Supporting Information

Oriented attachment growth of wurtzite ZnTe nanoplatelets from metastable magic-size nanoclusters

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DFT calculations of surface energies.

We employed the first-principles method based on the density function theory (DFT) and the first-principles pseudo-potential method to investigate the surface energy of ZnTe NPLs. The DFT calculations were carried out by the Vienna Ab Initio Simulation Package (VASP) code with the projector-augmented wave (PAW) method using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.¹⁻³ The plane wave cutoff was set as 500 eV, with the total energy convergence at 10⁻⁶ eV for the self-consistent iterations. The Gaussian smearing method with σ =0.05 eV was considered for Brillouin-zone integration and the geometry optimizations were stopped until the forces on the atoms were < 0.01 eV/Å. We used the finite-sized slab technique to investigate the surface energy of ZnTe NPLs. The slab models were built from the wurtzite ZnTe crystal structure determined by Kart *et al.*⁴ The lattice parameters of bulk wurtzite ZnTe, optimised with a 12×12×6 k-point grid, were a=b=3.996Å, c=6.626 Å, which are in good agreement with experimental values. According to the exposed surfaces of ZnTe NPLs, four different surfaces that are related to the growth of ZnTe NPLs were studied: two non-polar surfaces, i.e. (110) and (100), and two polar surfaces (Zn-terminated (002) and Te-terminated (00²) (Fig. S5). All these slab models in periodical super cell were separated by a vacuum region of 20 Å thick. Each slab of nonpolar surface models contains four zinc and four tellurium atoms within each Zn-Te layer in a repeated slab configuration, whereas for the polar surface models each one contains eight zinc or eight tellurium atoms within each Zn-Te layer in a repeated slab configuration. The surface free energy of the particular slab with a repeated geometry is given by the equation:

$$\sigma = \left(E_{slab} - \sum_{i} n_{i} \mu_{i}\right) / 2A$$

where E_{slab} is the total energy of the particular slab; n_i and μ_i are the number of atoms and the chemical potential of the *i*th constituent of the slab, respectively; A is the surface area. The factor of 2 accounts for two equivalent surfaces in the particular slab. The surface energies of non-polar surface were found to converge with slab thickness and were converged to smaller than 0.001 eV/Å² with respect to eight-layer slab thickness. We therefore used the eight-layer thick ZnTe slabs for studying the surface energy of (110) facet and of (100) facet with 3×6×1 and 6×3×1 Monkhorst-Pack k-point grid, respectively. Special care should be taken with the computational treatment of the polar surface, in particular to avoid the build-up of an overall artificial dipole field. Here, we adopted symmetric structures of the nine-layer slab model for the Zn-terminated (002) and Te-terminated ($00^{\overline{2}}$) surfaces as shown in Figure S5. The surface free energy equation is a thermodynamic function of the chemical potential of the constituent in the slab. Therefore, the surface energy is governed by the chemical potentials of the constituents of the slab, i.e. μ_{Zn} and μ_{Te} . Invoking equilibrium of ZnTe bulk, $\mu_{Zn+} \mu_{Te} = E_{bulk}^{ZnTe}$, the dependence of the surface free energy on the chemical potential can be further simplified by eliminating μ_{Te} , leading to a dependence on μ_{Zn} only. We restricted the values of μ_{Zn} to μ_{bulk}^{Zn} + $\Delta H_f(ZnTe) \le \mu_{Zn} \le \mu_{bulk}^{Zn}, \text{ i.e. } \Delta H_f(ZnTe) \le \Delta \mu_{Zn} = \mu_{Zn} - \mu_{bulk}^{Zn} \le 0, \text{ according to thermodynamically}$ allowed ranges. These ranges were determined by the assumed constraints, $\mu_{Zn} \leq \mu_{bulk}^{Zn}$ and $\mu_{Te} \leq \mu_{bulk}^{Te}$, which means that Zn and Te do not crystalline on the surface. In addition, the fromation enthalpy of bulk ZnTe was given by $\Delta H_f(ZnTe) = E_{bulk}^{ZnTe} - \mu_{Zn} - \mu_{Te}$. We have calculated the surface energy as linear function of μ_{Zn} , -2.360 eV $\leq \Delta \mu_{Zn} \leq 0$. The chemical potential

 $\Delta \mu_{Zn} = 0$, i.e. $\mu_{Zn} = \mu_{bulk}^{Zn}$, represents the Zn-rich condition while $\Delta \mu_{Zn} = -2.360$ eV represents the Terrich condition.

DFT calculations for simulating UV-Vis absorption spectra of (ZnTe)₃₄ isomers and the growth of wurtzite ZnTe NPLs.

We used DFT as implemented in the Gaussian 09 to simulate the growth of ZnTe NPLs. We have chosen the hybrid density functional B3LYP with def2-svp basis set. UV-Vis absorption spectra of model systems were calculated at the time-dependent density functional theory (TDDFT) level. The convergence thresholds for total energy and the forces were set to 10^{-8} eV and 10^{-3} eV/Å respectively. Solvent effects were simulated using the polarized continuum model (PCM) with the appropriate dielectric constant-propylame, as incorporated the Gaussian-09 software package.



Figure S1. ¹H NMR spectrum of TBP and TBP-Te.



³¹P

Figure S2. ³¹P NMR spectrum of TBP and TBP-Te.



Figure S3. TEM image of stacking self-assembled ZnTe MSC-323.



Figure S4. HAADF-STEM image of self-assembled ZnTe MSC-398.



Figure S5. The SAED profile fitted by PASAD tools. Red curve (reduced background), green curve (residual plot), blue curve (final fitted profile).

k (nm ⁻¹)	Fitted lattice spacings d (Å)	Miller indices (hkl)	Standard lattice spacings d (Å) (JCPDS No. 19-1482)	Lattice contraction (%)
2.72	3.47	(002)	3.55	2.2
2.95	3.24	(101)	3.31	2.1
3.78	2.50	(102)	2.57	3.1
4.19	2.11	(110)	2.16	2.3
4.86	1.96	(103)	2.00	2.0
5.34	1.79	(200)	1.86	3.7
6.65	1.44	(203)	1.46	1.4

Table S1. Lattice spacings of ZnTe NPLs fitted by using PASAD tools.



Figure S6. The fitted SAED profile by using PASAD tools annotated to the original SAED pattern with labeled Miller indices.



Figure S7. The slab model structures of (110), (100), Zn-terminated (002) and Te-terminated (00

²) surfaces of wurtzite ZnTe NPLs.

References

- 1 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
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- P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186. 3
- C. Soykan and S. Özdemir Kart, J. Alloy. and Compd., 2012, 529, 148-157. 4