

Supporting Information

Aqueous Growth of Titania Subnanoparticle: Understanding of the Ultrasmall Visible-light-absorbing Unit of $(\text{TiO}_2)_8(\text{H}_2\text{O})_{16}$

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Table S1. The energies (in eV) of 20 gas-phase structures in the testing set calculated by the NN-potential and DFT, respectively.

No	Energy _{NN} (eV)	Energy _{DFT} (eV)
1	-280.33	-279.38
2	-281.41	-280.48
3	-282.35	-281.52
4	-282.44	-281.55
5	-282.50	-281.72
6	-282.63	-281.73
7	-282.97	-281.80
8	-283.34	-281.91
9	-283.53	-281.95
10	-283.54	-281.97
11	-283.61	-282.14
12	-283.77	-282.40
13	-283.79	-282.49
14	-283.84	-282.62
15	-283.88	-282.66
16	-283.92	-282.89
17	-283.97	-283.11
18	-284.10	-283.43
19	-284.42	-283.96
20	-284.56	-284.19

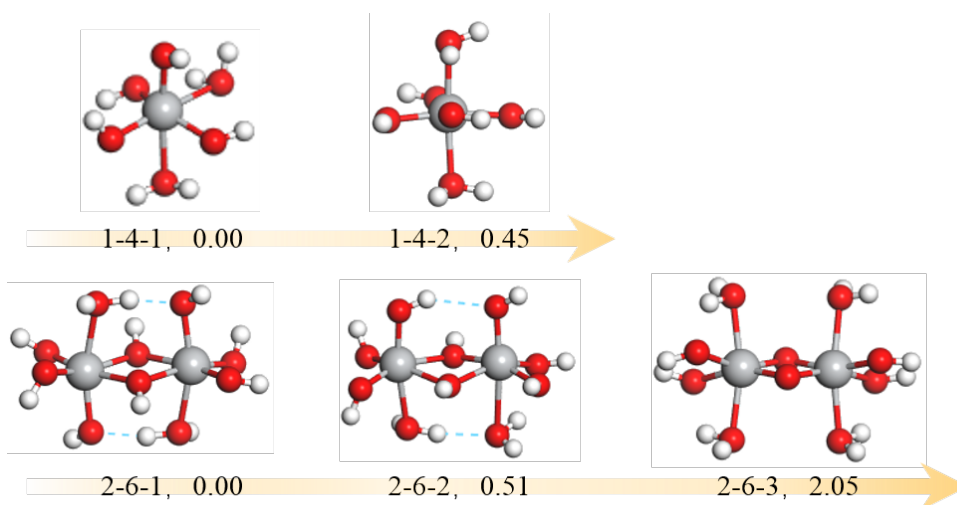


Figure S1. The representative structures for $n=1$ and $n=2$ liquid-phase particles. The relative energies (eV) of these structures are listed. The hydrogen bonds are depicted in blue dash lines. Color scheme: grey: Ti atoms; red: O atoms; white: H atoms.

Gas-phase particle growth. Figure S2 shows some selections of representative nanoclusters that we have sampled. For $n=1-5$ clusters, structures that have two mono-dentate O atoms usually grow via the terminal dangling Ti-O bonds, leading to the in-plane aggregation of monomers. Specifically, monomer has a bent structure with C_{2v} symmetry, where Ti-O bond and O-Ti-O angles are 1.71 Å and 115.11°, respectively. The global minima of dimer possessing C_{2h} symmetry is formed exothermically with -5.18 eV. The most stable structures of trimer and pentamer, containing three-fold coordinated O, have C_s symmetry while the tetramer has a C_{2v} symmetry.

In the case of $(TiO_2)_6$ clusters, structure **6a** is generated by connecting cluster **5** with the monomer, forming a 4-fold coordinated O atom located at the center of the cage. The average length of four Ti-O bonds around the central O is 2.08 Å. By contrast, the sub-stable structures **6b** and **6c**, which are 0.33 eV or 0.34 eV less stable compared to **6a**, only possess 3-fold and 2-fold coordinated O atoms. Both of them can be regarded as the structures that connect two clusters **3** through the bridging O, resulting in the triangular prism configurations. Subsequently, one Ti-O bond around 4-fold coordinated O atom in **6a** is broken when the structure connects with an additional monomer. This leads to the appearance of $(TiO_2)_7$ structure. **7a** (C_s symmetry) structure with two terminal dangling Ti-O bonds is 0.47 eV more stable than the **7c** structure (C_{3v} symmetry) with one terminal dangling Ti-O bond. For $(TiO_2)_8$ clusters, in comparison with the spherical **8d** structure, **8a/8b/8c** structures that exhibit the cubic-like or tubular-like

configurations are identified with increased stability. Similarly, the **9a** structure with tubular-like geometry is the lowest energy structure compared to other spherical geometry and is 0.04 eV more stable than the structure from literature.

For $(\text{TiO}_2)_{10}$, the global minimum **10a** is of S_4 symmetry and is comprised of four 4-fold coordinated Ti, four 5-fold coordinated Ti and two 6-fold coordinated Ti atoms. The particle formation proceeds via the upward growth of **9a** particle and finally leads to a tetrahedral configuration (**10a**). Notably, **10b** cluster with tubular-like geometry is less stable than **10a** by 0.79 eV, while spherical structures **10c** and **10d** with one monovalent O atom are less stable than **10a** by 1.47 eV and 1.78 eV, respectively. From the energy sequence, the most stable structures of $(\text{TiO}_2)_{11}$ and $(\text{TiO}_2)_{15}$ both show preference for the spherical formation, during which monomers adhere to the particle surface. In addition, the structure **20a** with a tetrahedral stacking, which can be seen as the transition state during the tubular to spherical growth of particle, was also observed. Our results demonstrated that the formation of gas-phase $(\text{TiO}_2)_n$ in this size range ($n=10-20$) has an inclination to grow towards spherical geometry.

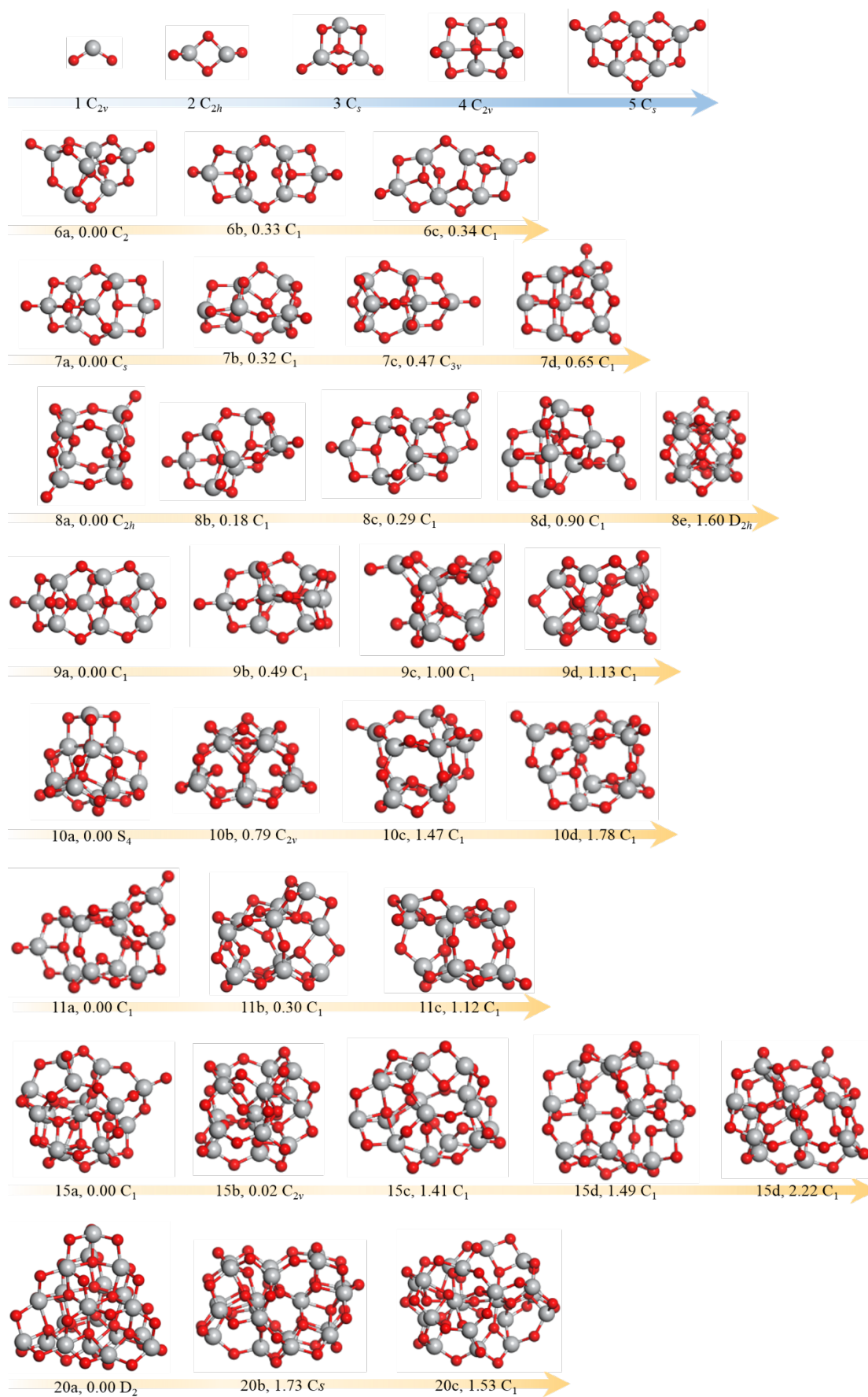


Figure S2. Structures for $(TiO_2)_n$, $n=1-20$. Relative energy (eV) and point group of the stable structure are

listed.

Table S2. Calculated reaction energy (ΔG) and differential energy ($d\Delta G/dn$) at different H₂O coverages for the reaction from (TiO₂)₁ to (TiO₂)₁·4H₂O. N_c is the coordination number of Ti atoms. a is the number of H₂O adsorbed in structures.

a	1	2	3	4
N_c	2	3	4	5
ΔG (eV)	-2.87	-4.66	-5.06	-5.27
$d\Delta G/dn$ (eV)	-2.87	-1.79	-0.40	-0.21

Table S3. The number of dissociative adsorbed H₂O (q), molecular adsorbed H₂O (p) and the total number of H₂O (m) in $n=1-20$ liquid-phase particles and the ideal number of H₂O (N) adsorbed in the stable gas-phase structures.

	q	p	m	N
(TiO ₂) ₁	2	2	4	4
(TiO ₂) ₂	4	2	6	6
(TiO ₂) ₃	6	2	8	7
(TiO ₂) ₄	7	1	8	8
(TiO ₂) ₅	7	2	9	9
(TiO ₂) ₆	11	1	12	12
(TiO ₂) ₇	8	4	12	14
(TiO ₂) ₈	14	2	16	16
(TiO ₂) ₉	17	2	19	18
(TiO ₂) ₁₀	6	4	10	12
(TiO ₂) ₁₁	8	8	16	21
(TiO ₂) ₁₅	20	4	24	22
(TiO ₂) ₂₀	5	8	13	20

Solvation energy. The solvation energy (ΔG_{sol}) is defined as the free-energy change of the solvation process of $(\text{TiO}_2)_n$ and the equation can be expressed as:

$$\Delta G_{sol} = G_{tot} + G_{water} - G((\text{TiO}_2)_n) - mG(\text{H}_2\text{O}) \quad (1)$$

where G_{tot} , G_{water} , $G((\text{TiO}_2)_n)$ and $G(\text{H}_2\text{O})$ are the Gibbs free-energies of the liquid system, solution, $(\text{TiO}_2)_n$ and H_2O . The solvation energy, which consists of the interaction between $(\text{TiO}_2)_n$ and the first solvation shell and the interactions from the second or third solvation shell, shows an overall decreasing trend that varies with the particle sizes (Figure S3). This further rationalizes the thermodynamic inclination of the $(\text{TiO}_2)_n(\text{H}_2\text{O})_m$ structures in titania preparation and practical applications when in contact of water.

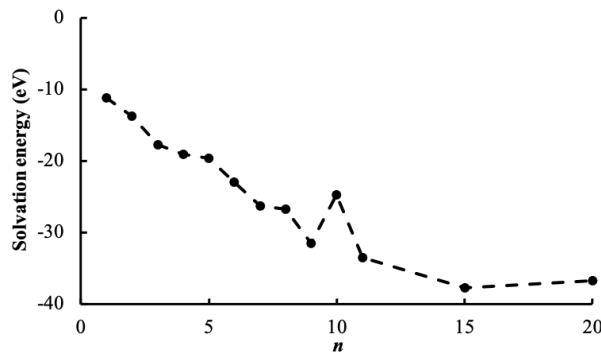


Figure S3. The solvation energies as a function of sizes for the lowest energy structures of $(\text{TiO}_2)_n$.

Stoichiometric structures. Essentially, titania particles grow via the dehydration-polymerization of octahedral monomers, and whether the stoichiometric or non-stoichiometric structures are formed in the process depends on the presence of reductant in the system. In this work, it does not involve evident oxidation-reduction reaction in the liquid-phase system and thus the titanium in the particle exhibits an oxidation state of +4. We note that the non-stoichiometric Ti-O structures may form under the influence of the reductant. Taking $\text{Ti}_8\text{O}_x \cdot y\text{H}_2\text{O}$ (x is the number of O atoms in Ti-O framework and y is the number of adsorbed H_2O in liquid-phase titania) as an example, we can examine the stabilities of stoichiometric and non-stoichiometric structures. To obtain the stable geometry of the non-stoichiometric structure, we immersed $\text{Ti}_8\text{O}_{15} \cdot 16\text{H}_2\text{O}$ into water and performed AIMD simulations with a durability of 5 ps at 400 K. In this process, H_2O dissociates at the O-vacancy site of $\text{Ti}_8\text{O}_{15} \cdot 16\text{H}_2\text{O}$ and the dissociative H_2O ($-\text{OH}/\text{H}$) connects with the unsaturated Ti/O to form $\text{Ti}_8\text{O}_{15} \cdot 17\text{H}_2\text{O}$; the Ti-O framework of this non-stoichiometric structure is similar to that of the stoichiometric structure. Thermodynamically, the process, $\text{Ti}_8\text{O}_{16} \cdot 16\text{H}_2\text{O} + \text{H}_2 \rightarrow \text{Ti}_8\text{O}_{15} \cdot 17\text{H}_2\text{O}$, is endothermic ($\Delta G=0.43$ eV). It suggests that, in the system with high H_2 pressure ($P_{\text{H}_2}>29.2$ atm),

$\text{Ti}_8\text{O}_{15}\cdot 17\text{H}_2\text{O}$ forms in the liquid-phase system ($\Delta G < 0$).