

Supporting Information (SI)

CdTe Magic size clusters synthesis via cation exchange method and conversion mechanism

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Experimental section

Chemicals.

Zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$) and toluene (Tol, $\geq 99.5\%$) were purchased from General-reagent. Cadmium acetate dihydrate ($\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 99%), octylamine (OTA, 99%) were purchased from Aladdin. Tellurium powder (Te, 99.99%), 1-octadecene (ODE, 90%) and trioctylphosphine (TOP, 90%) were obtained from Aldrich, Adamas-beta and Strem Chemicals, respectively. Acetonitrile (ACN, 99%) and Acetic acid (HAc, 98%) were purchased from Titan. Oleic acid (OA, 90%), Oleylamine (OLA, 80%–90%) and diphenylphosphine (DPP, 98%) were purchased from Alfa Aesar, Acros Organic and J&K, respectively. All chemicals were used as received.

Synthesis and purification of MSCs

Preparation of $\text{Zn}(\text{OA})_2$ precursors. To a 50 mL three-necked flask was added 2.65 g of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (12.0 mmol), 8.4 mL of oleic acid (OA, 26.4 mmol) and 12.6 mL of octadecene (ODE, 19.8 mmol). The above mixture was heated to 100°C under vacuum and left at this temperature for 2 hours until $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was completely dissolved and no bubbles were emerging from the solution. Subsequently, the reaction system was filled with N_2 after 3 evacuation/ N_2 -filling cycles. The reaction system was heated to 120°C under a N_2 atmosphere and kept at this temperature for 30 min to obtain a clear $\text{Zn}(\text{OA})_2$ solution, which was cooled to room temperature and then transferred to a glass vial for further use.

Preparation of $\text{Cd}(\text{OA})_2$ precursors. 0.48 g of $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (0.6 mmol) and 18.0 mL of OA (57.0 mmol) were added to a 50 mL three-neck flask and the above mixture was heated to 100°C under vacuum. Heating was continued at this temperature for 40 minutes until the $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ solution was completely dissolved and no bubbles appeared in the solution. After 3 evacuation/ N_2 -filling cycles, the reaction system was heated to 120°C under a N_2 atmosphere and kept at this temperature for 30 min to obtain a transparent $\text{Cd}(\text{OA})_2$ solution. After cooling to room temperature, the $\text{Cd}(\text{OA})_2$ solution was transferred to a glass vial for further use.

Preparation of $\text{Cd}(\text{Ac})_2/\text{OLA}$ precursors. 0.48 g of $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (1.8 mmol) and 18.0 mL of oleylamine (OLA, 39.0 mmol) was added to a 50 mL three neck flask, which was heated to 100°C under vacuum and kept at this temperature for 40 min until $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was completely dissolved and no bubbles were emerging from the solution. After 3 evacuation/ N_2 -filling cycles, the reaction system was then heated to 120°C under a N_2 atmosphere and maintained at this temperature for 20 min to obtain a transparent $\text{Cd}(\text{Ac})_2/\text{OLA}$ solution. After cooling to room temperature, the

$\text{Cd}(\text{Ac})_2/\text{OLA}$ solution was transferred to a glass vial for further use.

Preparation of TOP-Te. 1.15 g of Te powder (1.8 mmol) and 18.0 mL of TOP (36.0 mmol) were added to a 50 mL three-necked flask and the above mixture was heated to 100°C under vacuum. Heating was continued at this temperature for 40 min until the Te powder was dissolved and no bubbles were emerging from the solution. After 3 evacuation/ N_2 filling cycles, the reaction system was heated to 310 °C under N_2 and kept at this temperature for 30 min to obtain a clear light green solution, TOP-Te. After cooling to room temperature, the TOP-Te solution was transferred to a glass vial and stored in a refrigerator for further use.

Synthesis of ZnTe MSCs. The synthesis of ZnTe MSCs is based on the two-step synthesis method reported by Yu's group, with appropriate modification. First, ZnTe precursor compounds (PCs) were synthesized. 4.2 mL of $\text{Zn}(\text{OA})_2$ (2.4 mmol) and 5.3 mL of ODE (16.6 mmol) were added to a 50 mL three-necked flask, which was heated to 100°C under vacuum and kept at this temperature for 40 min. After three evacuation/ N_2 filling cycles, the reaction system was heated to 190°C under N_2 followed by the rapid injection of a mixture of 1.2 mL of TOP-Te (0.6 mmol), 104 μl of DPP (0.6 mmol) and 1.4 mL of HAc (18 mmol). After 10 min of reaction at this temperature, a clear light yellow ZnTe PCs solution was obtained. Then, ZnTe MSCs were obtained by adding ZnTe PCs solution to an excess of toluene solution.

Synthesis of CdTe MSCs. CdTe MSC-448 were synthesized at room temperature by cation exchange using ZnTe MSCs as a template. Typically, CdTe MSCs were obtained by adding a certain amount of $\text{Cd}(\text{Ac})_2/\text{OLA}$ to the above freshly prepared ZnTe MSCs solution and leaving it at room temperature for 12 hours. CdTe MSC-448 were synthesized by direct synthesis. 1.5 mL of $\text{Cd}(\text{OAc})_2/\text{OLA}$ (0.9 mmol) and 3.0 mL of OLA were added to a 50 mL three-necked flask, which was heated to 100°C under vacuum and kept at this temperature for 30 min. After three evacuation/ N_2 filling cycles, the reaction system was heated to 140°C under N_2 followed by the rapid injection of a mixture of 0.39 mL of TOP-Te (0.22 mmol) and 1.5 mL of OLA. After 10 min of reaction at this temperature, a clear light yellow CdTe PCs solution was obtained. Then, CdTe MSCs were obtained by adding CdTe PCs to a mixture solution of toluene (3.0 mL) and methanol (0.1 mL).

Purification of MSCs. 1.0 mL of ZnTe MSCs or CdTe MSCs solution and 1.0 mL of toluene were loaded into a 5 mL centrifuge tube, into which 2.0 mL of acetonitrile was added. The mixture was centrifuged at 8000 rpm for 5 min and the supernatant was discarded. The precipitate was mixed with 1.0 mL of toluene, into which 2.0 mL of acetonitrile was added. The mixture was then centrifuged at

8000 rpm for 5 min and the supernatant was discarded. The precipitates were dried and loaded in a glass vial and stored in the refrigerator for subsequent characterization.

Characterization

The UV–vis optical absorption was recorded on a spectrophotometer (Shimadzu UV-2600). The transition electron microscopy (TEM) images were photographed using a microscope (JEM-2100, JEOL). The X-ray diffraction (XRD) patterns of the samples were collected using an X-ray powder diffractometer from Rigaku (D/MAX-2550). The size of ZnTe MSC-389 was calculated by Scherrer equation: $D_{hkl} = K\lambda/(B_{hkl}\cos\theta)$, $K = 0.89$ (a numerical factor referred to as the shape factor), $\lambda = 1.5418 \text{ \AA}$ (the wavelength of the X-ray), B is the full width at half maxima (FWHM) of the diffraction peak. Fourier transform infrared spectra (FTIR) were obtained from Shimadzu IR Prestige-21. ^{113}Cd Nuclear magnetic resonance spectra (NMR) spectra of the samples were tested on Avance Neo 600 MHz.

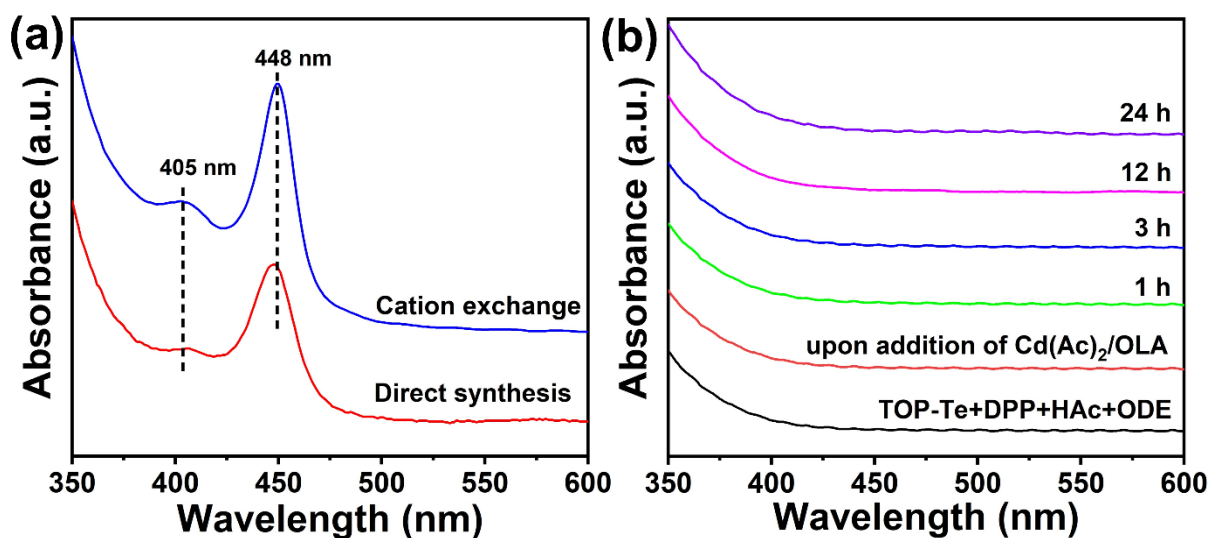


Fig. S1 (a) Absorption spectra of directly and indirectly synthesized CdTe MSCs. (b) Compare the absorption spectra of the experiment. Absorption spectra of TOP-Te, DPP, HAc, ODE mixture and Cd(Ac)₂/OLA were added to toluene solution.

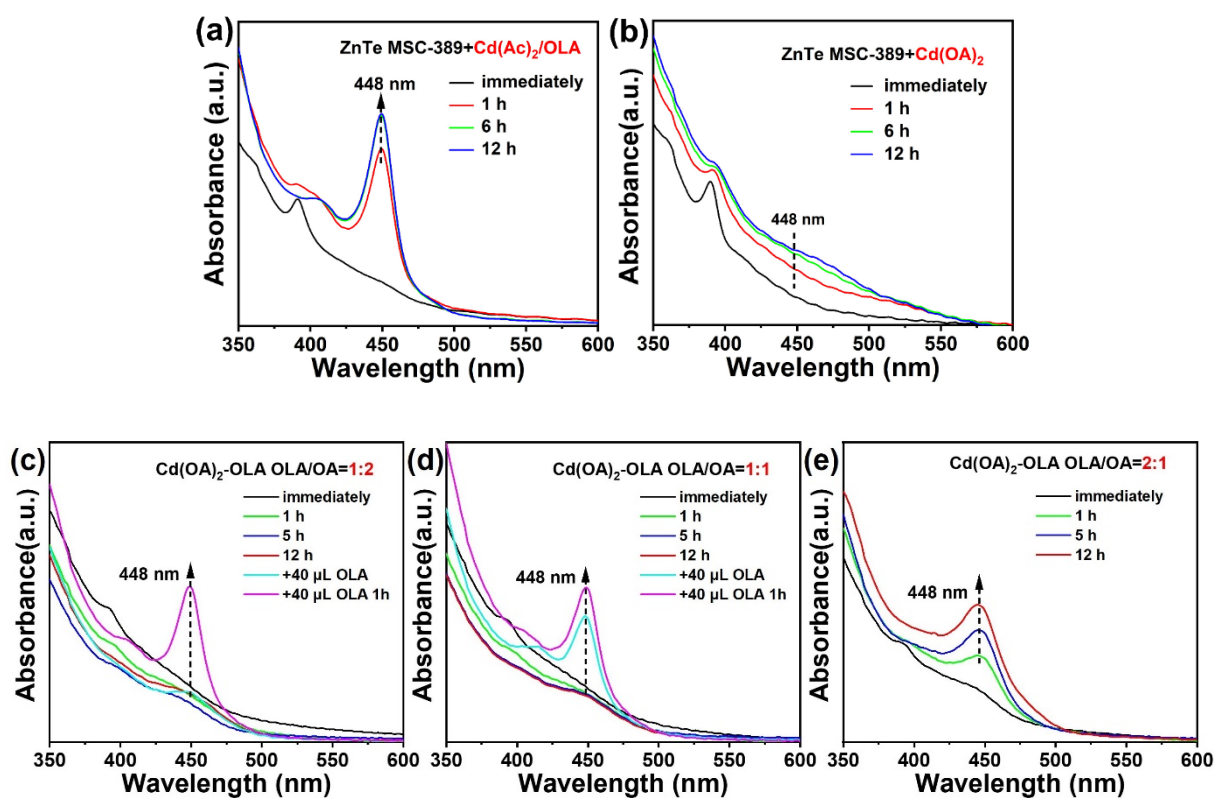


Fig. S2 Absorption spectra of ZnTe MSCs after adding different Cd precursors. (a) Cd(Ac)₂/OLA, (b) Cd(OA)₂, Cd(OA)₂-OLA with OLA/OA ratio of (c) 1:2, (d) 1:1 and (e) 2:1.

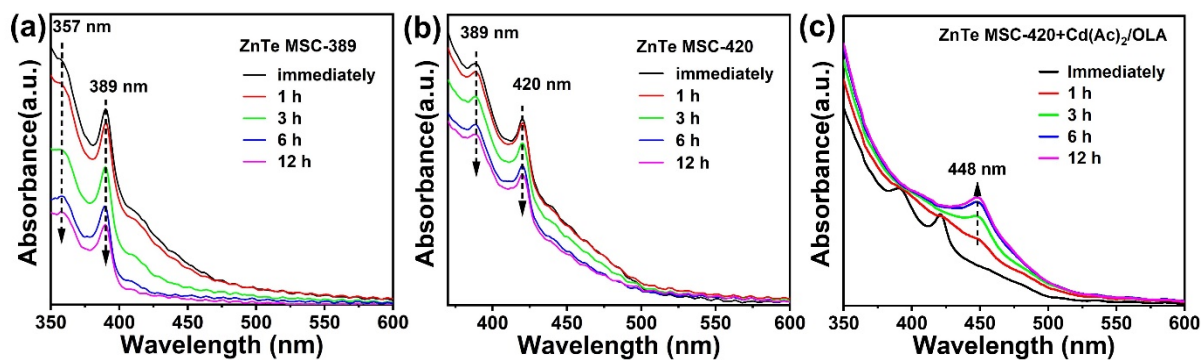


Fig. S3 (a, b) Absorption spectra of ZnTe MSC-389 and ZnTe MSC-420 dispersed in toluene. (c) Absorption spectra of ZnTe MSC-420 with immediate addition of Cd(Ac)₂/OLA.

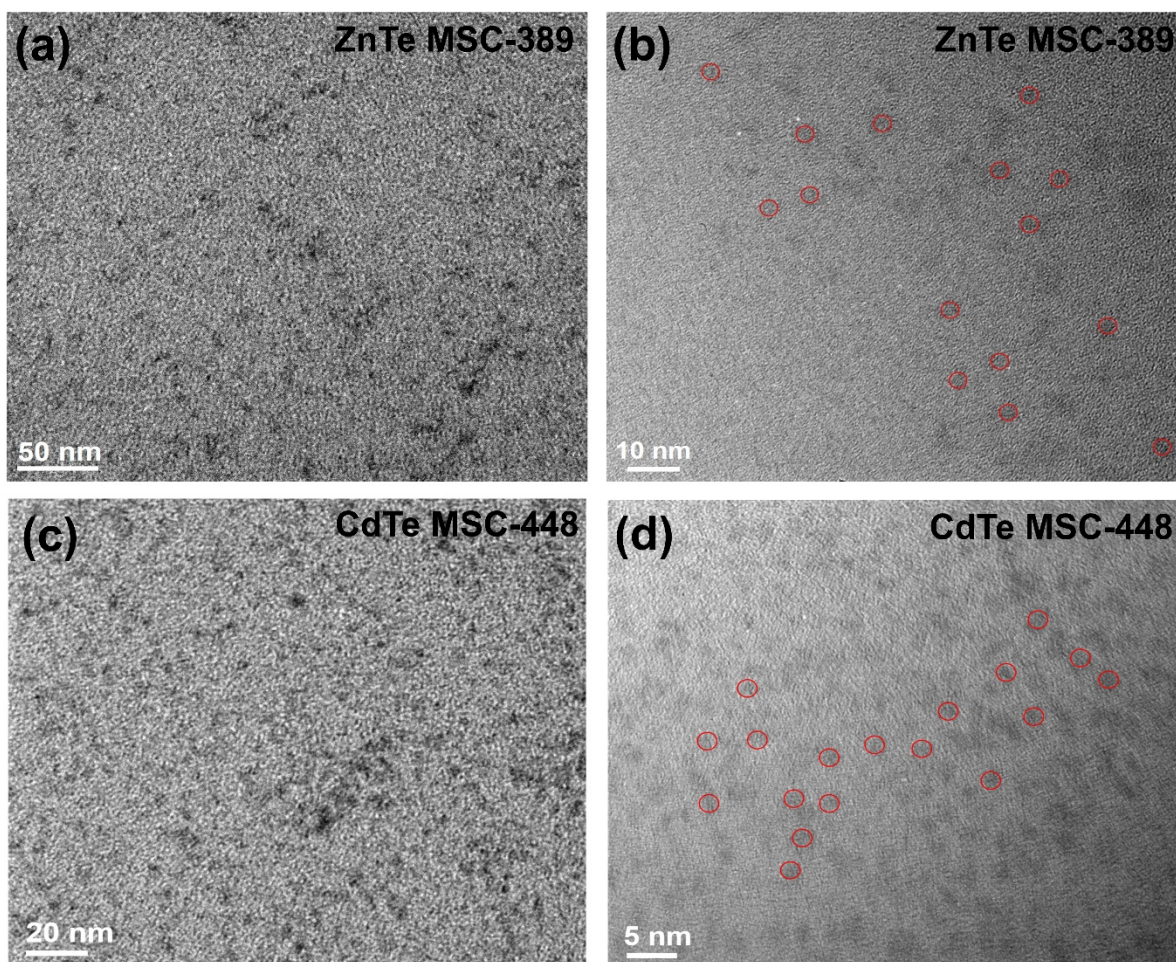


Fig. S4 TEM images of (a, b) ZnTe MSC-389 and (c, d) CdTe MSC-448.

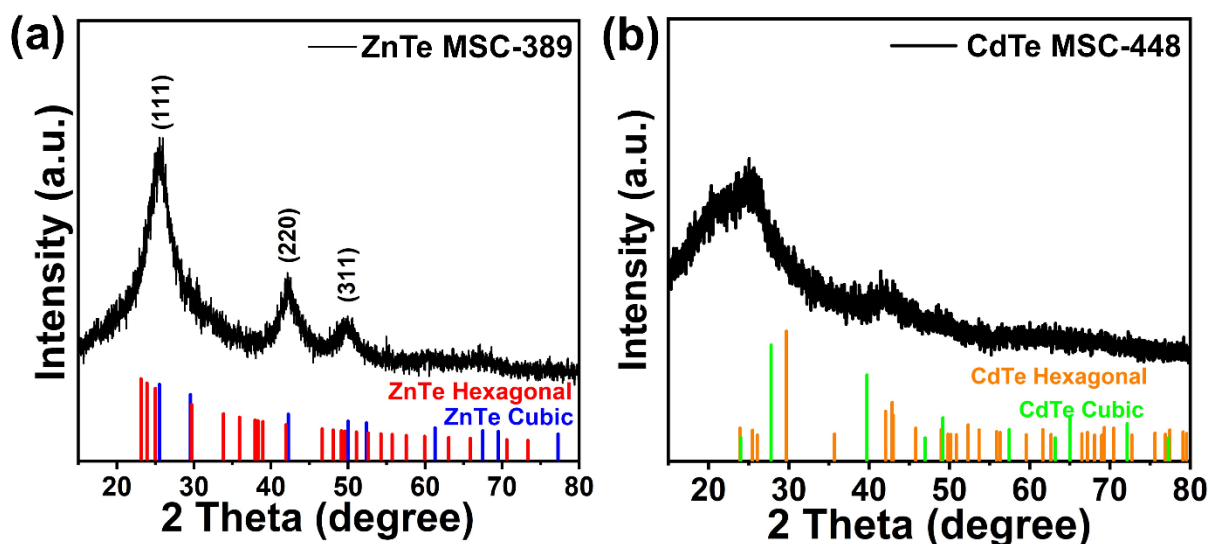


Fig. S5 XRD patterns of ZnTe MSC-389 (a) and CdTe MSC-448

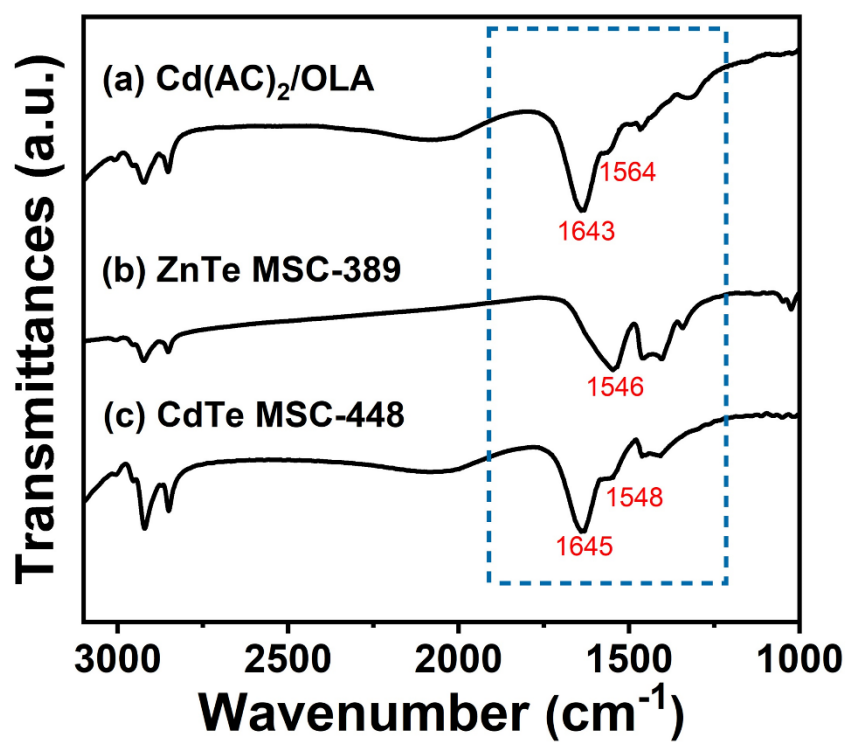


Fig. S6 FT-IR spectra of Cd(Ac)₂/OLA (a), ZnTe MSC-389 (b) and CdTe MSC-448 (c).

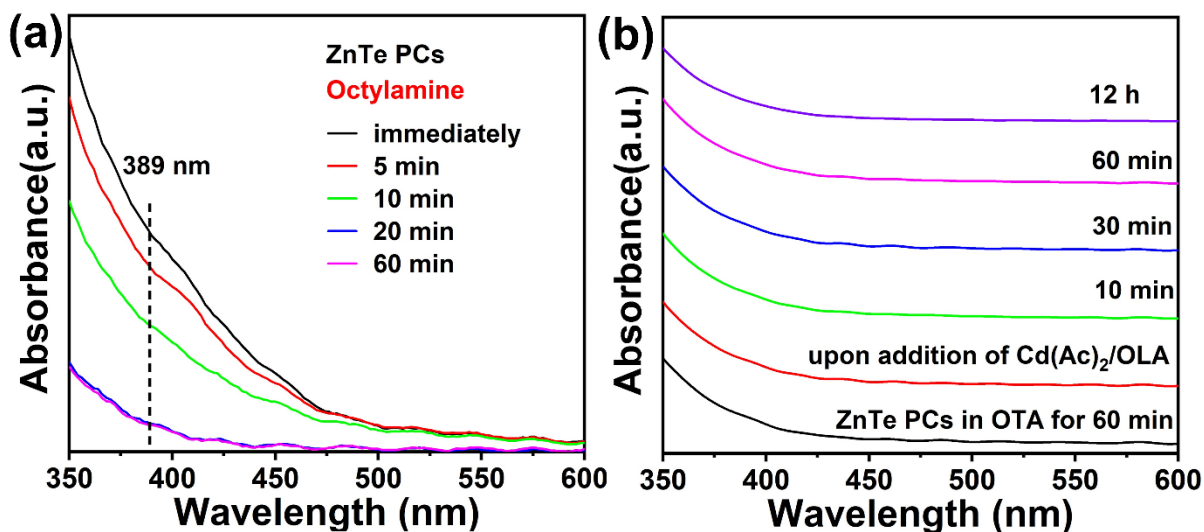


Fig. S7 (a) Absorption spectra of ZnTe PCs dispersed in octylamine. (b) Absorption spectra after addition of $\text{Cd}(\text{Ac})_2/\text{OLA}$ to octylamine solution of ZnTe PCs (after 60 min of dispersion).

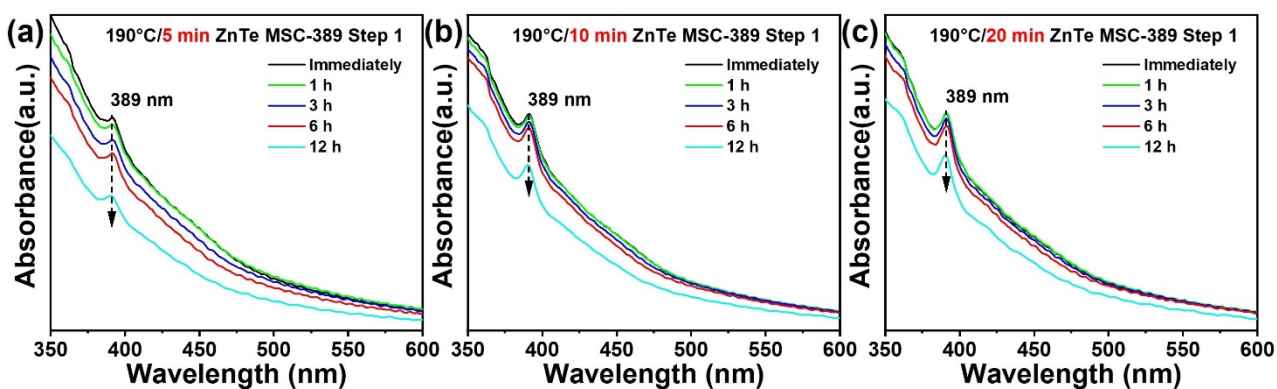


Fig. S8 Absorption spectra of ZnTe MSC-389 obtained by adding ZnTe PC into toluene. The ZnTe PCs react at 190°C for (a) 5 min, (b) 10 min and (c) 20 min, respectively.