

Two-dimensional CdX (X=Se, Te) nanosheets controlled synthesis and their photoluminescence properties

Yasir A. Haleem, Qiumei Di, Bing Bai, Meng Xu, Wenxing Chen, Jiajia Liu, Jia Liu, Hongpan Rong, Jiatao Zhang*

Beijing Key Laboratory of Construction-Tailorable Advanced Functional Materials and Green Applications, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing-100081, China

Electronic Supplementary Information

*Correspondence Email: zhangjt@bit.edu.cn

Materials:

Cadmium Acetate Dihydrate ($\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 99.99%), Oleic acid (OA, 85%), and Stearic Acid (SA, 80%) were purchased from Aladdin Industrial Co., Ltd. Diphenyl Ether (DPE, 90%), Selenium (Se, 99%) and Tellurium (Te, 99%) were bought from Sinopharm Chemical Reagent Co., Ltd. 1-octadecene (ODE, 90%) were obtained from Sigma-Aldrich Co., Ltd. Trioctylphosphine (TOP, 90%) were obtained from Shanghai Macklin Biochemical Co., Ltd. Toluene (99%) were obtained from Beijing Chemical Works. All the chemicals were used without further purification. The reaction assembly, used for synthesis, were contained of a three-necked flask, a condenser, a septum, a Teflon based magnetic stirrer and a thermocouple attached with the heating mantle.

Methods:

CdSe Nanosheets Synthesis:

CdSe-OA Nanosheets: These nanoplates were synthesized according to reported protocol with some modification.¹ Typically, 0.5 mmol of cadmium acetate dihydrate (133 mg) and 0.25 mmol of oleic acid (80 μL) and 6.0 mL of DPE were mixed in a three-necked flask at 80 °C for 10 minutes in the presence of N_2 flow. In the next step, the temperature of the reaction mixture was raised to 160 °C and kept for 3 min under N_2 purge. After that, the temperature of the reaction mixture was lowered again down to 80 °C. Subsequently, stop the N_2 flow and degassed the reaction mixture under vacuum at 80 °C for 90 min. During degassing, 1 mol solution of Se and TOP was prepared (0.03948 mg Se in 0.5 mL TOP). Afterward, the reaction solution was heated again up to 180 °C under N_2 flow and 10 min later, 0.1 mL of a 1 M TOP-Se solution was injected. Following this, the solution turned from colorless to orange color during 10 min of reaction time. Eventually, the reaction temperature was reduced back to 80 °C. During temperature dropping when it reached 100 °C, 0.5 mL of oleic acid was added into the reaction mixture. The reaction solvent was removed by purification through precipitation with methanol using a centrifuge machine. The resulting CdSe nanosheets were collected by the removal of the supernatant and re-suspension in toluene for further characterization. The samples synthesis by this method is named as CdSe-OA.

CdSe-SA Nanosheets: These nanoplates were synthesized according to reported protocol with some modification.² In a three-neck flask, 0.20mmol Cadmium acetate dihydrate (0.0533g), 0.05mmol Selenium Powder (0.0040g), 0.05mmol Stearic Acid (SA, 0.0142g) and 6.0 mL of ODE were mixed and heated up to 170 °C and kept at this temperature for 10 min under N_2 environment. In the next step, the heating mantle was removed and the reaction mixture was cooled down to room temperature. The reaction solvent was removed by purification through precipitation with ethanol using a centrifuge machine. The resulting CdSe-SA nanosheets were collected by the removal of the supernatant and re-suspension in toluene for further characterization. This sample was named as CdSe-SA.

CdTe Nanosheets Synthesis:

CdTe-OA Nanosheets: The synthesis was carried out according to reported protocol with some modification.³ Briefly, 0.3 mmol of cadmium acetate dihydrate, 0.45 mmol of oleic acid and 10 ml of ODE were introduced into a three-necked flask and degassed at 90 °C for 30 minutes. After that, the flask was purged with N₂. The whole reaction mixture temperature was raised to 210 °C. At this point, 200 µl of 0.1 M TOP-Te solution in ODE was swiftly injected and the reaction mixture was heated for another 15 minutes at the same temperature to increase the reaction yield. Eventually, the reaction mixture temperature was reduced back to 50 °C. During temperature dropping when it reached 90 °C, 0.5 mL of oleic acid was added into the reaction mixture. The reaction solvent was removed by purification through precipitation with methanol using a centrifuge machine. The resulting CdTe nanosheets were collected by the removal of the supernatant and re-suspension in n-hexane for further characterization. The samples synthesis by this method was named as CdTe-OA.

CdTe-SA Nanosheets: This synthesis was carried out according to reported protocol with some modification.² In a three-neck flask, 0.20mmol Cadmium acetate dihydrate (0.0533g), 0.05mmol Tellurium Powder (0.0064g), 0.05mmol SA (Stearic Acid, 0.0142g) or OA (80 µL) and 6.0 mL of ODE were mixed and heated up to 210 °C and kept at this temperature for 15 min under N₂ environment to increase the reaction yield. In the next step, the heating mantle was removed and the reaction mixture was cooled down to room temperature. The reaction solvent was removed by purification through precipitation with ethanol and TBP mixture using a centrifuge machine. The resulting CdTe nanosheets were collected by the removal of the supernatant and re-suspension in toluene for further characterization. The samples synthesis by this method was named as CdTe-SA.

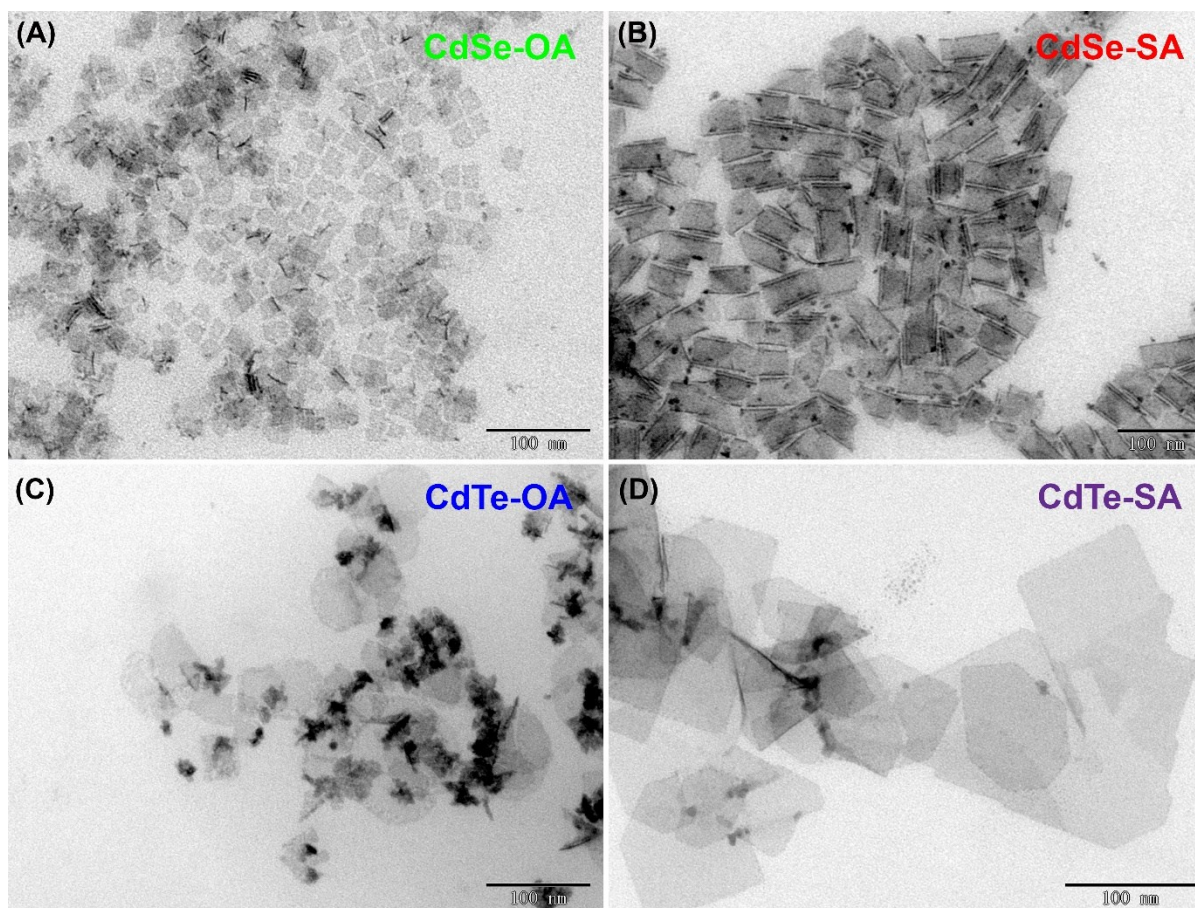


Fig. S1 TEM images of (A) CdSe-OA, (B) CdSe-SA, (C) CdTe-OA, (D) CdTe- SA nanosheets.

Table S1: XPS elemental data of CdSe-OA, CdSe- SA, CdTe-OA, and CdTe-SA nanosheets.

Samples	Cd (%)	Se or Te (%)
CdSe-OA	70.30	29.70
CdSe-SA	75.27	24.73
CdTe-OA	62.15	37.85
CdTe-SA	77.53	22.47

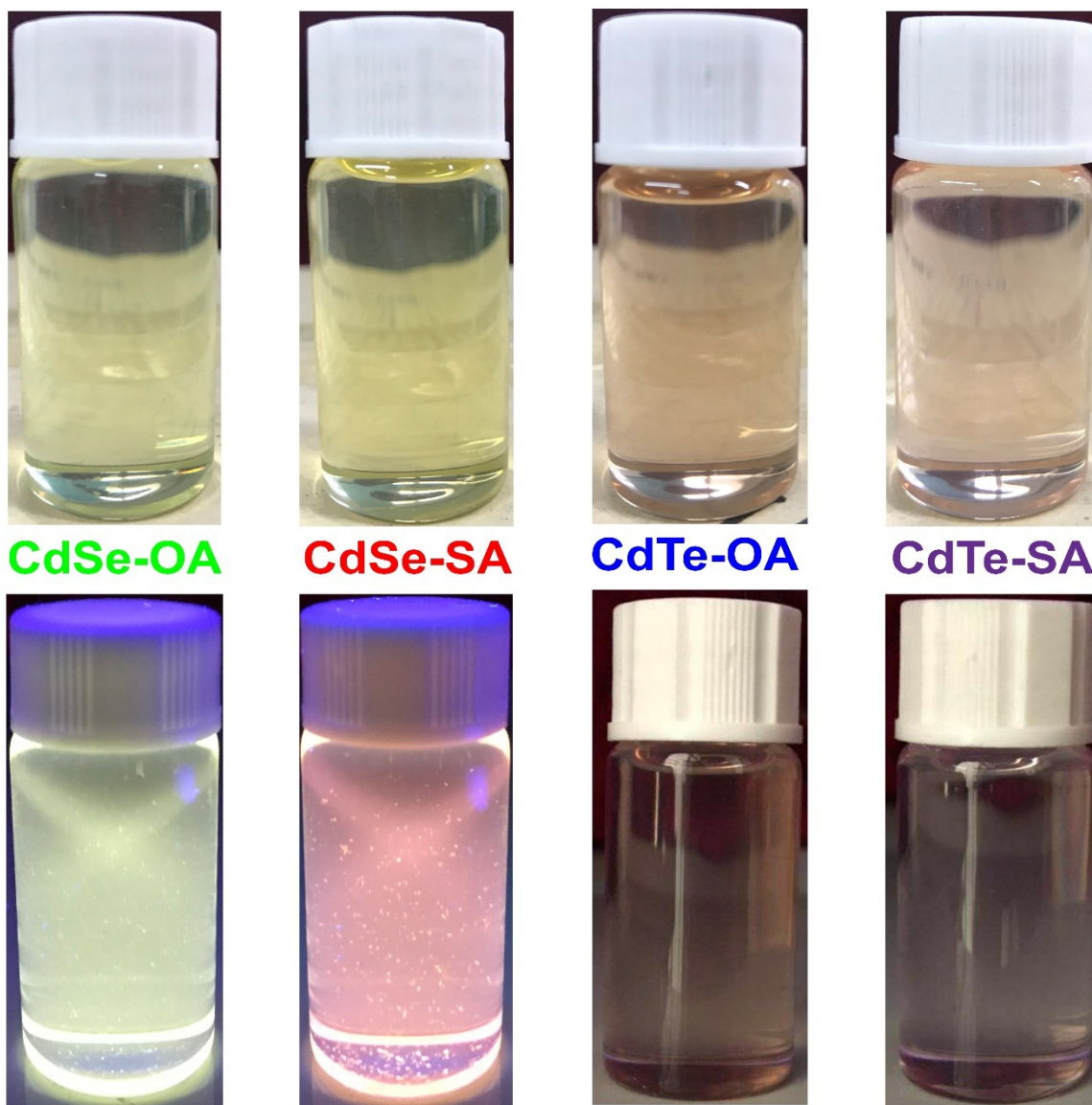


Fig. S2 Sample Photographs of nanosheets colloid under ordinary illumination (Top) and under illumination of 365 nm radiations (Bottom).

Table S2: Photoluminescence Quantum Yields (PLQYs) of CdSe-OA, CdSe- SA, CdTe-OA, and CdTe-SA nanosheets.

Samples	Band-edge PL Peak	Trap-states PL Peak
CdSe-OA	$1.09 \pm 1 \times 10^{-3}\%$	$18.66 \pm 9 \times 10^{-3}\%$
CdSe-SA	$0.93 \pm 1 \times 10^{-4}\%$	$9.31 \pm 3 \times 10^{-3}\%$
CdTe-OA	$0.28 \pm 1 \times 10^{-4}\%$	-----
CdTe-SA	$0.09 \pm 1 \times 10^{-4}\%$	-----

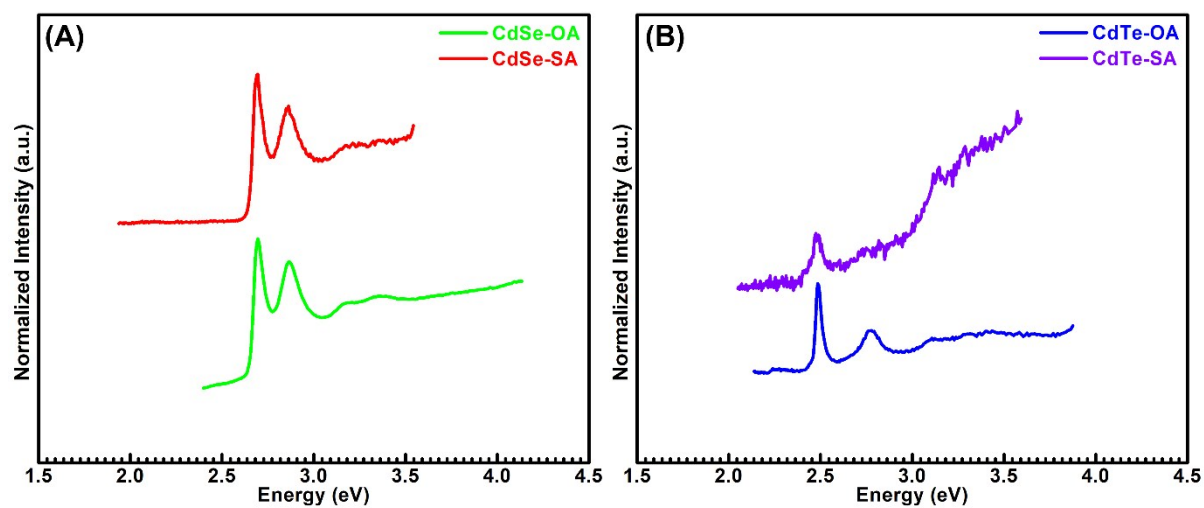


Fig. S3: Excitation spectra of (A) CdSe-OA, CdSe- SA, (B) CdTe-OA, and CdTe-SA nanosheets Colloid measured at 610 nm and 560 nm emission wavelengths for CdSe and CdTe respectively.

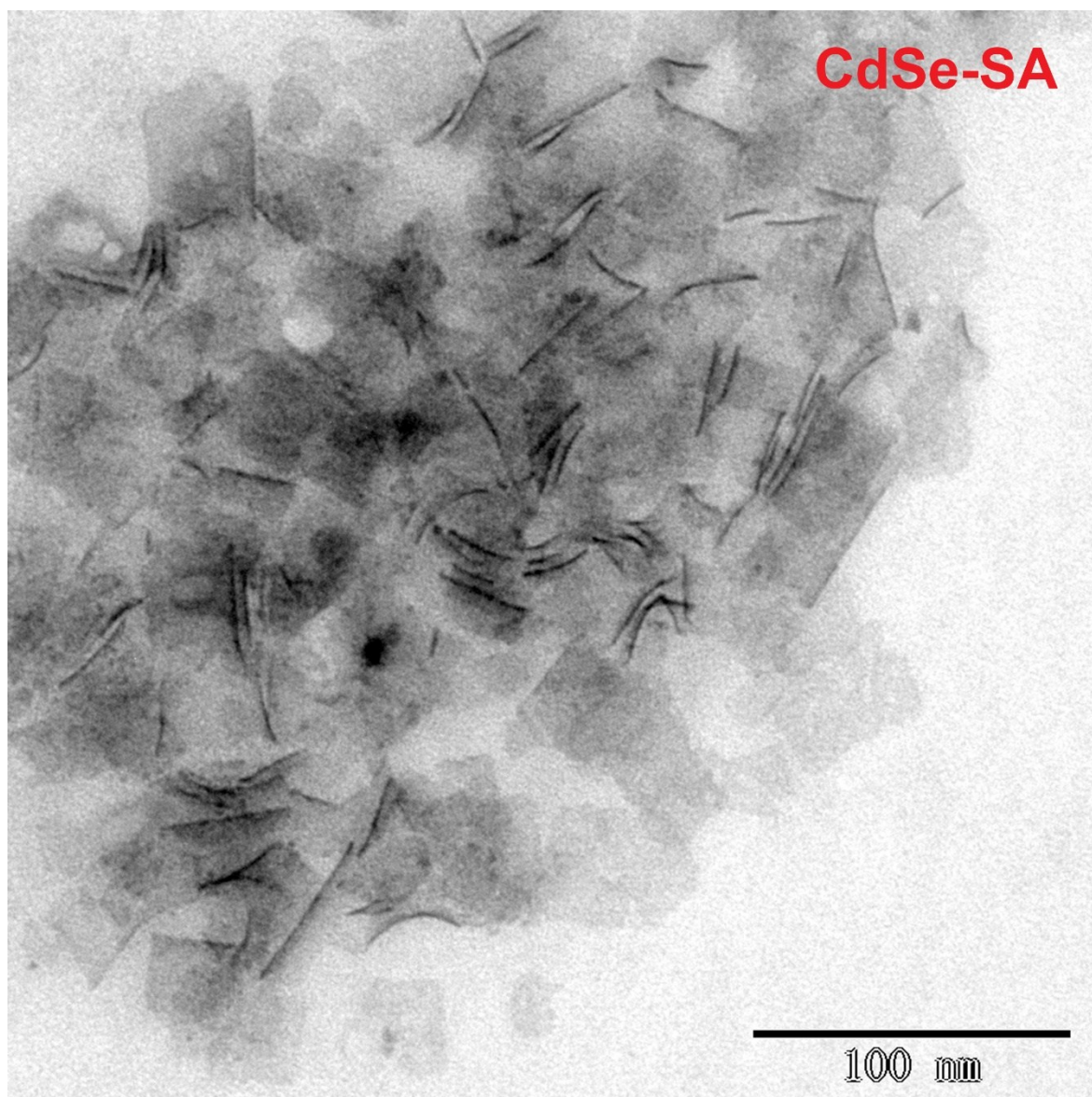


Fig. S4 TEM image of CdSe-SA nanosheets taken after two weeks of temperature-based PL testing.

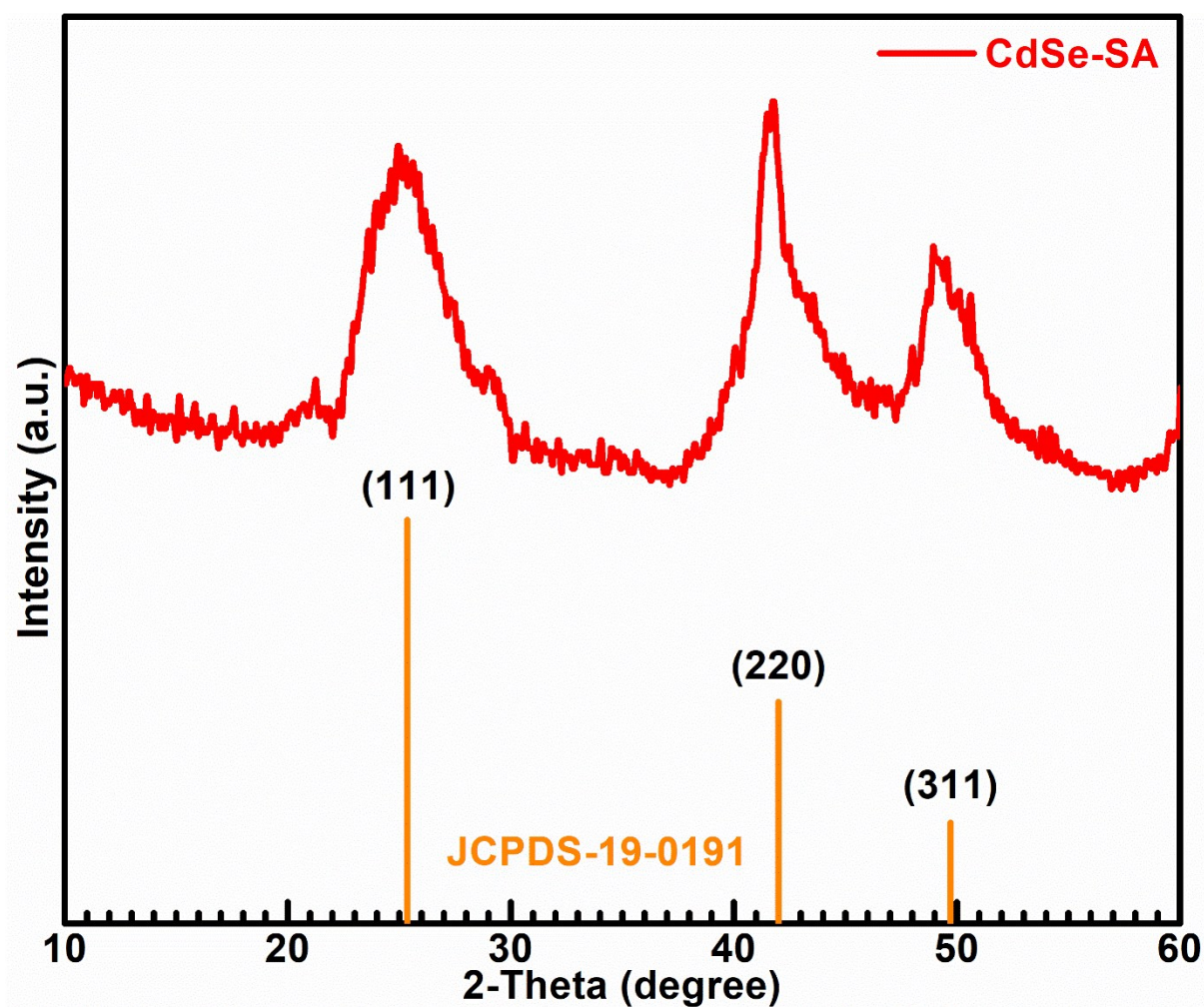


Fig. S5 XRD spectrum of CdSe-SA nanosheets taken after two weeks of temperature-based PL testing.

References:

- 1 F. Gerdes, C. Navío, B. H. Juárez and C. Klinke, *Nano Lett.*, 2017, **17**, 4165–4171.
- 2 Z. Li and X. Peng, *J. Am. Chem. Soc.*, 2011, **133**, 6578–6586.
- 3 A. V. Antanovich, A. V. Prudnikau, D. Melnikau, Y. P. Rakovich, A. Chuvilin, U. Woggon, A. W. Achtstein and M. V. Artemyev, *Nanoscale*, 2015, **7**, 8084–8092.