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Supplementary Materials for

Ligand induced shape transformation of thorium dioxide nanocrystals

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1. Convergence of the surface energies

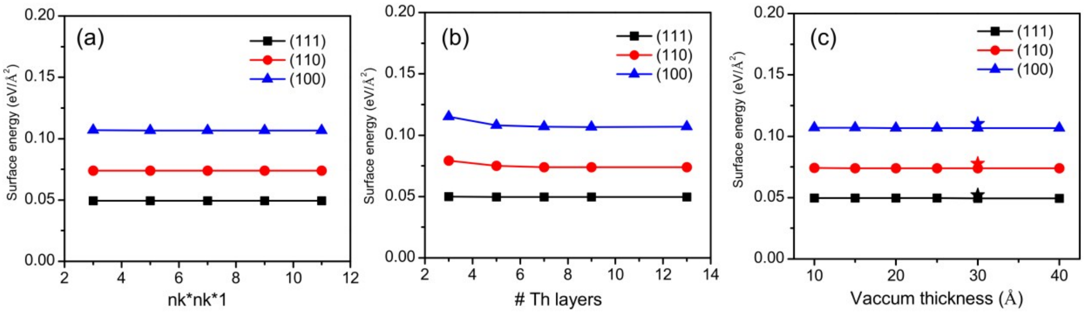

Figure S1. Convergence of surface energies with respect to the number of k-points (a), thickness of the slab (b), as well as the thickness of the vacuum region (c).

	$\gamma_{(111)}$	$\gamma_{(110)}$	$\gamma_{(100)}$
Rak et al. [1] *(GGA-PBE)*	0.79 J/m^2	1.18 J/m^2	
Alexandrov et al. [2] *(GGA-PBE)*	0.8 J/m^2	1.10 J/m^2	1.6 J/m^2
Skomurski et al.[3] *(GGA-PW91)*	0.72-0.81 J/m^2	0.98-1.30 J/m^2	1.55-1.75 J/m^2
This work	50 meV/Å^2 (~0.801 J/m^2)	75 meV/Å^2 (~1.202 J/m^2)	110 meV/Å^2 (~1.762 J/m^2)

Table S1. A comparison of the surface energies from our calculations and the reported values in the literatures.

References

1. Z. Rák, R. C. Ewing and U. Becker, *Surface Science*, 2013, **608**, 180-187.
2. V. Alexandrov, T. Y. Shvareva, S. Hayun, M. Asta and A. Navrotsky, *The Journal of Physical Chemistry Letters*, 2011, **2**, 3130-3134.
3. F. Skomurski, L. Shuller, R. Ewing and U. Becker, *Journal of Nuclear Materials*, 2008, **375**, 290-310.

2. Ligand model

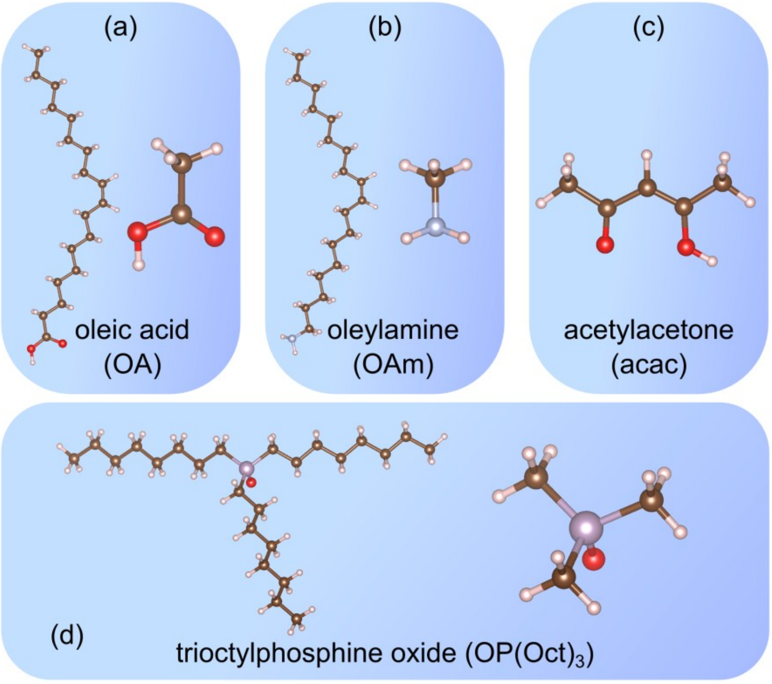

Figure S2. Surfactant ligands and the corresponding small ligand models used in our simulations.

3. *Steric correction to the binding energies* $\Delta_{correction}$

The steric correction to the binding energy was calculated using

$$\Delta_{correction} = E_{\Theta} - E_{\Theta \to 0}$$

where $E_{\Theta \to 0}$ is the energy of a ligand when the coverage Θ is closer to 0, and E_{Θ} is the energy of the ligand at coverage of Θ. $\Theta \to 0$ represents that a ligand is far away from the other ligands (one ligand in the area of 3×3 nm^2 in our calculations), thus there is no interaction between the ligands. When the coverage of the ligand increases as shown in Figure S3 for OA, the distance between the ligands gets smaller, and the interaction between the ligands appears, which changes the energy of the ligand to E_{Θ}.

Figure S4 shows the calculated steric correction for OA/OAm, acac, and OP(Oct)$_3$. From Figure S4(a), it is seen that when the coverage of OA ligands is smaller than 4 ligands/nm^2, the correction term is negative with the inclusion of the vdW interaction, which corresponds to the attraction between the ligands. When the coverage of OA is larger than 4 ligands/nm^2, the correction term increases rapidly, corresponding of the repulsion between the ligands. Since OA and OAm have the same hydrocarbon tails, so they are expected to have the same steric correction. For acac ligand, the correction term increases rapidly when the coverage is larger than 3 ligands/nm^2. For OP(Oct)$_3$, the correction term increases quickly when the coverage is larger than 1.5 ligands/nm^2.

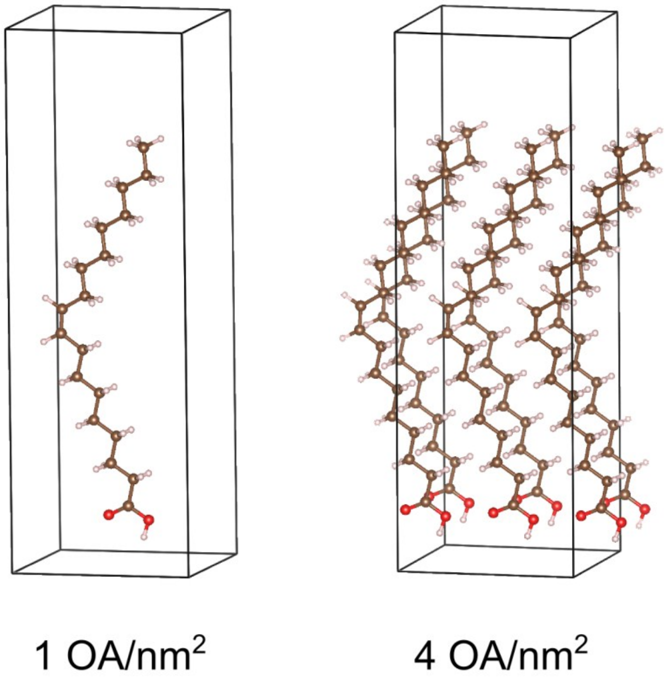

Figure S3. Configurations for calculating the steric correction ($\Delta_{correction}$) to the binding energies.

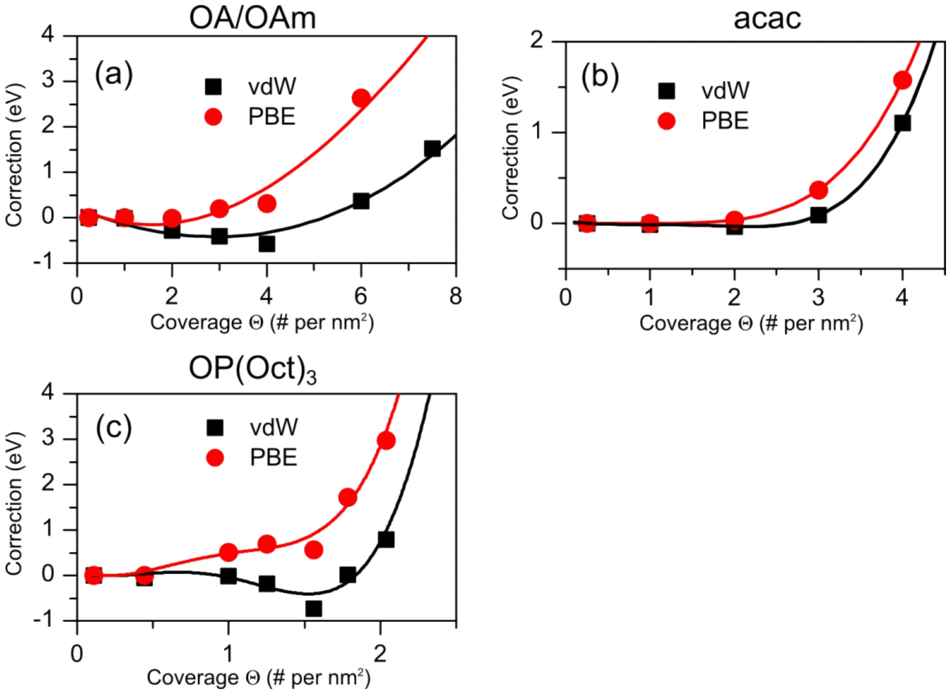

Figure S4. Calculated steric correction to the binding energy. The black squares are the results at GGA-PBE level of theory, the red dots are the results with the inclusion of van der Waals (vdW) interactions. The results with the vdW interactions were used for the calculation of surface energies in this paper.

4. Adsorption configuration of ligands on the surfaces

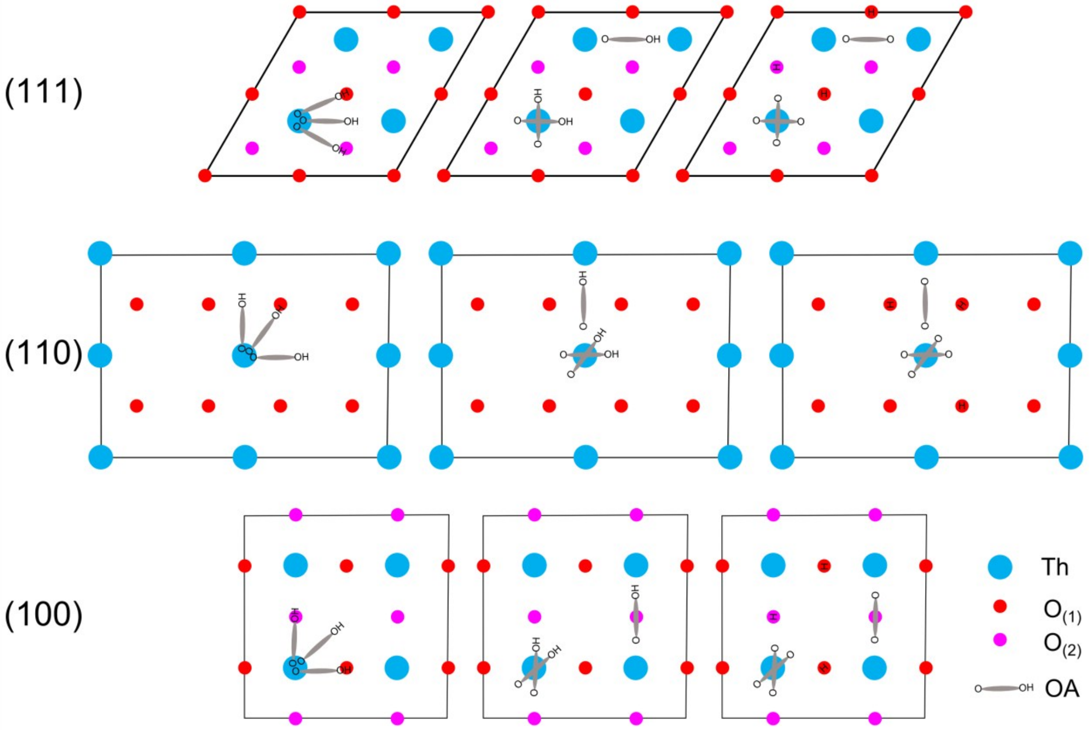

Figure S5. Initial adsorption configurations of OA ligands on different surfaces of ThO_2*. For acac ligand, the similar staring configurations were used. Nine different configurations were considered on each surface. The* 1^{st} *layer and* 2^{nd} *layer of O atoms are labeled as* $O_{(1)}$ *and* $O_{(2)}$*, respectively*

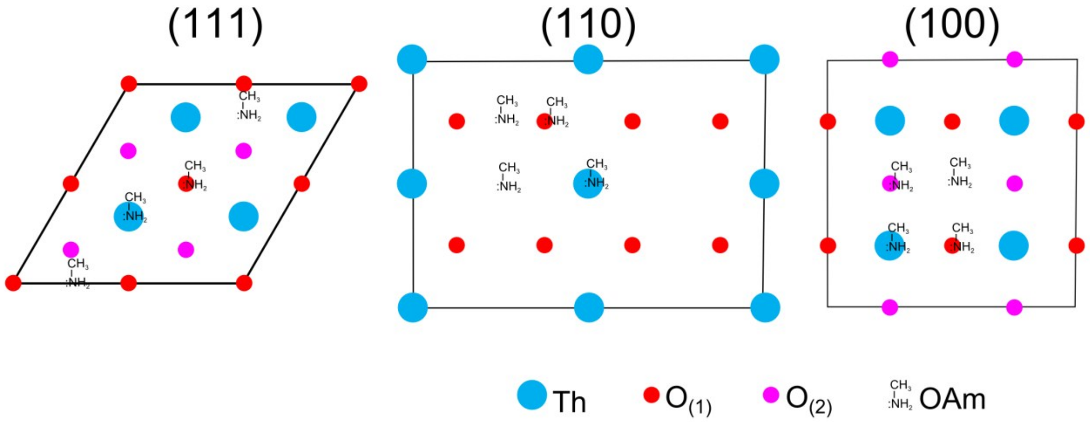

Figure S6. Initial adsorption configurations for methylamine *on different surfaces of* ThO_2*. Four different adsorption configurations were considered for each surface. The* 1^{st} *layer and* 2^{nd} *layer of O atoms are labeled as* $O_{(1)}$ *and* $O_{(2)}$*, respectively.*

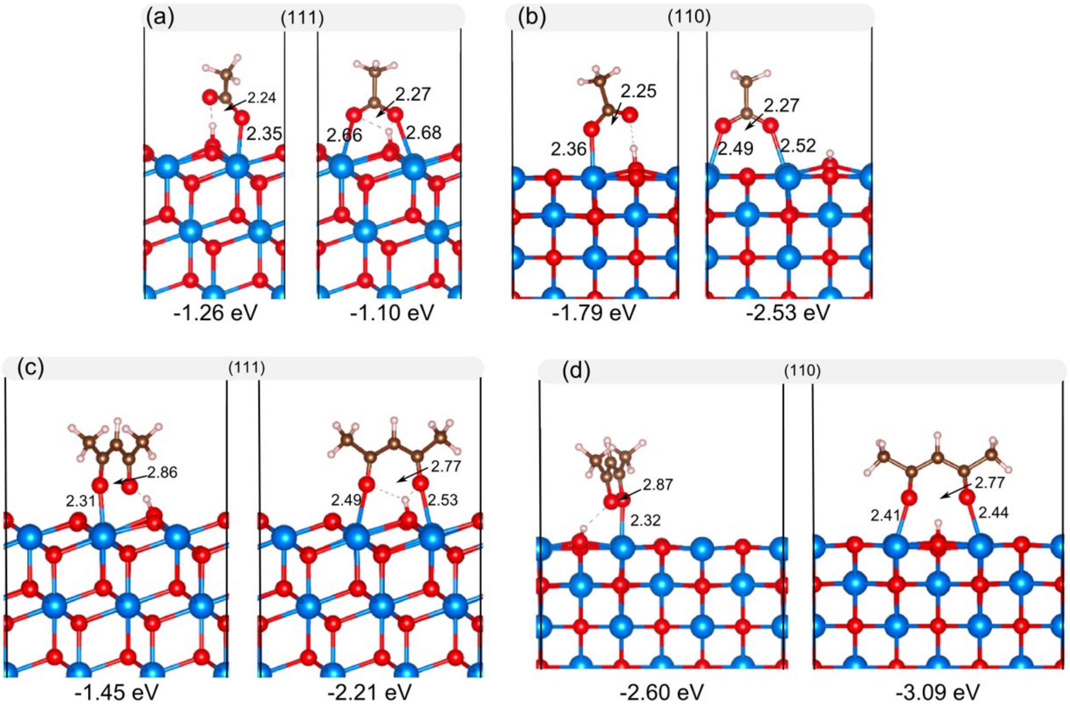

Figure S7. Comparison of the adsorption configurations of acetic acid (a, b) and acetylacetone (c, d) on (111) and (110) surfaces in the monodentate or bidentate bridging form. The O_{ligand}*-*O_{ligand} *distances of the ligands (illustrated by arrows) and bond length of* O_{ligand}*-*$Th_{surface}$ *are in unit of Å.*

		acetic acid		*acetylacetone*	
O_{ligand}-O_{ligand}	Free-standing molecule	2.28		2.65	
		monodentate	*bidentate*	*monodentate*	*bidentate*
	On (111)	2.24	2.27	2.86	2.77
	On (110)	2.25	2.27	2.87	2.77
O_{ligand}-$Th_{surface}$	On (111)	2.35	2.66, 2.68	2.31	2.49, 2.53
	On (110)	2.36	2.49, 2.52	2.32	2.41, 2.44
Minimum O_{ligand}-$O_{surface}$	On (111)	2.61	2.62	2.67	2.59
	On (110)	2.67	2.93	2.75	2.94

Table S2. Summary of the O_{ligand}*-*O_{ligand} *distances of the ligands, the* O_{ligand}*-*$Th_{surface}$ *bond length and the minimum* O_{ligand}*-*$O_{surface}$ *distances for ligands on the (110) and (111) surfaces of* ThO_2*. The length is in unit of Å.*