Investigating the Role of Polytypism in the Growth of Multi-Shell CdSe/CdZnS Quantum Dots

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Electronic Supplementary Information (ESI)

***Experimental**:* Control experiments annealing CdSe cores Wurtzite crystal structure, (*d* = 3.5 nm) were performed for 2.5 hr at 240 °C in presence of oleic acid (OAc) and dioctylamine (DOA) separately to investigate if the crystallographic preference of the two ligands affect the core structure prior to shell addition. Briefly, 2.9 x 10 $^{-8}$ moles of dried *W* CdSe were added to a 25 mL four necked flask with ~4 mL OAc (OAc, 0.013 moles) and 5 mL octadecene (ODE). The mixture was degassed at 110 °C for 1 hr, followed by annealing at 240°C under Ar flow. Figure S7 (a-b) shows the change in UV-Vis absorption spectra during the course of the annealing process by sampling out aliquots at regular intervals. Considerable etching of the CdSe core in presence of excess OAc ligand in the reaction medium at the initial stages, followed by ripening with the increase of temperature is depicted by the shift of λ_{Abs}.

Similar experiments were performed using ZB-CdSe cores (diameter *d* = 3.7 nm). Briefly, 1.5 x 10 $^{-7}$ moles of dried *ZB* CdSe were taken into a 25 ml four-necked flask with 5 mL OAc (0.016 moles) and 5 mL ODE. The mixture was degassed at 110 °C for 1 hr, followed by heating up and annealing at 240°C under Ar flow for 1.5 hr. Figure S7 (c-d) shows the change in UV-Vis absorption spectra during the course of the annealing process by sampling out aliquots at regular intervals. Considerable etching of the CdSe core in presence of excess OA ligand in the reaction medium at the initial stages is observed, followed by ripening with the increase of temperature is depicted by the shift of λ_{Abs}.

Supporting Figures

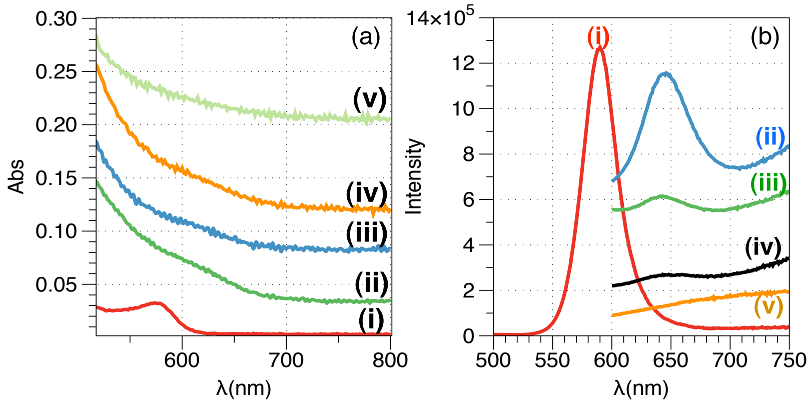

Figure S1: UV-vis (a) and PL emission (b) results characterizing the gQD growth at *ZB*-core at *n* = 0 (i) 4 (ii), 8 (iii), 12 (iv) and 18 (v). PL excitation carried out at 400 nm.

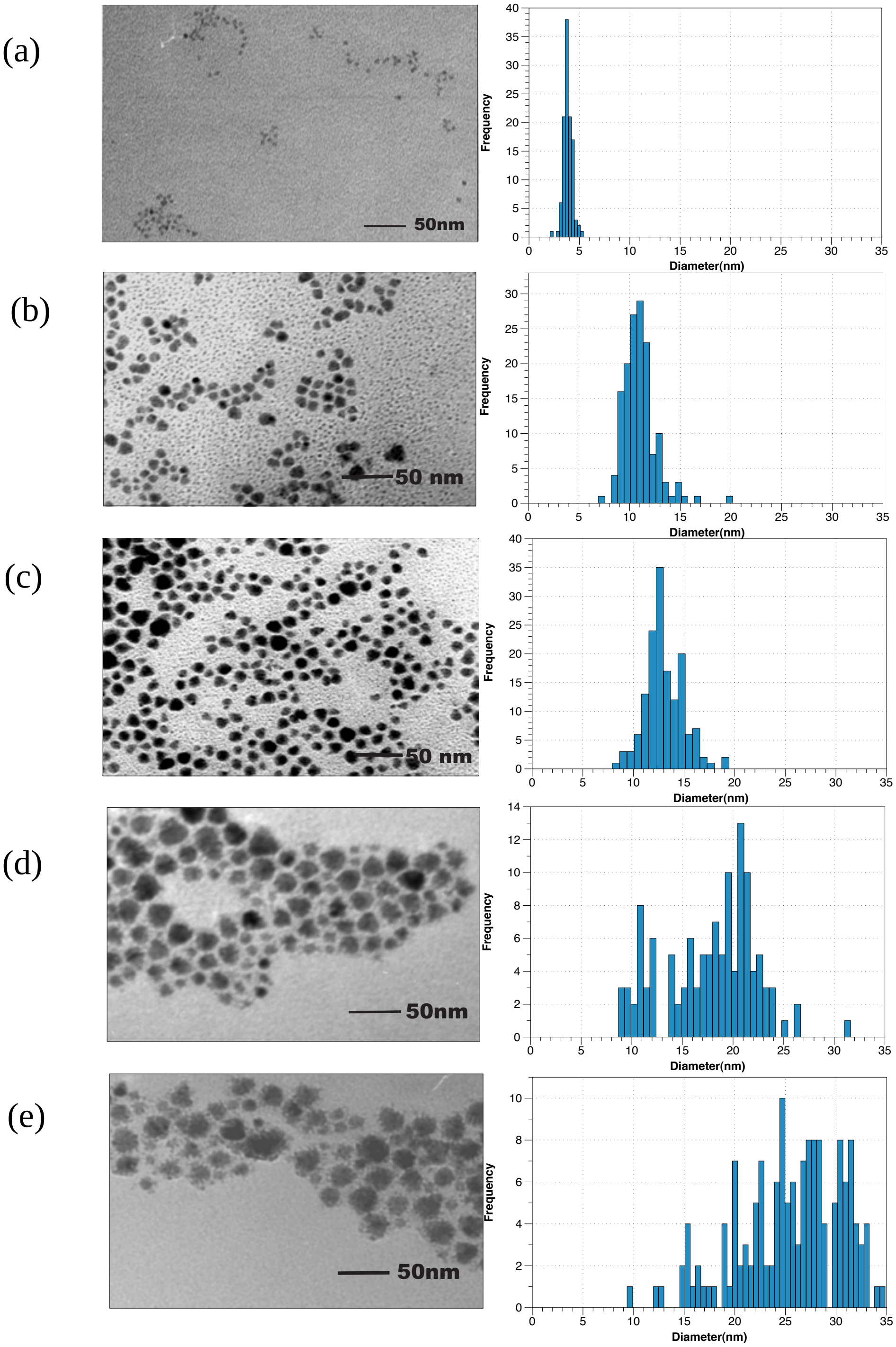

Figure S2: Representative TEM micrographs and size distribution of the *ZB*-core (d = 3.8 ± 0.4 nm) (a), and gQD at shell growth layers of n = 4 (d = 10.9 ± 1.6 nm) (b), 8 (d =13 ± 1.9 nm) (c), 12 (d = 17.7 ± 4.9 nm) (d) and 18 (d = 25.7 ± 5.3 nm).

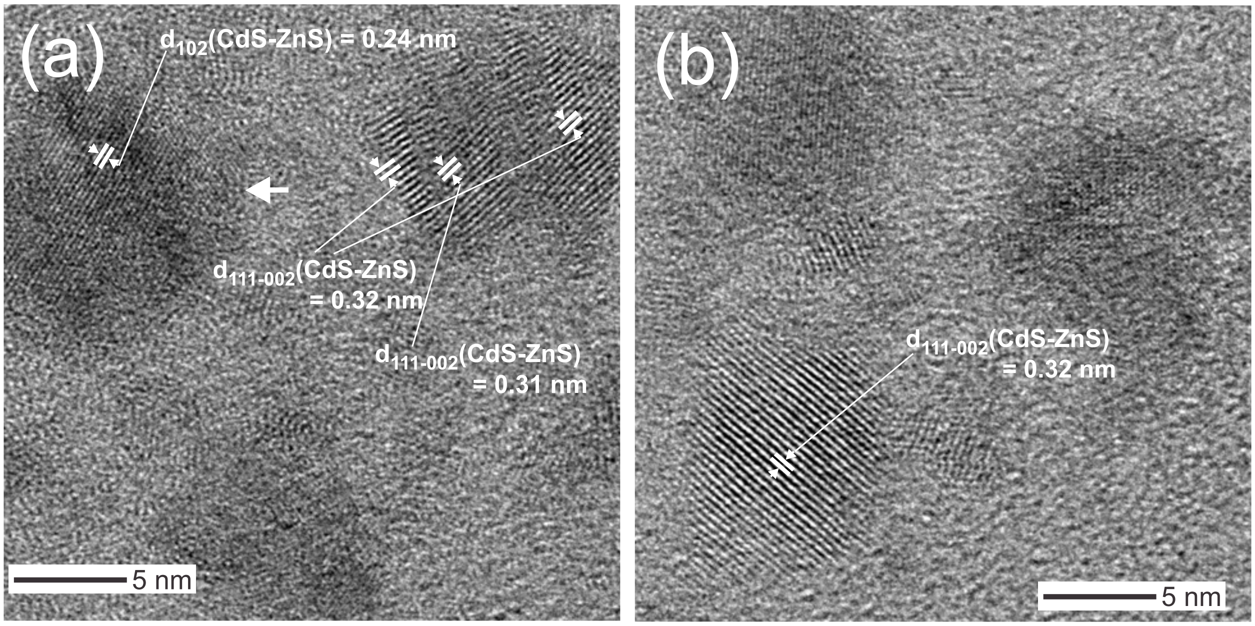

Figure S3: Additional HRTEM micrographs (a-b) of the gQD products at *n* = 18 using ZB-cores. Inserted arrows highlight crystalline protrusions.

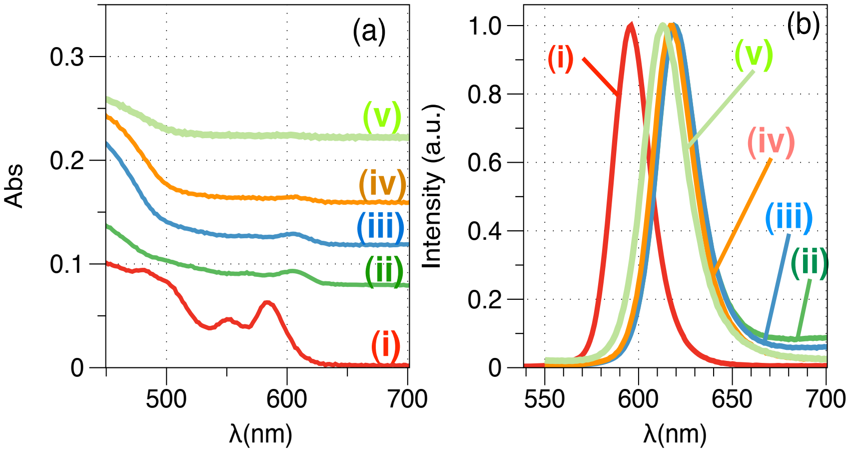

Figure S4: Representative UV-vis (a) and PL emission (b) results characterizing the gQD growth at *W*-core at *n* = 0 (i) 4 (ii), 8 (iii), 12 (iv) and 18 (v). PL excitation carried out at 400 nm.

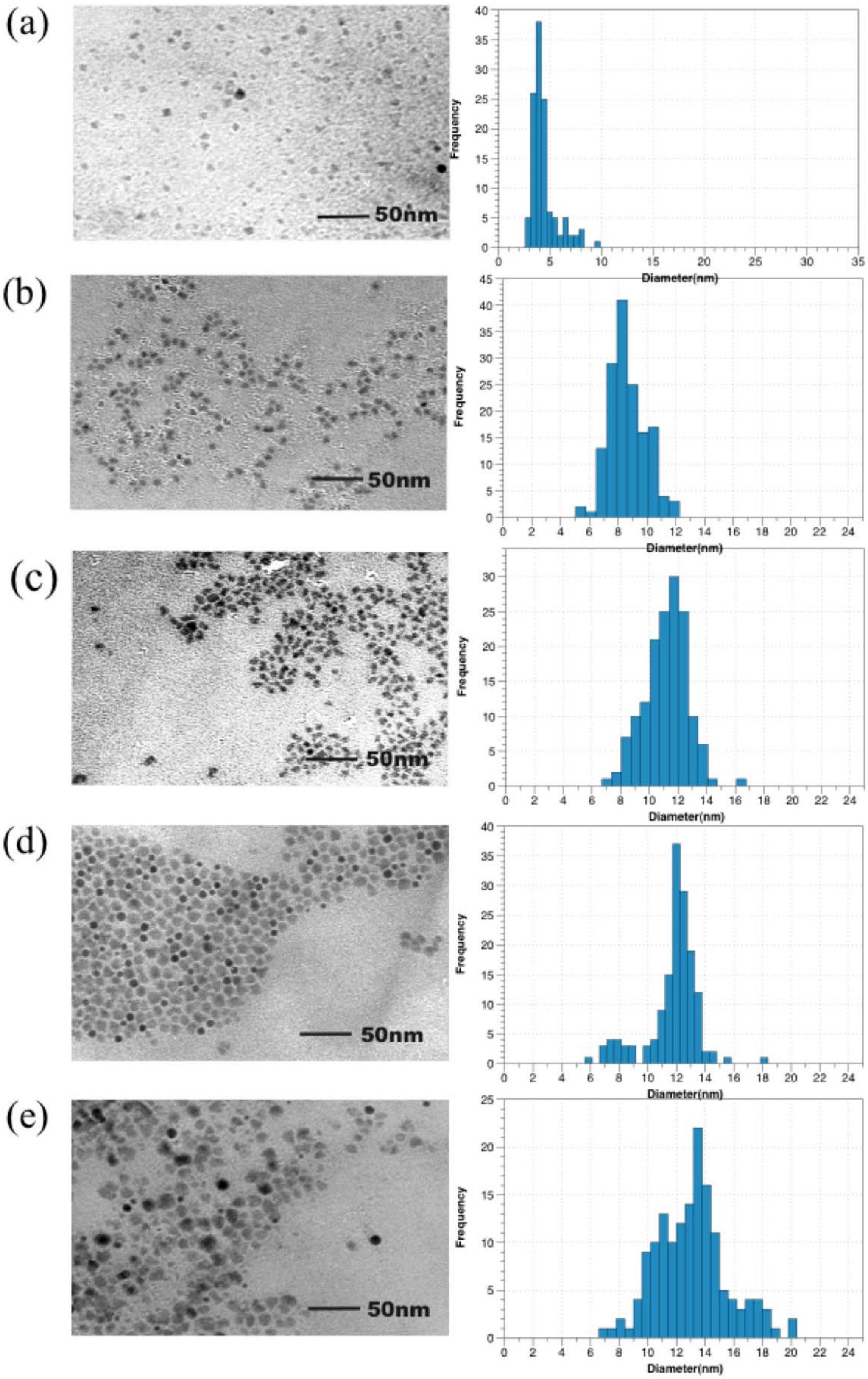

Figure S5: Representative TEM micrographs and size distribution of the *W*-core (d = 4.4 ± 0.9 nm) (a), and gQD at shell growth layers of n = 4 (d = 8.6 ± 1.2nm) (b), 8 (d = 11.3 ± 1.4nm) (c), 12 (d = 11.8 ± 1.8 nm) (d) and 18 (d = 13.1 ± 2.5 nm) (e).

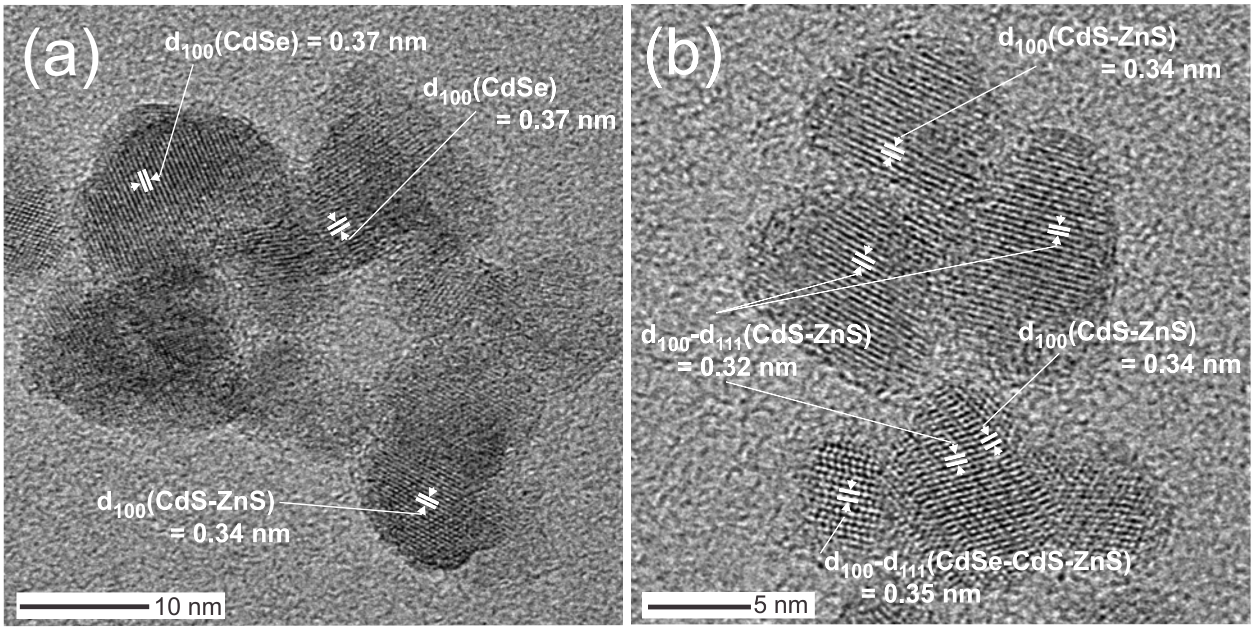

Figure S6: Additional HRTEM micrographs (a-b) of the gQD products at *n* = 18 using *W*-cores. Inserted arrows highlight crystalline protrusions.

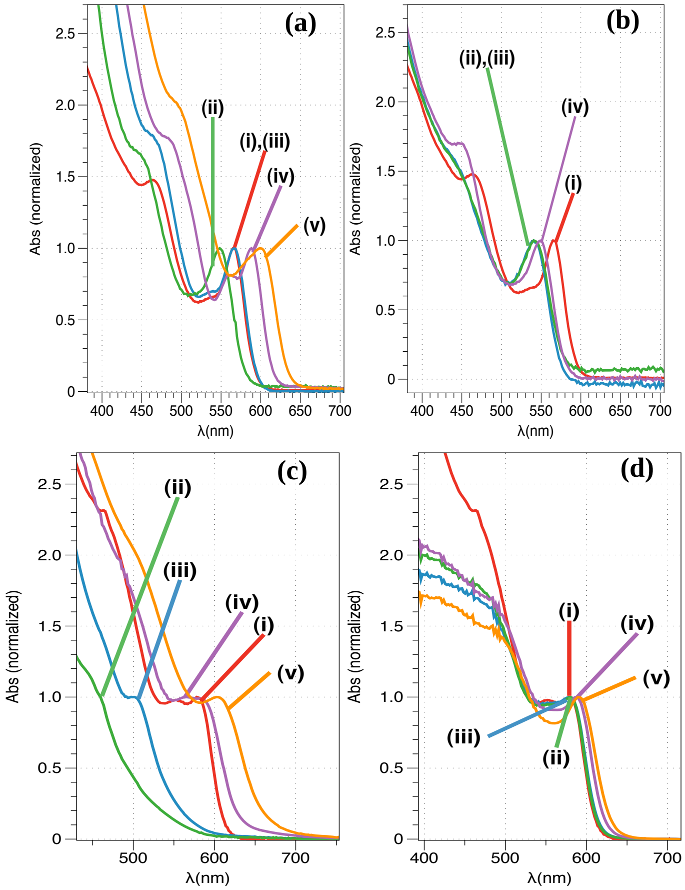

Figure S7: (a-b) UV-vis spectra monitoring of *W*-CdSe cores during annealing in excess OAc (a) or DOA (b) from room temperatures (i), to 110°C for 1h (ii), to 190°C for 1hr (iii), to 240°C for 0.5h (iv) and 1.5 hr (v). (c-d) Similar UV-vis monitoring for annealing of *ZB*-CdSe core in excess OAc (c) and DOA (d) for similar temperatures and annealing times.

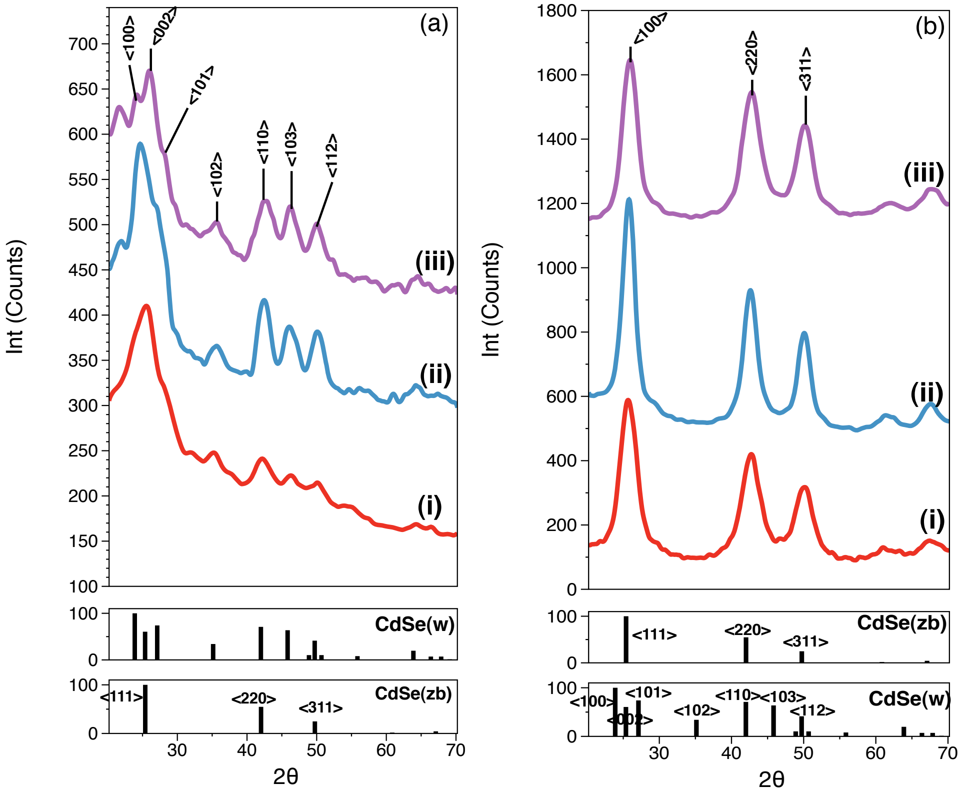

Figure S8: Powder XRD results characterizing the *W*- (a) and *ZB*- (b) CdSe cores (i) after completing the annealing cycle described in Fig. S7 with excess OAc (ii) and excess DOA (iii). CdSe (*W*, *ZB*) standards are provided for reference. XRD offset vertically for clarity.