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TiO_2 Phase Transformation Mechanisms at Atomic Scale under Heating and Electron Beam Irradiation

Miao Song[1] and Dongsheng Li[1*]

[1.] Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352
* Corresponding author: Dongsheng.Li2@pnnl.gov

Titanium oxide (TiO_2) has been extensively studied due to its low cost and promising applications, such as photo catalysis [1, 2], solar energy conversion in dye-sensitized solar cell [3, 4], energy storage [5, 6], and biomedicine [7, 8]. It has been reported that crystal phases play key role in determining crystal properties as well as particle size, morphology, and the exposed surface. For example, photocatalytic efficiency was optimized by mixed phases of anatase and rutile, such as degussa P-25 (~85 wt% anatase and ~15 wt% rutile) [9] due to an effective separation of charge carriers in the different phases, which suppresses the electron–hole recombination mechanism [10]. Therefore, understanding the structure evolution during TiO_2 phase transformation and the relationships between phases is necessary for improving and controlling its properties. Although the phase transformation has been extensively studied, the mechanisms and their relationships to properties are still not fully understood especially at atomic scale. Anatase, brookite, and rutile are three common phases of TiO_2. Here we investigated the atomic structure evolution of the three phases, as well as electron beam effects during *in situ* TEM heating experiments.

A Protochips heating holder was employed to conduct the *in situ* TEM experiments and to directly observe the atomic structure transformation between TiO_2 phases. We hypothesize that anatase can transform into different phases based on experimental conditions, such as heating rate, temperature, and particle morphologies. Our preliminary results revealed that platelet anatase particles of 100-200 nm transformed into brookite (Figure 1a-c) and octahedron anatase nanoparticles of ~10-100 nm transformed into rutile under heating of 600-1000°C. In addition, under e-beam irradiation, Ti^{4+} can be reduced to Ti^{2+} or Ti^{3+} or transformed into a different phase of TiO_{2-x} (Figure 1 d-f). Our results revealed that particle size, morphology, and temperature play important role in phase transformation (Figure 2). Further analysis is undergoing to investigate the atomic structure evolution and reveal the structure-function relationship. The resulting analysis enables the control of the phase transformation and crystal structure of TiO_2 nanoparticles that have unique properties. [11]

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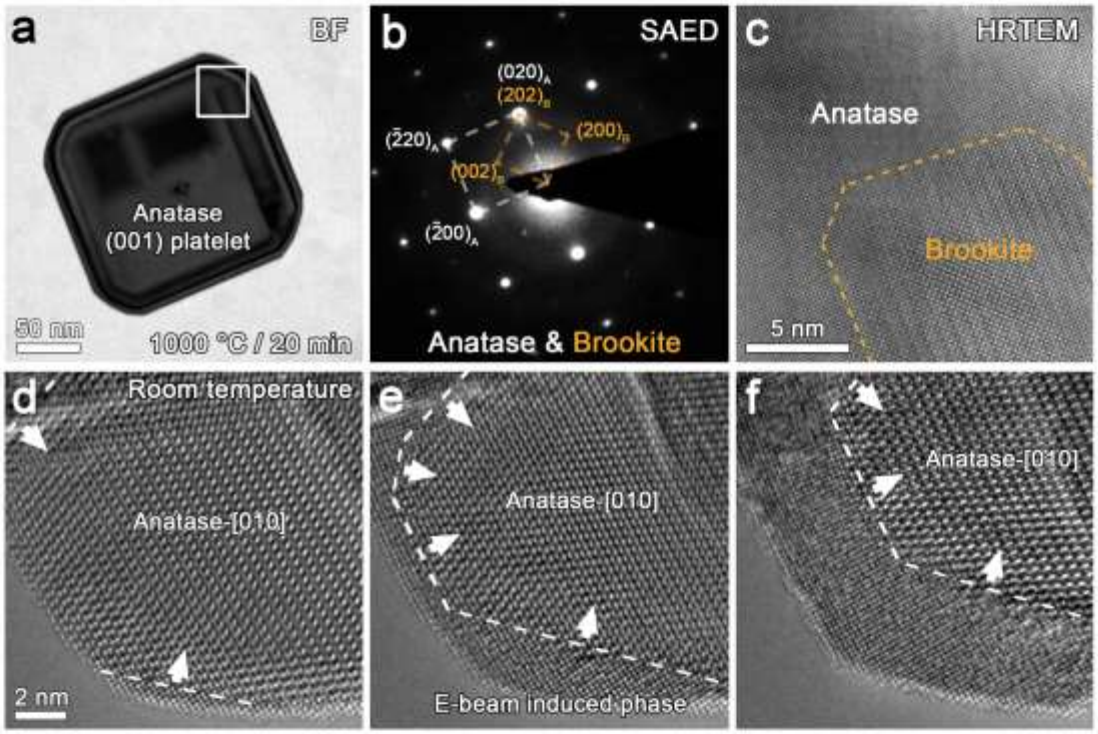

Figure 1. TEM analysis of anatase phase transformation into brookite and an unknown phase under heating (a-c) and electron beam irradiation (d-f), respectively.

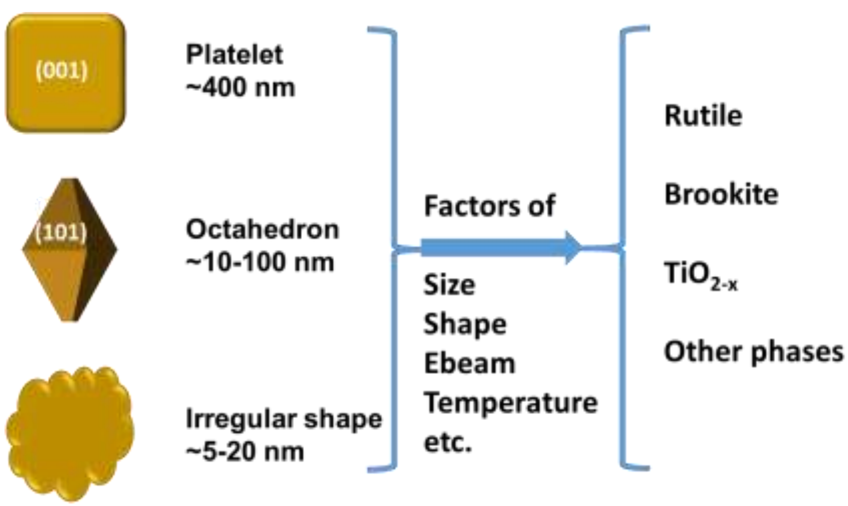

Figure 2. Schematic summary of phase transformations and its controlling factors.

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