Multiple wurtzite twinning in CdTe nanocrystals induced by methylphosphonic acid

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Supporting Information

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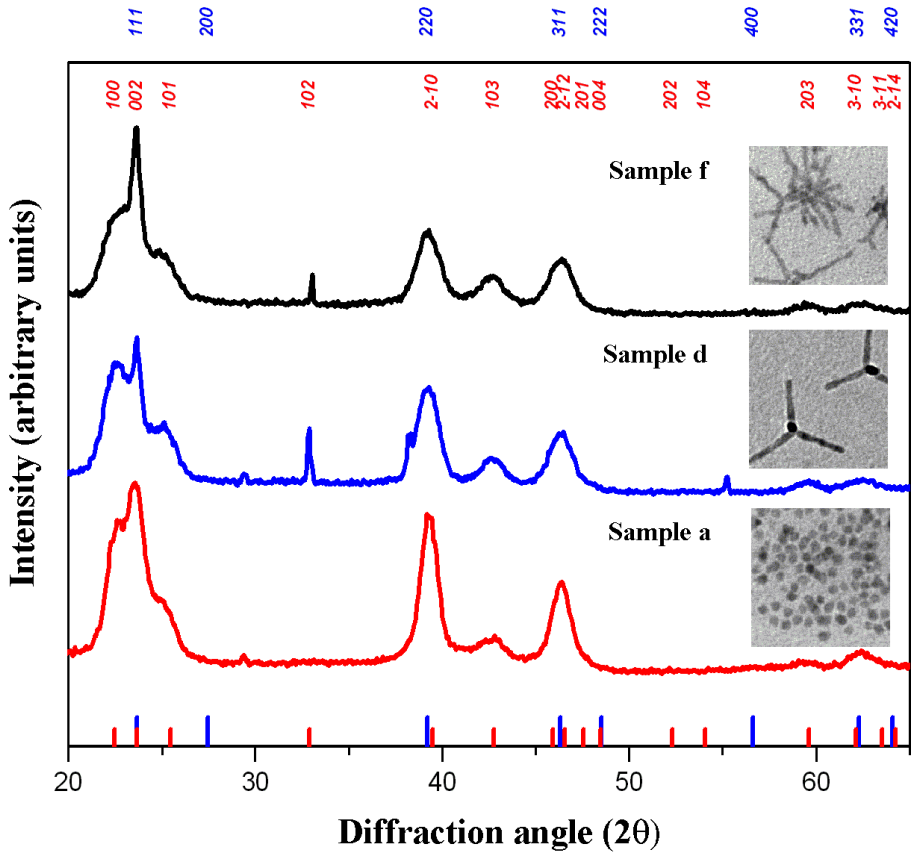
Impurities in old batches of Octadecylphosphonic acid

The impurities previously present in ODPA, as declared by the vendor (Polycarbon Industries Inc.), were the following: ethyl phosphonic acid, ethyl esters of ethyl phosphonic acid (mono and di-esters), octadecyl esters of ethyl phosphonic acid (mono and di-esters), mixed esters of the above, ethyl esters of ODPA (mono and di-esters), octadecyl esters of ODPA (mono and di-esters), mixed esters of the above. It is likely that other vendors provided ODPA with similar impurities in the past.

Diffraction Data

Figure S1. We report here the XRD spectra of the samples shown in Figure 2a, 2d and 2f of the manuscript. These samples are prepared at the following MPA:OPDA ratios: (a) 0.026; (d) 0.081; (f) 0.111. At the bottom of the plot, on the x-axis, the red lines correspond to the positions of the peaks in bulk wurtzite CdTe, while the blue lines correspond to the positions of the peaks in bulk sphalerite CdTe. On the top of the plot, these diffraction peaks are indexed.



Model of a multiple wurtzite twinned nanocrystal (a dipod) viewed at different tilts

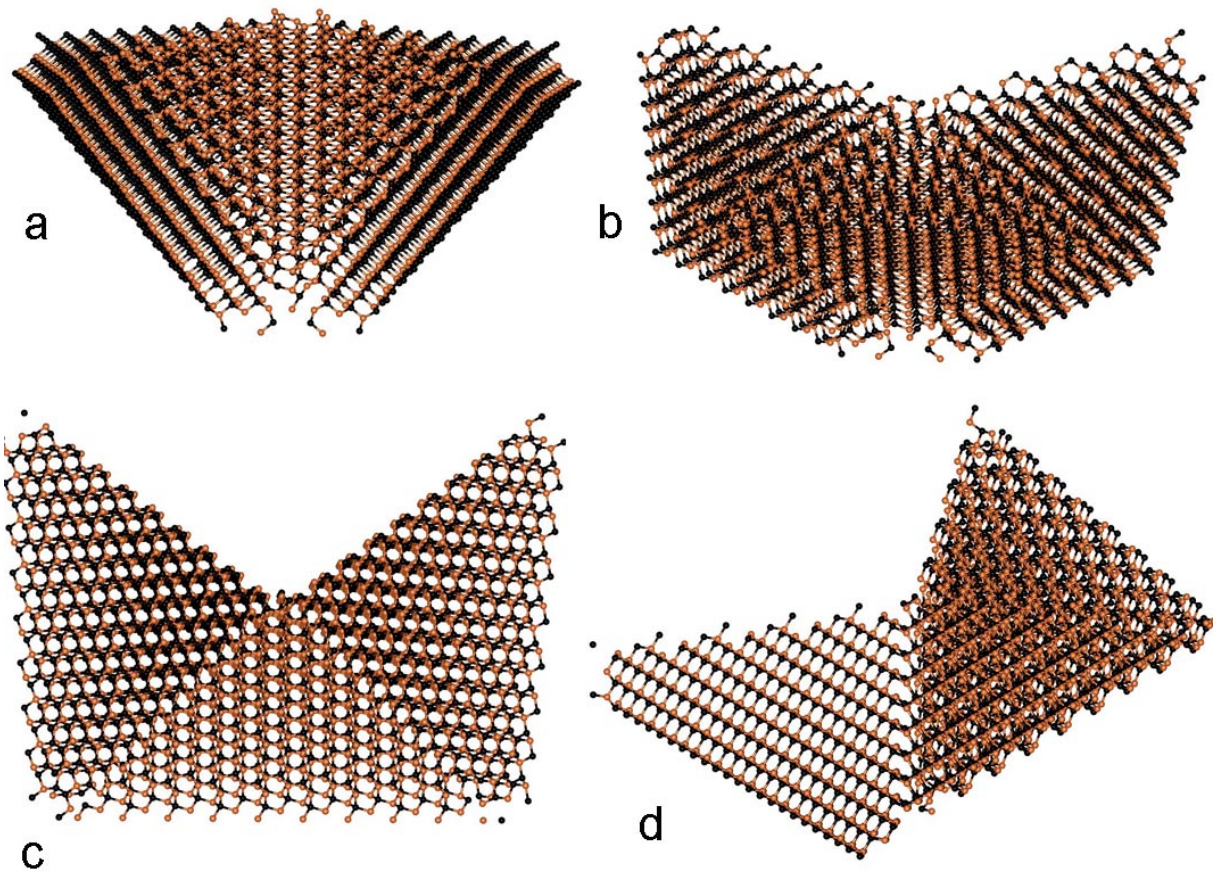


Figure S2. Different views of a dipod based on a multiple wurtzite twinned nanocrystal (the one used for the HRTEM image simulation, see figure 6 of the manuscript). The images have the purpose to show that the unambiguous identification of a given type of twin plane is difficult to achieve, unless the crystal has a particularly favourable orientation. This favourable orientation is for instance the one depicted in Figure S2-d. In this case, the domain on the left and the central domain are both viewed along their $(10\bar{1}0)$ zone axes (the same as in figure 1d of the manuscript). Unfortunately, the central domain overlaps with the domain on the right and this makes the view less clear. Moreover, this orientation is rather difficult to achieve in a real TEM experiment, as the domain on the right should be pointing upwards (or downwards), while the domain on the left should lie flat. The atomic positions near the twin boundaries have not been relaxed, as opposed to

the case depicted in figures S3 and S4. As a consequence, some stretched or compressed bonds are present in the model (See also the structure file of the dipod included as supporting material).

Geometrical details of the LDA-DFT computations

We report here the geometrical parameters of the *orthorombic* supercell used to model the $11\bar{2}2$ twin boundary, along with the atomic positions in the cell. The supercell used to model the twin boundary contained 64 atoms (for a total of 576 valence electrons) and was adapted from the supercell used by Yan and coworkers to model the same type of defect in ZnO. If we indicate with a and b the lattice parameters for the hexagonal cell of bulk wurtzite CdTe, the lattice parameters for the supercell are calculated as follows:

$$l_1 = 8a \cdot \cos(\arctan(a/c))$$
$$l_2 = a/\sin(\arctan(a/c))$$
$$l_3 = 2a \cdot \cos(\pi/6)$$

As can be seen from Figures S3 and S4, each cell intersects two twin planes. Therefore, the twin plane formation energy is calculated as follows:

$$E_{boundary} = \left(E_{\sup ercell} - E_{bulk}\right)/2A$$

Here, E_{bulk} corresponds to the energy per unit cell of bulk wurtzite CdTe, and *A* is the twin plane area intersected by a single supercell, which corresponds to $l_2 \cdot l_3$.

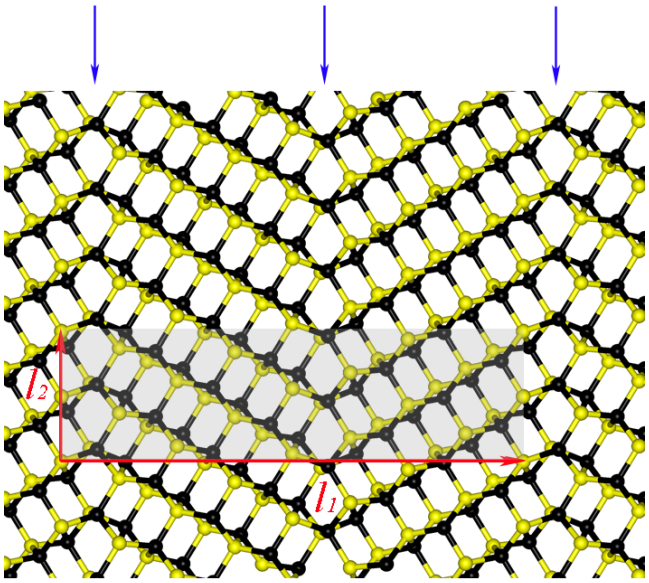


Figure S3. Lattice used to model the $11\bar{2}2$ twin boundary, side view. The shaded area corresponds to a single supercell. It contains 64 atoms (32 Cd and 32 Te). The blue arrows indicate the positions of the twin planes in the lattice.

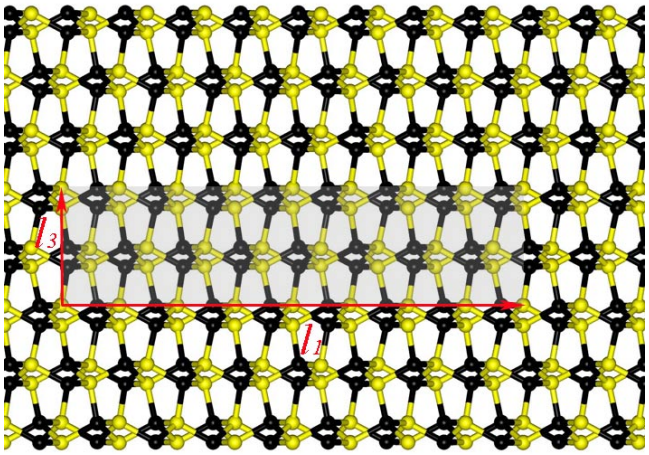


Figure S4. Lattice used to model the $11\bar{2}2$ twin boundary, top view. The shaded area corresponds to a single supercell.

Cell parameters: l_1= **31,167 Å**
l_2= **8,777 Å**
l_3= **7,897 Å**

Atomic positions in the cell (along l_1, l_2, and l_3, respectively):

Te	0.484792276	0.633448318	0.324374777
Te	0.233392040	0.604490987	0.166535178
Te	0.733472620	0.515843578	0.166811465
Te	0.608373364	0.797662140	0.165787235
Te	0.233379049	0.104510736	0.333489332
Te	0.173644375	0.468289588	0.666978980
Te	0.858289392	0.240028713	0.169650262
Te	0.985103391	0.481757787	0.323249028
Te	0.298257572	0.746371744	0.666868506
Te	0.357990061	0.880996596	0.169781022
Te	0.484790563	0.133538251	0.175475216
Te	0.985108023	0.981646755	0.176654796
Te	0.923687838	0.089965769	0.665745972
Te	0.108712461	0.316856571	0.165816202
Te	0.423143530	0.029659331	0.664457596
Te	0.048567065	0.213537898	0.663091435
Te	0.673477765	0.648150368	0.666419799
Te	0.798451074	0.372105969	0.666741280
Te	0.858281818	0.740041814	0.330316217
Te	0.923696982	0.589943934	0.834213598
Te	0.733463989	0.015816978	0.333195193
Te	0.548306016	0.401534209	0.837154643
Te	0.423155068	0.529593575	0.835656800
Te	0.673470407	0.148162723	0.833614020
Te	0.798433581	0.872113709	0.833210129
Te	0.608375126	0.297563898	0.334124197
Te	0.298266182	0.246378969	0.833223467
Te	0.548316701	0.901520767	0.662924548
Te	0.357988170	0.380999617	0.330297088
Te	0.048557743	0.713554190	0.836929973
Te	0.173628787	0.968322287	0.833040397
Te	0.108698262	0.816892118	0.334182017
Cd	0.686618827	0.243985207	0.167595774
Cd	0.436411445	0.410196024	0.165305761
Cd	0.626940885	0.376372416	0.669010243
Cd	0.876104177	0.818334074	0.664720095
Cd	0.561195117	0.525452266	0.164364859
Cd	0.311289989	0.653441076	0.332069133
Cd	0.811383223	0.967764761	0.167411188
Cd	0.311295934	0.153412033	0.168008686
Cd	0.186642217	0.876791973	0.168241434
Cd	0.251591100	0.018322254	0.666437799
Cd	0.000573802	0.493013763	0.669020638
Cd	0.811375055	0.467741180	0.332571203
Cd	0.936381515	0.705155239	0.165893797
Cd	0.375930490	0.302332568	0.664695957
Cd	0.061515589	0.588568611	0.163542439
Cd	0.127095141	0.239595986	0.830498095
Cd	0.436356734	0.910155787	0.334713877
Cd	0.561189496	0.025562910	0.335637689
Cd	0.375940155	0.802281292	0.835506562
Cd	0.000544187	0.992992967	0.831080659
Cd	0.876120646	0.318287959	0.835262600
Cd	0.061511231	0.088560233	0.336334779
Cd	0.686605102	0.743942927	0.332367216
Cd	0.751510776	0.100169144	0.667013214
Cd	0.936379525	0.205231275	0.334049430
Cd	0.751512256	0.600128771	0.832996492
Cd	0.186638706	0.376619323	0.331688504
Cd	0.626923189	0.876364310	0.830986891
Cd	0.251598903	0.518360155	0.833592253
Cd	0.500329278	0.122571993	0.830104151
Cd	0.500325435	0.622319394	0.670091488
Cd	0.127091959	0.739548454	0.669596226