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Structure, Reactivity, Photoactivity and Stability of Ti-O Based Materials: A Theoretical Comparison

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Ti-O based materials have attracted great attention recently for their potential applications in clean energy generation and environment remediation. To screen Ti-O based materials for specific applications, the atomic-level understanding of the subtle discrepancy of their properties is of paramount importance. In this regard, the density functional theory computations have been performed to systematically compare the physicochemical properties of three selected Ti-O based materials: anatase titanium dioxides, sodium trititanates and sodium hexatitanates. Due to their structure discrepancy, sodium trititanates show the highest chemical reactivity. However, titanium dioxides are found to be the most photoactive materials. The reactivity and photoactivity of sodium hexatitanates fall between those of titanium dioxide and sodium trititanates. At the mean time, our energetic analysis also confirms that the thermal stabilities of Ti-O based materials are strongly dependent on the acid-base conditions. Titanium dioxides are preferred under acidic conditions, while titanates are more stable in basic solutions.

1. Introduction

Ti-O based materials are an important class of materials comprised of TiO₆ octahedra, which include titanium dioxides (TiO₂) and titanates.¹⁻³ Traditionally, TiO₂ is used as pigments; and titanates are well-known as functional ceramic materials.⁴ Recently, more advanced applications of Ti-O based materials have been proposed, such as catalysis,⁵⁻⁶ sensors,⁷ hydrogen storage,⁸ lithium ion batteries,⁹ environmental remediation,¹⁰ absorption of radioactive ions in water treatment,¹¹ electronics,¹² solar cells¹³⁻¹⁵ and biomedicine.¹⁶ The applications in catalysis, hydrogen storage, water treatment and sensors are dependent on their chemical reactivities of materials.² The efficiencies of Ti-O based solar cells and photocatalysts are determined by their photoactivity.² Meanwhile, their thermal stability is also crucial for their practical applications. Since the physicochemical properties of Ti-O based materials are strongly related to their atomic configurations,¹⁷⁻¹⁸ the understanding of the discrepancy of the atomic configurations of Ti-O based materials and the corresponding structure-function relationship becomes essential for their development. However, based on our knowledge, there is no systematical comparison of the reactivity, photoactivity and thermal stability of Ti-O based materials. This comparison is

therefore dedicated in this study based on density-functional theory (DFT) calculations. DFT is employed because it is the most popular quantum chemistry method which reduces the computation consumption sharply with chemistry accuracy.¹⁹

Up to date numerous Ti-O based materials have been discovered or synthesized. It is impossible to compare the properties of all Ti-O based materials. Representative Ti-O based materials are hence screened in this study. Firstly, anatase TiO₂ phase is chosen since the previous experimental and theoretical studies have demonstrated that anatase is the most active TiO₂ phase.^{1, 20} Meanwhile, sodium titanates (Na₂Ti_nO_{2n+1}) are selected because they are widely employed in many practical applications.²⁻³ In general, titanates with higher sodium content possess layered structures, while the titanates with lower sodium content have tunnelled structures. Among them, sodium trititanates (Na₂Ti₃O₇) are the best studied titanates with a layered structure;²¹ and sodium hexatitanates (Na₂Ti₆O₁₃) are the most widely used titanates with a tunnelled structure.²² Based on these considerations, anatase TiO₂, Na₂Ti₃O₇ and Na₂Ti₆O₁₃ are deliberately selected in this study. The structures of three Ti-O based materials are shown in Fig. 1.

The DFT studies focusing on anatase TiO₂ have been comprehensively performed previously.²⁰ And recently, the structural and electronic properties of Na₂Ti₃O₇ were also investigated.²³⁻²⁵ However, there is no theoretical analysis on the physicochemical properties of titanates with a tunnelled structure. In this regard, the structural and electronic properties of Na₂Ti₆O₁₃ are firstly investigated in this study. Then, the structural discrepancy of three Ti-O based materials is analyzed

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by using our DFT optimized atomic structures. After that, their chemical reactivity and photoactivity are compared according to their electronic structures. Finally, the thermal stability of three Ti-O based materials is compared based on the energetic data.

2. Computation Details

All DFT computations are performed using the Quantum Espresso (QE) package.²⁶ Electron-ion interactions are described using the Vanderbilt-type ultrasoft pseudopotentials.²⁷ Valence states include the Ti 4s, 4p, 3d, and 4s states, the O 2s and 2p states, and the Na 3s states. A plane-wave basis set was used with the cut-off kinetic energy as 30 Ry. For the electron-electron exchange and correlation interactions, the functional of Perdew, Burke and Ernzerhof (PBE),²⁸ a form of the general gradient approximation (GGA), is used throughout. When the geometry is optimized, all atoms are allowed to relax. Since there are four structure parameters to determine the optimized lattice of the bulk systems of sodium titanates, to obtain the theoretical values of these parameters through traditional DFT calculations is quite time-consuming. Thus, the variable cell technique is employed to optimize these parameters. We perform Brillouin-zone integrations using Monkhorst-Pack grids of special points with a (4×4×2), (1×4×2) or (2×4×2) mesh for anatase TiO₂, Na₂Ti₆O₁₃ or Na₂Ti₃O₇, respectively. The supercell of anatase TiO₂, Na₂Ti₆O₁₃ or Na₂Ti₃O₇ includes 12, 42 or 24 atoms, respectively. The selected k-mesh densities and the cut-off kinetic energy have been justified in our previous studies.^{17, 25, 29} In the analysis of the thermal stabilities of three Ti-O based materials, the reaction energies between Ti-O based materials and isolated acidic or basic molecules are calculated. Even though experimental results for these reactions have been obtained in aqueous solution,³⁰⁻³² the calculations incorporating the solution effect will be unaffordable in terms of computation cost. Therefore a practical approach is to employ energies of average unit of crystals or isolated molecules for the thermal stability analysis since they are the major reactants and products. In this study, isolated molecules are in the cubic supercell with the lattice constant of 15 Å in calculations with the gamma-point only mesh. And the energy of the NaCl unit cell is calculated by using a (16×16×16) k-point mesh.

3. Results and discussion

3.1 Structural and electronic properties of Na₂Ti₆O₁₃

Na₂Ti₆O₁₃ was once used as a good supporter of photocatalysts for water splitting by Inoue and his co-workers.³³ Then, the Na₂Ti₆O₁₃ nanobelts themselves were found to exhibit good photocatalytic efficiency for the decomposition of organic pollutants in water under ultraviolet irradiation.³⁴ Meanwhile, they can also be used as the precursor to produce the important dielectric, ferroelectric, piezoelectric and electrostrictive material: barium titanates.³⁵ Recently, it was found that Na₂Ti₆O₁₃ was a good candidate to be used as anode materials of lithium ion batteries since it owns a low voltage range for the reversible insertion of lithium ions.³⁶⁻³⁷ Due to their tunnelled structures, Na₂Ti₆O₁₃ nanofibers have also been found to have potential to selectively absorb radioactive ions from water.³¹ However, most of the previous studies on Na₂Ti₆O₁₃ materials focused on the

synthesis techniques and their applications.^{22, 34, 38-42} To the best of our knowledge, there is no theoretical study on the structural and electronic properties of Na₂Ti₆O₁₃ materials. To compare the properties of selected Ti-O based materials, this theoretical study is therefore dedicated to investigate physicochemical properties of Na₂Ti₆O₁₃ materials firstly.

Fig. 1 The atomic configurations of (A) Na₂Ti₆O₁₃ with a tunnel structure, (B) Na₂Ti₃O₇, and (C) anatase TiO₂, with a layered structure. The black frame represents the size of a unit cell. Blue octahedron-[TiO₆], yellow Sodium, red-oxygen, and blue-titanium.

The structure of Na₂Ti₆O₁₃ was determined by Torres-Martínez *et al.* by a Rietveld refinement to simulate the experimental X-ray powder diffraction (XRD) patterns.³⁹ It is found that the Na₂Ti₆O₁₃ crystal is a monoclinic cell with space group C2/m.³⁹ Fig. 1A shows the optimized structure of a Na₂Ti₆O₁₃ crystal, and the lattice constants for a fully relaxed Na₂Ti₆O₁₃ structure, which are compared with the experimental values of Torres-Martínez *et al.*, are listed in Table 1. Our theoretical volume is about 1.6% larger than those from the experiments. Such discrepancy is ascribed to the approximation of GGA-DFT.⁴³ The atomic positions of Na₂Ti₆O₁₃ compared with the experimental data of Torres-Martínez *et al.* are listed in Table 2. After fully optimization, our theoretical fractional atomic coordinates are in agreement with the experimental observations greatly. The Ti-O bond length is with the range of 1.76 Å to 2.27 Å, which are also similar to those reported by Torres-Martínez *et al.*³⁹

Table 1 The theoretical lattice constants of Na₂Ti₆O₁₃ in comparison with the experimental data³⁹.

	theoretical	experiment
a (Å)	15.21	15.10
b (Å)	3.75	3.75
c (Å)	9.25	9.17
β (°)	98.9	99.0
V (Å ³)	520.8	512.3

Table 2. The theoretical fractional atomic coordinates of Na₂Ti₆O₁₃ in comparison with the experimental data³⁹. The number of the oxygen atoms is defined in Fig. 1B.

	x (theoretical)	x (experiment)	z (theoretical)	z (experiment)
Na1	0.46203	0.46102	0.26975	0.26595
Ti1	0.11455	0.11311	0.09562	0.09740
Ti2	0.16538	0.16716	0.43592	0.43740
Ti3	0.22718	0.22689	0.77015	0.77019
O1	-0.00002	0.00000	0.00000	0.00000
O2	0.06974	0.07020	0.29281	0.29497
O3	0.12649	0.12873	0.61489	0.61793
O4	0.16298	0.16904	0.91327	0.91716
O5	0.35657	0.35786	0.88228	0.88499
O6	0.29798	0.30113	0.57055	0.57074
O7	0.24065	0.23769	0.24576	0.24064

Fig. 2 Partial density of states of a titanium atom and seven distinctive oxygen atoms in $\text{Na}_2\text{Ti}_6\text{O}_{13}$. The number of the oxygen atoms is defined in Fig. 1A. The dashed line is the location of Fermi energy (E_f). The red area is low-energy range ($-6.0 \text{ eV} < E - E_f < -4.5 \text{ eV}$); the green area is the intermediate-energy range ($-4.5 \text{ eV} < E - E_f < -3.0 \text{ eV}$); and the yellow area is the high-energy range ($-3.0 \text{ eV} < E - E_f < -1.5 \text{ eV}$).

Recently, the layered $\text{Na}_2\text{Ti}_3\text{O}_7$ materials have been found that the lattice oxygen atoms show much diverse reactivity experimentally when the radioactive ions are absorbed by $\text{Na}_2\text{Ti}_3\text{O}_7$.⁴⁴⁻⁴⁵ The theoretical DFT calculations have revealed that the diverse reactivity is originated from the electronic properties of lattice oxygen atoms, which are determined by their chemical environments.²⁵ While $\text{Na}_2\text{Ti}_6\text{O}_{13}$ shows a various structure comparing with $\text{Na}_2\text{Ti}_3\text{O}_7$, the lattice oxygen atoms of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ also face various chemical environments, as shown in Fig. 1A. Since the diverse reactivity of lattice oxygen atoms in $\text{Na}_2\text{Ti}_3\text{O}_7$ has been found to play important role in their applications,^{31, 44} the similar diverse reactivity should be also expected to affect the applications of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ materials.

To analyze the electronic properties of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ materials, the partial density of states (PDOS) of each distinctive atom are calculated. Since each Ti atom is surrounded by six O atoms to form a TiO_6 octahedron, the chemical environments of all Ti atoms are similar. By contrast, the distinctive O atoms confront much different surroundings. The coordination number is two for O1, O2, O3 and O4, three for O5, and four for O6 and O7 in the TiO_6 octahedra, respectively. The number of O atoms is denoted in Fig. 1A. The PDOS images suggest that O1-O4 atoms are more active than O5-O7. As shown in Fig. 2, the peaks of O-2p states are divided into three classes: $-6.0 \text{ eV} < E - E_f < -4.5 \text{ eV}$ (red, low-energy range), $-4.5 \text{ eV} < E - E_f < -3.0 \text{ eV}$ (green, intermediate-energy range), and $-3.0 \text{ eV} < E - E_f < -1.5 \text{ eV}$ (yellow, high-energy range). The denser states of atoms at high-energy range indicate the higher reactivity. From Fig. 2, the main peaks of O1-O4 2p states locate at the high- and intermediate-energy ranges. With the increase of the coordination number of O atoms, the main peaks shift from the high-energy area to the low-energy area. For O6 and O7 atoms, their main peaks all fall within the low-energy ranges. The PDOS shifted from high-energy area to the low-energy area indicates a decreased reactivity for oxygen atoms. Thus, it demonstrates that the coordination number of O atoms is the dominate factor for their

reactivity. This conclusion is in agreement with the previous theoretical analysis on $\text{Na}_2\text{Ti}_3\text{O}_7$.²⁵

3.2 Structure discrepancy of Ti-O based materials

The most obvious difference of the three Ti-O based materials is their atomic structures, as shown in Fig. 1. Anatase TiO_2 is a materials with a small rhombus tunnel along $\langle 010 \rangle$ direction. The tunnel side length is about $3.0 \text{ \AA}$. Meanwhile, both $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ are monoclinic. $\text{Na}_2\text{Ti}_3\text{O}_7$ shows a layered structure. And Na ions are located in the space between Ti-O layers. On the other hand, $\text{Na}_2\text{Ti}_6\text{O}_{13}$ is with a typical tunnelled structure. There are two different sizes of tunnels: the big one is an $8.4 \text{ \AA} \times 2.7 \text{ \AA}$ rectangle, which accommodates two Na atoms in each tunnel; and the small rhombus one is similar as that of anatase TiO_2 . The different morphology is expected to affect their application greatly. Firstly, sodium titanates show exclusive ion-exchange properties due to sodium ions between TiO_6 octahedra can be replaced by protons or other transition-metal ions.⁴⁶ Secondly, layered $\text{Na}_2\text{Ti}_3\text{O}_7$ has the highest internal surface area, which will benefit the absorption of radioactive metal wastes.⁴⁴⁻⁴⁵ Thirdly, the specific tunnelled structure of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ gives its promising for applications in ion conductivity, or electron conductivity. So, $\text{Na}_2\text{Ti}_6\text{O}_{13}$ is a good candidate in lithium ion battery.³⁶

Another structure discrepancy of three Ti-O based materials is the coordination number of lattice oxygen atoms. Since Ti atoms locate at the centre of TiO_6 octahedra in anatase TiO_2 , $\text{Na}_2\text{Ti}_6\text{O}_{13}$, and $\text{Na}_2\text{Ti}_3\text{O}_7$, all their coordination numbers are six. However, the coordination numbers of distinctive lattice oxygen atoms are different. The coordination number is determined by the number of TiO_6 octahedra sharing the same oxygen atom. In anatase TiO_2 , all the lattice oxygen is chemical identical due to their high symmetry with the coordination number as three. However, there are seven distinctive oxygen atoms in $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_3\text{O}_7$. The seven distinctive O atoms have been marked as O1-O7, as shown in Fig. 1. In $\text{Na}_2\text{Ti}_6\text{O}_{13}$, each O1, O2, O3 or O4 atom bonds to two Ti atoms. As a comparison, each O5 atom interacts with three Ti atoms; and each O6 or O7 atom connects with four Ti atoms in the TiO_6 octahedra. In $\text{Na}_2\text{Ti}_3\text{O}_7$, the coordination number of O atoms is slightly different. The coordination number of O1 of $\text{Na}_2\text{Ti}_3\text{O}_7$ is merely one. And the coordination numbers of other lattice oxygen atoms are same as those in $\text{Na}_2\text{Ti}_6\text{O}_{13}$. Since the coordination number of lattice oxygen is the decisive factor to their electronic properties and reactivity,²⁵ the chemical properties of these Ti-O based materials are expected to be much diverse. The comparison about the reactivity of these materials will be discussed below.

3.3 Reactivity of Ti-O based materials

The chemical reactivity of Ti-O based materials is important to their applications in sensors, catalysis, absorption, and hydrogen storage. The previous theoretical studies have demonstrated that the reactivities of the lattice oxygen atoms in titanates are determined by their electronic properties.²⁵ Thus, the electronic properties of lattice oxygen atoms of three Ti-O based materials are compared based on their PDOS. The PDOS of the lattice oxygen atoms with the highest reactivity of the three Ti-O based materials are shown in Fig. 3. The PDOS peaks of $\text{Na}_2\text{Ti}_3\text{O}_7$ in the low-energy range (marked as the red area in Fig. 3) are the

lowest. And the peaks of TiO_2 in the low-energy range are the highest. On the other side, the PDOS peaks of the O1 atoms of $\text{Na}_2\text{Ti}_3\text{O}_7$ at the high-energy range (marked as the yellow area in Fig. 3) are the highest. The different shapes of the PDOS images indicate that $\text{Na}_2\text{Ti}_3\text{O}_7$ shows the highest chemical reactivity while anatase TiO_2 is the most chemically inert materials among them. This conclusion is supported by experiments of Yang *et al.* that $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanofibers have a lower ion-exchange capacity comparing with that for $\text{Na}_2\text{Ti}_3\text{O}_7$ nanofibers.⁹

Fig. 3 Partial density of states of the most reactive lattice O atom of the three Ti-O based materials: anatase TiO_2 , $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$. The red area is low-energy range ($-6.0 \text{ eV} < E - E_f < -4.5 \text{ eV}$); the green area is the intermediate-energy range ($-4.5 \text{ eV} < E - E_f < -3.0 \text{ eV}$); and the yellow area is the high-energy range ($-3.0 \text{ eV} < E - E_f < -1.5 \text{ eV}$).

The difference of reactivity can be explained according to their structural properties. In the analysis of the reactivity of lattice oxygen atoms in $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_3\text{O}_7$, lattice oxygen atoms with a smaller coordination number are reactivity.²⁵ Based on the discussion of the structure discrepancy of three Ti-O based materials, the coordination numbers of the most reactive oxygen atoms in different materials vary. In $\text{Na}_2\text{Ti}_3\text{O}_7$, the lattice O1 atoms bond to merely one Ti atom in TiO_6 octahedra.^{25, 45} However, in $\text{Na}_2\text{Ti}_6\text{O}_{13}$, the lowest coordination number for O atoms is two. And the coordination number of lattice oxygen in anatase TiO_2 is three. As a result, the $\text{Na}_2\text{Ti}_3\text{O}_7$ shows the highest reactivity among three Ti-O based materials.

3.4 Photoactivity of Ti-O based materials

Since all three Ti-O based materials have been proposed to the applications in photocatalysis,^{21, 39, 47} the understanding of their photoactivity is crucial for their further development. From the analysis of PDOS, as shown in Fig. 2 and previous literatures,^{25, 48} it is found that the contribution to the bands around Fermi energy level is similar for all Ti-O based materials. Most of the DOS of O-2p states locate at the highest valence bands (VB). As a comparison, the major composite of lowest conduction bands (CB) is Ti-3d states. The similar electronic structures of Ti-O based materials explain why all of them can be used as photocatalysts. Furthermore, their similar electronic structures also suggest that the photo-excitation mechanism based on TiO_2 photocatalysts can also be used for titanates.

To compare the photoactivity of three Ti-O based materials,

their bandgap energies (E_g) are calculated since E_g determines the efficiency of the visible sunlight absorption. Although the traditional DFT method underestimates the real E_g of semiconductors seriously,⁴⁹⁻⁵⁰ the previous theoretical studies have demonstrated that the DFT results can be used to get the optical properties of materials qualitatively.⁵¹ Based on our calculations, it is found that the E_g of sodium titanates are much higher than that of TiO_2 (the E_g is 2.14 eV, 3.03 eV and 3.09 eV

Fig. 4 UV-vis absorption spectra obtained from anatase TiO_2 , $\text{Na}_2\text{Ti}_6\text{O}_{13}$, and $\text{Na}_2\text{Ti}_3\text{O}_7$ nanofibers. The insert is the plot of Kubelka-Munk function vs. the energy of light.

for anatase TiO_2 , $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_3\text{O}_7$, respectively). It indicates that the corresponding photoactivity of titanates is lower than that of TiO_2 . To evaluate our theoretical prediction, we have investigated the UV-vis diffusion reflectance (UV-vis DR) spectra of $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$, and anatase TiO_2 nanofibers. The results are displayed in Fig. 4. All the materials are prepared by the hydrothermal method under the same conditions used in the previous experiments.⁴⁴⁻⁴⁵ The onset wavelength λ_{onset} of the spectrum recorded from $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$ or anatase TiO_2 is 350nm (3.54 eV), 360nm (3.44 eV) and 400 nm (3.10 eV) nm, respectively. Our UV-Vis diffusion reflectance spectra data for anatase TiO_2 and $\text{Na}_2\text{Ti}_3\text{O}_7$ are in agreement with the previous experimental data.⁵²⁻⁵³ Apparently, the experimental E_g data support the theoretical prediction that sodium titanates can only absorb UV light with shorter wavelength. To increase the photoactivity of titanates under visible sunlight, further bandgap engineering is required.

3.5 Thermal stability of Ti-O based materials

In the experiments, sodium titanates can be produced through the interaction between TiO_2 and NaOH.^{21-22, 32} Thus, we have calculated the formation energy of sodium titanates according to the equation:

or

Both reaction energies are negative: -4.94 eV and -5.20 eV for the formation energies of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$, respectively, which means that the reactions are energetically preferred. The recent XRD and SEM images have demonstrated that the sodium titanates are the more stable phase when the Ti-O nanocrystals are synthesized through hydrothermal methods under basic conditions.³² Our theoretical conclusions hence confirm the

experimental observation.^{21-22, 32}

The sodium titanates can also change into TiO₂ systems by interacting with acid, such as HCl.³² The overall reaction can be written as:

or

The reaction energy is -1.94 eV and -2.19 eV for Na₂Ti₆O₁₃ and Na₂Ti₃O₇, respectively. Our theoretical data support that the TiO₂ is more stable under acidic conditions. Thus, the thermal stability of Ti-O based materials strongly dependent on the acid-base conditions in the synthesis process. Meanwhile, the reverse reaction of (1)-(4) can be used to describe the reaction of TiO₂ or sodium titanates under the pH-neutral condition. Based on our theoretical results, all the reverse reactions are endothermic, which suggests that all Ti-O based materials are stable under pH-neutral solutions.

To compare the thermal stability of Na₂Ti₃O₇ and Na₂Ti₆O₁₃, we have calculated the reaction energy of the two phase change, as proposed according to the recent Raman spectra:³⁰

Based on our calculations, the reaction energy is positive: 9.35 eV, which indicates that the above reaction is not energetically favourable. This is contrary to the experimental observation that Na₂Ti₃O₇ can be converted into Na₂Ti₆O₁₃ at high temperature.³⁰ The theory-experiment discrepancy can be explained by considering the phase transformation condition from Na₂Ti₃O₇ to Na₂Ti₆O₁₃. In the experiment, Na₂Ti₆O₁₃ is produced by calcinating Na₂Ti₃O₇ at 300°C under air flow.³⁰ Since H₂O is continuously supplied and the NaOH is blown away by air flow, the reaction (5) can hence dynamically occur. Once Na₂Ti₆O₁₃ interacts with the basic solution, it should be changed back into Na₂Ti₃O₇ based on our theoretical prediction. Indeed, Morgado and his co-workers demonstrated that the Na₂Ti₃O₇ crystal is the most stable phase for sodium titanates at the basic condition.⁵⁴

Meanwhile, the phase change from Na₂Ti₃O₇ to Na₂Ti₆O₁₃ under the acidic condition is also considered:

The calculated reaction energy is -2.46 eV, which suggests that the Na₂Ti₃O₇ can be converted to Na₂Ti₆O₁₃ through facile wet chemistry under mild conditions. This phase transition process is novel since no such experiment is reported previously. Further experiments are then expected to confirm it. However, the amount of acid should be carefully controlled since Na₂Ti₆O₁₃ can be further converted to TiO₂ under acidic condition, as shown in the reaction (3).

4. Conclusions

In summary, the first principle DFT calculations have been performed to compare the physicochemical properties of Ti-O based materials. Although they are all comprised of TiO₆ octahedra, it is found that their physicochemical properties are much different. The layered Na₂Ti₃O₇ shows highest chemical reactivity and largest bandgap energy. As a comparison, anatase TiO₂ is chemically inert with the highest photoactivity. The physicochemical properties of Na₂Ti₆O₁₃ fall between those of anatase TiO₂ and Na₂Ti₃O₇. Meanwhile, our energetic analysis demonstrates that all Ti-O based materials are stable under the

pH-neutral solution. However, TiO₂ is more stable under acidic condition while titanates are preferred in basic solutions. Our theoretical results also predict that Na₂Ti₆O₁₃ can be generated by the interaction between Na₂Ti₃O₇ and weak acid, which proposes a novel way to produce sodium titanates with lower sodium content. According to our theoretical comparison, Ti-O based materials can therefore be pre-screened for their difference applications.

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