## Supplementary Information for Bandgap engineering and shape control of colloidal Cd<sub>x</sub>Zn<sub>1-x</sub>O nanocrystals

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Corresponding authors: yizhengjin@zju.edu.cn (Dr. Yizheng Jin) and yezz@zju.edu.cn (Prof. Zhizhen Ye) **Materials:** Myristic acid (MA, 98%), 1-octadecanol (ODA, 97%), tetramethylamonium hydroxide pentahydrate (TMAH, 98%), zinc stearate (Zn(St)<sub>2</sub>), and magnesium stearate (Mg(St)<sub>2</sub>) were purchased from Alfa Aesar. Cadmium acetate dihydrate (Cd(Ac)<sub>2</sub> 2H<sub>2</sub>O, 98%) and 1-octadecene (ODE, tech 90%) were purchased from Acros Organics. Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O, 98%) and stearic acid (SA, 95%) were purchased from Aldrich. Ethyl acetate, toluene, chloroform, hexane, methanol, ethanol, and acetone were analytical grade reagents (Sinopharm Chemical Reagent Co.). All chemicals were used as received.

**Preparation of Zn(Mt)**<sub>2</sub> and Cd(St)<sub>2</sub>: The zinc and cadmium precursors were synthesized according to a method developed by Chen et al.<sup>1</sup> For the syntheses of Zn(Mt)<sub>2</sub>, a methanol solution of MA (20 mmol) was neutralized by a methanol solution of TMAH (20 mmol). Then a methanol solution of Zn(NO<sub>3</sub>)<sub>2</sub>  $6H_2O$  (10 mmol) was introduced into the neutralized solution under vigorous stirring by dropwise addition. A white precipitate of Zn(Mt)<sub>2</sub> formed immediately. The precipitates were washed by methanol several times and dried under vacuum at 45 °C. For the synthesis of Cd(St)<sub>2</sub>, MA and Zn(NO<sub>3</sub>)<sub>2</sub>  $6H_2O$  were replaced by SA and Cd(Ac)<sub>2</sub>  $2H_2O$ , respectively, and all the other procedures were kept the same.

**TEM and HRTEM** images were taken with a JEOL JEM 1230 microscope operated at 80 keV and a FEI TECNAI G<sup>2</sup> F30 transmission electron microscope at 300 keV. Samples were prepared by dropping a dilute solution of nanocrystals onto carbon-coated Cu grids.

**XRD** measurements were performed on a X'Pert PRO system operated at 40 kV and 40 mA with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). XRD samples were prepared by dropping concentrated solutions of the purified nanocrystals onto glass substrates. The samples were allowed to dry and then measured in reflection geometry.

**FTIR spectra** were obtained with a Bruker Vector 27 spectrophotometer. The samples were prepared by directly spreading hot aliquots of the reaction mixture (0.3  $\mu$  L) onto CaF<sub>2</sub> plates.

**ICP-AES** analysis was carried out by using an IRIS Intrepid II XSP ICP-AES equipment. The samples for elemental analyses of zinc and cadmium were prepared by digesting the purified oxide nanocrystals in concentrated nitric acid (63%).

**UV-vis absorption spectra** of the colloidal oxide nanocrystal solutions were measured by using a Shimadzu UV 3600 UV/Vis/NIR spectrophotometer.

**The Cd K-edge EXAFS spectra** were recorded at beamline BL14W1 of Shanghai Synchrotron Radiation Facility (SSRF) using a double Si (311) monochromator in transmission and fluorescence mode. The electron beam energy of the storage ring was 3.5 GeV, and the maximal stored current was ~300 mA. The data were collected using Ge

solid detectors. The nanocrystals were dissolved in toluene. The EXAFS spectra for the nanocrystals from 15 mol.% Cd(St)<sub>2</sub> reaction and commercial CdO powder were obtained by the fluorescence mode and transmission mode, respectively.

**Thermo gravimetric analysis (TGA)** of the zinc and cadmium precursors were carried out on a SDT Q600 Simultaneous DSC-TGA analyzer. Samples were heated from 50 to 600  $^{\circ}$ C at a rate of 10  $^{\circ}$ C/min in an air flow.



**Figure S1**. Characterization of the cationic precursors. (a) and (c) are the FTIR spectra of  $Zn(Mt)_2$  and  $Cd(St)_2$ , respectively. (b) and (d) refer to the TG analyses of the  $Zn(Mt)_2$  and  $Cd(St)_2$ , respectively.



**Figure S2**. Purification of the oxide nanocrystals from the 15 mol.%  $Cd(St)_2$  reaction by extraction. The original reaction solution was extracted by a mixture of methanol/chloroform at 55 °C. FTIR spectra were taken for the original solution and the upper layer after every extraction. All the FTIR spectra were normalized to the relatively intense C=C vibration band at 1641 cm<sup>-1</sup> originating from ODE. The peak at 1598 cm<sup>-1</sup> refers to the asymmetrical vibration of carboxylate from metal precursors. The unreacted metal precursors were completely removed after the third extraction. The residual band in the FTIR spectrum corresponds to the ligand bonding onto the surfaces of the nanocrystals.



**Figure S3.** (a) A typical TEM image and (b) XRD pattern of the nanocrystals from the 10 mol.%  $Cd(St)_2$  reaction (without additional MA) by injecting alcohol into metal precursors at elevated temperature (250 °C). The red lines refer to the wurtzite structure of ZnO (PDF#36-1451). (\*) refers to the diffraction peak coming from the segregated CdO (PDF#65-2908). (c) FTIR spectra of  $Cd(St)_2$  (0.25 mmol) dissolved in ODE (5 mL) at 120 °C and 230 °C. Both spectra are normalized to the relatively intense C=C vibration band at 1641 cm<sup>-1</sup> originating from ODE as a standard.



Figure S4. The cadmium concentrations in the alloyed nanocrystals, determined by ICP-AES, as a function of the relative concentrations of  $Cd(St)_2$  in the reagents.



Figure S5. A typical SAED pattern of the alloyed  $Cd_xZn_{1-x}O$  nanocrystals.



**Figure S6.** Stability of  $Cd_xZn_{1-x}O$  nanocrystals from the 10 mol.%  $Cd(St)_2$  reaction. (a) The UV-vis spectra of the fresh nanocrystals and nanocrystals stored at ambient conditions for three days. (b) and (c) Typical TEM images of the fresh nanocrystals and nanocrystals stored at ambient conditions for three days, respectively.



**Figure S7.** TEM analyses of the  $Mg_xZn_{1-x}O$  nanowires from the 55 mol.%  $Mg(St)_2$  reaction. The average diameter of the nanowires was measured to be  $1.9\pm0.2$  nm. The synthetic details of  $Mg_xZn_{1-x}O$  ultrathin nanowires are described as following. A solution of ODA (2.5 mmol) dissolved in ODE (10 mL) was degassed and heated to 280 °C under an Ar flow. A separate solution of  $Zn(St)_2$  (0.225 mmol) and  $Mg(St)_2$  (0.275 mmol) in ODE (4 mL) at 150 °C was quickly injected into the reaction flask. The temperature dropped to 250 °C and stabilized afterwards. The reaction was allowed to proceed for 20 min. The resulting nanocrystals were precipitated by a mixture of ethyl acetate and ethanol. Then the precipitates were washed by hexane/methanol combinations several times. The purified nanocrystals were dissolved in toluene.



**Figure S8.** Quantum confinement effects of the pure ZnO nanocrystals on the bandgaps. The relationship between the optical bandgap and the diameter of the pure ZnO nanocrystals can be well described by an empirical equation,  $E_g = a + b/D^2 - c/D$ , in which a, b and c were determined to be 3.25, 49.06 and 9.16, respectively.

## References

1. Y. F. Chen, E. Johnson and X. G. Peng, *Journal of the American Chemical Society*, 2007, **129**, 10937-10947.