Shape Dependence of Pressure-Induced Phase Transition in CdS Semiconductor Nanocrystals

Lingyao Meng,[†] J. Matthew D. Lane,[‡] Luke Baca,[†] Jackie Tafoya,[†] Tommy Ao,[‡] Brian Stoltzfus,[‡] Marcus Knudson,[‡] Dane Morgan,[#] Kevin Austin,[‡] Changyong Park,[§] Paul Chow,[§] Yuming Xiao,[§] Ruipeng Li,[£] Yang Qin,^{*,†} and Hongyou Fan^{*,‡,⊥,∆}

[†]Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States

[‡]Sandia National Laboratories, Albuquerque, New Mexico 87123, United States

[#]Nevada National Security Site, New Mexico Operations-Sandia, Albuquerque, New Mexico 87123, United States

[§]HPCAT, X-ray Science Division, Argonne National Laboratories, Lemont, Illinois 60439, United States

[£]National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY, 11973, United States

¹Department of Chemical and Biological Engineering, University of New Mexico, Albuquerque, New Mexico 87131, United States

^ACenter for Integrated Nanotechnology, Sandia National Laboratories, Albuquerque, New Mexico 87123, United States

KEYWORDS: High pressure, phase transitions, CdS nanoparticles, shape effects, synchrotron X-ray, bulk modulus.

ABSTRACT: Understanding structural stability and phase transformation of nanoparticles under high pressure is of great scientific interest, as it is one of the crucial factors for design, synthesis, and application of materials. Even though high-pressure research on nanomaterials has been widely conducted, their shape-dependent phase transition behavior still remains unclear. Examples of phase transitions of CdS nanoparticles are very limited, despite the fact that it is one of the most studied wide band gap semiconductors. In this study, we have employed in-situ synchrotron wide-angle X-ray scattering (WAXS) and transmission electron microscopy (TEM) to investigate the high-pressure behaviors of CdS nanoparticles as a function of particle shapes. We observed that CdS nanoparticles transform from wurtzite to rocksalt phase at elevated pressure in comparison to their bulk counterpart. Phase transitions also vary with particle shape—rod-shaped particles show a partially reversible phase transition and the onset of the structural phase transition with relatively low phase transition pressure. In addition, TEM images of spherical particles exhibited sintering-induced morphology change after high-pressure compression. Calculations of the bulk modulus reveals that spheres are more compressible than rods in the wurtzite phase. These results indicate that the shape of the particle plays an important role in determining their high-pressure properties. Our study provides important insights into the understanding of the phase-structure-property relationship, which may guide future design and synthesis of nanoparticles for promising applications.

Wide band gap II-VI semiconductor nanoparticles have been intensively studied in recent years owing to their large optical absorption coefficients and high emission quantum efficiencies.¹ These nanoparticles have been considered as excellent candidates for various applications, such as thin film solar cells,² lasers,³ chemical and biological sensors,⁴ transistors,⁵ transparent electronics,⁶ and so on. In addition, their widely tunable band gaps and possibilities of doping with various metal ions allow great design and fabrication flexibility.^{1,7} Among these materials, CdS nanoparticles have been proven to possess excellent electronic and optical properties for solar cells,⁸⁻⁹ photocatalysis,¹⁰ and batteries.¹¹ In general, the properties of nanoparticles can be greatly affected by their size, shape, and crystal structure. Understanding structural stability is one of the key factors for determining optimal nanoparticle design and applications. It is well known that high-pressure studies are a powerful method for characterizing the phase stability and transformation of materials, and prior high-pressure experiments on nanoparticles have revealed their unique pressure-dependent properties. For example, greater phase transition pressure has been observed for nanoparticles, relative to the bulk.¹²⁻¹³ In addition, the phase transition pressure has been reported to shift with particle size for CdSe quantum dots¹⁴⁻¹⁶ and iron oxide nanoparticles¹⁷. In

addition to crystal structural changes, high-pressure has recently been applied as a controlled and effective means to alter nanomaterial morphologies at the mesoscale, leading to observations of new nanostructures that are difficult to obtain through solution synthesis methods.18-28



Figure 1. Transmission electron microscopy (TEM) images of (a) spherical CdS nanoparticles, (b) short CdS nanorods, and (c) long CdSe/CdS core/shell nanorods.

At ambient pressure, CdS can crystallize in either wurtzite (WZ) or zinc blende (ZB) structures. Bulk CdS undergoes phase transition from WZ to rocksalt (RS) at 2.6 GPa.²⁹ Previous studies on pressure tuned phase transition of CdS nanoparticles have revealed that both nanoparticle size³⁰⁻³¹ and doping³²⁻³³ can affect the phase transition behaviors, but the effect of particle shape has not yet been systematically studied. In fact, how the shape of the particle influences the phase transition has been rarely scrutinized. Lee et al.34 theoretically predicted that the phase transition pressure of CdSe nanorods decreased with rod length. Park et al.35 studied the shapedependent compressibility in rice-shaped and rod-shaped TiO₂ nanoparticles. To more thoroughly understand the shape effects on high-pressure phase transition of nanoparticles, detailed experimental studies on different kinds of nanoparticles are still needed. In this work, a systematic high-pressure study of CdS particles possessing various particle shapes was carried out by using in-situ synchrotron wide angle X-ray scattering (WAXS) and TEM.

Table 1. Sizes and surface-to-volume ratios of CdS nanoparticles.

CdS Shape	Average Size (nm)	Surface Area (nm ²)	Surface to volume ratio (nm ⁻¹)
Spheres	5.3±0.9	86.9	1.1
Short Rods	6.9±0.9 (width) 20.1±5.1 (length)	512.4	0.7
Long Rods	2.9±0.7 (width) 34.9±5.6 (length)	328.5	1.5

CdS nanoparticles were synthesized in three distinct shapes as previously reported.³⁶⁻³⁸ TEM was used to characterize the morphology of nanoparticles, and representative images are shown in Figure 1. All three types of CdS nanoparticles are monodisperse in size and uniform in shape. The average particle size and surface-to-volume ratio of different nanoparticles are summarized in Table 1. The average sizes were obtained by sampling at least 100 individual nanoparticles. It should be noted that the long CdSe/CdS core/shell nanorods are comparable with the other two samples in the current studies because the contribution of CdSe core to the overall pressure-induced behaviors can be neglected due to its relatively small volume ratio.39-40





Figure 2. Wide-angle X-ray scattering (WAXS) patterns under various applied pressure: (a) CdS nanospheres, (b) short CdS nanorods and (c) long CdSe/CdS core/shell nanorods. Pressures labeled with letter r are during decompression processes. The black, blue, and red curves represent the WZ, RS, and WZ/RS mixture crystal structures, respectively. Red asterisks mark diffraction peaks from the rhenium gaskets.

These CdS nanoparticles were then drop casted onto Si wafers to form uniform films, and small pieces of the resulting

films were scratched off and loaded into sample chambers of the diamond anvil cells (DACs) for high-pressure experiments. The DAC was compressed quasi-hydrostatically up to 15 GPa using silicon oil as pressure transmitting medium and WAXS experiments were performed after each pressure point was reached and stabilized. The resulting X-ray scattering patterns of different samples at different pressures are compiled in Figure 2. At ambient pressure before compression, the WAXS patterns of all three CdS nanoparticles can be indexed according to the hexagonal WZ crystal structure (wurtzite CdS, JCPDS card number 75-1545). With increasing pressures, all WAXS peaks shifted to higher q values, corresponding to smaller d spacings resulting from shrinkage of the nanoparticle atomic lattice under applied pressures. Clear phase transitions, as indicated by appearances of new scattering peaks, were then observed at higher pressures. The onsets of such phase transitions occur at ca. 6.0 GPa for nanospheres, ca. 6.9 GPa for short nanorods, and 8.0 GPa for long nanorods. These observed new peaks correspond to the cubic RS crystal structure (cubic CdS, JCPDS card number 21-829) in all three cases, and RS structures were stable up to the highest pressure applied, *i.e.*, 15 GPa. When the pressure was released back to ambient, some of the WZ peaks reappeared in both cases of the nanorod samples (Figures 2 (b) and (c)), indicating a partially reversible phase transition process. On the other hand, the high-pressure RS phase is maintained at ambient pressure for the nanospheres (Figure 2 (a)), representing an irreversible phase transition behavior. Compared with bulk materials, WZto-RS phase transitions have been found to take place at higher pressures for spherical nanoparticles, which is commonly explained by the increased surface energy with reducing particle size or increasing surface to volume ratio.¹² In the cases of our present studies, the nanospheres, short nanorods, and long nanorods possess surface-to-volume ratios at ca. 1.1 nm⁻¹, 0.7 nm⁻¹, and 1.5 nm⁻¹, respectively. It is thus expected that the long nanorods show the highest phase transition pressure due to its highest surface-to-volume ratio. However, the short nanorods, having lower surface-to-volume ratio than that of the nanospheres, display relatively higher phase transition pressure. Furthermore, the WZ-to-RS phase transition was found to be irreversible in nanospheres, while such transitions appear to be partially reversible in both nanorods with different aspect ratios. Our results suggest that, besides considering nanoparticle surface energies, the shape of nanoparticles also plays an important role in determining the pressure and reversibility of phase transitions. More precise determination and quantification of such shape-dependent phase transition effects will require more detailed and comprehensive studies on larger sets of nanoparticles with varying shapes, which is currently underway.

After the high-pressure experiments, residues from the DAC cells were dissolved in small amount of toluene and drop-cast onto TEM grids, and representative TEM images are shown in Figure 3. CdS nanospheres showed insignificant size changes after compression. Interestingly, some of the nanospheres were observed to sinter into continuous wires that have width comparable to that of individual nanospheres (Figure 3a) and high resolution TEM (HR-TEM) image (Figure 3d) reveals that the crystal lattice belongs to the RS phase, consistent with the WAXS results. The connection between sintered nanospheres appears to be non-epitaxial since the lattice fringes do not match one another in adjacent spheres as observed in HR-TEM images (Figure S1, Supporting Infor-

mation). As for the nanorods, the general shapes remain unchanged as seen in Figures 3b, 3c and Figure S2. However, the lengths of both nanorods have become shorter and less uniform. The average length of the short CdS nanorods decreases from ca. 20.1 ± 5.1 nm to ca. 16.3 ± 4.5 nm, while that of the core/shell long nanorods reduces from ca. 34.9 ± 5.6 nm to ca. 18.5 ± 5.2 nm. Since the widths of these nanorods remain unchanged, we suspect that the observed shortening of nanorods are resulted from pressure induced breakage, which is more severe in the case of the long nanorods. HR-TEM (Figures 3d to 3f) reveals the presence of both the RS (d₁₁₁ = 0.31 nm) and WZ (d₁₀₀ = 0.35 nm) crystal structures, consistent with the WAXS data and confirms that the phase transitions of nanorods are partly reversible.



Figure 3. TEM images of (a) CdS nanospheres, (b) short CdS nanorods, (c) long CdSe/CdS core/shell nanorods after high pressure studies; and high-resolution TEM (HR-TEM) images of (d) CdS nanospheres, (e) short CdS nanorods, and (f) long CdSe/CdS core/shell nanorods after high pressure studies.

Evolution of the unit cell volumes as a function of pressure is shown in Figure 4. It can be seen that there is ca. 17% volume reduction from WZ to RS crystal structure, which is in good agreement with previous studies.⁴¹ The volume change versus pressure data were then fitted into the second-order Birch-Murnaghan equation of state to calculate the bulk moduli of different samples,⁴²⁻⁴⁴

$$P=(3/2)B_0[(V_0/V)^{7/3}-(V_0/V)^{5/3}]$$
(1)

where B_0 is the bulk modulus. V_0 is the volume at zero applied pressure and can be calculated from the zero pressure WAXS data. The as-calculated bulk moduli of different samples at both WZ and RS phases are summarized in Table 2.

Table 2. Calculated unit cell volumes and bulk moduli of the three CdS samples.

CdS Shape		Wurtzite (WZ)		Rocksalt (RS)	
	pe	$V_0(Å^3)$	$B_0(GPa)$	V_0 (Å ³)	B ₀ (GPa)
Sphere	S	98.36	57.89±1.36	158.72	87.97±1.72
Short Ro	ds	98.92	66.67±1.89	160.91	85.45±1.32
Long Ro	ds	98.45	67.69±0.75	162.11	88.58±1.05



Figure 4. Pressure dependence of the unit cell volume for (a) CdS nanospheres, (b) short CdS nanorods, and (c) long CdSe/CdS core/shell nanorods. The black and red dots represent the compression and decompression process, respectively.

Materials that show higher bulk modulus values are less compressible. The CdS bulk material was reported to have a bulk modulus of 54.0 GPa for the WZ phase, and 68.0 GPa for the RS phase.⁴⁵ The bulk moduli of all three samples in both WZ and RS phases are higher than that of the bulk CdS, which is in agreement with earlier studies.⁴⁶⁻⁴⁷ In addition, WZ particles are found to be more compressible than RS particles. Bulk moduli of nanoparticles in the WZ phase also shows shapedependent features, with nanorods being less compressible than spherical nanoparticles, while RS phase behaves similar for all shapes. A similar trend has been observed for ZnO nanowires and nanobelts.⁴⁸⁻⁴⁹ But opposite behavior was also observed for rice-shaped TiO₂ nanoparticles.³⁵ Therefore, there is still no agreement on how the shape of the particle affect the value of the bulk modulus, and more research on other types of particles is necessary to fully understand this phenomenon.

In summary, we have employed high-pressure synchrotron WAXS to investigate the effects of particle shape on the phase transition behaviors of nanoparticles by applying CdS nanoparticles with three different shapes: CdS nanospheres, short CdS nanorods, and long CdSe/CdS core/shell nanorods. The results show that the WZ to RS phase transition pressure and the process reversibility are both closely associated to the particles' sizes and shapes. Spherical nanoparticles were found to possess the lowest phase transition pressure and showed sintering phenomena after the high pressure studies. Both nanorods showed higher phase transition pressures despite the fact that the short nanorods have smaller surface-to-volume ratio than that of the nanospheres. On the other hand, both nanorods display similar bulk moduli in both WZ and RS phases, but differ significantly in phase transition pressures. Furthermore, the WZ-to-RS phase changes were found to be irreversible in nanospheres but partially reversible in both nanorods. These observations clearly demonstrate that the shape plays an important role in phase changes of nanoparticles under pressure. Our study provides a rudimentary understanding of nanoparticle shape-dependent mechanical and phase properties, which will contribute to the design and development of novel functional nanomaterials.50-52

ASSOCIATED CONTENT

Supporting Information

Experimental details and additional data. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

- * hfan@sandia.gov
- * yangqin@unm.edu

ACKNOWLEDGMENT

This was supported by the National Science Foundation (DMR-1453083 and CHE-1904659) and research reported in this publication was supported by an Institutional Development Award (IDeA) from the National Institute of General Medical Sciences of the National Institutes of Health under grant number P20GM103451. This work was supported by the Sandia's Laboratory Directed Research & Development (LDRD) program. This paper describes objective technical results and analysis. Portions of this work were performed at HPCAT (Sector 16), Advanced Photon Source Argonne National Laborato-(APS), ry. HPCAT operations are supported by DOE-NNSA's Office of Experimental Sciences. The Advanced Photon Source is a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. DOE or the United States Government. Research was carried out, in part, at the Center of Integrated Nanotechnology (CINT), a US Department of Energy, Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This manuscript has been authored by Mission Support and Test Services, LLC, under Contract No. DE-NA0003624 with the U.S. Department of Energy, National Nuclear Security Administration, Office of Defense Programs and supported by the Site-Directed Research and Development Program. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The U.S. Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

REFERENCES

(1) Jie, J.; Zhang, W.; Bello, I.; Lee, C.-S.; Lee, S.-T. Onedimensional II-VI nanostructures: Synthesis, properties and optoelectronic applications. *Nano Today* **2010**, *5*, 313-336.

(2) Mathew, X.; Thompson, G. W.; Singh, V.; McClure, J.; Velumani, S.; Mathews, N. R.; Sebastian, P. Development of CdTe thin films on flexible substrates. *Sol. Energy Mater. Sol. Cells* **2003**, *76*, 293-303.

(3) Fang, X.; Bando, Y.; Gautam, U. K.; Zhai, T.; Zeng, H.; Xu, X.; Liao, M.; Golberg, D. ZnO and ZnS nanostructures: Ultraviolet-light emitters, lasers, and sensors. *Crit. Rev. Solid State* 2009, *34*, 190-223.
(4) Bailey, R. E.; Smith, A. M.; Nie, S. Quantum dots in biology and medicine. *Physica E. Low Dimens. Syst. Nanostruct.* 2004, *25*, 1-12.

(5) Ma, R.-M.; Dai, L.; Huo, H.-B.; Xu, W.-J.; Qin, G. Highperformance logic circuits constructed on single CdS nanowires. *Nano Lett.* **2007**, *7*, 3300-3304.

(6) Sato, K.; Katayama-Yoshida, H. Materials design for transparent ferromagnets with ZnO-based magnetic semiconductors. *Jpn. J. Appl. Phys.* **2000**, *39*, L555-L558.

(7) Henini, M. Wide bandgap electronic materials. *Microelectron. J.* **1992**, *23*, 500-506.

(8) Wang, Y.; Fu, H.; Wang, Y.; Tan, L.; Chen, L.; Chen, Y. 3-Dimensional ZnO/CdS nanocomposite with high mobility as an efficient electron transport layer for inverted polymer solar cells. *Phys. Chem. Chem. Phys.* **2016**, *18*, 12175-12182.

(9) Zhang, Q.; Guo, X.; Huang, X.; Huang, S.; Li, D.; Luo, Y.; Shen, Q.; Toyoda, T.; Meng, Q. 3-Dimonsional ZnO/CdS nanocomposite with high mobility as an efficient electron transport layer for inverted polymer solar cells. *Phys. Chem. Chem. Phys.* **2011**, *13*, 4659-4667.

(10) Cheng, L.; Xiang, Q.; Liao, Y.; Zhang, H. CdS-based photocatalysts. *Energy Environ. Sci.* **2018**, *11*, 1362-1391.

(11) Zhang, Z.; Dai, S.; Fan, X.; Blom, D. A.; Pennycook, S. J.; Wei, Y. Controlled synthesis of CdS nanoparticles inside ordered mesoporous silica using ion-exchange reaction. *J. Phys. Chem. B* **2001**, *105*, 6755-6758.

(12) Tolbert, S. H.; Alivisatos, A. High-pressure structural transformations in semiconductor nanocrystals. *Annu. Rev. Phys. Chem.* **1995**, *46*, 595-626.

(13) Bai, F.; Bian, K.; Huang, X.; Wang, Z.; Fan, H. Pressure induced nanoparticle phase behavior, property, and applications. *Chem. Rev.* **2019**, *12*, 7673-77178.

(14) Tolbert, S.; Alivisatos, A. Size dependence of a first order solidsolid phase transition: the wurtzite to rock salt transformation in CdSe nanocrystals. *Science* **1994**, *265*, 373-376.

(15) Jacobs, K.; Zaziski, D.; Scher, E. C.; Herhold, A. B.; Alivisatos, A. P., Activation volumes for solid-solid transformations in nanocrystals. *Science* **2001**, *293*, 1803-1806.

(16) Wickham, J. N.; Herhold, A. B.; Alivisatos, A. Shape change as an indicator of mechanism in the high-pressure structural transformations of CdSe nanocrystals. *Phys. Rev. Lett.* **2000**, *84*, 923.

(17) Clark, S.; Prilliman, S.; Erdonmez, C.; Alivisatos, A. Size dependence of the pressure-induced γ to α structural phase transition in iron oxide nanocrystals. *Nanotechnology* **2005**, *16*, 2813.

(18) Wu, H.; Bai, F.; Sun, Z.; Haddad, R. E.; Boye, D. M.; Wang, Z.; Fan, H. Pressure-Driven Assembly of Spherical Nanoparticles and

Formation of 1D-Nanostructure Arrays. Angew. Chem. Int. Ed. 2010, 49, 8431-8434.

(19) Li, B.; Wen, X.; Li, R.; Wang, Z.; Clem, P. G.; Fan, H., Stressinduced phase transformation and optical coupling of silver nanoparticle superlattices into mechanically stable nanowires. *Nat. Commun.* **2014**, *5*, 4179.

(20) Li, B.; Bian, K.; Zhou, X.; Lu, P.; Liu, S.; Brener, I.; Sinclair, M.; Luk, T.; Schunk, H.; Alarid, L.; Fan, H. Pressure compression of CdSe nanoparticles into luminescent nanowires. *Sci. Adv.* **2017**, *3*, e1602916.

(21) Wu, H.; Wang, Z.; Fan, H. Stress-induced nanoparticle crystallization. J. Am. Chem. Soc. 2014, 136, 7634-7636.

(22) Wu, H.; Bai, F.; Sun, Z.; Haddad, R. E.; Boye, D. M.; Wang, Z.; Huang, J. Y.; Fan, H., Nanostructured gold architectures formed through high pressure-driven sintering of spherical nanoparticle arrays. *J. Am. Chem. Soc.* **2010**, *132*, 12826-12828.

(23) Wang, Z.; Schliehe, C.; Wang, T.; Nagaoka, Y.; Cao, Y. C.; Bassett, W. A.; Wu, H.; Fan, H.; Weller, H. Deviatoric stress driven formation of large single-crystal PbS nanosheet from nanoparticles and in situ monitoring of oriented attachment. *J. Am. Chem. Soc.* **2011**, *133*, 14484-14487.

(24) Li, W.; Fan, H.; Li, J. Deviatoric stress-driven fusion of nanoparticle superlattices. *Nano Lett.* **2014**, *14*, 4951-4958.

(25) Wang, Z.; Wen, X. D.; Hoffmann, R.; Son, J. S.; Li, R.; Fang, C. C.; Smilgies, D. M.; Hyeon, T. Reconstructing a solid-solid phase transformation pathway in CdSe nanosheets with associated soft ligands. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 17119-17124.

(26) Wang, Z.; Chen, O.; Cao, C. Y.; Finkelstein, K.; Smilgies, D. M.; Lu, X.; Bassett, W. A. Integrating in situ high pressure small and wide angle synchrotron x-ray scattering for exploring new physics of nanoparticle supercrystals. *Rev. Sci. Instrum.* **2010**, *81*, 093902.

(27) Zhu, H.; Nagaoka, Y.; Hills-Kimball, K.; Tan, R.; Yu, L.; Fang, Y.; Wang, K.; Li, R.; Wang, Z.; Chen, O. Pressure-enabled synthesis of hetero-dimers and hetero-rods through interparticle coalescence and interparticle fusion of quantum-dot-Au satellite nanocrystals. *J. Am. Chem. Soc.* **2017**, *139*, 8408-8411.

(28) Nagaoka, Y.; Hill-Kimball, K.; Tan, R.; Li, R.; Wang, Z.; Chen, O. Nanocube superlattices of cesium lead bromide perovskites and pressure-induced phase transformations at atomic and mesoscale levels. *Adv. Mater.* **2017**, 29, 1606666.

(29) Owen, N.; Smith, P.; Martin, J.; Wright, A. X-ray diffraction at ultra-high pressures. J. Phys. Chem. Solids **1963**, 24, 1519-1520.

(30) Mishra, A.; Garg, N.; Pandey, K.; Singh, V. Effect of the surfactant CTAB on the high pressure behavior of CdS nanoparticles. *J. Phys.: Conf. Ser.* **2012**, *377*, 12012.

(31) Martín-Rodríguez, R.; González, J.; Valiente, R.; Aguado, F.; Santamaría-Pérez, D.; Rodríguez, F. Reversibility of the zinc-blende to rock-salt phase transition in cadmium sulfide nanocrystals. *Int. J. Appl. Phys.* **2012**, *111*, 063516.

(32) Zhao, R.; Wang, P.; Yao, B.; Hu, T.; Yang, T.; Xiao, B.; Wang, S.; Xiao, C.; Zhang, M. Co effect on zinc blende–rocksalt phase transition in CdS nanocrystals. *RSC Adv.* **2015**, *5*, 17582-17587.

(33) Zhao, R.; Yang, T.; Luo, Y.; Chuai, M.; Wu, X.; Zhang, Y.; Ma, Y.; Zhang, M. Structural phase transition and photoluminescence properties of wurtzite CdS: Eu³⁺ nanoparticles under high pressure. *RSC Adv.* **2017**, *7*, 31433-31440.

(34) Lee, N. J.; Kalia, R. K.; Nakano, A.; Vashishta, P. Pressureinduced structural transformations in cadmium selenide nanorods. *Appl. Phys. Lett.* **2006**, *89*, 093101.

(35) Park, S.-w.; Jang, J.-t.; Cheon, J.; Lee, H.-H.; Lee, D. R.; Lee, Y. Shape-dependent compressibility of TiO2 anatase nanoparticles. *J. Phys. Chem. C* **2008**, *112*, 9627-9631.

(36) Arora, V.; Soni, U.; Mittal, M.; Yadav, S.; Sapra, S. Synthesis of trap emission free cadmium sulfide quantum dots: Role of phosphonic acids and halide ions. *J. Colloid. Interf. Sci.* **2017**, *491*, 329-335.

(37) Joo, J.; Na, H. B.; Yu, T.; Yu, J. H.; Kim, Y. W.; Wu, F.; Zhang, J. Z.; Hyeon, T. Generalized and facile synthesis of semiconducting metal sulfide nanocrystals. *J. Am. Chem. Soc.* **2003**, *125*, 11100-11105.

(38) Carbone, L.; Nobile, C.; De Giorgi, M.; Sala, F. D.; Morello, G.; Pompa, P.; Hytch, M.; Snoeck, E.; Fiore, A.; Franchini, I. R. Synthesis and micrometer-scale assembly of colloidal CdSe/CdS nanorods prepared by a seeded growth approach. *Nano Lett.* **2007**, *7*, 2942-2950.

(39) Ludescher, L.; Dirin, D.; Kovalenko, M. V.; Sztucki, M.; Boesecke, P.; Lechner, R. T. Impact of crystal structure and particles shape on the photoluminescence intensity of CdSe/CdS core/shell nanocrystals. *Front. Chem.* **2018**, *6*, 672.

(40) Greytak, A. B.; Allen, P. M.; Liu, W.; Zhao, J.; Young, E. R.; Popović, Z.; Walker, B. J.; Nocera, D. G.; Bawendi, M. G. Alternating layer addition approach to CdSe/CdS core/shell quantum dots with near-unity quantum yield and high on-time fractions. *Chem. Sci.* **2012**, *3*, 2028-2034.

(41) Kennedy, J.; Benedick, W. Shock-induced phase transition in single crystal CdS. J. Phys. Chem. Solids **1966**, 27, 125-127.

(42) Murnaghan, F. D., Amer. Finite deformations of an elastic solid. *J. Math.* **1937**, *59*, 235-260.

(43) Murnaghan, F. The compressibility of media under extreme pressures. *Proc. Natl. Acad. Sci. U.S.A.* **1944**, *30*, 244.

(44) Birch, F. Finite elastic strain of cubic crystals. *Phys. Rev.* 1947, 71, 809.

(45) Grünwald, M.; Zayak, A.; Neaton, J. B.; Geissler, P. L.; Rabani, E. Transferable pair potentials for CdS and ZnS crystals. *J. Chem. Phys.* **2012**, *136*, 234111.

(46) Jiang, J.; Olsen, J. S.; Gerward, L.; Mørup, S. Enhanced bulk modulus and reduced transition pressure in γ -Fe2O3 nanocrystals. *EPL* **1998**, *44*, 620.

(47) Gu, Q.; Krauss, G.; Steurer, W.; Gramm, F.; Cervellino, A. Unexpected high stiffness of Ag and Au nanoparticles. *Phys. Rev. Lett.* **2008**, *100*, 045502. (48) Wang, L. H.; Liu, H. Z.; Qian, J.; Yang, W. G.; Zhao, Y. S. Structural Stability and Compressibility Study for ZnO Nanobelts under High Pressure. *J. Phys. Chem. C* **2012**, *116*, 2074–2079.

(49) Dong, Z. H.; Zhuravlev, K. K.; Morin, S. A.; Li, L. S.; Jin, S.; Song, Y. Pressure-Induced Structural Transformations of ZnO Nanowires Probed by X-ray Diffraction. *J. Phys. Chem. C* **2012**, *116*, 2102–2107.

(50) Wang, J.; Zhong, Y.; Wang, X.; Yang, W.; Bai, F.; Zhang, B.; Alarid, L.; Bian, K.; Fan, H. pH-dependent assembly of porphyrin– silica nanocomposites and their Application in targeted photodynamic therapy. *Nano lett.* **2017**, *17*, 6916-6921.

(51) Fei, L.; Xu, Y.; Wu, X.; Chen, G.; Li, Y.; Li, B.; Deng, S.; Smirnov, S.; Fan, H.; Luo H. Instant gelation synthesis of 3D porous MoS 2@ C nanocomposites for lithium ion batteries. *Nanoscale* **2014**, *6*, 3664-3669.

(52) Zhang, N.; Wang, L.; Wang, H.; Cao, R.; Wang, J.; Bai, F.; Fan, H. Self-assembled one-dimensional porphyrin nanostructures with enhanced photocatalytic hydrogen generation. *Nano lett.* **2018**, *18*, 560-566.



For Table of Contents Only