Supplementary Information (SI) for Nanoscale.

Cd_3P_2 QDs Emitting in the SWIR Through Overgrowth of Cadmium Phosphide Clusters

Supplementary Material

Materials: Cadmium oxide (CdO, ≥ 99.99%) and 1-octadecene (ODE, 90%) was purchased from Sigma-Aldrich and Acros Organics. Oleic acid (OA, 90%). *Tris*(trimethylsilyl)phosphine (TMSP, 98%) was purchased from Strem. All chemicals were used without any purification.

Instrumentation: Absorption spectra were measured on a Jasco V-780 spectrophotometer with a $In_xGa_{1-x}As$ near-IR detector. PL spectra were measured on a Horiba FluoroMax spectrofluorometer with with a $In_xGa_{1-x}As$ near-IR detector with the 475 nm excitation.

MALDI Mass Spectrometry Cadmium Phosphide Clusters and QDs

The mass spectra shown in Figure S1 are labeled with average mass due to the complex Cd isotopes (Cd-106, Cd-108, Cd-110, Cd-111, Cd-112, and Cd-114). Putative assignments for QD fragments are proposed in Table S1, demonstrating similar repeating pattern with clusters (Table 1) but slightly different ion composition.

Table S1. Analysis of major peaks in the mass spectra of the QDs emitting at 1010 nm in the low-mass region.

QD Fragment Formula	Theoretical Average Mass (Da)	MALDI Fragment Average Mass (Da)
$Cd_{29}P_{18}(C_{17}H_{33}CO_2)_7^+$ / $Cd_{27}P_{16}(C_{17}H_{33}CO_2)_8^+$	5787.6/5782.3	5787.2
$Cd_{32}P_{21}(C_{17}H_{33}CO_2)_5^+$ / $Cd_{28}P_{14}(C_{17}H_{33}CO_2)_7^+$	5654.9/5551.3	5653.3
$Cd_{23}P_{13}(C_{17}H_{33}CO_2)_9^+$ / $Cd_{21}P_{11}(C_{17}H_{33}CO_2)_{10}^+$	5521.2/5515.9	5519.5
$Cd_{26}P_{16}(C_{17}H_{33}CO_2)_7^+$ / $Cd_{24}P_{14}(C_{17}H_{33}CO_2)_8^+$	5388.5/5383.1	5385.7
$Cd_{29}P_{19}(C_{17}H_{33}CO_2)_5^+$ / $Cd_{27}P_{17}(C_{17}H_{33}CO_2)_6^+$	5255.7/5250.4	5253.2
$Cd_{22}P_{13}(C_{17}H_{33}CO_2)_8^+$ / $Cd_{20}P_{11}(C_{17}H_{33}CO_2)_9^+$	5127.3/5122.0	5123.3
$Cd_{53}P_{33}(C_{17}H_{33}CO_2)_9^+$ / $Cd_{51}P_{31}(C_{17}H_{33}CO_2)_{10}^+$	**9513.0/9507.7**	**9510.7**

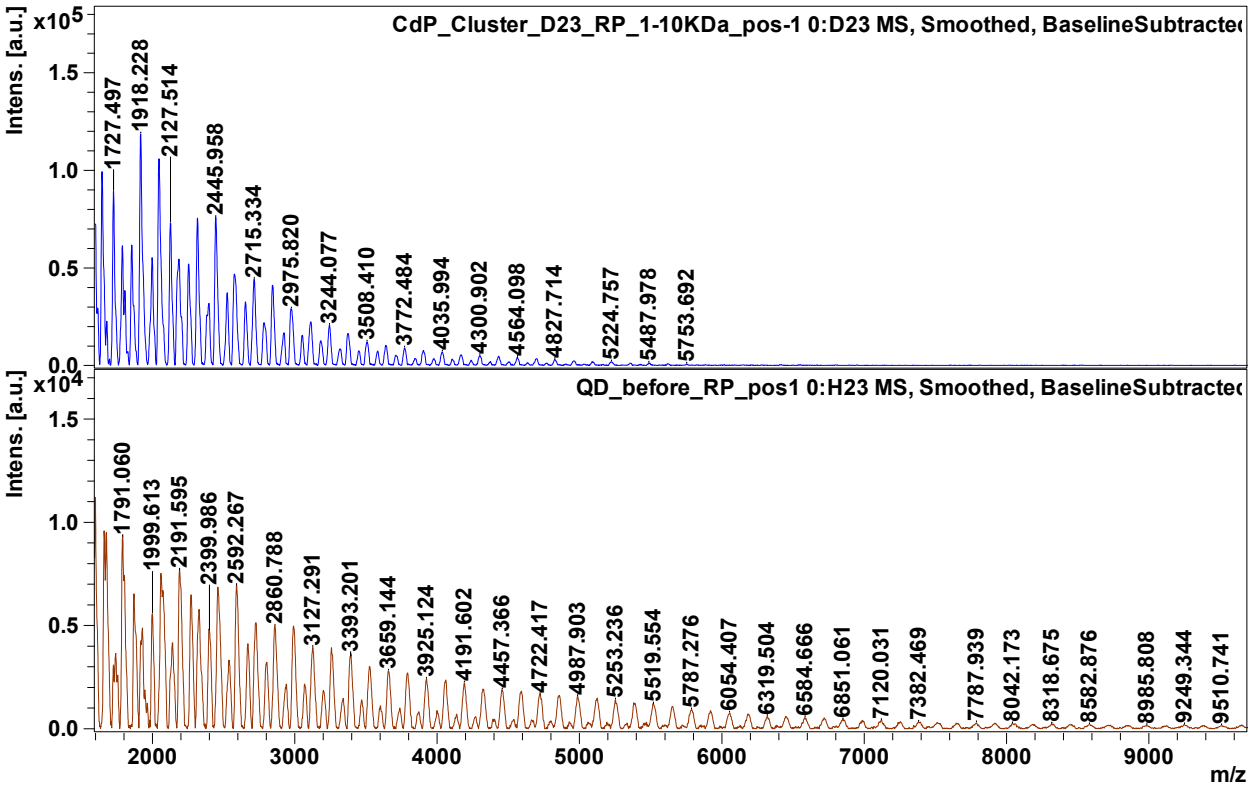

Figure S1. MALDI MS spectrum of cadmium phosphide MSCs and QDs emitting at 1010 nm taken in the positive refelctron mode using matrix DCTB in the 1:1 sample: matrix ratio of (a) MSCs and (b) QDs.

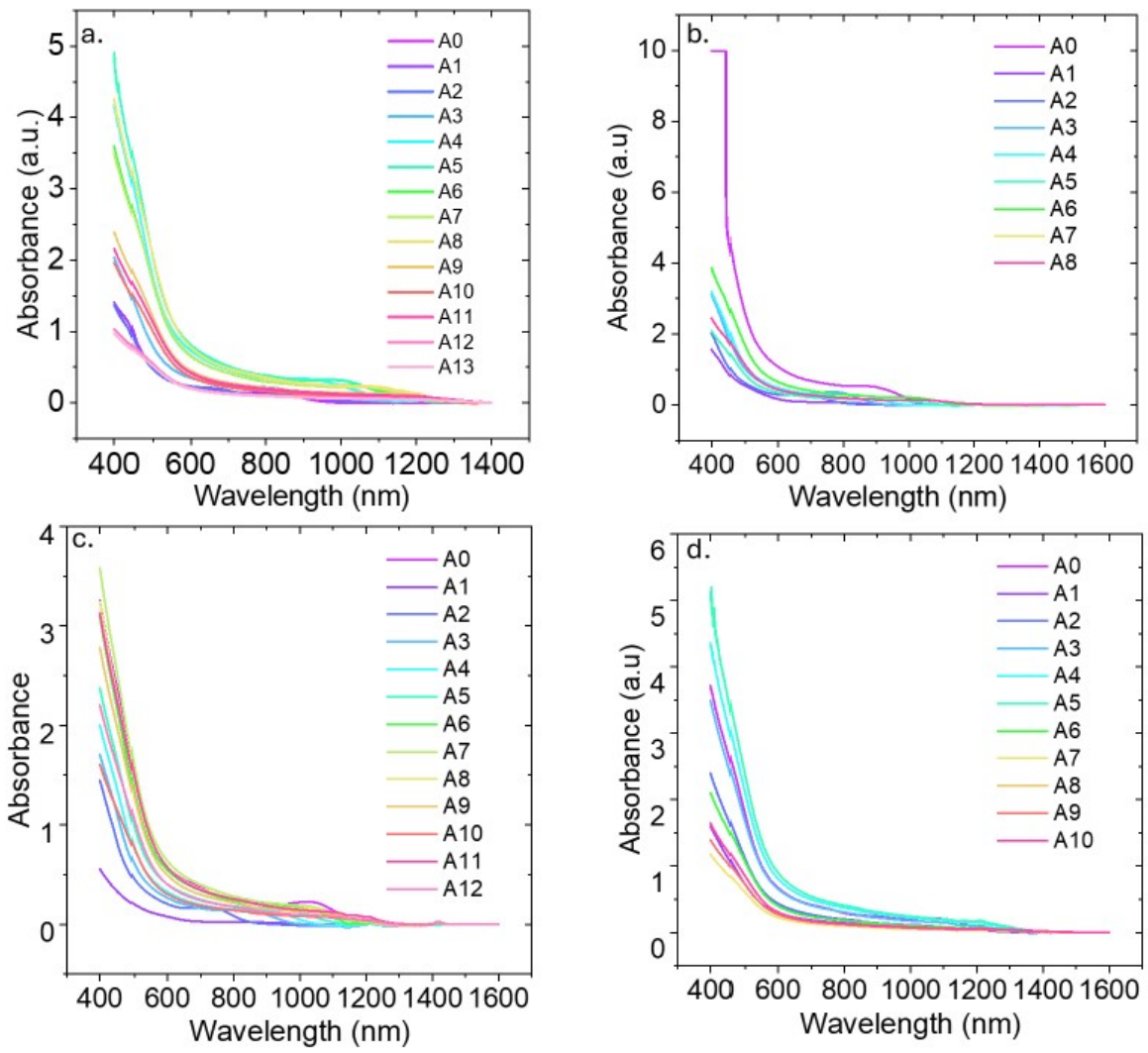

Figure S2. Absorption spectra of cluster overgrowth trials on (a) 965 nm emitting QDs, (b) 1010 nm emitting QDs, (c) 1102 nm emitting QDs, and (d) 1145 nm emitting QDs.

Quantum Yield Calculations

We measured the PL QY of the final products of the overgrowths in tetrachloroethylene (TCE) with a 1025 nm excitation in an integrating sphere.

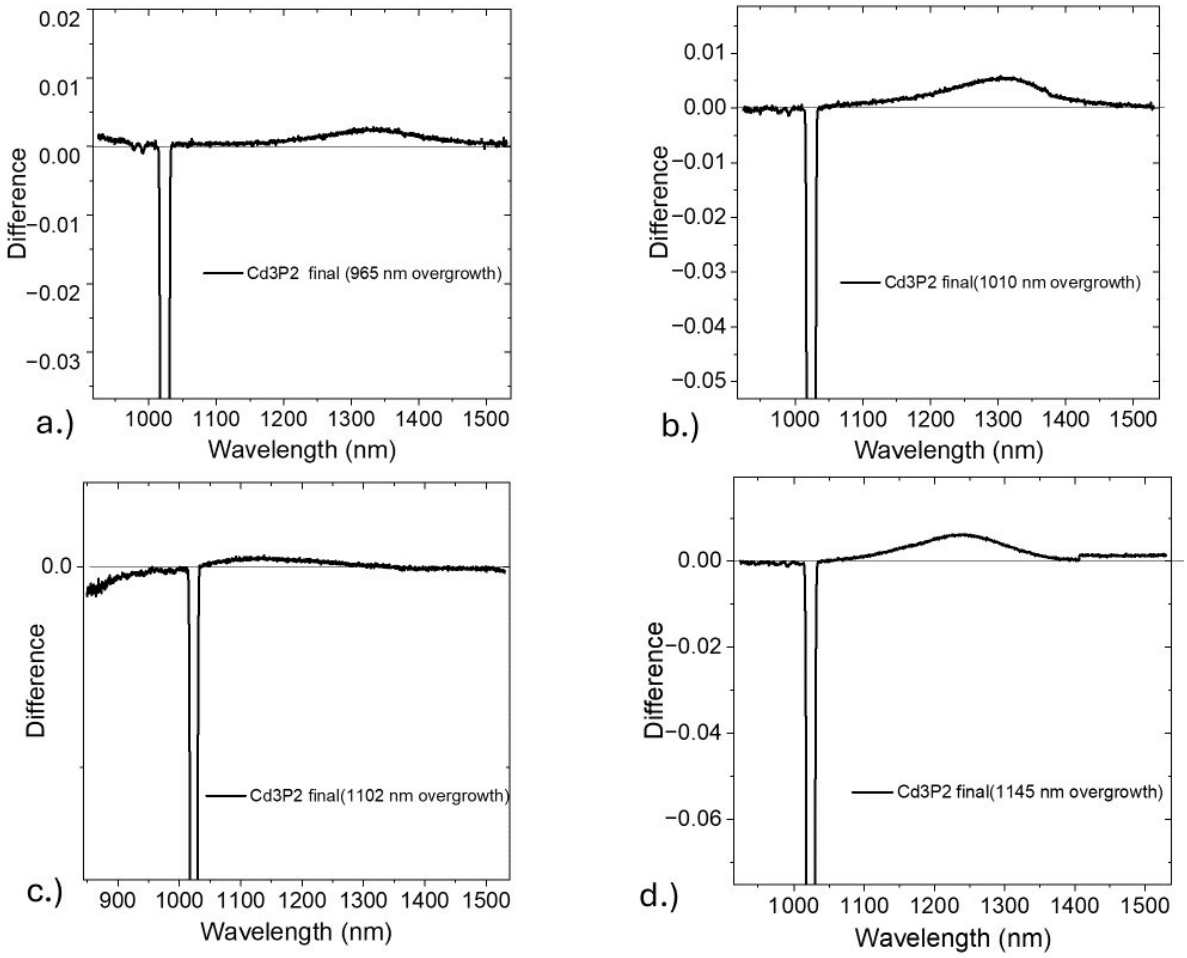

Figure S3. PLQY of the final product of the cluster overgrowths on (a) 965 nm, (b) 1010 nm, (c) 1102 nm, and (d) 1145 nm emitting QDs.

Table S2. Spectroscopic properties of the initial QDs and products of overgrowth.

First exciton of QDs used for overgrowth	Emission wavelength of QDs used for overgrowth	Quantum yield of the product
834 nm	965 nm	7.3%
912 nm	1010 nm	14.8%
1015 nm	1102 nm	6.7%
1048 nm	1145 nm	17.6%

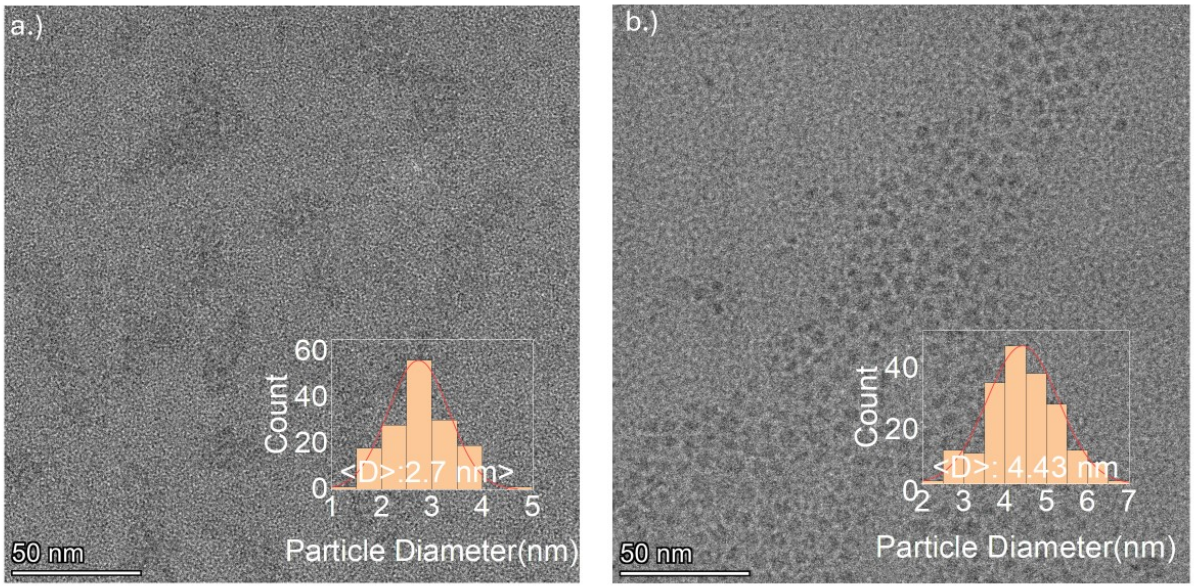

Figure S4. TEM images of overgrowth treatment of 1025 nm emitting QDs: (a) initial QDs with average size of 2.7 nm (b) final QDs with average size 4.4 nm

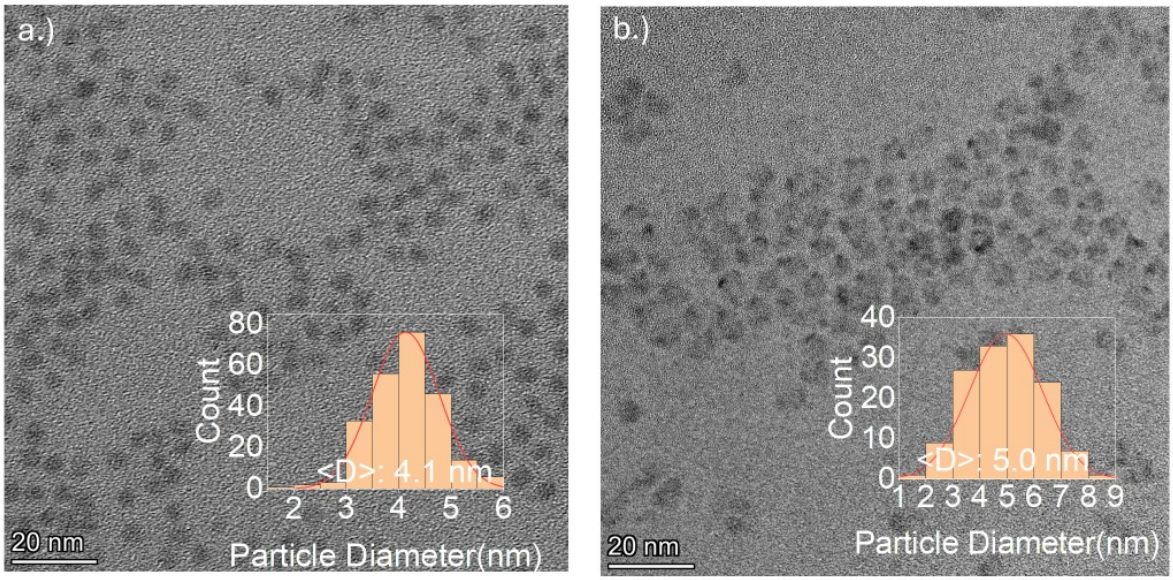

Figure S5. TEM images of overgrowth treatment of 1145 nm emitting QDs: (a) initial QDs with average size of 4.1 nm (b) final QDs with average size of 5.0 nm.

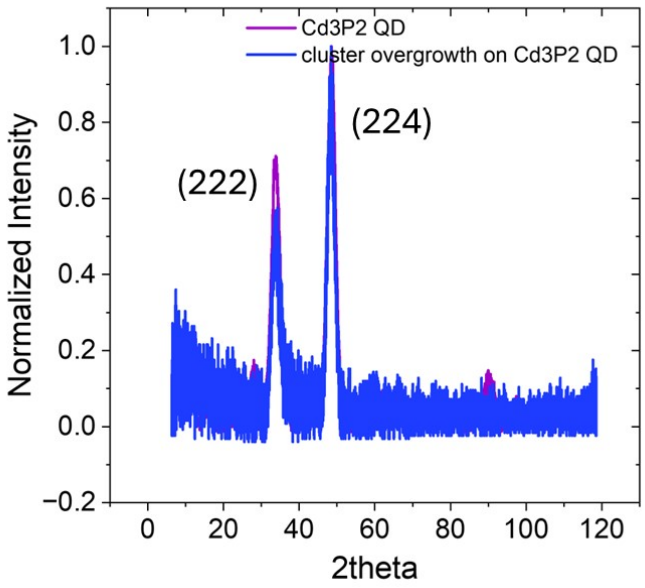

Figure S6. Powder X-ray diffraction of Cd_3P_2 QDs on the **Co-K*α*** line before and after cluster overgrowth. The characteristic (222) and (224) peaks[1-3] indicate the tetragonal crystal structure is preserved.

1. R. Xie, J. Zhang, F. Zhao, W. Yang and X. Peng, *Chemistry of Materials*, 2010, **22**, 3820-3822.
2. S. Miao, S. G. Hickey, C. Waurisch, V. Lesnyak, T. Otto, B. Rellinghaus and A. Eychmüller, *ACS Nano*, 2012, **6**, 7059-7065.
3. L. Smith, K. E. Harbison, B. T. Diroll and I. Fedin, *Materials*, 2023, **16**, 6346.