Structural characterizations of photo-catalytic titanium oxide nanoparticles made from amorphous building blocks

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I am submitting herewith a dissertation written by Mengkun Tian entitled "Structural characterizations of photo-catalytic titanium oxide nanoparticles made from amorphous building blocks." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Materials Science and Engineering.

Gerd Duscher, Major Professor

We have read this dissertation and recommend its acceptance:

Kurt Sickafus, Kalyanaraman Ramakrishnan, Gong Gu

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
Structural characterizations of photo-catalytic titanium oxide nanoparticles made from amorphous building blocks

A Dissertation Presented for the Doctor of Philosophy Degree
The University of Tennessee, Knoxville

Mengkun Tian
August 2015
Dedications

To my parents, grandparents, my wife, and my son.
Acknowledgements

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Abstract

TiO$_2$ [titanium dioxide] nanoparticles (NPs) exhibit a variety of properties substantially departed from the optical and catalytic properties of the known bulk phases. A special interest in the engineering of functionality is how structures and bandgaps interact to enhance the photo-activity of TiO$_2$. However, fundamental understanding of bandgap-related changes is difficult at these length scales because of scarcity of methods capable of probing the bandgap and the structure of isolated small particles. In this research, we adopt a series of highly spatially resolved transmission electron microscopy (TEM) techniques to characterize the structures of amorphous TiO$_2$ nanoparticles (NPs) used as precursors and the TiO$_2$ NPs with narrowed band gap derived from these amorphous precursors. The results show: (1) The amorphous TiO$_2$ precursors consist of TiO$_6$ [titanium atom surrounded by six oxygen atoms] octahedra randomly connected with each other; (2) An unconventional phase transformation occur wherein anatase and TiO$_2$(B) coexist when annealing the amorphous TiO$_2$ NPs in a temperature range from 400°C to 900°C in oxygen gas; (3) Chromium and nitrogen co-doped TiO$_2$ NPs have significantly narrowed band gaps originating from extra states on the top of valence band; (4) Black rutile NPs are produced by annealing amorphous TiO$_2$ NPs at 700 °C in argon gas, which have a (crystalline TiO$_2$) core-(amorphous Ti$_2$O$_3$ [titanium sesquioxide]) shell structure. Formation of Ti$_2$O$_3$ originates from diffusion of oxygen vacancies towards vacuum in the amorphous precursors; (5) The black anatase NPs are produced by annealing amorphous TiO$_2$ NPs at 400 °C in argon gas, whose structures are (i) core-shell, or (ii) randomly distributed phases. These two structures originate from different degrees of crystallization and diffusion rate of oxygen vacancies; (6) Cubic-TiO$_2$ is induced by the electron beam, which originates from the migration of interstitial Ti atoms grown on a rutile template; (7) We also discuss the origins of deviations from known phases’ EELS spectra which is the most important tool of electronic structure characterizations in this research; (8) Finally, we found a group of intense peaks in the interface between silicon and TiO$_2$. These peaks may originate from interface plasmon excitations.

Keywords: TiO$_2$, band gap narrowing, amorphous precursors, TEM techniques, monochromated EELS.
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Chapter 1. **Introduction**

### 1.1 Structure and properties of TiO$_2$

TiO$_2$, known as titania, has been used as white pigment from ancient times. It is usually called the ‘perfect white’, or ‘the whitest pigment’. TiO$_2$ doesn’t show any absorption of visible light, but it becomes active in the UV range. In nature, there are three common forms of TiO$_2$: anatase, rutile, and brookite. The anatase and rutile have been used and investigated mostly because of easy availability and relatively high performance in photo-catalysis. The crystal structure of rutile is tetragonal, P4$_2$/mm, $a = b = 4.584$ Å, $c = 2.953$ Å, and of anatase is tetragonal as well, I4$_1$/amd, $a = b = 3.782$ Å, $c = 9.502$ Å. Table 1-1 lists some basic properties of anatase and rutile.

**Table 1-1 Properties of anatase and rutile**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>~80 g/mol</td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>No, due to anatase to rutile</td>
<td>2116</td>
</tr>
<tr>
<td>Boiling point</td>
<td>phase transformation at high temperature</td>
<td>3246</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.488</td>
<td>2.609</td>
</tr>
<tr>
<td>Density</td>
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<td>3.78 g/cm$^3$</td>
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<td>$a = b = 4.584$ Å</td>
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<td>$c = 9.502$ Å</td>
<td>$c = 2.953$ Å</td>
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<tr>
<td>Band gap</td>
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<td>3.0 eV</td>
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There are several metastable forms of TiO$_2$ such as TiO$_2$(B)$^1$, hollandite-like TiO$_2$$^2$ and ramsdellite-like TiO$_2$$^3$, and high pressure forms: TiO$_2$(II)$^4$, baddeleyite-like TiO$_2$$^5$, cubic-TiO$_2$ (fluorite forms and pyrite form)$^6$, TiO$_2$-O$^7$ and cotunnite (PbCl$_2$-like) TiO$_2$-O$^8$. Selected structures of different
TiO$_2$ phases are shown in Figure 1-1. Due to the opacity, exposure to sunlight, and whiteness, these materials have been used in numerous industries in powder form. The most common applications in daily life involve paper making, tooth paste, food and medicine because TiO$_2$ powder is extremely white and non-toxic. Some rare polymorphs of TiO$_2$ possess distinctive properties, i.e. cotunnite-type phase, which was reported as the hardest oxide in the nature by Dubrovinsky, L. S. et al.\textsuperscript{8} with the Vickers hardness of 38 GPa and the bulk modulus of 431 GPa, close to diamond's value of 446 GPa.

![Selected polymorphs of TiO$_2$. Three main types of TiO$_2$: (a) rutile, (b) anatase, (c) brookite, metastable form (d) TiO$_2$(B) and high pressure forms (e) Baddeleyite-like TiO$_2$ and (f) cubic-TiO$_2$](image)

1.2 **Synthesis of TiO$_2$ nanomaterials**

Single crystals of TiO$_2$ are widely available through companies such as Sigma-Aldrich, Kelpin Kristallhandel, Plasma Chem, Nano Amor and many others. TiO$_2$ nanomaterials are often synthesized in the form of thin films and nanoparticles (NPs). Historically, TiO$_2$ thin films are widely used as reflective optical coating or dielectric mirrors due to the high refractive index and white color. TiO$_2$ thin films can be synthesized by a variety of methods, such as sol-gel\textsuperscript{9}, chemical vapor deposition (CVD)\textsuperscript{10-12}, electron-beam evaporation\textsuperscript{13,14}, pulse laser deposition (PLD)\textsuperscript{15,16}, molecular beam epitaxy (MBE)\textsuperscript{17,18} and plasma spray\textsuperscript{19,20}. More details of synthesizing TiO$_2$ nano-materials methods were summarized by Chen et al.\textsuperscript{21}. By coating the TiO$_2$ thin films, the materials have numerous applications.
in the photocatalysis\textsuperscript{22}. For example, deposition of TiO\textsubscript{2} at the surface of the tiles makes them self-cleaning self-sterilizing, self-purification and anti-fogging\textsuperscript{23}. Nowadays, the thickness of TiO\textsubscript{2} thin films can be controlled as precisely as in atomic range. King D. M. et al\textsuperscript{24} controlled the thickness of TiO\textsubscript{2} thin films as precise as in 0.61 Å/cycle. By such synthesis method, they found quantum size effect on the band gap of TiO\textsubscript{2} thin films from 1 to several layers of TiO\textsubscript{2}.

TiO\textsubscript{2} NPs attract a great interest because they exhibit a variety of properties that substantially depart from those typical of the known bulk phases\textsuperscript{25}. A great number of techniques have been developed to fabricate TiO\textsubscript{2} NPs. A comprehensive introduction of these techniques involving sol–gel, hydro- and solvo-thermal, sonochemical, microwave, electrodeposition, physical vapor deposition (PVD), and CVD were explicitly summarized by Chen et al.\textsuperscript{26}. In contrast to the quantum size effects that are governed purely by spatial confinement of bulk phases, NPs properties are primarily related to disruption of bulk periodicity localized at or near the surface layer where TiO\textsubscript{2} directly interacts with the surrounding materials. Though the size of quantum effect is highly disputed\textsuperscript{27-29}, the reported critical size is very small (typically <2nm). This characteristic is unique for TiO\textsubscript{2} NPs compared to the much larger critical size of other photo-catalysts, as shown in Figure 1-2\textsuperscript{29}. Therefore, in most case we don’t need to consider the negative impact of quantum confinement on the band gap of TiO\textsubscript{2}.

![Figure 1-2 Size dependent band gap for different photo-catalysts from Ref [28].](image-url)
In the past, synthesis of a specific structure of TiO$_2$ is difficult to control because the crystal structure, appearance planes and the phase stabilities of the TiO$_2$ NPs are highly sensitive to the chemical environment. In 2005, Barnard et al.\textsuperscript{30} investigated the morphology of anatase and rutile in hydrogenated, hydrogen-rich, hydrated, hydrogen-poor and oxygenated surface. As shown in Figure 1-3 a-j, they calculated the energy of different surfaces and reconstructed the evolution of appearance facet of the NPs, i.e. the \{010\} planes tend to appear from hydrogen-rich to oxygenated ambient.

Figure 1-3 Morphology predicted for anatase (top) from Ref [29] with (a) hydrogenated surfaces (b) with hydrogen-rich surface adsorbates, (c) hydrated surfaces, (d) hydrogen-poor adsorbates, and (e) oxygenated surfaces, and rutile (bottom) with (f) hydrogenated surfaces, (g) with hydrogen-rich surface adsorbates, (h) hydrated surfaces, (i) hydrogen-poor adsorbates, and (j) oxygenated surfaces.

Barnard et al.\textsuperscript{30} also pointed out that the phase stabilities of anatase and rutile highly depend on the chemical surroundings. In a hydrogenated ambient, rutile is not stable under 22.7nm, while this value decreases to 6.9nm in an oxygenated environment. As the techniques evolve, TiO$_2$ NPs sized 10-50nm with stable phases and controllable morphologies can be easily prepared recently. In the following we will use the term ultra-small NPs as a definition of NPs smaller than 10 nm in diameter. Synthesizing ultra-small crystalline NPs is still challenging because high temperature annealing, which is the conventional approach to stabilize NPs, causes the growth of those NPs, and a phase transformation of TiO$_2$. The conventional low-temperature methods i.e. sol-gel are usually considered to fail to control the
crystallinities of NPs. Here we summarize several most recent modified so-gel methods for synthesizing the ultra-small crystalline NPs. Wang et al.\textsuperscript{31} used ethylene glycol (EG) to control the hydrolysis and condensation rates, and then successfully synthesize highly crystalline anatase of 2-4nm size at low temperature. Szeifert et al.\textsuperscript{32} used tert-butyl alcohol, a new sol-gel reaction medium, to synthesize 3nm anatase NPs with a high dispersity from TiCl\textsubscript{4} starting materials. Very recently, Burunkaya\textsuperscript{33} fabricated TiO\textsubscript{2} NPs <5nm using titanium ethoxide as precursors. A combination of sol-gel medium such as ethanol has been used in that experiment.

However, the modified sol-gel method still cannot synthesize sub-10nm ultra-small rutile which is highly metastable at low temperature and highly size-dependent as we discussed before. Very few reports of synthesizing ultra-small rutile NPs are associated with the laser deposition techniques\textsuperscript{34,35}. Investigation on ultra-small rutile is still in the infant state due to the difficulties in synthesis. This fact and the unexplored properties and uses, makes ultra-small NPs an interesting field to explore. For example, in 2015, Li et al.\textsuperscript{36} reported that ultra-small rutile NPs possess a great potential in enhancing the hydrogen production by increasing efficiency of visible light absorption.

1.3 Historical review of TiO\textsubscript{2} in photo-catalysis

Unlike other newest synthesized materials, TiO\textsubscript{2} is demonstrated to be an environmental friendly and non-toxic material through a long time of use by human beings. TiO\textsubscript{2} is even safe enough for government-permitted pigment in food. This material nowadays has wide applications such as self-sterilizing surfaces, anti-fogging surfaces, water purification, air purification, heat transfer and heat dissipation, anti-corrosion applications, and photo-catalysis. More advanced applications of TiO\textsubscript{2} are associated with photo-catalysis. For example, because the TiO\textsubscript{2} surface can decompose organic materials under ultraviolet light, the TiO\textsubscript{2} can be coated on the surface of the materials as a ‘self-cleaning’ layer. Fujishima\textsuperscript{22} showed many examples of this application: the MM tower built in Yokohama of Japan is coated with self-cleaning tiles, the Matsushita Denso building is covered with self-cleaning glass, self-cleaning sound-proof walls, eco-life-type houses using self-cleaning tiles and glass. One of the most promising applications of TiO\textsubscript{2} in photo-catalysis is water splitting producing H\textsubscript{2}, which is considered as a low-cost and environmental friendly candidate fuel to replace the non-renewal energy resources. Here we made a brief overview of the history\textsuperscript{22} of pivotal breakthroughs in TiO\textsubscript{2} photo-catalysis.
A century ago, the pioneer named Renz, in the University of Lugano (Switzerland), made a series of experiments by putting the CeO$_2$, TiO$_2$, Nb$_2$O$_5$ and Ta$_2$O$_5$ into organic compound. Surprisingly, he found that the color of these oxides turned from white to dark color, and he suggested that these oxides were partially reduced under sunlight illumination. The reaction was given as follows:

$$\text{TiO}_2 + h\nu \rightarrow \text{Ti}_2\text{O}_3 \text{ or Ti}$$

In 1924, Baur and Perret discovered that ZnO decomposed photo-catalytically the silver salt into pure silver. They guessed both the oxidation and reduction exist at the same time and proposed the reaction equation:

$$\text{ZnO} + h\nu \rightarrow h^+ + e^-$$

$$h^+ + \text{OH} \rightarrow \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O}$$

$$e^- + \text{Ag}^+ \rightarrow \text{Ag}^0$$

Then Baur and other researchers performed a series of experiments, and found that the ZnO can also be used as producing hydrogen peroxide as following reactions:

$$2e^- + 2\text{H}^+ + \text{O}_2 \rightarrow \text{H}_2\text{O}_2$$

These researches resulted in a great number of follow-up experiments on the photocatalytic properties of ZnO. TiO$_2$, however, was often just used as comparison to the ZnO, although a few breakthroughs from Japan, Germany, Russia and Switzerland came out. The milestone of TiO$_2$ in photo-catalysis research is that Fujishima and Honda found the photocatalytic water splitting of TiO$_2$ under UV illumination. They gave the reaction equation of water splitting as follows:

$$\text{TiO}_2 + 2h\nu \rightarrow 2e^- + 2h^+ \text{ (excitation of TiO}_2 \text{ by the UV light)}$$

$$2h^+ + \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ \text{ (at the TiO}_2 \text{ electrode)}$$

$$2e^- + 2\text{H}^+ \rightarrow \text{H}_2 \text{ (at the Pt electrode)}$$

The overall reaction then is:

$$\text{H}_2\text{O} + 2h\nu \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2$$

This process involves the (1) charge generation, (2) charge separation and (3) reaction at a surface of TiO$_2$, as shown in Figure 1-4. The initial step is the formation of photo-generated electron-hole pairs. When the energy of incident light is larger than the band gap of TiO$_2$, the electrons in the valence band (VB) will be excited into the conduction band (CB), leading to electron-hole pairs. The holes migrate to the TiO$_2$ side and react with water. As a result, oxygen gas and protons are generated. The most
important reaction occurs at the platinum side where the electrons react with protons and then H₂ is formed. The production of H₂ is limited by the charge separation, mobility of electrons and so on. This discovery then stimulated a large number of following researcher to focus on the water splitting of TiO₂, because one of the products, the H₂, is considered as the ideal replacement of the non-renewal fossil fuels. Another milestone of TiO₂ photocatalytic application also indirectly started from that year. Tributsch used ZnO electrodes to successfully convert visible light into electric current. Very soon, this technique was applied to TiO₂, and then ZnO was replaced by the TiO₂ because TiO₂ is much more stable under the illumination of light.

![Figure 1-4 Water splitting process in TiO₂. This process involves the generation and migration of electrons and hole pairs under illumination of light sources. The associated products in this process are O₂ and H₂. H₂ is considered as a potential clean fuel.](image)

These two findings attracted attention of scientists who realize the potentially tremendous applications in photocatalysis of TiO₂, and thus TiO₂ enjoyed a rapid development from then on. TiO₂ has the advantage of excellent photocatalytic activity, stability, non-toxicity and low cost. However, the intrinsic disadvantage of TiO₂ as a photo-catalysts are the large optical band gaps (3eV for rutile and 3.2eV for anatase), which significantly limit the absorption of solar energy in both rutile and anatase because they only absorb ultraviolet lights which only makes up <5% of sunlight.
1.4 Review of gap narrowing engineering techniques of TiO$_2$

To overcome the bandgap problem of TiO$_2$, starting ~30 years ago, a growing number of research focused on the modifying the TiO$_2$ to be active in the visible light range. The term ‘band gap narrowing’ means (1) the intrinsic band gap is narrowed by pushing down the CB and/or pushing up the VB, or (2) creating mid-gap defect state in band gap of TiO$_2$. Because it is nearly impossible to comprehensively summarize and categorize all the methods associated with band gap narrowing, here we introduce the most common approach (doping) and two novel and attractive methods involving synthesizing new polymorphs of TiO$_2$ and defective TiO$_2$.

1.4.1 Doping

The conventional effort involved doping element(s) in the TiO$_2$ such as Cr, Cu, Fe, S, C and N. Doping has been demonstrated to be an effective way to narrow the band gap of TiO$_2$ especially the non-metal doping, which has been intensely studied recently. In 2001, Asahi et al.$^{37,38}$ discovered the N-doping TiO$_2$ absorbed light at less than 500nm. This N-doping TiO$_2$ thin films showed obvious activity under visible light exposure, and decomposed acetaldehyde and decolorize methylene blue solution. Starting from that breakthrough, a growing number of associated studies have originated. Now, N doping TiO$_2$ can be achieved by a variety of methods including sol-gel, ion implantation, chemical vapor deposition (CVD), sol-gel, sputtering and many others.

In 2002, Khan et al.$^{39}$ successfully extended the absorption threshold into the visible light range by doping carbon into TiO$_2$. From their report, substitutional carbon atoms replace oxygen atoms in the TiO$_2$ lattice. The band gap of the C doped TiO$_2$ (in rutile form) was estimated as 2.3eV instead of 3.0eV in pure rutile. Fantastic water splitting photo-conversion efficiency of 8.4% was reported by them. However, this unbelievable high photo-conversion efficiency was highly criticized and nobody could reproduce such a high efficiency.

Furthermore, several other elements such as F were used as dopants in TiO$_2$. Yu et al.$^{40}$ used F ions to dope TiO$_2$ by hydrolysis of titanium tetraisopropoxide in a mixed NH$_4$F-H$_2$O solution. TiO$_2$ in anatase and brookite form show stronger absorption in the UV-visible range, and a red shift of the band gap was observed. However, the photo-conversion efficient was not given and is supposed to be lower than the N or C doping ones.
It should be noted that doping elements into TiO$_2$ would also cause phase transformation among different polymorphs. Since photo-activities of the different polymorphs of TiO$_2$ vary significantly, this effect of doping element has to be considered. The impact of doping element on phase transformation is well studied in the rutile-anatase systems: Hanaor et al.\textsuperscript{41} made an excellent review on the influence of doping elements on the rutile-anatase phase transformation. As shown in Figure 1-5, they summarized the inhibition or promotion effects of different doping elements on anatase-rutile phase transformation by experiments or predictions. The prediction is based on four deductive considerations of the potential effects of dopants:

i) Most common valence of metallic elements in titanium dioxides is proportional to the ionic radii of substitutional cationic dopants as follow equation:

\[ y = -0.0455x + 0.2045 \]

**Eq. 1-10**

where \( x \) is the valence and \( y \) is the ionic radius.

ii) The potential for valence change in dopant cations should be considered (i.e. Fe$^{3+} \rightarrow$ Fe$^{2+}$);

iii) The potential for oxygen vacancy formation through reduction should be considered (e.g., C and N doping);

iv) Effects of anioic dopants cannot be understood intuitively. Therefore, only known effects of anioic dopants (e.g. F$^-$ and Cl$^-$) reported by literatures can be used for the prediction.

Another drawback of doping is that the added dopants may create defect state in the mid-band gap acting as recombination centers. The mechanism and the effects are still highly disputed\textsuperscript{42} because the electron-hole recombination is highly sensitive to synthesis methods, temperatures, charge trapping and excitation intensities.

1.4.2 New form of TiO$_2$

Another approach is associated with exploring new polymorphs of TiO$_2$ with narrower band gaps. Though TiO$_2$ has been used for thousands of years, new polymorphs have been continuously discovered with the development of synthesis technologies. In 2004, Mattesini M. et al\textsuperscript{6} reported that they synthesized the cubic-TiO$_2$ phase at high temperature and high pressure. Although this phase is transformed from the anatase, it can be only thermo-dynamically stabilized over the TiO$_2$-OII phase at
Dopant experimentally observed to inhibit the transformation of anatase to rutile

Dopant experimentally observed to inhibit the phase transformation under certain conditions (mixed effect)

Dopant predicted to inhibit the transformation of anatase to rutile

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Dopant experimentally observed to promote the transformation of anatase to rutile

Dopant experimentally observed to promote the phase transformation under certain conditions (mixed effect)

Dopant predicted to promote the transformation of anatase to rutile

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Figure 1-5 Experimental and predicted inhabitation and promotion of anatase to rutile transformation based on the preceding four considerations from Ref [34].
a pressure of 48GPa and a temperature of ~2000K. However, they also pointed out that cubic-TiO$_2$ can possibly be obtained in room conditions by doping, i.e. yttrium. The transformation mechanism between cubic-TiO$_2$ and anatase was investigated by Tsai et al$^{43}$ using in-situ TEM. They found that fluorite-type TiO$_2$ was transformed to anatase through a martensitic transformation. The crystallographic relationship is $<001>_f || [100]_a$ with a habit plane similar to $\{100\}_f || (001)_a$.

Interestingly, no publications reported the transformation of rutile to cubic-TiO$_2$. However, this doesn’t mean this transformation cannot happen because the transformation from rutile structure to cubic structure in other oxides has been well investigated by many researches, i.e. Haines, J et al$^{44}$. It was reported by Mattesini, M. et al.$^{45}$ that cubic TiO$_2$ (either of pyrite type or of fluorite type) can be considered as a potential solar-energy absorber based on ab-initio calculation. Later on, cubic TiO$_2$ has been intensely investigated. Mahmood et al$^{46}$ did a great work to summarize the electronic, elastic, acoustic, and optical properties of cubic TiO$_2$ by comparing different first principle calculation methods. However, due to the difficulty in synthesizing cubic TiO$_2$, most research associated with the properties are still restricted to calculations.

The newest form of TiO$_2$ was discovered by Tao et al.$^{47}$ in 2011, who found a single layer of TiO$_2$ stoichiometry whose band gap is 2.1eV. They first produced a rutile crystal with (011) terminal plane. This crystal was reduced in vacuum, and then showed a blue color. The reduced layer originating from surface reconstruction$^{48}$ has a symmetry called ‘add row Ti$_2$O$_3$’$^{49,50}$. They re-oxidized this layer and it transformed into this new form of TiO$_2$ which exhibits a 2.1eV band gap as measured by scanning tunneling spectroscopy (STS) and ultraviolet photoemission spectroscopy (UPS). However, though this new form of TiO$_2$ is considered a promising photo-absorber, there is a major problem of this material for applications: it is too thin to harvest an appreciable amount of solar energy and it seems not to be possible at this time to grow a thicker layer of this material. Even the synthesis of a single layer under the similar conditions is hard to reproduce$^{51}$.

1.4.3 Defective TiO$_2$

Synthesizing these new forms of TiO$_2$ is still challenging and costly i.e. high temperature and high pressure for synthesizing cubic TiO$_2$. It has been shown empirically that the formation of structural imperfections govern the properties$^{52,53}$ of TiO$_2$ NPs. The most common defects in TiO$_2$ are oxygen vacancies$^{54}$. The oxygen-deficient TiO$_2$ has been demonstrated as a visible light responsive photocatalyst$^{55-60}$. Theoretically, the existence of oxygen vacancies are accomplished with unpaired
electrons or Ti$^{3+}$, which may form donor levels in the band structures of TiO$_2$\textsuperscript{51,52}. Pan et al.\textsuperscript{54} did an excellent review on the formation of oxygen vacancies via different methods, in which they discuss how oxygen vacancies influence the electronic structures of TiO$_2$, and potential photocatalytical applications. According to their review, the oxygen vacancies can be introduced by thermo-annealing in a reducing atmosphere, bombardment using high energy particles, and doping. Defective TiO$_2$ with oxygen vacancies has unique physical and chemical properties, and can be a candidate for a visible light absorber. However, further investigation of oxygen vacancies still need to be developed, but this research is very difficult to perform in experiment and has been perused only through calculations. For example, defects formation energy is usually challenging to measure in the experiment but readily accessible through density functional theory (DFT). Chretien et al.\textsuperscript{63} investigated the positions and energy of the unpaired electrons by taking oxygen atoms out of unit cell from DFT+U. They found if $U< 2.5 \text{eV}$, the unpaired electrons are delocalized; $3.0 \text{eV} < U < 6.0 \text{eV}$, they are both localized on different Ti atoms, reducing them (formally) from Ti$^{4+}$ to Ti$^{3+}$. The formation energy of the vacancies depends on the location of the pair of reduced Ti atoms. This calculation will be very important for us when we determine the reduced phase at the surface.

A particularly intriguing example of defective TiO$_2$ that has been intensely studied recently is that of “black” TiO$_2$ NPs\textsuperscript{64,65}. The enhanced photocatalytic activity of this form of TiO$_2$ is attributed to the bandgap narrowing in the surface layer that is produced by crystallization of amorphous material in a variety of highly reducing atmospheres, for example in a H$_2$ stream. It has been shown that reducing stable, white crystalline TiO$_2$ powders (Degussa P25) produces only pale blue samples with no red shift in the absorption spectra. Though this material was reported very recently by Chen et al.\textsuperscript{64}, tremendous volume of research has been performed due to the prominently enhanced photo-activities and narrowed band gap of TiO$_2$. In 2015, Chen et. al.\textsuperscript{66} performed a great job in summarizing comprehensively the synthesis approaches, properties and applications of black TiO$_2$. It generally accepted that the reduction annealing ambient gives rise to a unique core-shell structure of black TiO$_2$, a stoichiometric core with an amorphous shell. It is argued that black TiO$_2$ is uniquely stable because the metastable defective phase containing oxygen vacancies and Ti$^{3+}$ is frozen in. However, it is highly possible that oxygen vacancies of a high amount should react with the stoichiometric TiO$_2$ and form reduced structures, i.e. magnéli phases or Ti$_2$O$_3$. Therefore, a systematically characterization of structures need to be
performed on the black TiO$_2$. In this study, we characterized a form of black TiO$_2$ in great details and the results are shown in chapter 3-4.

1.5 Summary and motivation

In summary, TiO$_2$ is an easy fabricated, low cost and high photo-activity material in photocatalytic application, i.e. water splitting. However, the current application of TiO$_2$ is hindered by its intrinsic property-the large band gap. Dopants injection is the most conventional way to narrow the band gap but it is disputed that the defect states in the band gap may act as recombination center of electron-hole pairs. Directly synthesizing the new form of TiO$_2$ with narrowed band gap can fundamentally solve this problem. The recent intensely developed way involving creating defects can significantly decrease the band gap of TiO$_2$ in a low-cost way.

The motivation of this work is to find a low-cost but effectively way to obtain the TiO$_2$ NPs with narrowed band gap. We focus on the fundamental understanding in the evolution of the TiO$_2$ structures during different process, i.e. thermo-annealing by taking advantage of a combination of high spatially resolved techniques which we will introduce in next chapter.
Chapter 2. *Experimental methodologies*

2.1 *Synthesis and sample preparation*

Pulsed laser deposition (PLD), a well-known and versatile synthesis method, typically used for epitaxial thin film growth, was used here as a clean way of synthesizing ultra-small TiO$_2$ NPs by gas phase condensation. By adjusting the density and thermalization dynamics of the ablation plume through the choice of laser fluence and background gas density, different phases and sizes of TiO$_2$ NPs could be synthesized. Temporally- and spatially-resolved gated-ICCD imaging is employed as *in situ* diagnostic to study the propagation of the ablation plume over which the high kinetic energy species in the laser plasma are thermalized to condense and deposit as NP aggregates onto substrates for subsequent analysis by HRTEM. Pulsed KrF (248nm, 1 J cm$^{-2}$, 1 Hz) laser vaporization of a TiO$_2$ targets in room temperature and 200 mTorr oxygen background pressure were determined to produce a spatially confined laser ablation plasma plume that thermalized over different stopping distances and resulted in the formation of ultra-small (< 5 nm) NPs. These ultra-small NPs were deposited as loosely assembled aggregates onto room-temperature Si substrates. The experimental setup and representative plume images are shown in Fig 2-1.

![Figure 2-1(a) Schematic of the experimental setup. (b) Time resolved imaging of visible plasma plume luminescence at the indicated times after laser ablation in 1Torr Ar and 873 K substrate temperature.](image)
These as-synthesized ultra-small NPs appeared amorphous under examination by electron diffraction as shown in Fig 2-2. However, we found that these NPs produced by our non-equilibrium synthesis route can serve as versatile “building blocks” to form a variety of morphologies and phases when deposited at different rates and temperatures. In Chapter 3-1, we will first focus on the characterization of the ultra-small NPs “building blocks” that were deposited at room temperature. Then, we will study the structure of larger TiO$_2$ NPs of anatase, TiO$_2$(B), and rutile phases that were formed by post-annealing UNPs at 400-900°C, for 1-2 hours in different background gas.

Figure 2-2 Electron diffraction patterns taken from morphous NPs synthesized in room temperature.

2.2 Analysis Methodologies:

Characterization of the TiO$_2$ NPs was performed with the transmission electron microscopy (TEM); Aberration-corrected scanning transmission electron microscopy (STEM); electron energy loss spectrum (EELS); selected area diffraction (SAD); nano-beam electron diffraction (NBED) and Energy dispersive X-ray spectroscopy (EDS). The TEM characterization of the samples was performed with a Zeiss Libra 200 MC TEM at an acceleration voltage of 200 kV. The information limit in high resolution TEM images in this microscope is ~0.1nm, and the energy resolution of the EELS with monochromator is ~0.1eV measured at the full width at half maximum (FWHM) of the zero-loss peak in the vacuum. In STEM mode in this microscope, the beam size of nano-beam diffraction varies from 0.5-2 nm depending on experimental requirements. The overview of the structure of Zeiss libra200 MC TEM is shown in Figure 2-3. The parts from number 1 to 16 are: 1. field emission gun (FEG), 2.

2.2.1 Conventional TEM methods

The conventional electron microscopy methods used in this paper involved SAD, HRTEM and EDX. Since these techniques are well explained in microscopy textbooks, here we will only make a short introduction of these techniques.

2.2.1.1 SAD

Electron diffraction originates from constructive interferences of the coherently scattered electron waves when incident electrons are scattered by a specimen with a periodic structure. The scale of periodicity can be in long range order (~hundreds of nanometers) in crystalline materials, or short range (a few angstroms) order in amorphous materials. Diffraction patterns (DP) in the TEM has long been used to determine material phases, orientations of single crystals, degree of crystallinity, poly-crystallinity and so on. The specimen is illuminated with either a parallel electron beam (strictly speaking, an extremely low convergence angle) or a convergent electron beam. The Köhler illumination method is used in Libra200 MC, which produces extremely uniform illumination on the sample and ensures the electron source not visible in the resulting image. In the parallel condition, if we insert an aperture in the image plane of the objective lens to select a specific region of interest (ROI), the diffraction pattern in the focal plane is called selected area diffraction (SAD) pattern. The aperture is called the SAD aperture, whose function is to create a selective virtual aperture at the plane of the real specimen conjugate with the image plane. In comparison, if we insert an aperture in the back focal plane to select a certain reflection in the DP, then a dark field (DF) image is formed.

Figure 2-4a shows a representative DP from a single crystalline WS2 triangle film shown in Figure 2-4b. Because the zero beam is too strong, we must blank it in the center. Indexing the reflections in such a single crystal is not difficult once the crystal is tilted to a specific zone axis, i.e. [001] direction for the DP in Figure 2-4a. However, the orientations of the NPs are random. As a result, all possible reflections will exist in the DP and each reflection which fulfills Bragg’s law will diffract creating a ring pattern. Figure 2-4c shows a representative polycrystalline anatase DP. Figure 2-4d is
Figure 2-3 Overview of Zeiss libra200 MC TEM
the intensity profile derived from Figure 2-4c. Indexing the diffraction rings from a single phase is accomplished by measuring the d-spacing of each ring and comparing it with reference electron diffraction patterns or X-ray diffraction pattern (XRD) or comparing with d spacing calculations from the crystal structure. However, it is extremely challenging to extract the phase information from a DP of multiple phases. As shown in Figure 2-4e, a DP from a mixture of rutile (R), anatase (A), TiO$_2$(B), and brookite (Br) shows very complicated reflections. From the intensity profile shown in Figure 2-4f, the phase from the strongest peak locating at 2.8±0.1 /nm cannot be unambiguously distinguished because it can belong to reflections from anatase, TiO$_2$(B), or brookite. Therefore, alternative tools such as EELS and HRTEM imaging are necessary. We will introduce HRTEM imaging in the following section.

2.2.1.2 HRTEM image

A brief definition of HRTEM image from a TEM textbook written by Fultz$^{68}$ is: “The HRTEM image is an interference pattern of the electron wavefunction with itself after it is diffracted from the specimen”. The contrast in HRTEM image originates from the difference in the phase of electron waves scattered from a specimen. The mechanism of the contrast is quite hard to interpret because it depends on many factors: thickness, orientation, scattering factor of the specimen, variations in the focus or astigmatism of the objective lens$^{67}$. By using HRTEM imaging, one can determine the phase of a NP assuming the NP is a single crystal. Figure 2-5a is a HRTEM image taken from a rutile NP. The atomic structure of this NP is clearly resolved, and we can see there are two distinct grains (labeled A and B) and an edge dislocation in the top of grain A. The inset of Figure 2-5a is a conventional technique to interpret the HRTEM image called fast Fourier transformation (FFT) image or diffractogram, which provides useful information about the periodicity of a crystal. From the FFT, we can easily distinguish that the zone axis (the viewed direction) is (111) by calculating the d-spacing and inter-plane angles. We can also distinguish the twinning relationship between grain A and grain B by observing the reflection spots in the diffractogram: The reflections inside the red and green circles come from grain A and B, respectively. The (110) mirror symmetry is evident as all the reflections from grain A are mirrored to those from grain B. This information is critical in understanding how the atomic structure changes in the NP, i.e. the TiO$_6$ octahedra change orientation across the mirror plane, as shown in Figure 2-5b.
Figure 2-4 Diffraction patterns of single crystalline, polycrystalline and multiple phases, respectively. (a) Diffraction pattern of WS\(_2\) thin films. The DP was taken from an area of this film hanging in vacuum in (b). (c,d) Diffraction pattern of anatase and its intensity profile. (e,f) Diffraction pattern of different polymorphs of TiO\(_2\).
However, the HRTEM image is more difficult to interpret if the material is not single crystalline. It is problematic to obtain material phase information from a defective, polycrystalline or amorphous material where moiré patterns from mixed phases may obscure the true d spacing. Additional characterization methods (i.e. EELS) are necessary for a reliable phase identification. In the following we will introduce these methods.

Figure 2-5 HRTEM of a rutile NP and a model of its interface. (a) HRTEM image of a rutile particle viewed in [111] direction with twin boundary, and fast fourier transformation (FFT) diffractogram of the interface area. The reflections highlighted in red come from grain A, while those in green come from grain B. The mirror plane is (101), of which the corresponding reflections are indicated in yellow. (b) Atomic model of the interface structure. The interface is highlighted by the purple line.

2.2.1.3 EDS

When the high energy electron beam hits the sample, the core electrons in deep energy levels may be kicked from the atoms and leave holes. As a result, electrons from higher energy levels will fall into these newly created holes by emitting a characteristic X-ray to release the energy. Because each element (of different valences) has its unique atomic structure, the corresponding X-ray spectrum has a unique set of peaks. This spectrum is called the X-ray energy dispersive spectrum (EDS), which is a very convenient tool to distinguish elemental types in the sample. Figure 2-6a shows a high angle annular dark field (HAADF) image of TiO$_2$ NP aggregations, and the inset is the EDS taken from this area of energy ranging from 0 eV to 10 keV. The corresponding elemental maps of Ti, O and Cr are shown in Figure 2-6b-d. From these maps, we can quickly check that Cr was successfully doped in the sample and observe the distribution of Cr. However, elemental quantification from EDS is challenging.
It is impossible to prevent X-ray radiation from areas outside the ROI. X-rays of this nature are termed “spurious X-rays”\(^6\). As shown in Figure 2-6e, the copper signal in this map originates from the copper TEM grid rather than the TiO\(_2\) aggregations. Since Ti and O are common impurities in Cu, an elemental quantitative analysis is not possible as there is an unknown contribution of spurious x-rays from outside the ROI.

2.2.2 Advanced TEM methods

2.2.2.1 Monochromated EELS

Electron energy-loss spectroscopy (EELS) involves analyzing the energy distribution of initially monoenergetic electrons after they have interacted with a specimen\(^6\). We compare these band structure characterization techniques: EELS, Auger electron spectroscopy (AES), EDS, X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and Ultraviolet photoelectron spectroscopy (UPS), because these techniques have many similarities and differences, as shown in Figure 2-7. The analogue of EELS is XAS. Instead of using an electron beam, XAS is obtained from synchrotron radiation sources, which provide a series of tunable X-ray beams. Both EELS and XAS can be used to investigate the electronic structure of the CB associated with the excitation of electrons from deep core-levels. The corresponding feature in EELS or XAS is called energy-loss near edge structure (ELNES) or X-rays near edge structure (XANES) and the peak(s) in this feature is (are) called ionized edge(s). However, it is also possible that the excited electrons are removed from the atoms and behave like a free electron wave. The associated feature in the XAS or EELS is called extended X-ray absorption fine structure (EXAFS) or extended energy-loss fine structure (EXELFS) which usually starts 50 eV above the ionization edges\(^6\). Because the free electron gas is weakly bonded, we can determine atomic positions in a relatively short range order. With associated the partial radial distribution function (RDF) can be obtained from EXAFS or EXELFS. UPS and XPS is used to measure binding energy \(E_b\), which equals the total energy of the source of the exciting radiation, \(E\), minus the sum of work function \(\Phi\) and kinetic energy of excited photoelectrons \(E_k\). In this case, the electrons are excited to vacuum level rather than staying within the CB. Depending on the excitation source, either X-ray or ultraviolet light, the spectrum is called XPS or UPS. Because the energy limit of ultraviolet light is much smaller than that of X-rays, the spectrum usually ranges from 0eV to 60eV. However, the resolution of UPS is
Figure 2-6 EDS of Cr doped TiO$_2$ NP aggregations. (a) HAADF image of Cr doped TiO$_2$ nanoparticle aggregations. The inset is the EDS of this area. (b-e) Elemental maps of Ti, O, Cr, Cu from EDS.
usually much higher than XPS, and, therefore, scientists often use UPS to investigate the detailed electronic structure of VB. Because an electron-hole will be created when an electron is kicked from its original energy level, the electron above this energy level will fill into this hole. As a result, the atom will either emit characteristic X-rays or excite an electron from a higher energy level to vacuum. EDS is used to measure the energy of characteristic X-rays and AES measure the kinetic energy \( E_k \) of the eject electron which is called an Auger electron.

The recent monochromator (MCR) technology remarkably improves EELS spectroscopy’s resolution which is now comparable to that of X-ray absorption spectroscopy (XAS). The development of MCR is explicitly introduced by Egerton\(^6^9\), and here we just made a comparison showing how the TiO\(_2\) ELNES features change at different energy resolution by tuning the MCR slit in the Libra 200 MC. In the EELS spectrum, a peak located at 0 eV is formed by electrons which are elastically scattered or not scattered. Therefore, this peak is termed the zero-loss peak (ZLP). We determine the energy resolution of the EELS spectrum by measuring the full width at half maximum (FWHM) of the
ZLP in the vacuum. Figure 2-8 shows various ZLPs taken using MCR slits of different widths: 0.5μm (black), 3μm (green), 5μm (pink), and 60μm (blue). The energy resolution of each spectrum is 0.1, 0.18, 0.28 and 0.3eV respectively. The energy resolution becomes worse with increasing the MCR slit width. The higher the resolution, the more fine structure we can resolve in the core-loss spectrum. Figure 2-8b shows EELS spectra of Ti-L₂,₃ edges taken using different MCR slits. The intensity difference of two L₃-ε₈ peaks in the EELS spectra taken with an MCR slit width of 0.5μm is clearly resolved. The L₃-t₂₆ peak is relatively sharp with a FWHM of ~0.4eV, and two pre-peaks are also clearly resolved. L₃ edge of EELS spectra become slightly broadened with increasing MCR slit width from 0.5μm and 5μm. However, EELS spectra with an MCR slit width of 60μm become significantly featureless: the two pre-peaks cannot be resolved and the intensity difference between the two L₃-ε₈ peaks is not easy to recognize. Interestingly, the energy resolution measured by FWHM of the ZLP only decreases by 0.02eV from 5μm to 60μm but a significant change of features appears. The reason is that the effective energy resolution for the 60μm slit is worse than 0.3 eV because the ZLP is asymmetric in this case. Therefore, using a smaller slit is necessary for investigating the fine structures of EELS. In our research, all the experiments are performed at 0.5μm.

Figure 2-8 ZLP (a) and core-loss spectra including Ti-L₂,₃ edges (b) of EELS spectra taken with different MCR slit widths from 0.5μm to 60μm

2.2.2.2 NBED mapping

The inability of SAD to characterize a single NP is obvious: The size of the selected area (a few hundred nanometers in diameter) is large compared to the dimensions of NPs. Compared to SAD,
convergent beam electron diffraction (CBED) is performed by converging the electron beam into a small spot (0.3-1nm in Libra 200 TEM). Therefore, this technique can be used to determine the crystal structure of a small volume. CBED can also give you 3-D information about the sample such as sample thickness and 3D symmetry (space group). If one uses a small condenser aperture to confine the converged beam size making it close to parallel illumination, then this type of CBED is called NBED. The smallest condenser aperture in the Libra 200 TEM is 5μm, which limits α (the convergence angle) to 1.25mrad, while α is 0.02mrad in SAD. In STEM mode, because the electron probe is already converged, you can easily switch to the NBED mode by just inserting the smallest condenser aperture. The advantage of performing NBED in STEM is that we can move the electron beam by tuning the scanning coils and then map the NBED patterns in a specific ROI. This function was realized through a custom script within the Digital Micrograph software (© Gatan). NBED mapping is important for us to investigate the short range order (SRO) of an individual defective TiO$_2$ NP, while SAD always provides overall information about the SRO of large number of NPs, as shown in Figure 2-9

![Figure 2-9 Comparison of NBED and SAD](image)

(a) $2\alpha \approx 2.5$ mrad
(b) $2\alpha \approx 0.04$ mrad

Beam size $d < 1$ nm

Selected area $d \approx 200$ nm

Figure 2-9 Comparison of NBED and SAD. (a) NBED patterns are taken from a small volume of the material and they show the local symmetry $< 1$ nm. (b) SAD patterns are taken by selecting an area in the image plane with a diameter of $\sim 200$ nm and it represents the overall structures of the materials.
2.2.2.3 Atomic resolution in STEM

The formation of a STEM image is different from that of HRTEM image. The HRTEM image is formed in a ‘stationary’ way under parallel electron illumination, while in STEM mode, the electron beam is converged into a small probe. With this electron probe, the ROI of a sample is scanned by the scan coils. An electron detector receives electrons from the specimen at each location, and then amplifies and displays the corresponding signals on the computer pixel by pixel. The magnification of STEM isn’t modified through lenses but is controlled by the scan dimensions on the specimen. The detectors are placed in the back focal plane and act as an objective aperture to let only a portion of the electrons participate in forming image. As shown in Figure 2-10, the bright field detector uses electrons from the direct beam to form an image which is termed a bright field (BF) image. If we want to image with the scattered electrons, then we need place an annular shaped detector around the direct beam. The associated image taken by this detector is termed the annual dark field (ADF) image. Depending on the angle of scattering angle of electrons contributing to image, the ADF image can be a low angle annular dark field (LAADF) image, medium angle annular dark field (MAADF) image, or high angle annular dark field (HAADF) image. Because electrons participating in forming a HAADF image are incoherently elastically scattered, the HAADF image is sensitive to the atomic number of the atoms. Therefore, HAADF image is also called a Z-contrast image.

The resolution of STEM imaging depends on how fine the probe is. The electron beam diameter $d$ is determined by the intrinsic electron-beam intensity distribution, Rayleigh criterion, and aberrations. Aberrations play a major role in influencing the diameter of electron beam since the first two factors have very limited contribution. With the development of aberration correctors, resolution in STEM images can easily approach a sub-angstrom level. Principles of aberration correction are well discussed by Pennycook et al. Here we introduce the idea of an aberration function and its parameter. A quantitative description of wavefront distortions are determined by the aberration functions:

$$\chi(\theta, \phi) = \sum_n \sum_m \left( C_{n,m,a} \theta^{n+1} \cos(m\phi) + C_{n,m,b} \theta^{n+1} \sin(m\phi) \right) / (n + 1)$$

Eq. 2-1

Where $\theta$ and $\phi$ are the axial angle and azimuthal angle respectively, $n$ refers to the order of aberration, $m$ is angular multiplicity, $C$ is the aberration coefficient, and $a$ and $b$ refer to orientations. Figure 2-11 shows electron wavefront distortions due to different aberrations.

In this research, we use a state-of-art 5th order Nion aberration-corrected UltraSTEM 200 STEM.
The resolution limit of this machine is ~50pm. A measurement of the resolution can be obtained by measuring the d-spacing of reflections without periodicity (to avoid multiple scattering) in the FFT image. Figure 2-12 shows a rutile NP with multiple twin boundaries taken by the UltraSTEM 200. The inset is the FFT image as an example for estimating the resolution. With a sub-angstrom resolution (<80pm measured from the in FFT), the periodicity of the surface shell of this rutile NP is clearly resolved. We will discuss in details about this shell in Chapter 3-4. We also use STEM equipped in Libra 200MC. The resolution is 0.3nm.

Figure 2-10 Formation of BF, LAADF, and HAADF images. BF = bright field detector, LAADF = low angle annual dark field detector, HAADF = high angle annual dark field detector. These detectors use (1) the electrons scattered from direct beam to form BF image, (2) the electron scattered from low angle to form LAADF image, and (3) the electron scattered from high angle to form HAADF image.
Figure 2-11 Distortions of electron wavefront due to aberrations from 0th to 5th order from Ref [71].
2.2.3 Analysis methods

2.2.3.1 EELS spectra quantification

EELS spectrum quantifications have been performed using a versatile software called ‘Quantifit’. With this software, we can accurately determine elemental fractions of (doped) TiO$_2$ NPs, determine the thickness of TiO$_2$ NPs, fit the low energy-loss or core-loss spectra, and analyzing the EELS spectra, NBED patterns and STEM images for many other functions. The background of the EELS spectrum is subtracted by a combination of a power law and a polynomial: $E^r + aE^2 + bE + c$, here $a$, $b$, $c$ and $r$ are fitting parameters and $E$ is the energy. We fit the background between 400eV-455eV for the Ti-L$_{2,3}$ edges and 510-525eV for the O-K edges. Then the background subtracted intensities, $I$, of the ionization edges are directly related to the areal density, $N$, of the element as given by:

$$I(\beta, \Delta) = N(\beta, \Delta) \times \sigma(\beta, \Delta) \times I_T.$$  \hspace{2cm} \text{Eq. 2-2}

Where $N$ is the absolute number of atoms per unit area, $\sigma$ is the inelastic scattering cross-section, $I_T$ is the total transmitted intensity, $\beta$ and $\Delta$ represent the dependence of the integration energy window and
collection angle respectively. If $I_T$ and $\beta$ are kept constant in this experiment, the ratio between two elements $a$ and $b$ are determined by the cross-section and ionization edge intensities:

$$\frac{N_a(\Delta a)}{N_b(\Delta b)} = \frac{I_a(\Delta a)}{I_b(\Delta b)} \times \frac{\sigma_b(\Delta b)}{\sigma_a(\Delta a)}$$

Eq. 2-3

In equation 2-3, if we know the total number of transmitted electrons striking the detector, then we can calculate the areal density, $N$, of a certain element because the inelastic scattering cross-section is known for specific elements. The total number of electrons is obtained through measuring the conversion factor between beam current and electron counts. The beam current can be directly read through putting the electron beam on the phosphor screen. Electron counts are measured by imaging the Ronchigram of vacuum in STEM mode. The ionization edge signal comes from the total scanned volume which equals $\text{width} \times \text{length} \times \text{sample thickness}$ (see Figure 2-13). Since the areal density is total electrons in an area whose size is determined by $\text{width} \times \text{length}$, the thickness $t$ of a sample is areal density divided by volume density ($N/\rho$). For a known crystal, $\rho$ is easy to calculate. Coupled with STEM imaging, this technique enables us to reconstruct the whole 3-D profile of a NP. We will show how to use this technique to reconstruct the a core-shell structure NP in Chapter 3-4

Figure 2-13 Right: Schematic of the electrons within a certain volume, all of which contribute to the intensity of ionization edges in EELS spectra (Left).
2.2.3.2 Linear combination and linear least-square fit

In an EELS spectrum, if two mixed phases have the same elements but different ELNES (for example anatase and rutile), then we can use a linear combination and linear least-square fit to identify these phases. We show an example for identifying Ti$_2$O$_3$ and TiO$_2$ in a reduced titanium oxide in this section. To make a reasonable comparison among different EELS spectra, the intensities of the Ti-L$_{2,3}$ edge and O-K edge in the EELS spectra must be normalized within a certain energy window, specifically, 450eV-470eV for Ti-L$_{2,3}$ edge and 525-550eV for O-K edge, respectively. Then we used linear combinations of EELS spectra from pure TiO$_2$ and Ti$_2$O$_3$ for the Ti-L$_{2,3}$ edge and O-K edge to reconstruct the spectrum. As shown in Figure 2-14, fine features in the Ti-L$_{2,3}$ edge and O-K edge ELNES change significantly with increasing Ti$_2$O$_3$/TiO$_2$ ratios.

![Figure 2-14 Reconstructed EELS spectra of Ti-L$_{2,3}$ edge and O-K edge at different Ti$_2$O$_3$/TiO$_2$.ratios.](image)

It should be noted that the energy dispersion of reference spectrum from pure rutile used in this linear combination is 0.1eV/channel in order to acquire Ti L$_{2,3}$ and O-K edges at the same time. Thus, there is a small reduction of energy resolution (<0.1eV) because the zero-loss peak cannot be focused as precise as in the highest energy dispersion (0.025eV/channel) case.

We then use least-square fitting to find the best fit between the experimental spectra and the reconstructed spectra, yielding the coefficients. The spectrum range before any ionization edge allows for determination of the average noise after background subtraction. The energy window was 430eV-455eV for the Ti-L$_{2,3}$ edge and 510-525 eV for the O-K edge. To judge the quality of fit, we can compare the fit difference and this noise. However, as the EELS spectra may have a small energy drift.
(≤ 0.1eV) during acquisition, we need to align the EELS spectra by using some fine features as reference positions (the L₃-t₂g peak, for example). We will discuss how useful this technique is to identify the Ti₂O₃ component in a black TiO₂ NP in Chapter 3-4.

2.2.3.3 Band gap determination

In the low energy-loss spectrum, we can directly measure the band gap of a TiO₂ NP. In the past, the broad energy spread of the ZLP made it difficult to extract the signal from interband transitions. The asymmetry of ZLP further complicates band gap measurements. However, recent breakthroughs in monochromator technology for EELS significantly reduce the energy spread of the ZLP and therefore lead to precise band gap determination of semiconductors with 0.1eV error by using different EELS spectrum fit methods such as Fourier-log deconvolution to obtain single scattering distributions, power law to fit the tail of ZLP, and visual determining the band gap without fitting. However, though monochromated EELS highly suppresses the impact of the ZLP on band gap determination, there are still many factors that influence the accuracy of band gap determinations. For example, accuracy of the band gap determination for anatase may be lower than that of rutile because anatase has an indirect band gap while rutile has a direct band gap. In indirect band gap materials, excitation of electrons from the top of the VB to the bottom of the CB isn’t through the Γ-Γ transition but is associated with momentum transfer. Therefore the cross-section for interband transitions of indirect band gap materials is lower than that of direct band gap materials. Other transitions such as Cerenkov radiation, surface plasmon or excitonic excitation can also occur in the energy range of the band-gap and complicate band gap measurements in many materials. This is however not the case in our TiO₂ nano-particles.

In this research, we used EELS spectra taken from a standard rutile (Degussa 25) of known band gap (3eV) to compare different measurement methods. The maximum of the ZLP is shifted exactly to 0eV because there is a 0.1eV-0.2eV uncertainty due to high tension energy instability. The electron beam is placed at the center of the rutile NPs. The measured band gap is constant in most TiO₂ NPs synthesized in our experiments. One may need to consider quantum size effects when measuring NPs below 2 nm in diameter, and however the particles examined here were substantially larger. Figure 2-15a shows the simplest method to estimate the band gap by reading the minimum between the ZLP’s right tail and the onset of the first TiO₂ interband transition (VB-3d) peak located at 3-7eV. This point can be precisely measured by taking the first derivative of the EELS spectrum, as shown in Figure
2-15b. Though this method is simple we obtain very accurate band gap measurement (3eV) which is the same as bulk rutile. The reason that we can accurately estimate the onset of the TiO₂ first interband transition peak is that the monochromator significantly suppresses the influence of ZLP’s tail.

Another method of band gap determination is to find the intersection between the tangent line at the inflection point of the TiO₂ VB-3d interband transition peak and the x axis. This is shown in Figure 2-15c. This method requires calculating the second derivative of the spectrum. However, this method is sensitive to noise which can easily alter the curvature of the peaks, as shown in Figure 2-15d. Therefore, the measured band gap values usually vary by 0.1-0.2eV. To improve this noise problem we would have to use a long integration time during acquisition but this tends to damage the TiO₂ NPs. Even in bulk TiO₂, finding the inflection point of the first interband transition peak is not trivially accomplished by just taking the second derivative of the spectrum, because this peak actually split into two peaks associate with VB-t₂g and VB-e_g transitions due to the crystal field splitting effect in rutile. Therefore, we use Quantifit to separate these two peaks and then make a corresponding estimation.

As shown in Figure 2-15e, we use a combination of a Gaussian peak and a Lorentzian peak to model the ZLP. The Gaussian peak represents the intrinsic energy distribution of the zero-loss beam and the Lorentzian peak is used to fit the asymmetric tail of the ZLP. The first interband transition peak is fitted by two Gaussian peaks located at 4.5eV and 6.1eV respectively. Whether the peaks are fitted by Gaussian or Lorentzian peaks depend on the calculated “goodness of fit”, \( \chi^2 \). This method is also applied to the core-loss peak fitting. From the fit we can also get the area and FWHM of the peak. A Gaussian peak \( f(x) \) is defined by:

\[
f(x) = a \times \exp \left( -\frac{(x - b)^2}{2c^2} \right)
\]

where, \( a \) modifies the height of the Gaussian peak, \( b \) is position of the intensity maximum, and \( c \) modifies the width of the Gaussian peak. The relationship between FWHM and \( c \) is:

\[
\text{FWHM} = 2c\sqrt{2\ln 2} \approx 2.35482c
\]

To obtain \( a \), we integrate the whole Gaussian from negative infinity to positive infinity, to obtain:

\[
a = \frac{1}{c\sqrt{2\pi}}
\]
Figure 2-15 Comparisons of different methods for TiO$_2$ band gap determinations. (a)-(b) Directly observing band gap from the lowest point in EELS spectra, (c)-(d) Measuring the band gap associated with finding inflection points. (e) Fitting EELS spectrum by Quantifit. (f) Defining the band gap at the x where $f(x) = \max \{f(x)/e\}$ of the Gaussian peak which represents for transition from VB to Ti-$t_{2g}$. 

~2.8eV
The inflection point occurs at $x = b \pm c$. We then use the peak located at 4.5eV associated with VB-t_{2g} transition to estimate the band gap. Using the FWHM of this peak, 1.6eV, from Quantifit, we get $a = 2.64eV$ and $c = 0.68eV$. The left inflection point occurs at 3.8eV. Then the band gap value (3eV) is obtained using the inflection point minus half the FWHM. This method provides most accurate band gap values.

Another method for band gap estimation is to use the location where the intensity decays to 1/e of the maximum ($e$ is Euler constant). This method doesn’t need complicated calculation as with the previous one. One just needs to use peak height divided by $e$ and find this value in the spectrum. The cross point of EELS spectrum and x axis is the onset of the peak, as shown in Figure 2-15f. However, this method gives about 0.2eV error.

We found that the EELS spectrum is influenced by the acquisition position. Figure 2-16 shows EELS spectra acquired at different locations designated 1-9. The peak position of the first interband transition is redshifted by about 0.5eV in vacuum or at the surface of the NP, and the intensity maximum of this peak is much higher than that of the second interband transition peak shown in Figure 2-16c. Artifacts arising from thickness effects such as Cerenkov effect or multiple scattering are highly depressed because the dimensions of the TiO$_2$ NPs are quite small (<50nm). Figure 2-16c shows peak position, area, and intensity maximum which also change with varying thickness. We assume that we measure the electronic structure of the surface, which is reportedly non-stoichiometric and obviously has a broken symmetry compared to bulk. No publication has reported this phenomenon yet. A strategy to minimize these impacts of surfaces is to take EELS spectra from ~30nm thick TiO$_2$, either from a thin area of a large NP or from an aggregation of small NPs.

2.2.3.4 Crystalline/amorphous ratio determination

Crystalline/amorphous ratio determination is extremely difficult to perform in TiO$_2$ NPs. The hardest part here is the definition of crystalline and amorphous. Ideally, a single crystal is a solid material whose atoms, molecules or ions are arranged periodically through the whole crystal. However, crystals may have defects. The defect breaks the periodicity of a crystal, and therefore crystal becomes ‘defective’. Depending on the type of defects and defect concentrations, a defective crystal can become ‘more defective’ to the extent that the range of ordered structure becomes shorter. However, amorphous material still has SRO whose dimensions and types vary with many factors such as synthesis methods. For example, Bertoni et al. used the sol-gel method to synthesize amorphous TiO$_2$ with no crystal
field splitting in EELS spectra. Then they quantified the amorphous/crystalline ratio using a method called Cramer–Rao lower bound by analyzing EELS spectra taken from reference crystalline TiO$_2$ and as-synthesized amorphous TiO$_2$. However, in Chapter 3-1, we will see ELNES of EELS taken from amorphous TiO$_2$ NP synthesized by PLD at room temperature show crystal field splitting features because these amorphous consist of TiO$_6$ octahedra. Due to differing distortions in each TiO$_6$ octahedra, crystal field splitting features in EELS spectra differ with each other. The crystal field splitting features even disappear in some defective crystalline TiO$_2$ NPs, and we will show this in Chapter 3. Therefore, ELNES of EELS is sensitive to TiO$_6$ octahedra in both amorphous and crystalline TiO$_2$ but cannot used to quantify crystalline/amorphous ratio. However, RDF retrieved from EXELFS of EELS spectra or EXAFS of XAS spectra of Ti-K edge can provide local bonding information. RDF shows how the local bond (ion-ion pair) length deviates from that of standard crystalline TiO$_2$. The drawback of taking RDF is evident: it is time-consuming to acquire almost noise-free XAS spectra or EELS spectra. It is also impossible to extract the crystalline/amorphous ratio from RDF.

In this research, we used DPs to estimate crystalline/amorphous ratios. The whole process of analyzing DPs is shown in Figure 2-17: First, we took SAD patterns from TiO$_2$ NP aggregations hanging in the vacuum using a condenser aperture ~500nm in diameter. Then we subtracted the intensity profile from this DP. By using a two-window method performed in Digital Micrograph, we subtract the intensity profile’s background which results from scattering in amorphous TiO$_2$ to get peaks arising from scattering in crystalline TiO$_2$ NP. The crystalline/amorphous ratio is obtained by comparing the intensity of the background subtracted peaks and the intensity of the subtracted background.

Results from this method may have large errors. The first error originates from crystalline or amorphous NPs which may aggregate together. If we only perform a limited number of measurements, we may unfortunately select an amorphous aggregation area or crystalline aggregation area. This results in either a higher or lower crystalline/amorphous ratio. In this case, analysis from XRD patterns can better represent the crystalline/amorphous ratio of the sample. The second error involves inability to accurately estimating the contribution of scattering intensity. Scattering intensities are different for different crystal planes, and calculation of scattering intensities in amorphous material is different from that of crystalline materials. Therefore, the crystalline/amorphous ratio is related to but not equal to scattering intensity of the background subtracted peaks and subtracted background. Moreover, many
Figure 2-16 EELS spectra taken at different locations of TiO$_2$ NPs. (a) STEM image of TiO$_2$ NPs. The numbers, 1-9, represent the locations where EELS spectra were taken. (b) EELS spectra taken from a. (c) Selected EELS spectra with fitting by Quantifit.
other factors such as reduction, strain, multiple phases, and method of background subtraction also strongly influence the result. Hence, analyzing DPs only provides a rough estimation of the crystalline/amorphous ratio. However, this method is still more accurate than using EELS spectra.

![Figure 2-17](image)

**Figure 2-17** Procedure of estimation of crystalline/amorphous ratio from DP. This procedure involves taking DPs from NPs hanging in vacuum, extracting the intensity profile from the DP, subtracting the background from the DP, and comparing the intensity scattered from the crystalline and amorphous material.

### 2.2.3.5 DFT calculation

We performed first-principles density functional theory (DFT) calculations to understand thermodynamic stabilities of TiO$_2$ (rutile) and Ti$_2$O$_3$ crystals at a given experimental condition. Our total calculations adopt the Perdew-Burke-Ernzerh version of exchange-correlation functional$^{80}$ and the projector augmented wave method$^{81}$ for ionic potentials as implemented in the Vienna Ab Initio Simulation Package$^{82}$. We compare the changes in the Gibbs free energy (G) between TiO$_2$ and Ti$_2$O$_3$, where we assume that extra oxygen atoms upon the structural transformation return to O$_2$ ideal gas.
The free energy changes incorporated with those changes in bulk volumes are negligible for the
considered pressure condition. Difference Gibbs free energies (G) between the two phases can be
expressed as:

\[
\Delta G(T,P) = U_{TiO_2} + \mu_{TiO_2}(T,P) - \frac{1}{2}[(U_{Ti_2O_3} + \mu_{Ti_2O_3}(T,P) + \frac{1}{2} (\mu_{O_2}(T,P_0) + U_{O_2} + k_B T \ln (\frac{P}{P_0}))]
\]

Eq. 2-7

Where we obtained the internal energies U from the DFT calculations and the chemical potentials
of each species for a given temperature (T) and oxygen pressure (P) were obtained from the
NIST-JANAF thermochemical table\(^{83}\). The phase diagram was constructed based on G for a given P
and T.

For the TiO\(_2\) NP structure search, we developed a hybrid global structure search algorithm to
explore feasible NP structures. The algorithm find metastable configurations starting from randomly
generated structures using differential evolution, conjugate gradient method, and the BFGS
quasi-Newton method.
Chapter 3. **Experimental results and discussions**

3.1 Amorphous TiO$_2$ NPs as tunable building blocks

3.1.1 TiO$_2$ NPs synthesized at different target-sample distances.

We first synthesized TiO$_2$ NPs by PLD at room temperature as precursors for different functional crystalline NPs by post-annealing. Diameters of these NPs are functions of the distances from samples to target. As shown in Table 3-1, TiO$_2$ NPs’ sizes (either defined by average size or median sizes) have very weak relationship with target-sample distance, which slightly increase from 7.5cm to 4.5cm away from target. However, TiO$_2$ NPs’ sizes increase by 35% from 4.5cm to 2.5cm away from target, of which the crystalline/amorphous ratio is 1-30%, while almost no crystalline NPs are synthesized at distances from 4.5cm to 7.5cm. Surprisingly, the crystalline TiO$_2$ NPs are mainly in rutile form. As mentioned in Chapter 1-2, stable form of crystalline TiO$_2$ at room temperature is anatase. Even rutile NPs are reported to produce by sol-gel method in room temperature, the minimum size of rutile NPs is 7 nm which is much less than those synthesized in this experiment. We attribute this phenomenon to our unique synthesis method-PLD because synthesis of rutile NP with size < 5nm are mostly reported by laser related synthesis method.

Distance dependent degree of crystallinity originates from the nonlinearity of the kinetic energy of the plume species as a function of distance from the target. This relationship is investigated by in situ gated-intensified CCD-array imaging and ion probe measurements. Figures 3-1a and 1b show the ICCD

<table>
<thead>
<tr>
<th>Distance from target (cm)</th>
<th>Maximum size (nm)</th>
<th>Minimum size (nm)</th>
<th>Standard deviation</th>
<th>average size (nm)</th>
<th>Median size (nm)</th>
<th># of counted NPs</th>
<th>Crystalline/amorphous ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>7.15</td>
<td>2.2</td>
<td>0.85</td>
<td>3.81</td>
<td>3.8</td>
<td>102</td>
<td>1%-30%</td>
</tr>
<tr>
<td>4.5</td>
<td>6.97</td>
<td>1.55</td>
<td>0.85</td>
<td>3.06</td>
<td>2.82</td>
<td>123</td>
<td>&lt;&lt;1%</td>
</tr>
<tr>
<td>5</td>
<td>5.62</td>
<td>1.64</td>
<td>0.80</td>
<td>2.94</td>
<td>2.76</td>
<td>141</td>
<td>&lt;&lt;1%</td>
</tr>
<tr>
<td>5.5</td>
<td>6.72</td>
<td>1.61</td>
<td>0.80</td>
<td>2.91</td>
<td>2.74</td>
<td>142</td>
<td>&lt;&lt;1%</td>
</tr>
<tr>
<td>6</td>
<td>6.44</td>
<td>1.7</td>
<td>0.79</td>
<td>2.83</td>
<td>2.70</td>
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<td>&lt;&lt;1%</td>
</tr>
<tr>
<td>7.5</td>
<td>5.62</td>
<td>1.15</td>
<td>0.62</td>
<td>2.53</td>
<td>2.45</td>
<td>134</td>
<td>&lt;&lt;1%</td>
</tr>
</tbody>
</table>
images of the plume evolution and R-t plot of the leading edge of the plume at a pressure 200 mTorr at room temperature in oxygen gas. We use a phenomenological $a = -a v^2$ drag model, where $v = v_0/(1 + av_0t)$; $R = a^{-1} \ln(1 + av_0t)$ to fit the curve. The nonlinearity of the curve in the plot indicates that velocity of the ejecta (associated with kinetic energies) increase towards the target nonlinearly. Figure 3-1c shows the ion probe measurement of time for the ejecta to approach the ion probe at distance range 2.5-7.5 cm away from the target.

Figure 3-1c-e show the SEM images, TEM image and electron diffraction patterns of TiO$_2$ NPs deposited at 2.5, 5, 7.5 cm away from the target. At 2.5 cm, there are some highly crystalized NPs non-uniformly distributed in this sample. At this distance, these NPs are close with each other. The dense and high crystalline/amorphous ratio is associated with the higher kinetic energy, and possibly due to temperature of the plume. In contrast, as the distance increases to ~ 4.5 cm, the morphology significantly changes into more fractal hyperbranched structures. Further increase of the distance resulted in the formation of loose aggregates.

3.1.2 Experimental characterization and simulation of amorphous TiO$_2$ NPs

Structures of amorphous TiO$_2$ NPs are firstly characterized by NBED. As shown in Figure 3-2, we
selected an amorphous NP ~3nm in diameter, and performed NBED mapping 5 pixels × 5 pixels on this NP. From the NBED patterns map, a few NBED patterns show reflections whose periodicities are quite different from anatase, rutile, TiO$_2$(B), and brookite. These NBED patterns containing reflections are different from nearby NBED patterns. If we summed up the whole 25 NBED patterns, then this summed NBED pattern is very close to SAD which is taken from a large area of amorphous NPs. This result indicates that the reflections originate from independent structures with ~0.5nm SRO, but these structure randomly connect with each other and thus they didn’t show any periodicity in a larger scale. This conclusion that amorphous NP is SRO is explained explicitly as following:

In an amorphous material, the electron scattering intensity, I, is expressed by

$$I(k) = N|f(k)|^2(1 + \sum_{i\neq j} \exp(-2\pi ik \cdot r_{ij}))$$

Eq. 3-1

Where k is scattering vector, N is number of atoms, f(k) is form factor, and $r_{ij}$ is interatomic vector between ith and jth atoms in a cluster. If this NP doesn’t have any SRO like single atom gas, the second term in this equation is zero, and thus $I(k) = N|f(k)|^2$. In this case, electron scattering intensities only decay with k, and no reflections exist in DP. If atoms are packed in a SRO way, then I is a function of interatomic vector $r_{ij}$ and scattering vector k. Obviously, in the summed-up NBED pattern or in the SAD pattern, the amorphous-TiO$_2$ (a-TiO$_2$) NPs have SRO because there are several broad peaks. Figure 3-1 shows background subtracted peaks from SAD pattern. However, the position of these peaks are different with those in XRD patterns of pure anatase, rutile, TiO$_2$(B) or brookite. Therefore, the amorphous NPs have their own periodicities in the SRO. The reflections of NBED patterns represent for the SRO periodicities of a-TiO$_2$ NPs. Hirata et al. used simulation and NBED experiments data to build atomic structure of a bulk metallic glass (BMG). They found the BMG consists of polyhedral based a method called ‘Voronoi polyhedral analysis’. However, this Voronoi polyhedra analysis is too simple to describe polyhedra in TiO$_2$. As shown in Figure 3-3 titanium oxides including all TiO$_2$ polymorphs, Magnéli phases, which can be described as $\text{Ti}_n\text{O}_{2n-1}$, where $3 < n < 10$, and $\text{Ti}_2\text{O}_3$, consist of $\text{Ti}_6\text{O}_8$ octohedra. Due to different connectivities, distortions, and sizes, these unique $\text{Ti}_6\text{O}_8$ octohedra build up different crystal structures of titanium oxide. In Voronoi polyhedra analysis, six folder polyhedra (octahedra) have perfect shapes, which only exist in SrTiO$_3$ (STO) but not TiO$_2$. Therefore, we cannot investigate the structure of a-TiO$_2$ NPs by just using ‘Voronoi polyhedral analysis’ retrieved from NBED patterns.
To further investigate the structure of a-NPs in SRO, we took EELS spectra from these amorphous NPs because EELS spectra can reveal the energy levels splitting due to to TiO$_6$ octahedra in TiO$_2$. Specifically, TiO$_6$ octahedra result in two $t_{2g}$ and $e_g$ sub energy levels in both TiO$_2$ L$_2$ and L$_3$ edges due to crystal field splitting (CFS). The $e_g$ level further splits into two sub-levels due to distortion of TiO$_6$ octahedra. Figure 3-3 shows EELS spectra taken from pure TiO$_2$ NPs, Cr-doped TiO$_2$ NPs, and a-TiO$_2$ NPs synthesized by pulse laser ablation in water (PLA), compared with reference ones of TiO$_2$(B), anatase, rutile, and STO. It should be noted that EELS spectra were taken from a-TiO$_2$ NP aggregations because signal-to-noise ratio is very high if we took EELS from individual NP with such small size. Peak positions in the EELS spectra taken from different a-TiO$_2$ NP are very similar. Therefore, we suppose that these three types of a-TiO$_2$ NPs should have same distorted TiO$_6$ octahedra. The only difference among the EELS spectra taken from these a-TiO$_2$ NPs is peak’s width. The broadening effect in the peaks seems sensitive to the synthesis conditions: EELS spectra taken from Cr-doped a-TiO$_2$ NPs have the narrowest peaks, while those from pure a-TiO$_2$ NPs have the broadest peaks.

Interestingly, ELNES of a-TiO$_2$ looks very similar with that of TiO$_2$(B): their similarities are the peak’s position and the asymmetry of L$_3$-$e_g$ peak. TiO$_2$(B) has lowest symmetry in all TiO$_2$ polymorphs, which is ‘closer to’ a disordered structure. Therefore, we conclude that a-TiO$_2$ have very similar distorted TiO$_6$ octahedra as those in TiO$_2$(B).

We calculated the coordination number (CN) and bond length of Ti atoms in a-TiO$_2$ NPs, which provide the information whether TiO$_6$ octahedra exist in amorphous TiO$_2$ NPs. As shown in Figure 3-4, CN strongly depends on the particle’s size. If the TiO$_2$ clusters only contain two units ($n = 2$), then Ti atoms are only surrounded with 3 oxygen atoms. However, if TiO$_2$ clusters have 50 units ($n = 50$), then a-TiO$_2$ NPs are mostly surrounded by 6 or 7 O atoms. This calculation reveals that a-TiO$_2$ NPs with this size consist of TiO$_6$ octahedra and TiO$_7$ dextohedra. However, 50×TiO$_2$ clusters are too small. The volume of one TiO$_2$ unit in rutile is only 0.031nm$^3$. Considering a density of a-TiO$_2$ close to that of crystalline TiO$_2$, 50×TiO$_2$ clusters represent only a sphere with a diameter of 1.4 nm i.e. Approximately 500×TiO$_2$ clusters form a sphere of ~3nm in diameter which is close to the size of a-TiO$_2$ NPs in this experiment. Simulating such large volume of NP is time-consuming. Further investigation on these a-TiO$_2$ will be done when this calculation result come out.
Some individual NBED shows a certain periodicity in SRO (~0.5nm). The summed NBED pattern is similar as SAD, whose periodicity is different from those in anatase, rutile, TiO$_2$(B), and brookite.
Figure 3.3 Crystal structures and the corresponding TiO$_6$ building blocks of (a) Rutile P4$_2$/mnm, (b) anatase P4$_1$/amd, (c) Ti$_2$O$_3$ R$ar{3}$mH, (d) Ti$_4$O$_7$ I$ar{1}$, (e) Ti$_5$O$_9$ P$ar{1}$. The distortions and connectivities of the TiO$_6$ differ from each other. The dashed line represents the boundary of the unit cell.

Figure 3.4 EELS taken from pure, Cr-doped and pulse laser ablation in water synthesized (PLA) a-TiO$_2$, compared with reference ones of TiO$_2$(B), anatase, rutile, and STO.
Figure 3-5 CN and bond length of a-TiO$_2$ clusters with different sizes.
3.1.3 Summary

We investigate the deposition distance dependence on sizes, degrees of crystallinities, and morphologies of TiO$_2$ NPs synthesized at room temperature in O$_2$ gas. The results show that as approaching to the target, the TiO$_2$ NPs’ sizes, degrees of crystallinities, and morphologies slightly change from 7.5cm to 4.5cm, but change drastically from 4.5cm to 2.5cm.

The structures of a-TiO$_2$ NPs are systematically investigated in this research. Results of NBED mapping indicate the a-TiO$_2$ NPs have SRO ~0.5nm. This SRO originates from TiO$_6$ octahedra from EELS spectra analysis. The TiO$_6$ octahedra synthesized from different methods is quite different. We conclude that a-TiO$_2$ NPs synthesized by PLD or PLA consist of randomly orientated TiO$_6$ octahedra. Due to different distortions of TiO$_6$ octahedra, crystal field splitting features in Ti-L$_{2,3}$ edge of EELS spectra looks different. These results of structures of a-TiO$_2$ NPs have not been reported yet. Prospected simulations of larger TiO$_2$ cluster (i.e. ×500 TiO$_2$ units) need to be built to further investigate the connectivities, shapes, and distortion of a-TiO$_2$ NPs.

3.2 Unconventional phase transformation

3.2.1 Annealing a-TiO$_2$ NPs in O$_2$

a-TiO$_2$ NPs were annealed in oxygen ambient at different temperatures. When an energetic a-TiO$_2$ NPs obtains energy, it will transform into a thermodynamically equilibrium phase: a crystal, as shown in Figure 3-6. The duration time of this phase transformation is determined by temperatures, annealing time and many other factors. The growth of NP is associated with combining other crystalline or amorphous NPs. If the newly combined NP is amorphous, it tends to form crystal structure with the same orientation as the parent crystal. The STEM image in Figure 3-6 shows a defective NP matches with a big anatase NP viewed in [111] direction. This defective NP should transfer from a a-TiO$_2$ NP. Because the amorphous-crystalline transition didn’t finish, this NP is semi-crystalline.

The crystal phases are temperature dependent. As shown in Figure 3-7, the a-TiO$_2$ NPs were transformed into different phases at different temperatures. The NP’s sizes are $5 \pm 2$nm at 400°C, $9 \pm 3$nm at 500°C, $12 \pm 5$nm at 600°C, $20 \pm 7$nm at 700°C, $31 \pm 9$nm at 800°C, and $57 \pm 17$nm at 900°C, respectively. At 400°C, a-TiO$_2$ NPs were transformed into pure anatase. If annealing temperature increased to 500°C, anatase were partially transformed into rutile and TiO$_2$(B) which is a
unconventional phase of TiO₂. Surprisingly, in a temperature range 600°C-800°C, the fraction of rutile phases decreases, while the dominant phases are anatase and TiO₂(B). This transformation conflicts with classic phase transformation of TiO₂, which is that anatase or brookite should transform into rutile from 400°C-800°C⁸⁷. At 900°C, fraction of TiO₂(B) phase highly reduced, but anatase still dominate and the rutile is a minor phase.

Phase transformations of TiO₂ are influenced by many factors. Hanaor et al.⁴¹ made a review of anatase-rutile phase transformation which is most investigated in all TiO₂ polymorph transformation. He found that many factors influence this transformation such as particle size, particle shape, surface area, atmosphere, volume of sample, heating rate, and impurities. Particle size may be not the origin of this phase formation because Zhang et al.⁸⁸ found that smaller anatase tend to transforming into rutile at lower temperature. Rutile phase should begin to exist at very low temperature in our NPs (diameter < 5nm). To our knowledge, Zhou et al.⁸⁹ found most similar phase transformation as ours in a temperature range from 600°C to 1000°C, but they didn’t explain the origin of this phase transformation. They also have different starting precursors (H₂Ti₃O₇) and different phase at 400°C: the TiO₂(B) NPs. Therefore, no comparable results provide us the mechanism of this phase transformation.

Figure 3-6 Schematics of phase transformation of α-TiO₂ and crystalline TiO₂, and the growth process of TiO₂ NPs.
Figure 3-7 SAD patterns of TiO$_2$ NPs at different temperatures. A = anatase, B = TiO$_2$(B), and R = rutile.
3.2.2 The influence of defects on phase transformation

By comparing phase transformation at different experimental conditions, existence of rutile is usually accompanied by defects. Figure 3-8 shows rutile NP transformed from α-TiO₂ NPs annealed at 400°C for 1 hour. The particle’s size is 3.4 ± 0.8nm, determined from ~1000 NPs, as shown in Figure 3-8a. These NPs are pure rutile determined from the diffraction patterns as shown in the inset of Figure 3-8b. However, the reflection rings in the diffraction pattern are more or less broad, which indicates that the lattice of rutile is distorted. To confirm this, we took HRTEM images of the rutile NPs. As shown in Figure 3-8c, reflection spots in the FFT from a rutile NP viewed in [111] directions are stretched which is highlighted by the yellow dashed ellipses.

Figure 3-8 Rutile NP transformed from α-TiO₂ NPs annealed at 400°C. (a) Particle size distribution. (b) HRTEM image of aggregations of the rutile NPs. The inset is diffraction pattern taken from these aggregations. (c) HRTEM image of defective rutile NPs. The FFT shows that the reflection spots are stretched, indicating lattice distortion.

To further investigate the origin of the defects, we took core-loss and low-loss EELS spectrum image from these rutile NPs. As shown in Figure 3-9a, low-loss EELS spectrum shows an intense peak located at ~1.5eV. This peak may originate from mid-band gap Ti<sup>3+</sup> defect state<sup>61,90</sup>. From the intensity normalized core-loss EELS spectra, the Ti-L<sub>2,3</sub> ELNES of defective rutile NPs have both Ti<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> features, as shown in Figure 3-9b: peak a refers to Ti<sub>2</sub>O<sub>3</sub> L<sub>3</sub>-t<sub>2g</sub> peak and peak b refers to TiO<sub>2</sub> L<sub>3</sub>-t<sub>2g</sub> peak. In the O-K ELNES, two pre-peaks designated by a, and b also ambiguously distinguish these two phases: specifically a>b for rutile and a<b for Ti<sub>2</sub>O<sub>3</sub>. This O-K also confirmed that the defective rutile NPs contain a large amount of Ti<sub>2</sub>O<sub>3</sub>. Therefore, we conclude that the rutile NPs are
defective due to the existence of Ti$_2$O$_3$. The mid-band gap Ti$^{3+}$ interstitial atoms may be accompanied with the existence of oxygen vacancies which were created by annealing. We will discuss the formation of oxygen vacancies and Ti$_2$O$_3$ in chapter 3-4.

Figure 3-9 EELS spectra (in core-loss and low-loss range) of defective rutile, comparing with reference ones of perfect rutile or Ti$_2$O$_3$. (a) Low-loss EELS spectra taken from defective rutile and perfect rutile. (b) Core-loss EELS spectra of Ti-L$_{2,3}$ edge taken from defective rutile, perfect Ti$_2$O$_3$, and perfect rutile. Peak a, and b refer to Ti$_2$O$_3$ L$_{3}^{-1}t_{2g}$ and TiO$_2$ L$_{3}^{-1}t_{2g}$ peaks, respectively. (b) Core-loss EELS spectra of O-K edge taken from defective rutile, perfect Ti$_2$O$_3$, and perfect rutile. Peak a, and b ambiguously distinguish rutile and Ti$_2$O$_3$: a>b for rutile and a<b for Ti$_2$O$_3$.

3.2.3 Summary

In this section, we investigate the crystallization process and growth mechanism of a-TiO$_2$ NPs under annealing in O$_2$ gas. An unconventional phase transformation of TiO$_2$ is found at annealing temperatures ranged from 400°C to 900°C which is not reported yet. Annealed at 400°C, the phase of TiO$_2$ NPs is anatase. The TiO$_2$(B) starts to exist at 500°C, and co-exist with anatase until 900°C. However, because too many factors influence phase transform of TiO$_2$, the origin of this phase transformation still need to further investigated. Interestingly, the defects created by doping and reduction induce the existence of rutile phase. We shows an example from annealed at 450°C. The phase of TiO$_2$ NPs is rutile, which is defective from analysis of SAD, HRTEM, and EELS spectra.

3.3 Band gap modifications of doping in TiO$_2$ NPs

3.3.1 Formation of defects

In this research, we doped TiO$_2$ NPs with Cr$_2$O$_3$, N$_2$, and co-doped with Cr$_2$O$_3$-N$_2$, respectively.
The idea of doping with $\text{Cr}_2\text{O}_3$ is to use substitutional $\text{Ti}^{4+}$, with $\text{Cr}^{3+}$ which allows narrowing of the band gap of $\text{TiO}_2$. The band gap narrowing originates either from exciting the $\text{TiO}_2$ VB electrons into Cr mid-band gap levels or from these Cr levels into $\text{TiO}_2$ CB$^{91}$. The advantage of using $\text{N}_2$ as dopants is that $\text{N}$ has less electronegativity than O. By using $\text{N}$ to substitute O in the lattice, $\text{TiO}_2$ VB may be push up by N valence p-levels$^{42}$. However, the mechanisms of anion or cation doping are still highly disputed. The major question is whether the band gap narrowing is intrinsic or originates from defects$^{92}$. Although much confusion still exist about the origin of band gap narrowing in doped $\text{TiO}_2$, it has been recently reported that co-doping cations and anions into $\text{TiO}_2$ NPs can significantly narrow the band gap$^{42}$. Therefore, we also use $\text{Cr}_2\text{O}_3$-$\text{N}_2$ to dope $\text{TiO}_2$ NPs.

When the dopants are incorporated into $\text{TiO}_2$, the doped elements form either substitutional or interstitial defects. As a result, the $\text{TiO}_2$ lattices become defective. Using Kröger-Vink notation, a series of reactions of the doping process are represented by$^{90}$:

$$\text{Cr}_2\text{O}_3(\text{TiO}_2) = 2\text{Cr}^{′′}_\text{Ti} + 3\text{O}_0 + V^{**}_0$$  \hspace{1cm} \text{Eq. 3-2}$$

$$\text{N}_2(\text{TiO}_2) = \text{O}_2 + \text{TiN}_2$$  \hspace{1cm} \text{Eq. 3-3}$$

$$\text{O}_0 = \frac{1}{2}\text{O}_2 + V^{*}_0 + 2e^{′}(\text{Ti}^{3+}_\text{Ti})$$  \hspace{1cm} \text{Eq. 3-4}$$

$$2\text{O}_0 + \text{Ti}^{′}_{\text{Ti}} = \text{Ti}^{′′′}_{\text{Ti}} + 3e^{′} + \text{O}_2$$  \hspace{1cm} \text{Eq. 3-5}$$

$$2\text{O}_0 + \text{Ti}^{′}_{\text{Ti}} = \text{Ti}^{′′′′}_{\text{Ti}} + 4e^{′} + \text{O}_2$$  \hspace{1cm} \text{Eq. 3-6}$$

$$\text{O}_2 = 2\text{O}_0 + V^{'′′'}_{\text{Ti}} + 4h^{*}(\text{O}_0)$$  \hspace{1cm} \text{Eq. 3-7}$$

$$\text{nil} = e^{′} + h^{*}$$  \hspace{1cm} \text{Eq. 3-8}$$

Eq. 3-2 and Eq. 3-3 are substituional reaction by adding $\text{Cr}_2\text{O}_3$ or $\text{N}_2$ into $\text{TiO}_2$ lattice. Eq. 3-4,5 and 6 is the reduction reaction which usually occurs when heating in Ar gas. Eq. 3-4 reveals that an oxygen vacancy is created accompanied by $\text{Ti}^{3+}$ in the original Ti site of $\text{TiO}_2$. Eq. 3-7 is oxidation equation which explains the formation of holes accompanied with formation of Ti vacancies in the $\text{TiO}_2$ lattice. Eq. 3-8 represents charge carries (electrons and holes) recombination reaction. Those equations from Eq. 3-4 to Eq. 3-7 are temperature dependent$^{90}$. The corresponding reactions occur depending on the heating condition i.e. in $\text{O}_2$ gas or Ar gas. Figure 3-10 shows a scheme of defective $\text{TiO}_2$ lattice.
Figure 3-10 Schematic of defect species in defective TiO$_2$ lattice. The defect species involves Ti$^{4+}$ interstitial atoms, Ti$^{3+}$ interstitial atoms, Ti vacancies, O vacancies, Ti$^{3+}$, substitutional Cr$^{3+}$, substitutional N$^{2-}$, and substitutional N$^{3-}$.

3.3.2 Origins of band gap narrowing

Investigation on how the dopants influence the band gap narrowing of TiO$_2$ NPs is extremely challenging for two reasons: (1) The dopants i.e. N may vary valences, i.e. N$^{4-}$, N$^{3-}$, and N$^{2-}$ in TiO$_2$ NPs. Impacts of valence states of dopants on band gap narrowing are highly debated$^{42}$; (2) The band gaps are different in the N-TiO$_2$ samples even with the same valence state of N depending on the existence of defects i.e. oxygen vacancies, Ti$^{3+}$, and Ti interstitial atoms$^{92}$ which are created when adding dopants into TiO$_2$ lattice. We show an example how the valences vary and how the defects change the band gap of N-TiO$_2$ in the following.

Figure 3-11a shows EELS spectra of N-K edge taken at different locations of N-TiO$_2$ NP
aggregations annealed at 400°C. The N-edge in the ELNES of the EELS spectrum A shows two peaks: a, and b. This N-edge looks very similar to rutile O-K edge shown in Figure 3-9c. A possible reason for this similarity is that N$_{2}^{2-}$ replaces O$_{2}^{2-}$ in the TiO$_{2}$ lattice and thus N$_{2}^{2-}$ shows the same crystal field as O$_{2}^{2-}$. However, this N-K edge feature is also similar to the ELNES of TiN (N$_{4}^{4-}$). We determine the valence state of this N-edge feature to be N$_{4}^{4-}$ because there are no crystal field splitting features in either Ti-L$_{2,3}$ edge or O-K edge. In TiO$_{2}$,N$_{x}$ (N$_{2}^{2-}$), the crystal field splitting features in the Ti-L$_{2,3}$ edge and O-K edge are not influenced at all by adding N$_{2}^{2-}$, while these features changed in TiO$_{2-2x}$N$_{x}$ (N$_{4}^{4-}$).

In the EELS spectrum B, the valance of N is very difficult to estimate. Though we use Quantifit to fit peak a, and b in spectrum B, the features prior to these two peaks are hard to analyze. We even cannot even estimate how many peaks we should use to represent these pre-peak features. There is no obvious shift of these NPs’ band gaps.

Figure 3-11b shows EELS spectra taken from a N-TiO$_{2}$ thin film annealed at 500°C for 24hrs to let the N diffuse more sufficiently. The purpose to take EELS spectra from a thin film is that we can modify the thickness of the thin film so that signal-to-noise ratio of N-K edge in EELS spectra is high enough to resolve all the features in this edge. The N-K edge of EELS spectrum C taken from first 5nm layers (surface area) represents for TiN, and spectrum D from particle’s inner (>5nm away from surface) is very similar as that of TiN$_{1-x}^{93}$, where x~0.2-0.4. The peaks’ intensity and width of the N-edge in spectrum C slightly deviated from reference TiO$_{2}$,N$_{x}$ is due to existence of defects. Nitrogen concentrations are different at surface (10%) and in the NP’s interior (5%). Two new states exist in the band gap of these two types of N-TiO$_{2}$, as shown in the inset of Figure 3-11b. Though spectrum A shows the exactly same valence state of N as that of spectrum C, the band gaps of these N-TiO$_{2}$ are quite different because of the existence of two new states. As this N-TiO$_{2}$ thin film is more defective than the N-TiO$_{2}$ NPs in Figure 3-11a, the origin of these two new states is related to the defects. However, whether these two new states directly originate from defect states or originate from N is hard to analyze.

This example reveals how complicated the origin of TiO$_{2}$ band gap narrowing effect is in an element doped TiO$_{2}$ because of the changes of the dopants’ valence states and defects. Therefore, in this research, we only focus on the synthesis conditions in which we can get TiO$_{2}$ NPs with narrowed band gap.
Figure 3-11 EELS of and STEM images of nitrogen doped NPs and thin film. (a) STEM image of N-TiO$_2$ NPs, and EELS spectra taken from A and B sites, respectively. (b) STEM image of N-TiO$_2$ thin film, and EELS spectra taken from surface and particle’s interior, respectively.
3.3.3 Band gap and phase transformation of TiO₂ NPs synthesized with different dopants at different temperatures

Table 3-2 shows annealing temperatures, concentrations of dopants, measured band gaps, particle sizes and various other parameters and results of the doping experiments. The N or Cr concentration highly fluctuates in different areas. In both Cr₂O₃ and N₂ single doping samples, there are no obvious band gap narrowing effect. From EELS spectrum, only in Cr₂O₃ and N₂ co-doping samples at a temperature range from 400°C to 800°C, the band gaps of TiO₂ NPs are significantly narrowed. It should be noted that we didn’t use EELS spectra to measure band gap of Cr₂O₃ and N₂ co-doping samples synthesized at room temperature because there are no large aggregation of NPs from which the signal-to-noise ratio in the EELS spectra are high enough. The fluctuation of band gap values in the co-doped TiO₂ NPs is due to varying valences of dopants and defects. These band gap narrowing effects were also observed by our XPS results, as shown in Figure 3-12a. The XPS results show new local states on the top of VB whose is ~2eV close to VB. While in the EELS spectra as shown in Figure 3-12b, the VB-CB is 2eV, and no obvious new states on the bottom of CB exist. The EELS results are consistent with XPS results that band gap narrowing effect is due to new localized states at the top of the VB.

Figure 3-13 shows that rutile phase tend to form when the crystal structure of the doped TiO₂ is defective. As discussed in chapter 3-2, unconventional phase transformation from the PLD synthesized a-TiO₂ NPs occurs. In that unconventional phase transformation, the existence of the rutile phase is highly depressed at a temperature range from 25°C to 900°C. However, in the doped TiO₂ with a defective lattice, rutile dominates from 600°C-800°C. While at 400°C, rutile dominates in N-doped TiO₂ NPs whose lattice is highly defective. This interesting phenomenon is also found in the ‘black TiO₂’ NPs of crystalline core-amorphous shell structures which were annealed at Ar gas in 700°C. We will introduce this core-shell rutile NP in great details in the following section.

3.3.4 Summary

We introduce the formation of defects in TiO₂ lattices by doping. Due to the defects associated with adding dopants in TiO₂, the mechanism of band gap narrowing is extremely difficult to explore. The band gaps of N₂, Cr₂O₃, and N₂+Cr₂O₃ doped TiO₂ NPs annealed at different temperatures. Only N₂+Cr₂O₃ doped TiO₂ NPs have obvious band gap narrowing, which originates from extra states on the
top of valence band investigated by XPS and EELS spectra. We also show phase transformation of different doped TiO$_2$ NPs. The result is consistent with previous conclusion that defects will induce the existence of rutile in the TiO$_2$ phase transformation at a temperature range from 400°C to 800°C.

Table 3-2 Experimental conditions and results of doped TiO$_2$ NPs samples with different dopants at different temperatures, compared to those of non-doped TiO$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bandgap</th>
<th>Particle size (nm)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>25C-Pure</td>
<td>No shift</td>
<td>~2</td>
<td>Pure TiO$_2$ before/after annealing</td>
</tr>
<tr>
<td>400C-Pure</td>
<td>No shift</td>
<td>5±2</td>
<td></td>
</tr>
<tr>
<td>600C-Pure</td>
<td>No shift</td>
<td>11.4±4.5</td>
<td></td>
</tr>
<tr>
<td>800C-Pure</td>
<td>No shift</td>
<td>30.7±9.3</td>
<td></td>
</tr>
<tr>
<td>25C-N</td>
<td>No shift</td>
<td>~3</td>
<td>Nitrogen doped TiO$_2$ before/after annealing</td>
</tr>
<tr>
<td>400C-N</td>
<td>No shift</td>
<td>~10</td>
<td></td>
</tr>
<tr>
<td>600C-N</td>
<td>No shift</td>
<td>~20</td>
<td></td>
</tr>
<tr>
<td>800C-N</td>
<td>No shift</td>
<td>~40</td>
<td></td>
</tr>
<tr>
<td>25C-Cr</td>
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<td>2.8±0.6</td>
<td>Chromium doped TiO$_2$ before/after annealing</td>
</tr>
<tr>
<td>400C-Cr</td>
<td>No shift</td>
<td>4.7±1.4</td>
<td></td>
</tr>
<tr>
<td>600C-Cr</td>
<td>No shift</td>
<td>10.6±3.3</td>
<td></td>
</tr>
<tr>
<td>800C-Cr</td>
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<td>25.8±15.7</td>
<td></td>
</tr>
<tr>
<td>25C-Cr+N</td>
<td>/</td>
<td>3.8±0.9</td>
<td>Nitrogen and chromium co-doped TiO$_2$ before/after annealing</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>800C-Cr+N</td>
<td>2±0.3eV</td>
<td>30.3±22.4</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-12 Band gap determinations from XPS and EELS spectra taken from NPs annealed at a temperature range from 25°C to 800°C by Cr$_2$O$_3$-N$_2$ co-doping. (a) XPS spectra taken from 5mm area of sample (b) low energy-loss region in EELS spectra taken from ~100nm TiO$_2$ NP aggregation.
3.4 Characterization of black rutile NPs

In this section we describe TiO$_2$ NPs with core shell structures that, instead of defective but stoichiometric TiO$_2$, consist of a small bandgap Ti$_2$O$_3$ phase$^{94,95}$ not reported previously. These core shell Ti$_2$O$_3$/TiO$_2$ NPs were obtained by crystallization of a-TiO$_2$ NPs synthesized by PLD in O$_2$ background. This rutile NP has a stoichiometric core and a defective Ti$_2$O$_3$ shell.

3.4.1 EELS characterizations

The HRTEM images in Figures 3-14 reveal that the amorphous precursors consist of aggregates of particles, typically smaller than 5nm clearly identifiable by their shape. The inset of Figure 3-14a shows that no periodicity could be confirmed by SAD. After annealing in Ar for 2 hours at 700 these initially amorphous NPs crystallize into larger rutile particles (diameter of 90% NPs > 14nm). We took...
The use of the linear combination of Ti$_2$O$_3$ and rutile spectra to fit the experimental EELS data is also performed on the Ti-L$_{2,3}$ edge, which was acquired simultaneously with the O-K edge. Figure 3-16a shows that the ELNES of Ti-L$_{2,3}$ edge exhibits more distinct features than the O-K edge and is thus more sensitive to different TiO$_2$ phases. Both, pure anatase and rutile in Figure 3-16a exhibit two groups of peaks associated with transitions from 2p core electrons to t$_{2g}$ and e$_g$ sub-band in the conduction band. With the high energy resolution of monochromated TEM, one can easily distinguish anatase from rutile by the inverted ‘shoulder’ of the L$_3$-e$_g$ peaks in the EELS spectra. In contrast, the ELNES of Ti$_2$O$_3$ shows quite different crystal field splitting features in two sharp peaks associated with two small pre-peaks, relating to a different connectivity and distortion of the TiO$_6$ octahedral units.
The Ti-L_{2,3} edge data in 3-16b-f also confirms rutile as the phase in the interior of the NPs, but a high Ti_2O_3 concentration in the near surface region. As was done for the O-K edge, we fit the experimental spectra to a linear combination of Ti_2O_3 and rutile reference spectra. We discussed this method in detail in chapter 2-2-3-2, reconstructed spectra from linear combination of Ti_2O_3 and rutile reference spectra for O-K and Ti-L_{2,3} edge are shown in Figure 2-14. With the exception of the spectrum taken 1nm away from surface, the fractions of Ti_2O_3 derived from the two independent least-square fits of the Ti-L_{2,3} edge and the O-K edge agree within 0-2% error. The larger error (~10%) in the 1nm fit is attributed to a poor signal-to-noise ratio in the weaker O-K edge, as shown in Figure 3-15h. Consistent with the O-K edge case this fit reveals a constant but small contribution of Ti_2O_3 to the Ti-L_{2,3} ELNES in the NP interior 7 to 4nm away from vacuum (surface).

In Figure 3-17, the fraction of Ti_2O_3 dramatically jumps at the edge of the NP and the rutile intensity maxima associated with the L_3 edge features become inverted, which surprisingly resembles a smeared out anatase signal. The blurring of spectral features is indicative of the structural changes of the NPs associated with increasing Ti_2O_3 concentration in the near surface region, indicating that the inverted shoulder of L_3-e_g peaks is no longer a reliable feature for identifying the TiO_2 phases in the near surface region.

It should be noted that signal measured at the NP edge is affected by the 1) surface roughness of the NPs, 2) instrument drift during EELS acquisition of roughly one atomic layer and 3) electron-beam broadening. This combination of intrinsic and instrumental factors obscures the identification of Ti_2O_3 at the edge of NPs. The examples ‘S1’ and ‘S2’ in Fig. 3a represent surface spectra taken at grazing incidence from two different spots of the same rutile NP in overview. We can clearly observe TiO_2 crystal field splitting features in spectrum ‘S1’, while these features are almost unrecognizable in spectrum ‘S2’, indicating different Ti_2O_3 concentration. However, the significant increased surface-volume ratio in smaller NPs allows to acquire surface spectra with less delocalization. Figure 3-18b shows ~100% Ti_2O_3 from fitting the EELS spectrum taken at the surfaces (by summing spectra in order to increase signal-to-noise ratio) of a NP 4 times smaller the one in Figure 3-18a. The L_{2^{-1}2_g}
Figure 3-15 EELS spectra of O-K edge taken at different locations of a rutile NP and fit from linear combinations. (a) Reference spectra of the O-K edge of Ti$_2$O$_3$ and rutile, showing that the intensity pattern of the a and b peaks is uniquely different. (c,f) Experimental EELS spectra of O-K edge at different depth from the surface of this rutile NP compared with fits from linear combination of the reference rutile and Ti$_2$O$_3$ spectra. The coefficients determined by linear least-square fitting, representing the fractions of Ti$_2$O$_3$ of 11%, 13%, 17%, 31%, and 71% at locations from 7nm to 1nm away from vacuum, respectively. The residuals of the linear least-square fitting are given at the bottom of each plot.
Figure 3-16 EELS spectra of Ti-L\textsubscript{2,3} edge taken at different locations of a rutile NP and fit from linear combinations. (a) Reference spectra of the Ti-L\textsubscript{2,3} edge of anatase, rutile, and Ti\textsubscript{2}O\textsubscript{3}. (b-f) Experimental EELS spectra of Ti-L\textsubscript{2,3} edge at different depth from the surface of this rutile NP compared with fits from linear combination of the reference rutile and Ti\textsubscript{2}O\textsubscript{3} spectra. The coefficients determined by linear least-square fitting, representing the fractions of Ti\textsubscript{2}O\textsubscript{3} of 11\%, 14\%, 18\%, 33\%, and 60\% at locations from 7nm to 1nm away from vacuum, respectively. These fractions of Ti\textsubscript{2}O\textsubscript{3} are slightly different those of O-K edge except at 1nm where the signal-to-noise ratio is high. The residuals of the linear least-square fitting are given at the bottom of each plot.
peak of Ti$_2$O$_3$, whose position is quite different with rutile and anatase, ambiguously confirm highest Ti$_2$O$_3$ concentration in the surface. However, we didn’t perform systematic characterizations on small rutile not only due to the low signal-to-noise ratio, especially for O-K edge, but also concerning the influence of twin boundaries which is rich in the small rutile (<14nm) on the ELNES.

![Figure 3-17](image)

**Figure 3-17** Ti$_2$O$_3$ concentrations from fitting Ti-L$_{2,3}$ and O-K edge at 7, 5.5, 4, 2.5, 1nm away from vacuum.

![Figure 3-18](image)

**Figure 3-18** Comparison of EELS spectra taken from the rutile in Figure 3-14a and a rutile NP 4 times smaller. (a) HRTEM image of overview of the rutile NP in Figure 3-14a. EELS spectra (inset) of surface regions (S1 and S2) acquired at grazing incidence from two different spots, showing different Ti$^{4+}$ concentration. (b) HRTEM image of a rutile NP viewed in [111] direction. EELS spectrum (inset) was summed from the surfaces, showing Ti$_2$O$_3$ characteristic L$_{2-3}$ peak. The linear least-square fit shows ~100% Ti$_2$O$_3$ concentration.

### 3.4.2 STEM characterization and formation of core-shell structure

We use atomic-resolution STEM to image directly the surface of the rutile NP viewed in the [001] direction, as shown in Figure 3-19a. This image shows the surface layers of non-uniform thickness.
exhibiting periodicity different from rutile. The irregular periodicity of the top layers indicates that the outer shell is highly defective, below which is a defective rutile layers containing several interstitial Ti atoms (designated by yellow arrows in figure 3-19a) departed from the rutile basis. This defective layer is highlighted in a white dashed rectangular. The periodicity in the subsequent layers corresponds to that of perfect rutile, consistent with least-square fitting showing in Figure 3-15 and Figure 3-16 a low Ti$_2$O$_3$ fraction in layers deeper than 4nm from the surface. The atomic positions of Ti at the top of the defective rutile layers with periodicity clearly different from rutile (110) agree well with the excellent work from Shibata et al.$^{48}$, who reported a single layer which was reduced and reconstructed above the (110) surface by directly observing the surface of a rutile thin film using atomic resolution STEM. Thermal annealing is reported as a way to create this reconstructed layer$^{98}$, whose symmetry is commonly accepted as ‘added row Ti$_2$O$_3$$^{49,50}$. In our case, we found the Ti$_2$O$_3$ grow on this reconstruction layer. Stone et al.$^{51}$ reported that when annealed in O$_2$ atmosphere a stoichiometric TiO$_2$ can grow layer-by-layer on the surface reconstruction layer above the rutile (110) plane. The stoichiometric surface layers form by re-oxidation of Ti$^{3+}$ interstitials migrating from the interior of the particle. We rule out this mechanism because the background ambient is O$_2$ deficient. Tominaka, S$^{99}$ reported that the Ti$^{3+}$ ions would diffuse into the interstitial site of rutile in a reduction condition, and the Ti$_2$O$_3$ can be topotactically converted from the rutile. They claimed when TiO$_2$-Ti$_2$O$_3$ phase transformation is initialized, the Ti atoms in the light blue TiO$_6$ octahedra originate from the diffusion of Ti atoms nearby to the interstitial site in the rutile, as shown in Figure 3-19b. In the STEM image, the rutile structure combining with the ‘extra atoms’, which are Ti atoms in the surface reconstruction layer or the interstitial Ti atoms below this layer, generally match the crystal structure of corundum Ti$_2$O$_3$ in the [001] projection direction, as shown in Figure 3-19c. However, this transform is accompanied by a distortion of TiO$_6$ octahedra and a change of their connectivities, indicating a lattice distortion in the interface. The lattice mismatch becomes higher when the Ti$_2$O$_3$ grow on different rutile plane i.e. {110}. Considering the surface of the NP is not just a single well-define crystal plane, growth of Ti$_2$O$_3$ on different crystal planes of the rutile must cause strong lattice distortions, leading to collapsing the crystalline Ti$_2$O$_3$ into defect one.
Figure 3-19 Atomic resolution high-angle annular dark-field (HAADF) image of a rutile NP viewed in [001] direction and crystal structure models of TiO$_6$ octahedra for rutile and Ti$_2$O$_3$. (a) HAADF image of a rutile NP viewed in [001] direction. The surface reconstruction layer is located above the rutile {110} plane. The reduced layers form on top of the surface reconstruction layer. The yellow arrows designate a few Ti atoms near the surface that are displaced from the rutile basis. (b) Magnified image from the area highlighted by yellow dashed rectangular in a, and compared with the corundum Ti$_2$O$_3$ structure in (c). The formation of Ti$_2$O$_3$ is associated with the diffusion of Ti atoms nearby into the interstitial site of rutile in a reduction ambient, leading to rearrangement of the connectivities and shape of TiO$_6$ octahedra. This indicates that Ti atoms in the light blue octahedra in Ti$_2$O$_3$ originate from the diffusion of interstitial Ti atoms in rutile, associated with a unit cell distortion.
The distinct advantage of PLV has over conventional methods is its capability to control the oxygen stoichiometry of the particles during synthesis using O₂ mixtures in inert gas at different background pressures. The NPs for these studies were produced in 200mTorr of pure O₂ that is known to result in stoichiometric TiO₂. Annealing of these NPs in Ar at 973K sets-up a dynamic oxygen deficiency gradient during crystallization. The observation of the stoichiometric rutile core by EELS and STEM measurements reveals that the starting point of this gradient is located at the center of the particles. The oxygen deficiency reaches maximum in the surface layers. Oxygen vacancies which are the primary defects in reduced TiO₂ accumulate in the surface region during crystallization driven by the oxygen deficiency profile. When the concentration of oxygen vacancies reaches a saturation level beyond which the TiO₂ structure is no longer sustainable, Ti₂O₃ is formed. We attribute the unique surface structure of our rutile NPs to crystallization of amorphous PLV particles in a highly oxygen deficient environment maintained by the Ar atmosphere.

To test the hypothesis that the amorphous precursor is the key to the formation of the Ti₂O₃ shell at the surface, we compared the NPs annealing at different background gas but from the same amorphous precursors synthesized simultaneously. As shown in Figure 3-20a, black rutile firstly form after 1 hour annealing in Ar. Then we reheated this black rutile in air at 973K for 1 hour and the NP turn into white-a characteristic color of TiO₂ NPs. However, the change of color is irreversible when we reheated the NPs in Ar at 973K even repeating the experiments many times, as shown in Figure 3-20a, indicating the surface is stable in the crystalline rutile.

According to the TiO₂-Ti₂O₃ phase transformation diagram in our DFT calculations, crystalline rutile should transform to Ti₂O₃ at the surface in reduced oxygen environment as shown in Figure 3-20b. The fact that this transformation is not observed in crystalline TiO₂ points to a kinetically restricted reaction in crystalline rutile but this reaction is enabled in amorphous starting material like the one we used. This kinetic restriction was also confirmed by performing reference EELS experiments by annealing stoichiometric crystalline NPs (Degussa P25) in Ar background gas at 973K, showing no obvious changes in Ti-L₂,₃ ELNES as shown in Figure 3-21. Therefore, by just straight annealing of crystalline NPs in Ar we were unable to form similar Ti₂O₃ shells, while the amorphous precursors play a unique role in forming the black Ti₂O₃ shell, as shown in Figure 3-20c.
Figure 3-20 Comparison of amorphous/crystalline precursors by annealing. (a) NPs synthesized by PLV before/after annealing. The color of amorphous TiO₂ NPs is transparent, which turns into black after annealing in Ar at 973 K, resulting from formation of Ti₂O₃ shell. This shell can be oxidized by annealing in air, showing white color. This transformation is irreversible as the color of these NPs cannot turn back. (b) Thermodynamic stabilities of TiO₂ rutile and Ti₂O₃ on the temperature (T) and oxygen pressure (P). The solid line delineates the existence of two phases. (c) Conceptual diagram for formation of NP annealed from different precursors.
Figure 3-21 Comparison of EELS taken from crystalline precursor at room temperature (RT)/after annealing. (a,b) EELS spectra taken from Degussa at room temperature (RT)/after annealing in Ar at 973K and the Z-contrast image of the NPs. The yellow arrow indicates the direction where the spectrum image was taken. There is no obvious change in the Ti-L\textsubscript{2,3} and O-K ELNES of EELS spectra taken from different locations of the crystalline NPs (Degussa) before/after annealing. Scale bars are 20nm.

3.4.3 Further investigation of core-shell structure from NBED characterisation

We use NBED to explore further the structure of the core-shell NPs. The NBED pattern of the core in Figure 3-22a generally matches that of pure rutile, though it seems not quite ‘clean’ because of a small contribution from the Ti\textsubscript{2}O\textsubscript{3} shell and lattice distortions. As the surface is approached the NBED pattern for 2 to 4nm away from vacuum in Figure 3-22b shows the appearance of new reflections both kinetically and dynamically forbidden in pure rutile (\{100\} in the [001] zone axis). The existence of these forbidden reflections is an indication of Ti atoms away from the octahedral symmetry\textsuperscript{100}. The forbidden reflections is clear evidence that the Ti atoms suffered a distortion by traces of oxygen vacancies as they were expelled towards the surface during the crystallization of the core. This is consistent with the displacement of Ti atom from the rutile lattice in the corresponding area in the STEM image designated by yellow arrows. Low intensity forbidden reflections originating from the top and bottom surface regions may also be observed in NBED patterns of the interior of the...
particle. Simulation about forbidden reflections creation is shown in Figure 3-23. The forbidden reflections occur if the body-center atoms move outside of the rutile lattice or move into the interstitial site. Depending on the sites where the body-center atom move, the intensity of forbidden reflection is different.

Figure 3-22 Comparison of NBED between core and shell. (a,b) Nano-beam diffraction pattern taken from particle inner (core) and surface region, respectively. The yellow cross indicates the four-fold symmetry of \{200\} reflections in the core, while this four-fold symmetry is reduced into two-fold in the surface region because of the lattice distortion. The extra reflection with 0.256nm d-spacing is very close to Ti$_2$O$_3\ (1\bar{2}0)$ reflection (0.257nm), which unlikely comes rutile \(1\bar{2}0\) and \(2\bar{2}0\) reflections nearby as the d-spacings of them are 0.206nm, 0.162nm respectively, which cause 24.2% and 58.6% mismatch!

Figure 3-23 Calculation of diffraction pattern, comparing with pure rutile. The forbidden reflections occur when the body-center atom of a rutile move outside the rutile lattice or move into the interstitial site of the rutile lattice.
The NBED pattern of the shell region in Figure 3-22c corresponds to a highly defective crystalline structure with geometrically suppressed intensity. To probe the surface area, we slightly defocus the beam to increase the probe size to 1-2nm, and thus reduce the disturbance from roughness and sample-drift. The NBED patterns of this location contain the structure information of both the rutile core and the shell. A significant distortion of the rutile structure is apparent in Figure 3-22c, which originates from the increased oxygen vacancies in the surface region of rutile. These distortions are represented by the rotations of the (020) and (0\(\bar{2}0\)) reflections. A representative example of extra reflections (marked by the red circle) of varying intensity are attributed to the defective shell because the d-spacing is very close to \(\text{Ti}_2\text{O}_3\) (\(\bar{1}20\)). The highly defective crystallinity of the surface layer and off zone axis viewing direction limit us from fully mapping out the symmetry of \(\text{Ti}_2\text{O}_3\). However, the structural details of this core-shell NP obtained by NBED are highly consistent with the STEM image and EELS spectral fits.

3.4.4 3-D model of the black rutile nanoparticle

STEM (Z-contrast) image of rutile nanoparticle is shown in Figure 3-24a. Because the intensity in Z-contrast image is proportional to the number of atoms in atomic column associated with the sample thickness, we extracted the intensity profile from the inner part to surface (highlighted by the green dashed box) to obtain the geometry information of this nanoparticle. This area crosses the location where the EELS spectrum image (highlighted by red dash box) was acquired. We observe three distinct sections in the intensity profile plot: Intensity in the first section (0-3.5nm) is quite low, representing the noise level in the vacuum; Intensity in the second section (3.5nm-6nm) increases nonlinearly towards particle inner, indicating a round corner of the particle; In the third section (6nm-15.5nm), the intensity increase linearly with distance away from vacuum, indicating an oblique facet of the nanoparticle. According to this tomography, we reconstruct a conceptual diagram of this nanoparticle with the core part (yellow area) and the shell in black color and two magnified diagrams from corner and facet highlighted in purple boxes, as shown in Figure 3-24b. The green arrow represents the electron-beam direction, along which we took EELS spectra and STEM image. According to this geometry, the region from 4nm to 7nm away from vacuum should still be in in the facet region. The main reason of the small increase of \(\text{Ti}_2\text{O}_3\) concentrations (11%-18%) toward vacuum is that electron beam (in red color) pass through less rutile as the thickness of this particle decrease when approaching
to the vacuum, while the electron beam penetrate through more or less constant volume of Ti$_2$O$_3$. The two magnified diagrams clearly show that electron beam passes through more Ti$_2$O$_3$ than interior due to the curvature of the particle. Figure 3-24c shows a conceptual diagram illustrating the shape of this nanoparticle.

3.4.5 Summary

In summary, we describe a new form of reduced TiO$_2$ NPs produced by annealing in Ar atmosphere of amorphous NPs created by PLD at room temperature. By analyzing the change in crystal field splitting features from monochromated EELS spectra, we determine the presence of rutile in the core and Ti$_2$O$_3$ at the surface of post annealed NPs. The aberration corrected STEM images provide structural information with atomic resolution confirming the stoichiometric rutile core and a defective Ti$_2$O$_3$ shell. The structural evolution from the particle interior toward the surface was characterized by NBED and is also consistent with the results of EELS and STEM, confirming the core-shell structure of these TiO$_2$ NPs. This core-shell structure uniquely originates from annealing amorphous precursor synthesized by PLD rather than annealing the crystalline starting materials. Since Ti$_2$O$_3$ combined with TiO$_2$ was shown to exhibit higher photoactivity than TiO$_2$ alone\textsuperscript{101}, the increased photoactivity of the TiO$_2$/Ti$_2$O$_3$ core shell structures originates from the small bandgap semiconductor properties of the Ti$_2$O$_3$.

3.5 Characterizations of black anatase

3.5.1 STEM and EELS analysis of black anatase

The a-TiO$_2$ NPs transformed into anatase NPs after annealing at 400°C in Ar gas. These anatase NPs also show a black color. However, the structure of ‘black anatase’ is more complicated than that of black rutile. Figure 3-25a shows a STEM image of a small anatase NP (diameter <5nm) viewed in [100] direction. This anatase NP has a well-define crystal structure in the interior, and a highly defective shell. The separation of shell and inner is indicated by a yellow dash line in Figure 3-25a (right). We investigated the possibility that this shell is a reduced layer with the stoichiometry of Ti$_2$O$_3$. We took EELS spectra on an anatase NP a core-shell structure which shows the shell is Ti$_2$O$_3$ in Figure 3-25a. In the black anatase NPs, we also found another structure where the defective parts distribute randomly within this NPs. Figure 3-25b shows a NP with such a highly defective structure. In the magnified figure from the grey dashed area in Figure 3-25b, the particle interior which contains a great number of
Figure 3-24 (a) STEM image of Ti$_2$O$_3$ nanoparticle from Figure 3-14c. We compare the relative thickness of the nanoparticle across the green dashed box by using the intensity. This area crosses the red dash box where the EELS spectrum image was acquired. Three distinct sections in the intensity profile plot were observed: section I (0-3.5nm) represents the vacuum; section II (3.5nm-6nm) represents the round corner of the particle; section III (6nm-15.5nm) represents a facet of the nanoparticle. (b) Conceptual diagram of the TiO$_2$ nanoparticle with two magnified diagrams from the corner and facet highlighted by purple boxes. The black shell represents the Ti$_2$O$_3$ covered on the TiO$_2$ core (the yellow area). The red line represents the electron beam (EB) penetrating through the corner and the facet (in purple box) along the direction highlighted by green arrow. In the region from 4nm to 7nm which belong to section II, the electron beam passes through less rutile as it move towards vacuum, while the thickness of Ti$_2$O$_3$ is relatively constant. Consequently, this gives rises a small increase of Ti$_2$O$_3$ concentration toward vacuum. The two magnified diagrams from these two areas show the electron beam pass through more Ti$_2$O$_3$ than interior due to the curvature of the corner. (c) 3-D model this rutile nanoparticle.
interstitial atoms highlighted by dashed circle is more defective than the surface part. Because this NP is so defective, we don’t even know the zone axis of the viewed direction. The STEM image result indicates that the ‘black anatase’ NPs are actually either of a core-shell structure or of a highly defective crystalline structure.

In order to further investigate the ‘black anatase’ NPs of these two structures, we took EELS spectra of these black anatase NPs. Figure 3-26a shows an anatase NP viewed in [001] direction with a diameter < 5nm. This NP is covered by a defective shell of non-uniform thickness (~1nm). Figure 3-26b shows the EELS spectra taken from the surface area (shell) and the center (core) of the anatase NP in Figure 3-26a. EELS spectrum taken from the shell shows two characteristic peaks of Ti$_2$O$_3$: L$_3$+t$_2g$ and L$_2$+t$_2g$ peaks designated by purple arrows. While the EELS spectrum taken from the core of this NP shows an anatase ELNES with its characteristic crystal field splitting features. The peaks’ positions and widths in EELS spectrum taken from core part are slightly different from reference anatase spectrum in Figure 3-16a originating from the signals of the Ti$_2$O$_3$ shell. The EELS result indicates that this anatase NP has a stoichiometric core and a Ti$_2$O$_3$ shell, similar to that of black rutile. However, EELS spectra taken from some NPs don’t reflect a core-shell structure; Figure 3-26c shows a small (<5nm in diameter) TiO$_2$ NP, where ELNES in the EELS spectra taken from different locations is different. As shown in Figure 3-26d, EELS spectrum taken from area 1 which is in the center of this NP shows a Ti$_2$O$_3$ characteristic feature, while that from area 2 which is close to the surface shows an anatase crystal field splitting feature. This result indicates that Ti$_2$O$_3$ and anatase just randomly distribute in this NP. It should be noted that all the ELNES of EELS spectra looks ‘washed out’ (By washed out we mean the peaks width and the positions change in the ELNES). The reason may originate from the fact that annealing for 1hrs is not long enough for the a-TiO$_2$ NPs crystallization at this temperature (400°C). Therefore, these NPs still maintain lots of defects resulting in NPs far away from equilibrium.

3.5.2 Growth mechanism of black anatase

Based on the above results, we propose the formations of NPs at 400°C in Ar gas, as shown in Figure 3-27. When the a-TiO$_2$ NPs were annealed, these NPs started to crystalize from the core. However, the crystalline core may contain defects such as growth strains, interstitial atoms, and (Ti or O) vacancies. Depending on the concentration of defects, the core of NPs could be either close to
Figure 3-25 STEM images of TiO$_2$ NPs with a core-shell structure in (a) and a highly defective structure in the particle’s interior in (b).
Figure 3-26 Images and EELS spectra taken from black anatase. (a) HRTEM image of an anatase NP with a core-shell structure. The core is anatase and the shell is $\text{Ti}_2\text{O}_3$ characterized by EELS spectra in (b). (c) STEM image of an anatase NP, where $\text{Ti}_2\text{O}_3$ and TiO$_2$ are randomly distributed.
Formation of ‘black anatase’. Crystallization start from the cores of α-TiO$_2$ NPs accompanied by oxygen vacancies diffusion towards surface. Depending on the concentration of defects, the core is defective with varying degree. The growth of NPs is associated with combination of NPs. Sufficient diffusion of oxygen vacancies result in a core-shell structure, while insufficient diffusion of oxygen vacancies results in formation of Ti$_2$O$_3$ inside the NPs.

Figure 3-27
perfect crystal or highly defective crystal. The diffusion of oxygen vacancies toward the surface of NPs occurred accompanied with crystallization of the core. As a result, most oxygen vacancies would aggregate at surfaces of the TiO$_2$ NPs. The Ti$_2$O$_3$ would form depending on the oxygen vacancy concentrations.

When heating, the NPs tend to grow larger by combining with other NPs. A newly combined NP consists of the NPs directly transformed from a-TiO$_2$ NPs (we define them as ‘original NPs’) where the oxygen vacancies distribute at surface. When combined together, the surfaces of some original NPs may bury inside the newly combined NPs. It is possible that the oxygen vacancies of the original NPs didn’t diffuse to the surface of the newly combined NP due to some factors i.e. the heating stopped when the original NPs began to merge. As a result, each part of the NP still more or less keeps their original structure. While if the oxygen vacancies diffuse completely to the surface, then a core-shell structure would form. From the experimental observations, the core part in the NPs with core-shell structure is less defective than randomly distributed Ti$_2$O$_3$ and TiO$_2$. This phenomenon may indicate that (1) the core-shell structure is more thermodynamically stable than the mixed Ti$_2$O$_3$ and TiO$_2$ phases NPs because crystalline lattice is thermodynamically stable than defective lattice, and (2) oxygen vacancies indeed diffuse more rapidly in the NPs of core-shell structure and thus less defective.

It should be noted that we didn’t perform linear least-square fit in the EELS spectra taken from these NPs. The reason is not solely due to the low signal-to-noise ratio which results in a fit error. As discussed before, some defective small rutile (d < 4nm) annealed at 400°C didn’t show crystal field splitting features in the Ti-L$_2$,3 edge of EELS spectra due to distortion of TiO$_6$ octahedra. The same case also occurs in the anatase NPs annealed at 400°C in Ar gas. Therefore, EELS spectra with absence of anatase crystal field splitting doesn’t necessarily come from Ti$_2$O$_3$ but maybe come from defective anatase. However, Ti-L$_{2,3}$ ELNES of EELS spectra taken from the defective Ti$_2$O$_3$ doesn’t change so much possible because the peaks in Ti-L$_{2,3}$ ELNES of EELS spectra taken from Ti$_2$O$_3$ is very broad and thus less sensitive to the octahedra distortion, as shown in Figure 3-28. Therefore, if we find the L$_3$-t$_{2g}$ and L$_2$-t$_{2g}$ in the EELS spectra, we can ensure the existence of Ti$_2$O$_3$.

3.5.3 Summary

Structures of black anatase NPs synthesized by annealing a-TiO$_2$ NPs at 400°C in Ar gas have been investigated by STEM and EELS. The STEM images of black anatase NPs show that there are
two types of structures of black anatase NPs: one corresponds to core-shell structure of a crystalline core and an amorphous shell and the other corresponds to randomly distributed structures. EELS spectra taken from these black anatase NPs show (1) the core-shell structure of black anatase NPs is similar as black rutile, and (2) there is randomly distributed Ti$_2$O$_3$ and TiO$_2$ in the black anatase NPs. These two structures originate from different diffusion rate of oxygen vacancies inside a-TiO$_2$ NPs and degrees of crystallization. We proposed a model for the formation of black anatase NPs. These approaches may help people to further investigate and understand the structure of black TiO$_2$ NPs synthesized in other ways i.e. sol-gel.

![EELS spectra taken from defective Ti$_2$O$_3$ NPs and commercial Ti$_2$O$_3$ NPs of perfect crystal.](image)

3.6 Cubic TiO$_2$ growth and characterizations

In this research, we found a rare form of TiO$_2$, which is a great potential solar energy absorber. This TiO$_2$ has cubic structure which was created by the electron damage in the STEM. The interstitial atoms of rutile play an important role in growing this structure.

3.6.1 STEM images of cubic TiO$_2$

To avoid electron beam damage on TiO$_2$, we usually took STEM images in a lower magnification. Figure 3-29 shows a STEM image of a black TiO$_2$ NP viewed in [001] direction. The integration time of
the blue dashed area is ~0.5 second. It is unlikely that the structures of black rutile are damaged by such short integration time$^{103}$ because this structure is highly consistent with HRTEM images, NBED, and EELS spectra as we systematically discussed before. In this black rutile NP, the lattice constant of rutile lattice is ~4.6Å which is the same as bulk rutile$^{104}$.

Figure 3-29 STEM images of black rutile NP with a core-shell structure. The integration time of the whole NP is 6s, and the integration time of the area highlighted by the blue dashed rectangular is ~0.5s.
Figure 3-30 shows the STEM images of this black rutile under different integration time: 1.5min, 3min, and 5min respectively. In the 1.5min integration time STEM image, surprisingly, we observe a new crystalline structure start to exist in the near surface area of this NP. This new crystal structure is quite different with that of Ti$_2$O$_3$ shell which is highly defective separated with rutile by surface reconstruction layer. Below the surface area, we also observe a great number of interstitial Ti atoms (highlighted by white dashed circle) with varying intensity. Concentrations of these interstitial Ti atoms become much larger in the 3 minute integration time STEM image. A highly ordered structure exists which looks like rutile viewed in [001] zone axis with extra atoms shifted in the [100] and [010] directions by half a lattice constant of each direction. The inserted model highlights the extra atoms of this new surface phase. To find out which crystal structure and its orientation this structure belongs to, we checked the most common polymorphs of TiO$_2$ (rutile, anatase, brookite, PbO$_2$ type-TiO$_2$, B-type TiO$_2$, baddeleyite, TiO$_2$-II) and the reduced Ti-O compounds (the magneli phases (Ti$_x$O$_{2x-1}$ 3<x<10), Ti$_2$O$_3$, TiO, Ti$_2$O, Ti$_3$O). By the analysis, it is found this new structure matches very well with the cubic TiO$_2$ and the atomic arrangement in the image is consistent with the cubic TiO$_2$ in <001> projection direction. In the 5min integration time STEM image, the cubic TiO$_2$ is damaged which shows a distorted lattice. Therefore, this observation indicates that the cubic TiO$_2$ can be formed under electron beam exposure with a certain time, but it would be damaged after a long integration time.

By comparison, the intensity of extra atoms near surface is much higher than particle interior. This lower contrast indicates lower amounts of atoms in the projection direction, as shown in Figure 3-31a,b. We suspected that the surface must contain a special template structure for this new phase. The position of this extra Ti atoms are very similar as the one in surface reconstruction layer, as shown in Figure 3-31c. There are two models for surface reconstruction sites of Ti atoms proposed by Onishi-Iwasawa et al$^{49,50}$ and Park et al$^{105}$. Both of them suggested that the reconstructed atoms were actually in the interstitial sites. The difference between these two models is that the interstitial site is from either Ti columns only (iv sites) or Ti-O columns (ih sites) viewed in the [110] direction, whereas two models share the same interstitial positions in [001] direction. Compared to their work, in which the reconstructed atoms are only found at the surface, however, in the [001] projection direction, the extra atoms also exist inside the rutile particle with the same positions of surface reconstructed atoms. Therefore, we conclude the high energy of electron induced the Ti atoms diffusion. The final position of this Ti atom’s migration is the interstitial site. In Figure 3-31b we see three rows of rutile atomic planes at the bottom and three columns
of rutile on the left, while the top right is this new phase. In the cubic phase all atomic columns have
about the same intensity, while in the rutile phase the Ti columns are very bright but there is also some
intensity in between these Ti columns, which is not present in pure rutile. This intensity could come from
interstitials or from interface roughness, so that the cubic and the rutile phase mix in the projection of the
image.

3.6.2 Models of formation of cubic TiO$_2$

In order to understand how this new phase can be grown from the surface reconstruction template,
we used the schematics in Figure 3-32. Because we just wanted to highlight the new symmetry
introduced by the interstitial Ti atoms viewed in [001] direction, we ignored the oxygen atoms sublattices
here. Please note that the two different phases of cubic TiO$_2$ only differ in the position of the oxygen
atoms in this projection (see discussion below), and therefore, we cover both cases in this discussion.
Assuming all the interstitial positions, colored in pink, in a rutile unit cell were fully occupied as shown
in Figure 3-32a. The Ti atom at the (1/2, 1/2, 1/2) body center were intentionally colored black, while the
other Ti atoms at the 8 corners of the primitive tetragonal unit cell of rutile are shown in grey color.
Figure 3-32b shows the projection of pure rutile and reconstructed atoms viewed in the [001] direction.
An extended 1×2 unit cell highlights the different symmetry between rutile and this new structure
introduced by interstitial atoms. Inside the red dashed square, the reconstructed atoms composed a
perfect single layer of TiO$_2$ FCC {100}, which can be a template for growing cubic TiO$_2$. However, it is
also possible that the cubic TiO$_2$ is transformed from rutile by this template. As shown in Figure 3-32c,
this phase transformation will collapse two rutile unit cells into one fcc unit cell. Each of these two unit
cells of rutile collapses into a single plane, which means that Ti atoms moved from the base centered site
of rutile to the center of the other Ti atoms at the corners. The other plane came from the same movement
of the Ti base centered atoms plus a shift in [100] direction by half a unit cell. This position is equivalent
to an interstitial site in rutile. The distance of the planes has also to be re-arranged and form the face
centered cubic structure.

The lattice constant of rutile a=b=4.6Å is close to that of cubic TiO$_2$ ranging from 4.6-4.8Å because
the lattice constant of cubic TiO$_2$ deviate from different research slightly$^{6,96,102,106}$. From our
measurement, the lattice constant for cubic TiO$_2$ is about 4.7Å, which is slightly larger than lattice
constant of rutile. There are two cubic phases of rutile, which were synthesized at high temperature and
Figure 3-30 STEM images of black rutile NP under 1.5min, 3min and 5min integration time.
Figure 3-31 STEM images of rutile NP with cubic TiO$_2$ phase, comparing with STEM image with surface reconstruction layer. The atomic resolution image shows a new phase at the near surface area of the particle in (a). The non-uniform intensity distribution of these extra atoms was highlighted in a magnified image (b) from (a). The surface reconstruction atoms were clearly resolved in (c).
Figure 3-32 Schematic of phase transformation from rutile to cubic TiO$_2$ by a template. Interstitial Ti atoms in rutile are colored in red in (a). The grey circles represent the Ti atoms site before migration. Please note that the accompanying tetragonal distortion is not included in this schematic drawing. (b) shows a new symmetry introduced by interstitial Ti atoms. This new symmetry, highlighted insides the red square, originates from \{100\} plane of FFC TiO$_2$ viewed in [001] direction. Additional one unit cell was intentionally extended in [010] direction and present in dash grey line. (c) shows the motion of Ti atom during phase transformation from rutile to cubic TiO$_2$. The dash circles represent the site where the atoms migrate. (d) shows two cubic TiO$_2$ structures, the fluorite and pyrite type, respectively.
high pressure condition very recently. The first one has the fluorite structure, in which the Ti ion is surrounded by 8 oxygen atoms in cubic surrounding. The second phase is called pyrite-like with FeS$_2$ structure (Pa$\overline{3}$), and the position of oxygen atoms is the only structural difference between fluorite $\pm$(1/4, 1/4, 1/4) and pyrite $\pm$(0.34, 0.34, 0.34). From the [001] direction, there is no difference of Ti positions between these two cubic structures and hence it is impossible retrieve the oxygen positions in this rutile particle.

3.6.3 Summary

Our observations showed that the interstitial Ti atoms play a key role to grow the cubic TiO$_2$ phase on rutile. While interstitial Ti atoms were demonstrated in the previous researches at surface, the interstitial Ti atoms actually also existed inside the rutile particles at rutile {110} plane. We showed the process how the atoms moved and then formed the template of cubic TiO$_2$. The importance of our results is that this TiO$_2$ structure, conventionally synthesized at a high pressure and high temperature, can grow induced by electron beam. We expected that the cubic TiO$_2$ can also grow assisted with other high energy source, i.e. ion-implantation. Our analysis provides a pathway to optimize the growth of photo-active NPs with high concentrations of cubic-TiO$_2$.

3.7 Deviations of classic crystal field splitting features in known titanium oxides.

3.7.1 EELS experimental results and analysis

By tuning the connectivities, shapes, and distortion of TiO$_6$, we can obtain different titanium oxides, no matter these oxide are crystalline or amorphous. Therefore, TiO$_6$ octahedra are the building blocks of all titanium oxides. EELS or XAS spectra are the best tools for characterization of TiO$_6$ octahedra. However, deviations of standard TiO$_2$-L$_{2,3}$ ELNES of known titanium oxides were observed in the TiO$_2$ NPs synthesized in this research. Based on thousands of EELS spectra taken from titanium oxide NPs synthesized at different conditions, we found that deviations of crystal field splitting features in ELNES of EELS spectra are very popular in the NPs smaller than 5nm. However, unlike quantum size effect in which the electronic structure properties i.e. band gap increase with decreasing the size, deviations of crystal field splitting feature of EELS spectra aren’t always size-dependent. For example,
EELS spectrum taken from 5nm anatase NP can either show crystal field splitting feature or absence of crystal field splitting. According to the typical features of these changes of crystal field splitting, we classified the spectra into different types discussed below. The corresponding spectra are shown in Figure 3-33:

The classic TiO$_2$-L$_{2,3}$ crystal field splitting feature is hard to resolve in the spectra a-d, as shown in Figure 3-33a. However, the corresponding O-K ELNES in Figure 3-33b is quite different: The onset of O-K edge spectrum a blueshifts to ~532eV. There is only one peak in this spectrum’s O-K ELNES instead of two pre-peaks for TiO$_2$ and Ti$_2$O$_3$. This O-K ELNES is very similar as that of TiO$_9^6$ of which the splitting of both Ti-L$_{2,3}$ and O-K edge are hard to resolve and the O-K blueshift. Besides, there is another unique feature of spectrum a that the intensity of O-K edge is about 1/2 of TiO$_2$ after normalizing Ti-L$_{2,3}$ edge intensity. Quantification from Quantifit also show that the Ti:O ratio is 1:1. Therefore, spectrum a represents TiO. Spectrum a is taken from amorphous NPs synthesized at room temperature in Ar; Both O-K EELS spectra b-c show two pre-peaks with TiO$_2$ characteristics. The only difference between these two spectra is that spectrum c shows TiO$_2$ L$_{3,2}$-t$_{2g}$ peak, while this peak is too broad to resolve in spectrum b. In this case, both spectra b-c should come from TiO$_2$. The broadening effect of the TiO$_2$ L$_{3,2}$-t$_{2g}$ peak originates from TiO$_6$ octahedra distortion due to defects. The EELS spectra with spectrum b characteristics are taken from (amorphous or crystalline) NPs synthesized at room temperature in Ar and O. EELS spectra with spectra b characteristics taken from small anatase or rutile NPs (<5nm) annealed at 400°C; O-K edge in spectrum d show two pre-peaks with Ti$_2$O$_3$ characteristics. The Ti-L$_{2,3}$ shows both TiO$_2$ and Ti$_2$O$_3$. The ELENS of this EELS spectrum indicates the NPs have reduction. Interestingly, similar spectra as spectrum d can be taken from the NPs synthesized in many synthesis conditions: (1) amorphous and crystalline NPs synthesized at room temperature in Ar and O, (2) in small anatase or rutile NPs (<5nm) annealed at 400°C, and (3) in the surface area of large crystalline NPs synthesized in Ar at 700°C. Ti-L$_{2,3}$ edge in spectrum e show crystal field splitting with peaks’ widths broadening and peaks’ positions shifting. The ELNES of this spectra is representative for a-TiO$_2$ NPs synthesized by PLD at room temperature, which is quite different from that of anatase, rutile, TiO$_5$(B), brookite and Ti$_2$O$_3$, as discussed before. Depending on doped elements in the TiO$_2$ NPs or not, the widths of Ti-L$_{2,3}$ peaks vary. Spectrum f represents for the spectrum taken from crystalline particle (anatase or rutile) of small sizes (<5nm). In this type of spectrum, the ELNES is more or less ‘wash out’ which is possibly due to existence of defects. However, the defect
concentration should be low. As a result, TiO$_6$ octahedra aren’t distorted so much and hence we can clearly observe the crystal field splitting features.

We summarized the characteristics of Ti-L$_{2,3}$ and O-K ELMES of EELS spectra (a-f) and the corresponding condition where these EELS spectra were taken from in Table 3-3. We also summarized which types of crystal, and which types of structure of this crystal spectra a-f represent for. According to this summary, there are two reasons for the changes of crystal field splitting features in EELS spectra: (1) the reduction of TiO$_2$ NPs in the Ar annealing atmosphere, and (2) the distortion of TiO$_6$ octahedra due to defects.

![Diagram](image)

Figure 3-33 Ti-L$_{2,3}$ and O-K ELMES of EELS spectra (a-f) taken from the NPs synthesized at different conditions shown in Table 3-3.

3.7.2 Reduction

As discussed in Chapter 3-4, TiO$_2$ NPs annealed in Ar gas at 700°C are covered by Ti$_3$O$_5$ shells. In the EELS spectra taken from these black rutile NPs, we can retrieve the Ti$_3$O$_5$ signals in EELS spectra by linear least-square fit. It is not surprised that the Ti$_3$O$_5$ concentration exist the NPs synthesized in Ar at other temperature i.e. at 400°C from which we obtain black anatase NPs. The interesting point here is that we found TiO in the a-TiO$_2$ NPs synthesized at room temperature in Ar.
Table 3-3 Features of Ti-L$_{2,3}$ and O-K ELNES of EELS spectra (a-f) and the NPs where the spectra a-f are taken from. RT = room temperature, A = anatase, R = rutile, B = TiO$_2$(B), Br = brookite.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Ti-L$_{2,3}$ edge</th>
<th>O-K edge</th>
<th>Taken from</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>No splitting</td>
<td>No splitting</td>
<td>NPs synthesized at RT in Ar</td>
<td>TiO</td>
</tr>
<tr>
<td>b</td>
<td>Highly broadened</td>
<td>TiO$_2$ splitting features</td>
<td>(crystalline or amorphous) NPs synthesized at RT in Ar or O$_2$</td>
<td>TiO$_2$ with highly distorted TiO$_6$ octahedra</td>
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<td>c</td>
<td>Highly broadened but TiO$_2$ L$<em>3$-t$</em>{2g}$ peak can be resolved</td>
<td>TiO$_2$ splitting features</td>
<td>Small A or R NPs (&lt;5nm) annealed at 400°C</td>
<td>TiO$_2$ with distorted TiO$_6$ octahedra</td>
</tr>
<tr>
<td>d</td>
<td>Highly broadened but both TiO$_2$ and Ti$_2$O$_3$ L$<em>3$-t$</em>{2g}$ peak can be resolved</td>
<td>Ti$_2$O$_3$ splitting features</td>
<td>(1) amorphous and crystalline NPs synthesized at RT in Ar and O$_2$, (2) small A or R NPs (&lt;5nm) annealed at 400°C in Ar, and (3) in the surface area of large crystalline NPs synthesized in Ar at 700°C.</td>
<td>TiO$_2$ mixed with high concentration Ti$_2$O$_3$</td>
</tr>
<tr>
<td>e</td>
<td>Clearly resolve. Broadening splitting</td>
<td>Doped or non-doped amorphous and crystalline NPs synthesized at RT in Ar, O$_2$</td>
<td>Characteristic EELS spectra of amorphous NPs</td>
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<td>f</td>
<td>Slightly wash out TiO$_2$ splitting features</td>
<td>Small A or R NPs (&lt;5nm) annealed at 400°C</td>
<td>TiO$_2$ with slightly distorted TiO$_6$ octahedra</td>
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These TiO NPs aren’t found in any other synthesis conditions. Statistically, this type of NPs occupies less than 1 percent of the whole NPs. The formation of TiO NPs may be also related to oxygen diffusion like the formation of Ti$_2$O$_3$ in TiO$_2$ NPs in reduction atmosphere. Further investigation need to perform on the formation of the TiO synthesized at room temperature. In the reduced TiO$_2$ NPs, the reduced part is usually a shell covered by the stoichiometric TiO$_2$ core. Therefore, the size dependent crystal field splitting features in the EELS spectra is because surface-to-volume ratio is very high in a small NP. Figure 3-34 shows surface-to-volume ratio at different diameters of NPs with shells 0.5nm, 1nm, and 1.5nm thick, considering in the spherical shape or cubic shape cases. The surface-to-volume ratio is extremely high in the (<5nm ) NPs i.e. ~50% when diameter of NPs is 5nm with a 1nm thick reduced shell.

![Surface-to-volume ratio graph](image)

Figure 3-34 Surface-to-volume ratios of NPs in different diameters with the shells of different thickness, considering the NPs’ shape is spherical or cubic.

### 3.7.4 Defects

Distortions of TiO$_6$ octahedra in known phase i.e. rutile due to defects are hard to predict. From EELS spectra results, distortions of TiO$_6$ octahedra of TiO$_2$ lead to changes of peak’s positions, widths, and intensities in the EELS spectra. However, we found broadening effect play a major role in changing the crystal field splitting features of TiO$_2$ ELNES according to hundreds of experimental results. The broadening effect of the Ti-L$_{2,3}$ ELNES makes it hard to distinguish the phase between
defective TiO$_2$ and amorphous TiO$_2$. We have shown in Figure 3-4 that Ti-L$_{2,3}$ ELNES of EELS spectra taken from Cr doped a-TiO$_2$ look very similar with that of TiO$_2$(B). Slightly broadening peaks of these two ELNES would make them hard to distinguish. However, due to the broad peaks of Ti-L$_{2,3}$ edges, distortions of TiO$_6$ octahedra of Ti$_2$O$_3$ don’t significantly change the ELNES of perfect Ti$_2$O$_3$ ELNES. The broadening effects also applied to the O-K edge, but the two pre-peaks of O-K edge usually can be resolved. As discussed before, Ti-L$_{2,3}$ edge shows absence of crystal field splitting if the lattices of TiO$_2$ NPs are highly distorted. However, EELS spectra of TiO also show absence of crystal field splitting. The ways to distinguish them are (1) normalizing intensities of the Ti-L$_{2,3}$ edge of EELS spectra. The corresponding intensities of TiO O-K edge are about 1/2 of those of defective TiO$_2$; (2) observing the pre-peaks of O-K edge. There is only one pre-peak in TiO, and onset of this peak blueshifts to 532eV compared to 529eV in TiO$_2$. While there are two pre-peaks in the O-K edge of EELS spectra taken from defective TiO$_2$ NPs. These two differences of EELS spectra between TiO and TiO$_2$ allows to unambiguously distinguish these two phases. For example, Figure 3-35 shows EELS spectra taken from small defective rutile NPs annealed 400°C. We took EELS spectra from different NPs designated by 1-6. These NPs of sizes 5±1nm are stoichiometric confirmed by Quantifit with 5% fit error. As shown in Figure 3-35b, Ti-L$_{2,3}$ crystal field splitting features are different with those of standard rutile in spectra 1-6. In spectrum 2-3, the crystal field splitting features are hard to resolve. However, two pre-peaks of O-K are very easy to resolve in all the spectra. Therefore, we confirm the deviation of crystal field splitting can only originate from defects. The absence of crystal field splitting features in the EELS spectra due to defects is not size dependent, and it seems size dependent because the amorphous or highly defective NPs synthesized in this experiment are quite small (<5nm).

**3.7.5 Summary**

We summarized the origin of deviations of crystal field splitting features in the EELS spectra taken from TiO$_2$ NPs synthesized at different conditions. The deviations of crystal field splitting features in the EELS seem size dependent. There are two factors influencing the crystal field splitting features, which are reduction and defects. The TiO$_2$ can be reduced into Ti$_2$O$_3$ and TiO synthesized in Ar gas, and therefore the EELS spectra show different ELNES with TiO$_2$. Because the reduced layers in TiO$_2$ NPs consist of the shell, the significantly high surface-to-volume ratios in small NPs cause the
Figure 3-35 STEM images and EELS spectra taken from defective rutile NPs synthesized at 400°C. (a) STEM images of defective rutile NPs synthesized at 400°C. NPs 1-6 were selected to take EELS spectra shown in (b).
size dependent deviation of crystal field splitting features. The defects cause broadening the peaks’ width, positions, and intensities in EELS of TiO$_2$. The broadening effect plays a major role in changing crystal field splitting features in EELS. However, the changes of crystal field splitting features in EELS by defects are not size dependent.

### 3.8 Outlook: Si-TiO$_2$ interface plasmon

In the Cr$_2$O$_3$ and N$_2$ co-doped TiO$_2$ NPs samples annealed at 400°C-800°C, we found that the TiO$_2$ NPs were strongly attached to the debris of Si substrate, as shown in Figure 3-36a. TiO$_2$ and Si don’t show plasmonic effect by themselves. However, the low-loss spectra taken from the interface of these two materials show a series of peaks located from 1eV-2.8eV in the band gap of TiO$_2$. HRTEM image of TiO$_2$ NPs attached on Si substrate with an interface is shown in Figure 3-36b. Figure 3-36c shows an intense peak located at ~1.8eV in the EELS spectrum taken from Si-TiO$_2$ interface. The intensity of this peak decays in either Si or TiO$_2$ side. We attribute the origin of this peak to the interface plasmon excitation. This interface plasmon was found at different energy positions in different areas. In some cases, there are multiple interface plasmon peaks in a low-loss EELS spectrum. The intensity of this interface plasmon is slightly lower than Ag which is known as the metal with sharpest plasmon intensity. Since the positions of these interface plasmon peaks mostly concentrate on visible light range (1.5eV-3.0eV), we can take advantage of this phenomenon to enhance the photo-activities of TiO$_2$. However, we need to perform further research on the origin of this interface plasmon by synthesizing Si-TiO$_2$-Si multi-layers thin films. We also need to know whether this effect originate from the Cr and N dopants of TiO$_2$. 
Figure 3-36 HRTEM image and EELS spectra of Si-TiO$_2$ sample, where the Si-TiO$_2$ interface show multiple intense peaks in the band gap of TiO$_2$. (a) HRTEM image of TiO$_2$ NPs on the Si substrate. (b) HRTEM image of Si-TiO$_2$ interface. (c) EELS spectra taken from Si-TiO$_2$ interface, the locations 5nm from the interface in Si and TiO$_2$ sides, respectively. (d) EELS spectra of Si-TiO$_2$ interface plasmon and Ag plasmon, respectively.
Chapter 4. Conclusion

In this research, we focus on the structure characterizations of TiO$_2$ NPs with enhanced photo-activities by tuning the a-TiO$_2$ precursors using a series of methods: annealing at different background gases, doping elements, and electron beam inducement.

The sizes, degrees of amorphous/crystalline ratios, and morphologies of a-TiO$_2$ NPs are the functions of the distances between targets and samples. We investigate the unique structure of a-TiO$_2$ NPs in atomic scale synthesized at room temperature. NBED maps taken from these a-TiO$_2$ NPs show that these amorphous materials have ~0.5nm SRO. EELS spectra show that the SRO originates from the unique TiO$_6$ octahedra in a-TiO$_2$. The a-TiO$_2$ NPs annealed in O$_2$ have unconventional phase transformation: anatase-coexistence of anatase and TiO$_2$-(B)-anatase from a temperature ranged from 400°C to 900°C, in contrast to the anatase to rutile which is the conventional phase transformation in this temperature range. However, creating defects such as annealing in Ar gas, or doping can induce the rutile at temperatures from 400°C to 900°C.

We discuss the varying valences and defects in the doped TiO$_2$ NPs complicate the analysis of origin of band gap narrowing. From the experimental results, there is no obvious band gap narrowing effect in the NPs with single N- or Cr- doping. However, co-doping Cr$_2$O$_3$ and N$_2$ into TiO$_2$ NPs are demonstrated to significantly narrow the band gap of doped TiO$_2$ characterized by EELS and XPS. The band gap narrowing effect arise from extra states on the top of valence band.

The black TiO$_2$ NPs have been intensely studied recently. But no researches reported the structure of black TiO$_2$ NPs in atomic scale and their growth mechanism. The structures of black rutile NPs annealed from a-TiO$_2$ NPs at 700 °C in Ar are systematically investigated by HRTEM imaging, EELS spectrum imaging, atomic resolution STEM imaging, NBED patterns, and DFT calculations. From the linear least-square fit of EELS spectra taken from different locations of a black rutile NP, the Ti$_2$O$_3$ concentration increase towards surface. The atomic resolution STEM image shows that there is a defective Ti$_2$O$_3$ shell with thickness 1nm. Underneath this shell, there is a 1-2nm thick rutile layer which is defective due to the existence of interstitial Ti atoms. We conclude that the Ti$_2$O$_3$ originates from diffusion of oxygen vacancies towards vacuum when annealing the a-TiO$_2$ precursors in Ar gas. A comparison of EELS spectra taken from crystalline precursors and amorphous precursors show that the a-TiO$_2$ NPs, which are thermodynamically metastable, play a unique role in forming Ti$_2$O$_3$. The phase
transformation of Ti$_2$O$_3$-TiO$_2$ at 700°C in oxygen deficient background is kinetically forbidden derived from the DFT calculations. The corresponding NBED results show that (1) forbidden reflections exist in the defective rutile layer due to existence of interstitial atoms, and (2) distorted rutile lattice and existence of Ti$_2$O$_3$ reflections in the shell. The results of EELS spectra analysis, atomic resolution STEM image, and NBED pattern are consistent with each other; The black anatase are made from a-TiO$_2$ annealed at 400°C in Ar gas. Formation of Ti$_2$O$_3$ in black anatase NPs are similar as that of black rutile NPs. There are two types of structures for black anatase NPs: (1) a Ti$_2$O$_3$ core-anatase shell structure and (2) a random distributed TiO$_2$ and Ti$_2$O$_3$ structure. These two structures originate from different diffusion rate of oxygen vacancies inside a-TiO$_2$ NPs and degrees of crystallization.

Cubic TiO$_2$ has smallest band gap of all the TiO$_2$ polymorphs but can only synthesized at high temperature and high pressure condition. In this research, cubic TiO$_2$ is induced by the electron beam on rutile NPs. The origin of this phase comes from the migration of interstitial Ti atoms grown on rutile template. High concentrations of these interstitial Ti atoms result in collapse of the rutile lattice and thus forming the cubic TiO$_2$ structures. This result indicates that we may also take advantage of other high energy source, i.e. ion implantation to produce the cubic TiO$_2$ which has the smallest bandgap in all known TiO$_2$ polymorphs.

Assisted with highly spatial resolved TEM techniques, EELS is the best tool to investigate the electronic structure of TiO$_2$ in atomic scale, but much confusion about the origin of changes of ELNES in the EELS. In this research, we summarized two factors influencing deviations of unknown phases’ crystal field splitting features in EELS spectra which are strongly related to NPs’ size, based on a highly statistically valid EELS spectra data: One factor is the reduction. This factor results from annealing a-TiO$_2$ in Ar which leads to the formation of Ti$_2$O$_3$ whose ELNES is different with that of TiO$_2$. These Ti$_2$O$_3$ are the shells of TiO$_2$ NPs. Because the shell-core ratio in TiO$_2$ NPs increase dramatically with decreasing the NPs’ sizes, the Ti$_2$O$_3$ component may dominate in the small size NPs (<5nm). TiO$_2$ crystal field splitting features in the Ti-L$_{2,3}$ ELNES may disappear when the thickness of the shell is large and the size of a NP is small. TiO NPs, which occupy very small fractions of the whole NPs (<1%), is found in the samples synthesized at room temperature in Ar; The second factor is defect. The existences of defects result in changes of peak’s positions, widths, and intensities. However, the broadening effects of the peaks in Ti-L$_{2,3}$ ELNES play a major role in changing of standard crystal field splitting features of EELS spectra. Comparing to the featureless Ti-L$_{2,3}$ edge in highly defective
crystal, two pre-peaks of O-K edge can be easily resolve. The results show that there are no size dependences in these defective or amorphous TiO$_2$. The absence of crystal field splitting seems to correlate to the size because the sizes of most a-TiO$_2$ NPs are below 5nm.

Finally, we found a group of intense peaks in the interface between Si and TiO$_2$ both of which don’t show plasmonic effect. The energy of these peaks mainly concentrate on visible light range, which allows to enhance the photo-activities of TiO$_2$ NPs. These peaks seem to originate from interface plasmon excitations. A further confirmation and investigation need to perform in the future.


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VITA

Mr. Mengkun Tian was born in Yunyan district in Guiyang, capital city of Guizhou Province in China on May 5th 1986. He was admitted by Guiyang No.1 high school in 1999 and from then on he became interested in material science and engineering. In 2004, he enrolled in the department of materials science and engineering in China University of Mining and Technology (CUMT) in Xuzhou, Jiangsu. After he completed his Bachelor’s degree in CUMT in 2008, he enrolled in Central South University pursuing for his research in master program. His master program was related to synthesis of diamond thin films by chemical vapor deposition (CVD), and his advisor is Dr. Zhiming Yu.

After he obtained his master thesis degree in 2011, Mr. Mengkun Tian joined the materials science and engineering department to pursue a PhD degree in University of Tennessee, knoxville. His advisor is Gerd Duscher. He investigates the growth mechanism and structural evolution of TiO$_2$ nanoparticles and the associated band gap narrowing engineering for photocatalysis. He is also interested in structural characterizations of transition metal dichalcogenides 2D materials.