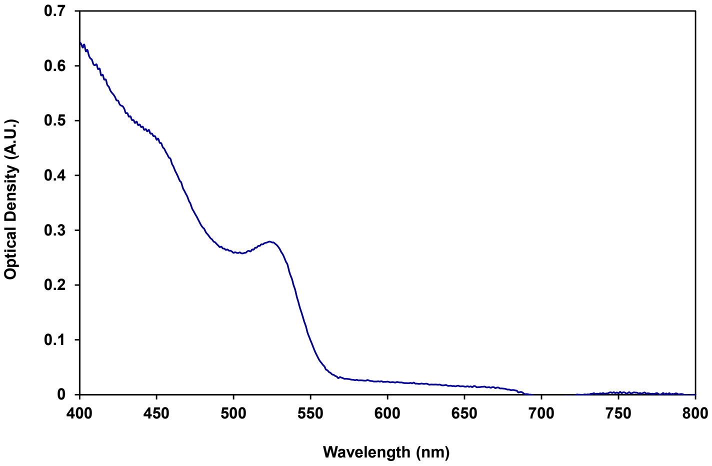

Figure 1. The UV-Vis absorption spectrum of the CdSe nanocrystals indicates a monodisperse sample due to the sharp band edge absorption peak.

If the shape dependent model were completely capturing all the factors which are involved in the melting point depression, then our observed melting points should closely agree with the size-dependent melting points they predict. However, if the experimentally observed melting points of the nanocrystals are different than the values predicted by the Gupta, it would indicate that factors other than surface to volume ratio are also involved in modeling the melting point depression of nanocrystals.

2. Experimental

2.1. Instrumentation

In situ melting experiments were performed using the Aduro® heating system (Protochips Inc.) in a scanning transmission electron microscope (STEM). STEM imaging conditions are similar to those we have described in a previous report [16]. Electron microscopy was performed utilizing a JEOL 2100 F 200 kV field emission gun (FEG)-STEM/TEM equipped with a Corrected Electron Optical System (CEOS). The geometrical aberrations were measured and controlled to provide less than a π/4 phase shift of the incoming electron wave over the probe-defining aperture of 17.5 mrad. At 200 kV this provides a nominal probe size of < 0.1 nm. High angle annular dark-field (HAADF) STEM images were acquired on a Fischione Model 3000 HAADF detector with a camera length such that the detector spanned 50-284 mrad. The scanning acquisition was synchronized to the 60 Hz alternating current electrical power to minimize 60 Hz noise in the images, and a pixel dwell time of 15.8 μs was utilized. Samples of nanocrystals were deposited by drop casting the nanocrystal solution onto the Aduro e-chip. During imaging, the temperature of the e-chip on which the nanocrystal sample was deposited was increased at a rate of 10 K/min, with a starting temperature for the experiments of 293 K. Images were taken every minute as the temperature was increased until the nanocrystals were observed to have melted.

2.2. Synthesis of CdSe Nanocrystals

The selenium precursor was prepared by dissolving Se (99.5%, 200 mesh, Acros Organics) in tri-*n*-butylphosphine (TBP, 95%, Alfa Aesar) in an oxygen free environment to prepare a 4 M stock solution. The stock solution was diluted in an oxygen free environment with 1-octadecene to make a 0.1 M Se solution.

The CdSe nanocrystals utilized in this study were synthesized following the methods previously reported [17,18]. The following reagents were combined in a three-neck flask: 1 mmol of CdO (99.998%, Alfa Aesar), 1.3 mL of oleic acid (Fisher Scientific), and 10 mL of 1-octadecene (90%, technical grade, Acros Organics). The three-neck flask was fitted with a temperature probe, a bump trap, and a rubber septum. The mixture was magnetically stirred and heated with an active argon purge until the temperature of the reaction mixture reached 120 °C. Upon reaching 120 °C, the purge needle was removed, and the reaction solution was heated under an argon atmosphere until it reached 310 °C. The conversion of the CdO into the reactive cadmium precursor was indicated by the reaction mixture changing to a clear and colorless liquid. Upon the solution becoming clear and colorless, 10 mL of the 0.1 M Se precursor was swiftly injected into the three-neck flask containing the reactive cadmium oleate solution, and CdSe nanocrystals nucleation and growth began. The reaction was monitored by UV-Vis absorption spectroscopy, and nanocrystal growth continued until the CdSe nanocrystals reached the desired size. When the nanocrystals reached the desired size, the heating mantle was removed, and the reaction was quenched by the addition on 20 mL of butanol to the reaction flask. The flask was further cooled with compressed air until the temperature of the reaction vessel was below 100 °C.

When the synthesis was completed, the nanocrystals were purified and isolated using a combination of precipitation and chromatography [19]. Equal volumes of nanocrystal reaction solution were decanted into six centrifuge tubes, and ethanol was added until the nanocrystals flocculated. The nanocrystals were collected by centrifugation, and the supernatant was discarded. The nanocrystals were dispersed in toluene and further purified by column chromatography with a silica gel stationary phase and a toluene mobile phase. The eluted nanocrystals were collected and stored in the dark prior to *in situ* melting experiments in order to prevent degradation.

3. Results and discussion

The synthesis resulted in monodisperse CdSe nanocrystals as demonstrated by the sharp band edge absorption feature (Figure 1). Since theory has predicted that the melting point of nanocrystals will be depressed as a function of size relative to the bulk melting temperature, it is necessary to have a monodisperse sample.

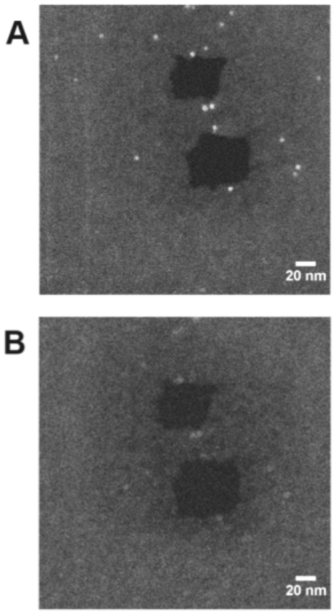

Figure 2. A) Prior to the onset of melting the CdSe nanocrystals are clearly observed in the STEM image. B) Upon reaching the melting point, the CdSe nanocrystals melt and then quickly evaporate from the e-chip surface due to the high vacuum conditions of the electron microscope.

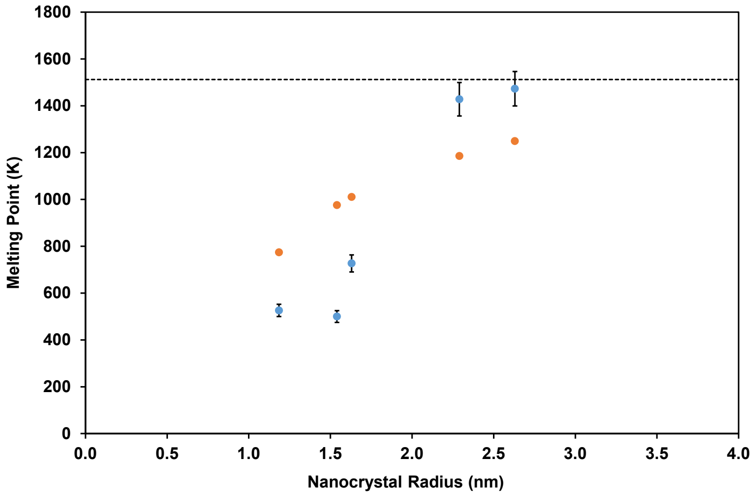

Figure 3. The blue circles indicate the experimentally observed melting point of the CdSe nanocrystals. The orange triangles represent the theoretical melting point based on the ratio of surface:interior atoms in the nanocrystal. The melting point of bulk CdSe is shown by the dashed line.

Previous reports on the melting point of CdS nanocrystals determined the melting point of the material based on the disappearance of the diffraction pattern [14]. While this was a reasonable criterion for determining the melting point of the nanocrystal, as a liquid would have no defined structure, in our study CdSe nanocrystals were observed prior to the onset of melting (Figure 2A, bright spots) and were observed to disappear from view in the electron microscope upon reaching their melting point (Figure 2B). During the heating process the nanocrystals remained stable and in the field of view as long as the temperature remained below the melting point. The vapor pressure of liquid CdSe has been reported to be in the range of 0.1-10 mmHg [20], and given the high vacuum nature of the electron microscope (~10^{-7} mmHg) the observed melting followed by almost immediate vaporization of the CdSe nanocrystals is not surprising.

The melting point for bulk CdSe with a zinc blende structure has been reported as 1512 K [21]. The CdSe nanocrystals that were synthesized for this study have a zinc blende structure due to weak binding of the oleic acid surface ligands [22]. As shown in Figure 3, we observe the melting point of CdSe nanocrystals (blue circles) to be depressed relative to the bulk melting point. As the size of the nanocrystal decreases, the surface to volume ratio increases. Because the surface atoms are not fully passivated, they have an increased energy relative to the interior atoms [13]. Building off of this concept, Gupta *et al.* developed a model of melting point depression dependent on the shape of the nanocrystal [13]. In their model, the melting point of the nanocrystal is depressed in proportion to the percentage of atoms at the surface.

A previous study by Taylor *et al.* has established the number of atoms at the surface of a CdSe nanocrystal [23]. The total number of atoms in a CdSe nanocrystal was calculated by assuming an approximately spherical shape for the CdSe nanocrystal with a FCC unit cell, and calculating the number of unit cells that could be contained within the spherical volume for a given nanocrystal radius. Using this method, we were able to calculate the number of total atoms for a given radius of nanocrystal, thus generating the parameters needed to test the shape dependent model proposed by Gupta *et al.* for melting point depression in CdSe nanocrystals.

The melting point predicted by Gupta's shape-dependent model [13] is shown in Figure 3 (orange triangles). It is apparent from our observations that shape alone does not accurately account for the melting point depression that has been observed in nanocrystals. At the smallest sizes (radius < ~2 nm), the shape dependent model overestimates the melting point of CdSe nanocrystals, while at larger sizes (radius > ~2 nm) the shape-dependent model underestimates the melting point. The overestimation of the melting point for the smallest sizes of nanocrystals is likely the result of the model's inability to capture the disorder which is inherent in a nanocrystal of this size (radius < ~2 nm). Previous efforts to image CdSe nanocrystals in this size regime using Z-contrast STEM at room temperature have revealed that the nanocrystals are highly disordered [24]. This observation has also been confirmed by molecular dynamics simulations of $Cd_{27}Se_{27}$ nanocrystals at 300 K [24]. The disorder that was reported at 300 K in the molecular dynamics simulation was reported to increase significantly when the temperature was raised to 500 K. The report of increased disorder at 500 K is consistent with our observation that CdSe nanocrystals with a radius of 1.5 nm and smaller have a melting point of ~500 K. The increased disorder, which previous authors have attributed to the fluxionality of ultrasmall CdSe nanocrystals, is likely the onset of the nanocrystal melting.

As molecular dynamics simulations have previously indicated that nanocrystals demonstrate increased fluxionality at higher temperatures, the likely reason for the shape dependent model underestimating the melting point is the uncertainty in the number of surface atoms at elevated temperatures caused by the fluxionality. With the increased temperature, the surface atoms will have a higher energy and rearrangement will be easier. It is likely that the rearrangement would result in a transition shape, which has fewer surface atoms than measured by previous studies. Thus with fewer surface atoms, the melting point would rise closer to the bulk melting point. In order for the shape-dependent model to more accurately predict the melting point of nanocrystals, the model should be modified to account for how the surface to volume ratio changes as the temperature is elevated; this is likely not a trivial correction, and would require significant molecular dynamics simulations.

An additional parameter which could play a role in explaining the difference between the observed melting point and the melting point predicted by the shape-dependent model is that different facets of the nanocrystals have different surface energies. This difference in surface energies for different facets of CdSe has been modeled previously by Puzder *et al.* and they reported differences in surface energy of up to ~0.75 eV between facets that were selenium terminated and those that were a mixture of cadmium and selenium [25]. This relatively large difference in surface energies for the different facets should also be taken into account as it will affect how well the surface ligands bind to the nanocrystal. The surface ligands themselves may also affect the melting point. In our study, the CdSe nanocrystal surface was passivated with oleic acid, which bonds to the surface via a carboxylic acid. Previous synthetic work on CdSe nanocrystals has demonstrated that the choice of surface ligands can influence the overall shape of a nanocrystal due to the surface ligands binding more tightly at certain facets [16,26]. It is possible that ligands which bind more tightly to the surface would prevent the surface atoms from rearranging at elevated temperatures; this could lead to nanocrystals of the same size having different melting points based upon their surface passivation.

4. Conclusion

Cadmium selenide nanocrystals were observed to have a size-dependent melting point, which was depressed relative to the bulk melting point. The actual melting point behavior of CdSe nanocrystals is sharper than was predicted by the simple shape-dependent model. The disagreement between the predicted value from the shape-dependent model and our observed values point to the importance of more fully considering the role that the surface atoms, and possibly surface ligands, play in determining the melting point of nanoscale systems.

Acknowledgements

We would like to thank the Lander Foundation for supporting this research.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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References

[1]. Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403-4408.
[2]. Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706-8715.
[3]. Landes, C.; Burda, C. Braun, M. *J. Phys. Chem. B* **2001**, *105*, 2981-2986.
[4]. Swafford, L. A.; Weigand, L. A.; Bowers, M. J.; McBride, J. R.; Rapaport, J. L.; Watt, T. L.; Dixit, S. K.; Feldman, L. C.; Rosenthal, S. J. *J. Am. Chem. Soc.* **2006**, *128*, 12299-12306.
[5]. Rosenthal, S. J.; McBride, J.; Pennycook, S.; Feldman, L. C. *Surf. Sci. Rep.* **2007**, *62*, 111-157.
[6]. Antoniammal, P.; Arivuoli, D. J. *J. Nanomater.* **2012**, *2012*, 415797.
[7]. Magomedov, M. N. *Tech. Phys.* **2016**, *61,* 730-733.
[8]. Pan, L. S.; Lee, H. P.; Lu, C. *Eur. Phys. J. D* **2008**, *50*, 27-33.
[9]. Delogu, F. *J. Mater. Sci.* **2008**, *43*, 2611-2617.
[10]. Pawlow, P. *Zeitschrift für Phys. Chemie* **1909**, *65*, 1-35.
[11]. Holloman, J. H.; Turnbull, D. *Prog. Met. Phys.* **1953**, *4*, 333-388.
[12]. Qi, W. H. *Physica B* **2005**, *368*, 46-50.
[13]. Gupta, S. K.; Talati, M.; Jha, P. K. *Mater. Sci. Forum* **2008**, *570*, 132-137.
[14]. Goldstein, A. N.; Echer, C. M.; Alivisatos, A. P. *Science*, **1992,** *256*, 1425-1427.
[15]. Jiang, H.; Moon, K. S.; Dong, H.; Hua, F.; Wong, C. P. *Chem. Phys. Lett.* **2006**, *429*, 492-496.
[16]. Cameron, M. T.; Rogerson, J. A.; Blom, D. A.; Dukes III, A. D. *Front. Mater. Sci.* **2016**, *10*, 8-14.
[17]. Yu, W. W.; Peng, X. *Angew. Chemie Int. Ed.* **2002**, *114*, 2368-2371.
[18]. Harrell, S. M; McBride, J. R.; Rosenthal, S. J. *Chem. Mater.* **2013,** *25,* 1199-1210.
[19]. Shen, Y.; Gee, M. Y.; Tan, R.; Pellechia, P. J.; Greytak, A. B. *Chem. Mater.* **2013**, *25*, 2838-2848.
[20]. Somorjai, G. A. *J. Phys. Chem.* **1961**, *65*, 1059-1061.
[21]. Lide, D. R. CRC Handbook of Chemistry and Physics, 83rd edition, CRC Press, 2002.

[22]. Liu, L.; Zhuang, Z.; Xie, T.; Wang, Y. G.; Li, J.; Peng, Q.; Li, Y. *J. Am. Chem. Soc.* **2009**, *131*, 16423-16429.
[23]. Taylor, J.; Kippeny, T.; Rosenthal, S. J. *J. Clust. Sci.* **2001**, *12*, 571-582.
[24]. Pennycook, T. J.; McBride, J. R.; Rosenthal, S. J.; Pennycook, S. J.; Pantelides, S. T. *Nano Lett.* **2012**, *12*, 3038-3042.
[25]. Puzder, A. Williamson, A. J.; Zaitseva, N.; Galli, G.; Manna, L.; Alivisatos, A. P. *Nano Lett.* **2004**, *4*, 2361-2365.
[26]. Li. Z.; Peng, X. *J. Am. Chem. Soc.* **2011**, *133*, 6578-6586.

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