

Supplementary information

Theoretical Study on the Surface Reaction of Tetrakis(dimethylamino)titanium on Titanium Oxide

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The energy of H₂O formation from surface hydroxyl groups

The energy of H₂O formation from surface hydroxyl groups ($E_{H_2O\text{ formation}}$) was calculated using the following equation:

$$E_{H_2O\text{ formation}} = E_{\text{after } H_2O\text{ formation}} - E_{\text{before } H_2O\text{ formation}} \quad (1)$$

where $E_{\text{after } H_2O\text{ formation}}$ is the total energy after the OH and H groups on the surface combine to form an H₂O molecule, and $E_{\text{before } H_2O\text{ formation}}$ is the total energy of the initial surface.

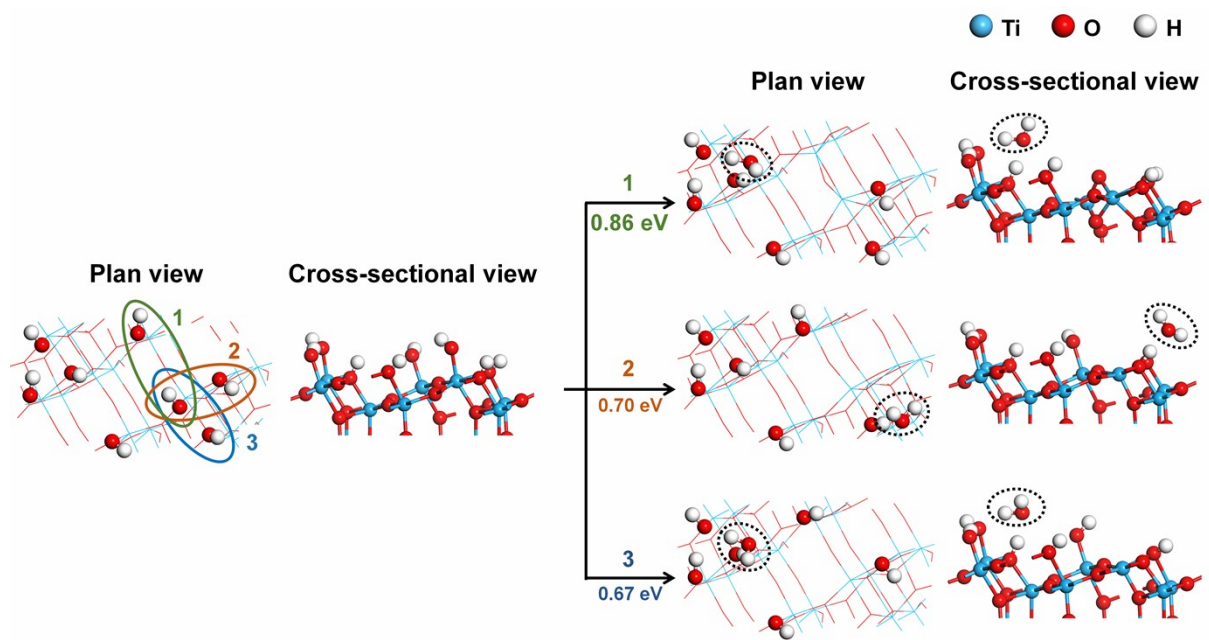


Fig. S1 The energy of H₂O formation from surface hydroxyl groups.

Temperature-dependent free energy change for the desorption of H₂O

We considered the formation of the H₂O from the structure (3) at an elevated temperature in Fig. S1. We then calculated the free energy of the initial substrate, the substrate after H₂O release, and the H₂O molecule at a given temperature using DFT.¹ The pressure of H₂O was assumed to be 1 Torr. The change in Gibbs free energy (ΔG_T) was determined by the following equation:

$$\Delta G_T = G_{T \text{ substrate after H}_2\text{O release}} + G_{T \text{ H}_2\text{O}} - G_{T \text{ initial substrate}} \quad (2)$$

The temperature-dependent change in free energy for releasing an H₂O molecule is shown in Fig. S2. The release of H₂O from the OH-passivated surface was expected to be spontaneous at 298°C or higher temperatures. Therefore, we concluded that it was unlikely that more water molecules would be released at the ALD process temperature compared to 0K.

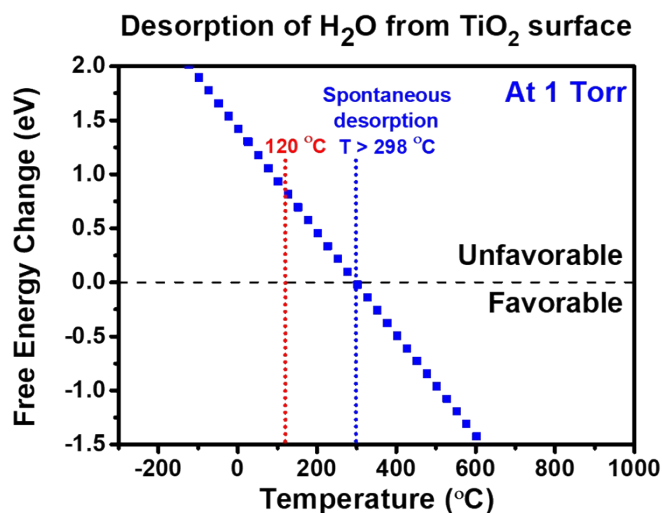


Fig. S2 The temperature-dependent free energy change for the desorption of an H₂O molecule at 1 Torr.

Slab thickness convergence

Surface energy (E_{surf}) of the hydroxylated surface slab model was calculated using the following equation:²

$$E_{surf} = \frac{(E_{slab} - nE_{bulk} - mE_{H2O})}{2A} \quad (3)$$

where the E_{slab} and E_{bulk} are the total energies of the bare slab and the bulk of TiO_2 , and m is the number of H_2O required to form the hydroxyl groups. The surface energy of hydroxylated TiO_2 almost converges at the two Ti layers, as shown in Fig. S3.

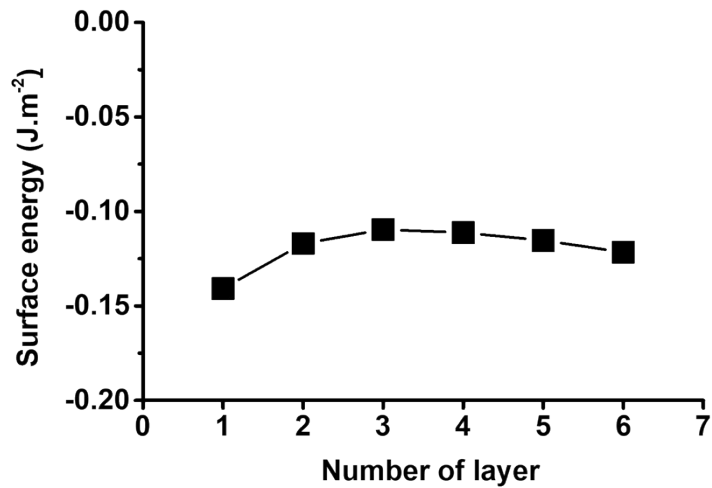


Fig. S3 The surface energy convergence on various layer thicknesses of the hydroxylated TiO_2 slab.

Adsorption energies (E_{ads}) of a TDMAT molecule on the optimized hydroxylated TiO_2 surface with various numbers of layers were calculated using the following equation:

$$E_{ads} = E_{phys} - (E_{slab} - E_{TDMAT}) \quad (4)$$

where the E_{phys} and E_{TDMAT} are the total energies of physisorbed TDMAT on the surface and a TDMAT molecule. The adsorption energies of TDMAT molecules converge at three Ti layers but almost converge at two Ti layers, as shown in Fig. S4.

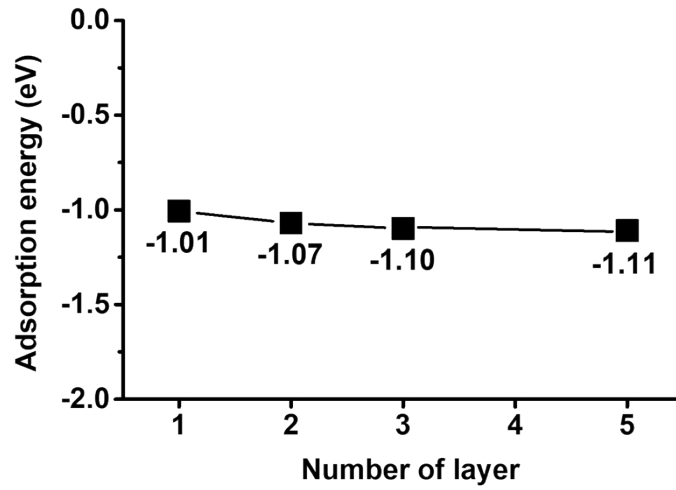


Fig. S4 The adsorption energy of a TDMAT molecule on various layer thicknesses of the hydroxylated TiO_2 surface. The bottom half layer was fixed.

References

- 1 S. Kim, R. Hidayat, H. Roh, J. Kim, H.-L. Kim, K. Khumaini, M. Park, J.-H. Seok, J. W. Park and W.-J. Lee, *J. Mater. Chem. C*, 2022, **10**, 6696–6709.
- 2 C. J. Lombard, C. G. C. E. van Sittert, J. N. Mugo, C. Perry and D. J. Willock, *Phys. Chem. Chem. Phys.*, 2023, **25**, 6121–6130.