Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Alloyed Multi-shell Quantum Dots with Tunable Dual Emission

Wenda Zhang,[abc] Weidong Zhuang,*[a] Xianran Xing,*[b] Bing Xu,[c] Dan Wu,[c] Haochen Liu,[c] Kai Wang,*[c] Ronghui Liu,[a] Xiao Wei Sun[c]

[a] National Engineering Research Center for Rare Earth Materials, General Research Institute for Nonferrous Metals, and Grirem Advanced Materials Co., Ltd., Beijing 100088, People's Republic of China

[b] Department of Physical Chemistry, University of Science & Technology Beijing, Beijing 100083, People's Republic of China

[c] Department of Electrical & Electronic Engineering, Southern University of Science and Technology, Shenzhen, 518055, China

***E-mail:**

wdzhuang@126.com

xing@ustb.edu.cn

wangk@sustc.edu.cn

sunxw@sustc.edu.cn

Listing of the contents:

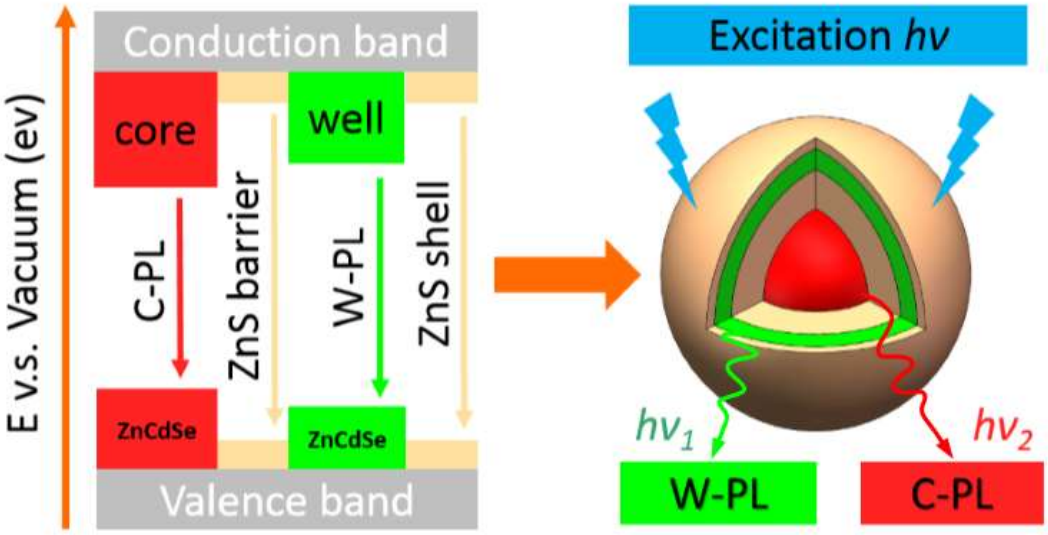

Figure S1. Schematic diagram of energy band structure

Experiment

Chemicals

Cadmium oxide (99.99%), selenium (99.5%), sulfur (99.98%), trioctylphosphine (97%) ,1-octadecene (ODE), and oleic acid (OA 90%) were purchased from Aldrich. zinc oxide (99.999%) was purchased from Aladdin， All chemicals were used directly without any further purification.

Synthesis of Zn，Cd，Se，S precursor

In a typical reaction, The Cd and Zn precursors (0.2 M) were made by dissolving CdO/ZnO in OA (1:4 molar ratio) and ODE under Ar. The mixture of CdO， OA and ODE was degassed for 60 min and then heated at 240 °C until the solution turned clear. Similarly, the mixture of ZnO， OA and ODE was degassed for 60 min and then heated at 310 °C until the solution turned clear .The Se precursor (0.2 M) was made by dissolving pure Se powder in trioctylphosphine (TOP) (1:2.25 molar ratio) and ODE. The S precursor (0.2 M) was made by adding pure S powder in trioctylphosphine (TOP) (1:2.25 molar ratio) and ODE.

Synthesis of $Zn_{0.5}Cd_{0.5}Se$ alloy QDs

12.78 mg (0.157 mmol) of ZnO, 20.17 mg (0.157 mmol) of CdO, 0.44 ml OA, 13.46 ml ODE were added to a three-necked bottle. The flask was vacuum-pumped and heated to 100 °C about 60 min to remove water and oxygen. Then the reaction was flooded with Ar and further heated to 310 °C. After the solution turned clear, the prepared 1.57 ml selenium precursor was then injected into the reaction solution quickly. QDs were completely alloyed after 45 min.

Synthesis of $Zn_{0.3}Cd_{0.7}Se$ alloy QDs

The process is the same as that of $Zn_{0.5}Cd_{0.5}Se$ alloy QDs. The only difference is that we changed the Zn and Cd precursors to 7.65 mg (0.094 mmol) and 28.22 mg (0.22 mmol) respectively.

Synthesis of $Zn_{0.7}Cd_{0.3}Se$ alloy QDs

The process is the same as that of $Zn_{0.5}Cd_{0.5}Se$ alloy QDs. The only difference is that we changed the Zn and Cd precursors to 17.9 mg (0.22 mmol) and 12.07 mg (0.094 mmol) respectively.

Synthesis of the first ZnS barrier layer on the $Zn_xCd_{1-x}Se$ core (Core/Barrier)

The solution containing $Zn_xCd_{1-x}Se$ was first cooled to 220 °C (prevent the barrier layer diffusion to core) for the growth of ZnS layer. Then 0.6 ml Zn precursor was added firstly followed by adding 0.6 ml S precursor 5 min later. The Zn and S were reacting about 30 min to allow epitaxial growth of first ZnS layer. Then sequentially adding 0.8 ml zinc precursor and 0.8 ml sulfur precursor with a time interval of 5 min. Then reacting 30 min to allow epitaxial growth of second ZnS layer. Then sequentially adding 1.1 ml zinc precursor and 1.1 ml sulfur precursor with a time interval of 5 min. Then reacting 30 min to allow epitaxial growth of third ZnS layer. This process can be repeated to grow more layers of ZnS barrier.

Synthesis of $Zn_{0.5}Cd_{0.5}Se$ QW layer on the surface of $Zn_xCd_{1-x}Se$ /ZnS QDs (Core/Barrier/QW)

For the growth of the $Zn_{0.5}Cd_{0.5}Se$ layer, the mixture of 2.36 ml Zn and 2.36 ml Cd precursors were added firstly into the three-necked bottle, followed by injecting

4.72 ml Se precursor 20 min later. Then after 10 min, we increase the temperature to 230 °C, which is maintained for 45 min to form alloy $Zn_{0.5}Cd_{0.5}Se$ outside the ZnS layer.

Synthesis of $Zn_{0.3}Cd_{0.7}Se$ QW layer on the surface of $Zn_xCd_{1-x}Se$ /ZnS QDs (Core/Barrier/QW)

The process is the same as that of $Zn_xCd_{1-x}Se$ /ZnS/$Zn_{0.5}Cd_{0.5}Se$ QDs. The only difference is that we changed the Zn and Cd precursors to 1.42 ml and 3.3 ml respectively.

Synthesis of $Zn_{0.7}Cd_{0.3}Se$ QW layer on the surface of $Zn_xCd_{1-x}Se$ /ZnS QDs (Core/Barrier/QW)

The process is the same as that of $Zn_xCd_{1-x}Se$ /ZnS/$Zn_{0.5}Cd_{0.5}Se$ QDs. The only difference is that we changed the Zn and Cd precursors to 3.3 ml and 1.42 ml respectively.

Synthesis of $Zn_{0.2}Cd_{0.8}Se$ QW layer on the surface of $Zn_xCd_{1-x}Se$ /ZnS QDs (Core/Barrier/QW)

The process is the same as that of $Zn_xCd_{1-x}Se$ /ZnS/$Zn_{0.5}Cd_{0.5}Se$ QDs. The only difference is that we changed the Zn and Cd precursors to 0.944 ml and 3.77 ml respectively.

Synthesis of outmost ZnS layer on the surface of $Zn_xCd_{1-x}Se$/ZnS/$Zn_yCd_{1-y}Se$ QDs (Core/Barrier/QW/Shell)

After growth of the alloy layer, ZnS shell was used to reduce surface defects and improvement of the quantum yield. The above reaction solution was first cooled to 220 °C for the growth of ZnS layer, 2.0 ml Zn precursor was added firstly followed by adding 2.0 ml S precursor 5 min later. The Zn and S were reacting about 30 min to allow epitaxial growth of first ZnS layer. Then sequentially adding 2.5 ml zinc precursor and 2.5 ml sulfur precursor with a time interval of 5 min. Then reacting 30 min to allow epitaxial growth of second ZnS layer. Then sequentially adding 3.2 ml zinc precursor and 3.2 ml sulfur precursor with a time interval of 5 min. Then reacting 30 min to allow epitaxial growth of third ZnS layer. This process can be repeated to grow more layers of ZnS barrier. The QDs were annealed after coating the outmost ZnS layer, first raise the temperature to 230 °C, then keep it for 60 min, which makes the QDs have better crystallinity and less defect states.

After annealing, the temperature is reduced to room temperature. The obtained QDs solution was mixed with 10 ml hexane and centrifuged at 10000 rpm for 3 min to remove the impurities, the obtained supernatant was mixed with ethanol in a ratio of 1:1, and centrifuged at 6000 rpm for 3 min, the obtained precipitation (about 660 mg) is dissolved in hexane for purification, which was repeated for 3 times. We could obtain 10 ml QDs that dissolved in hexane. About 100 μL QDs were dropped onto a glass slide, and n-hexane was removed on a heating table at 70 °C for 1 min. This specimen can be used for XRD analysis.

Characterization

The transmission electron microscopy (TEM) was carried out using a FEI Tecnai G2 F30 transmission electron microscope operating at an acceleration voltage of 300 kV. X-ray diffraction (XRD) measurements were carried out by an X-ray diffractometer (Bruker Advance D8 Ew Germany) with Cu Kα radiation (λ = 1.54178 Å). The operation voltage and current is 40 kV and 25 mA, respectively. The 2θ range was from 10 to 80 ° in a step of 0.02 °. The emission spectra were carried out using a FluoroSENS-9000 spectrophotometer with a static xenon lamp (150 W) as an excitation

source. The QY were taken using a Hamamatsu Quantaurus-QY, model no. C11347.

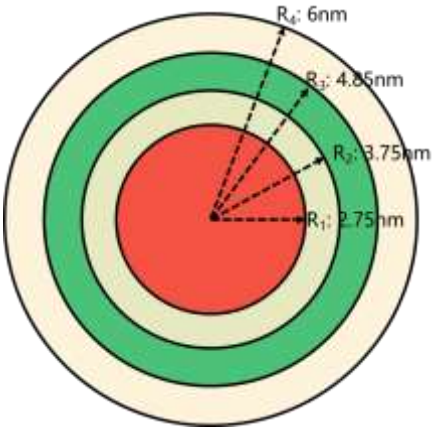

Figure S2. Schematic diagram of alloyed multi-shell QDs.

Table S1. Zn/Cd ratio of various QDs measured by ICP-Mass, for core QDs with different Zn/Cd in the precursor.

Core	Zn/Cd feed ratio	Zn/Cd ratio measured in QDs
$Zn_{0.3}Cd_{0.7}Se$	0.43	0.38
$Zn_{0.5}Cd_{0.5}Se$	1	0.89
$Zn_{0.7}Cd_{0.3}Se$	2.33	2.11

Zn/Cd feed ratio of $Zn_{0.3}Cd_{0.7}Se$ core:

$$\frac{Zn}{Cd} = \frac{0.3}{0.7} = 0.43$$

Zn/Cd feed ratio of $Zn_{0.5}Cd_{0.5}Se$ core:

$$\frac{Zn}{Cd} = \frac{0.5}{0.5} = 1$$

Zn/Cd feed ratio of $Zn_{0.7}Cd_{0.3}Se$ core:

$$\frac{Zn}{Cd} = \frac{0.7}{0.3} = 2.33$$

Table S2. Zn/Cd ratio of various QDs measured by ICP-Mass, for core/ZnS QDs with different Zn/Cd in the precursor.

Core/ ZnS	Zn/Cd feed ratio	Zn/Cd ratio measured in QDs
$Zn_{0.5}Cd_{0.5}Se/ZnS$	4.07	3.55

Zn/Cd feed ratio of $Zn_{0.5}Cd_{0.5}Se/ZnS$:

$$\frac{Zn}{Cd} = \frac{\frac{4}{3} * \pi * {R_1}^3 * 0.5 + \frac{4}{3} * \pi * ({R_2}^3 - {R_1}^3) * 1}{\frac{4}{3} * \pi * {R_1}^3 * 0.5} = 4.07$$

Table S3. Zn/Cd ratio of various QDs measured by ICP-Mass, for core/ZnS/QW QDs with different Zn/Cd in the precursor.

Core/ZnS/QW	Zn/Cd feed ratio	Zn/Cd ratio measured in QDs
$Zn_{0.5}Cd_{0.5}Se/ZnS/Zn_{0.3}Cd_{0.7}Se$	1.13	0.89
$Zn_{0.5}Cd_{0.5}Se/ZnS/Zn_{0.5}Cd_{0.5}Se$	1.77	1.41
$Zn_{0.5}Cd_{0.5}Se/ZnS/Zn_{0.7}Cd_{0.3}Se$	2.96	2.38

Zn/Cd feed ratio of $Zn_{0.5}Cd_{0.5}Se/ZnS/Zn_{0.3}Cd_{0.7}Se$:

$$\frac{Zn}{Cd}=\frac{\frac{4}{3}*\pi*{R_1}^3*0.5+\frac{4}{3}*\pi*({R_2}^3-{R_1}^3)*1+\frac{4}{3}*\pi*({R_3}^3-{R_2}^3)*0.3}{\frac{4}{3}*\pi*{R_1}^3*0.5+\frac{4}{3}*\pi*({R_3}^3-{R_2}^3)*0.7}=1.13$$

Zn/Cd feed ratio of $Zn_{0.5}Cd_{0.5}Se/ZnS/Zn_{0.5}Cd_{0.5}Se$:

$$\frac{Zn}{Cd}=\frac{\frac{4}{3}*\pi*{R_1}^3*0.5+\frac{4}{3}*\pi*({R_2}^3-{R_1}^3)*1+\frac{4}{3}*\pi*({R_3}^3-{R_2}^3)*0.5}{\frac{4}{3}*\pi*{R_1}^3*0.5+\frac{4}{3}*\pi*({R_3}^3-{R_2}^3)*0.5}=1.77$$

Zn/Cd feed ratio of $Zn_{0.5}Cd_{0.5}Se/ZnS/Zn_{0.3}Cd_{0.7}Se$:

$$\frac{Zn}{Cd}=\frac{\frac{4}{3}*\pi*{R_1}^3*0.5+\frac{4}{3}*\pi*({R_2}^3-{R_1}^3)*1+\frac{4}{3}*\pi*({R_3}^3-{R_2}^3)*0.7}{\frac{4}{3}*\pi*{R_1}^3*0.5+\frac{4}{3}*\pi*({R_3}^3-{R_2}^3)*0.3}=2.96$$

Table S4. Photoluminescence lifetime components of different reaction stages

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ_{avg}(ns)
ZnCdSe ($\lambda = 575$ nm)	14179	4.86	8353	16.41	860	42.48	10.36
Core/ZnS (λ=575 nm)	32144	5.20	10688	15.73	909	38.03	8.44
Core/ZnS/ QW/ZnS (λ=515 nm)	19342	4.72	17435	16.21	23438	39.29	22.63
Core/ZnS/ QW/ZnS (λ=575 nm)	18623	3.96	16094	15.81	22497	37.15	20.34

Absolute QY measurement

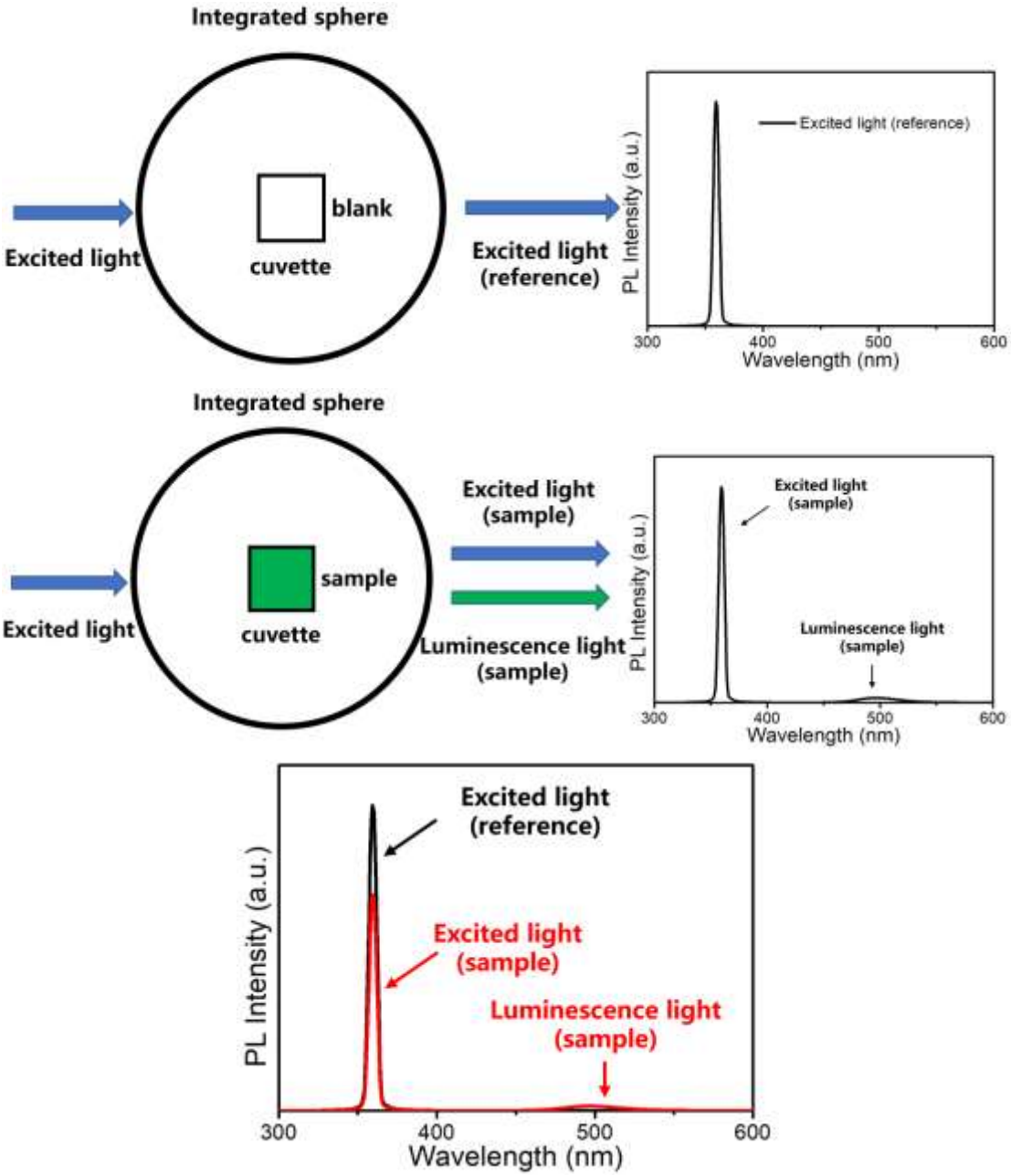

Figure S3. Absolute QY measurement. (Top) Light source intensity of blank sample measurement. (middle) Light source and PL intensity of sample measurement. (Bottom) The PL spectra of blank sample and QDs sample. (The QY were taken using a Hamamatsu Quantaurus-QY, model no. C11347).

The fluorescence quantum yield is defined as the ratio of the number of photons emitted to the number of photons absorbed.

$$\Phi = \frac{\text{photons emitted}}{\text{photons absorbed}} = \frac{I_{PL}}{I_{ELR} - I_{ELS}}$$

I_{PL}: Photon number integral of luminescence light of the sample

I_{ELR}: Photon number integral of excited light of the reference sample

I_{ELS}: Photon number integral of excited light of the sample

References

1 C. Yan, Z. Liu, W. Zhuang, R. Liu, X. Xing, Y. Liu, G. Chen, Y. Li and X. Ma, *Inorganic Chemistry*, 2017, **56**.

2 S. R. Chung, S. S. Chen, K. W. Wang and C. B. Siao, *Rsc Advances*, 2016, **6**, 51989-51996.

3 R. Xie, Z. Li and X. Peng, *J. Am. Chem. Soc.*, 2009, **131**, 15457-15466.

4 Y. Chen, M. Kim, G. Lian, M. B. Johnson and X. Peng, *J. Am. Chem. Soc.*, 2005, **127**, 13331-13337.

5 W. W. Yu, L. Qu, A. Wenzhuo Guo and X. Peng, *Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals*, St. Martin's Press in association with the Society for the Psychological Study of Social Issues, 2003.

6 Z. A. Peng and X. Peng, *J. Am. Chem. Soc.*, 2001, **123**, 183-184.

7 P. Jing, J. Zheng, Q. Zeng, Y. Zhang, X. Liu, X. Liu, X. Kong and J. Zhao, *Journal of Applied Physics*, 2009, **105**, 354.

8 C. Basilio, J. Oliva, T. Lopezluke and E. D. L. Rosa, *Electroencephalography & Clinical Neurophysiology*, 2014, **95**, P16.

9 K. Han, S. Yoon and W. J. Chung, *International Journal of Applied Glass Science*, 2015, **6**, 103-108.

10 C. Y. Shen, K. Li, Q. L. Hou, H. J. Feng and X. Y. Dong, *IEEE Photonics Technology Letters*, 2010, **22**, 884-886.

11 S. Bera, S. B. Singh and S. K. Ray, *Journal of Solid State Chemistry*, 2012, **189**, 75-79.

12 H. T. Nguyen, N. D. Nguyen and S. Lee, *Nanotechnology*, 2013, **24**, 115201-115205(115205).

13 G. Huang, C. Wang, S. Xu, Z. Qi, C. Lu and Y. Cui, *Nanotechnology*, 2016, **27**, 185602.

14 N. Razgoniaeva, M. Yang, C. Colegrove, N. Kholmicheva, P. Moroz, H. Eckard, A. Vore and M. Zamkov, *Chemistry of Materials*, 2017, **29**.

15 V. A. Vlaskin, N. Janssen, J. V. Rijssel, R. Beaulac and D. R. Gamelin, *Nano Letters*, 2015, **10**, 3670-3674.

16 R. Zeng, T. Zhang, G. Dai and B. Zou, *Journal of Physical Chemistry C*, 2011, **115**, 3005-3010.

17 Z. Zhang, D. Liu, D. Li, K. Huang, Y. Zhang, Z. Shi, R. Xie, M. Y. Han, Y. Wang and W. Yang, *Current Opinion in Microbiology*, 2015, **16**, 421–423.

18 C. X. Shan, X. W. Fan, J. Y. Zhang, Z. Z. Zhang, X. H. Wang, L. U. You ming, Y. C. Liu, D. Z. Shen, X. G. Kong and L. S. z. ptics, *Chinese Journal of Luminescence*, 2003.

19 X. Zhong, M. Han, Z. Dong, T. J. White and W. Knoll, *J. Am. Chem. Soc.*, 2003, **125**, 8589-8594.

20 B. P. Zhang, T. Yasuda, W. X. Wang, Y. Segawa, K. Edamatsu, T. Itoh, H. Yaguchi and K. Onabe, *Materials Science & Engineering B*, 1998, **51**, 127-131.

21 Z. H. Ni, H. M. Fan, J. Kasim, Y. M. You, Y. P. Feng, M. Y. Han and Z. X. Shen, *Journal of Physics Condensed Matter*, 2008, **20**, 325214.

22 Y. J. Zhao, *Advanced Materials Research*, 2011, **391-392**, 1338-1341.
23 J. Y. Jen, C. Y. Lin, J. R. Lee and C. R. Lu, *Journal of Physics & Chemistry of Solids*, 2008, **69**, 485-489.
24 S. L. Cumberland, K. M. Hanif, A. Javier, G. A. Khitrov, G. F. Strouse, S. M. W. And and C. S. Yun, *Cheminform*, 2002, **33**, 1576-1584.
25 H. Shen, C. Zhou, S. S. Xu, C. Yu, H. Wang, X. Chen and L. S. Li, *Journal of Materials Chemistry*, 2011, **21**, 6046-6053.
26 R. K. Čapek, I. Moreels, K. Lambert, D. D. Muynck, Q. Zhao, A. V. Tomme, F. Vanhaecke and Z. Hens, *Journal of Physical Chemistry C*, 2010, **114**, 6371-6376.
27 H. Shen, W. Sheng, H. Wang, J. Niu, Q. Lei, Y. Yang, A. Titov, J. Hyvonen, Z. Ying and S. L. Lin, *Applied Materials & Interfaces*, 2013, **5**, 4260-4265.
28 D. Battaglia, A. Bridgette Blackman and X. Peng, *J. Am. Chem. Soc.*, 2005, **127**, 10889.
29 W. C. W. Chan, D. J. Maxwell, X. Gao, R. E. Bailey, M. Han and S. Nie, *Current Opinion in Biotechnology*, 2002, **13**, 40-46.
30 F. Aldeek, C. Mustin, L. Balan, G. Medjahdi, T. R. Carmes, P. Arnoux and R. Schneider, *European Journal of Inorganic Chemistry*, 2015, **6**, 794-801.
31 C. C. Hung, S. J. Ho, C. W. Yeh, G. H. Chen, J. H. Huang, and H. S. Chen, *The Journal of Physical Chemistry C*, 2017, **51**, 28373-28384.
32 M. Braun, C. Burda and M. El-Sayed, *Chemical Physics Letters*, 2002, **361**, 446-452.
33 A. Mews, A. Eychmueller, M. Giersig, D. Schooss, and H. Weller, *J.phys.chem*, 1994, **98**.
34 S. H. T. And, and A. P. Alivisatos, *Annual Review of Physical Chemistry*, 1995, ***46***, 595.
35 B. Xie, Y. Cheng, J. Hao, W. Shu, K. Wang, and X. Luo, *Sci Rep*, 2017, **7**.
36 Z. Fei, and S. K. Jong, *Molecular Crystals & Liquid Crystals*, 2012, **566**, 120-125.
37 W. Qin, R. A. Shah, and P. Guyot-Sionnest, *Acs Nano*, 2012, **6**, 912-8.
38 P. Jing, X.Yuan, W. Ji, and M. Ikezawa, *Applied Physics Letters*, 2011, **99**, 093106-093106-3.