Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Materials

Phase Transition of Individual Anatase TiO_2 Microcrystals with Large Percentage of (001) Facets: A Raman Mapping and SEM Study

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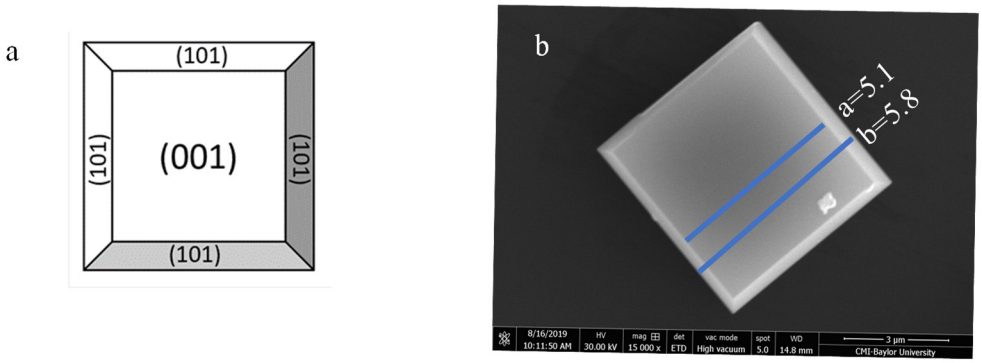

Figure S1. Calculation of percentage of (001) facet of anatase microcrystal. a: Sketch of anatase microparticles; b: Size measurement of the Particle #1 in Figure 1a.

The percentage of {001} facet is calculated using the following equation:

$$\frac{a^2}{\frac{(b^2-a^2)}{\mathrm{tg}\,(\theta)}+a^2}\,\mathrm{x100\ \%}$$

where a and b denote lengths of the side of the square {001} truncation and the side of bipyramid, θ, is interfacial angle between {001} and {101} facets. For the particle #1 in Figure 1a, a = 5.1 µm, b = 5.8 µm and θ = 68.3.

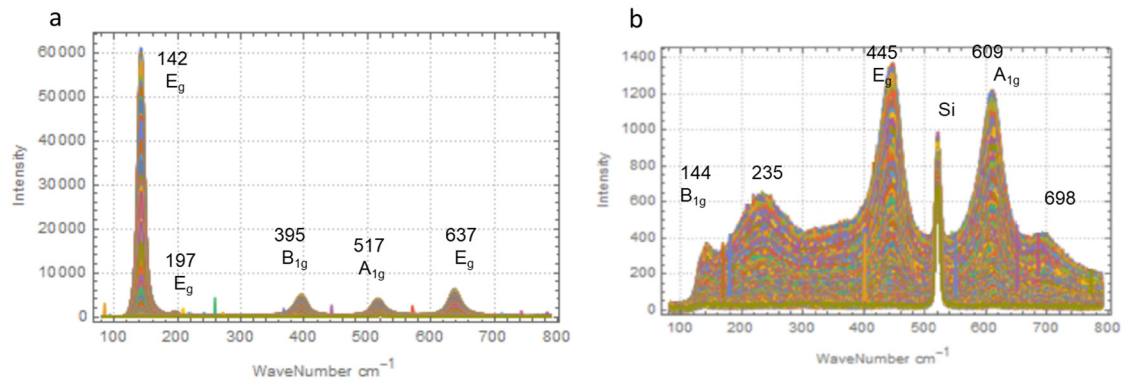

Figure S2. Raman spectra of the Particle #1 in Figure 1a before (a) and after ART (b) at 1100 ºC for 18 hours. Only anatase modes were observed before ART and only rutile modes together with Si substrate peak at 520 cm^{-1} were observed after ART.

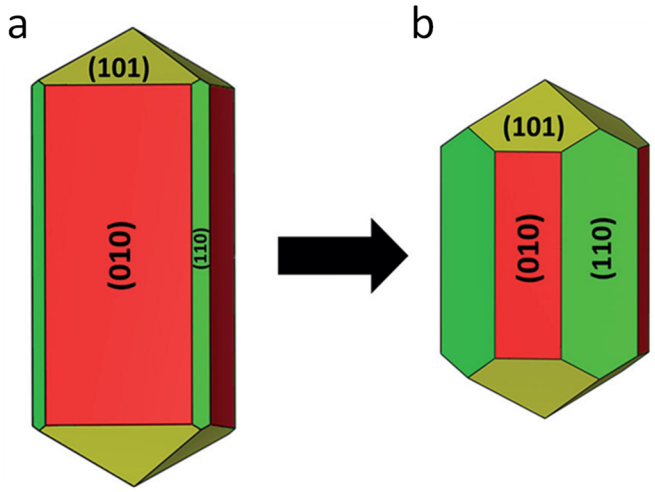

Figure S3. Rutile TiO_2 morphological Wulff reconstruction in a vacuum. (a) Unrelaxed structure. (b) Relaxed structure.[1, 2]

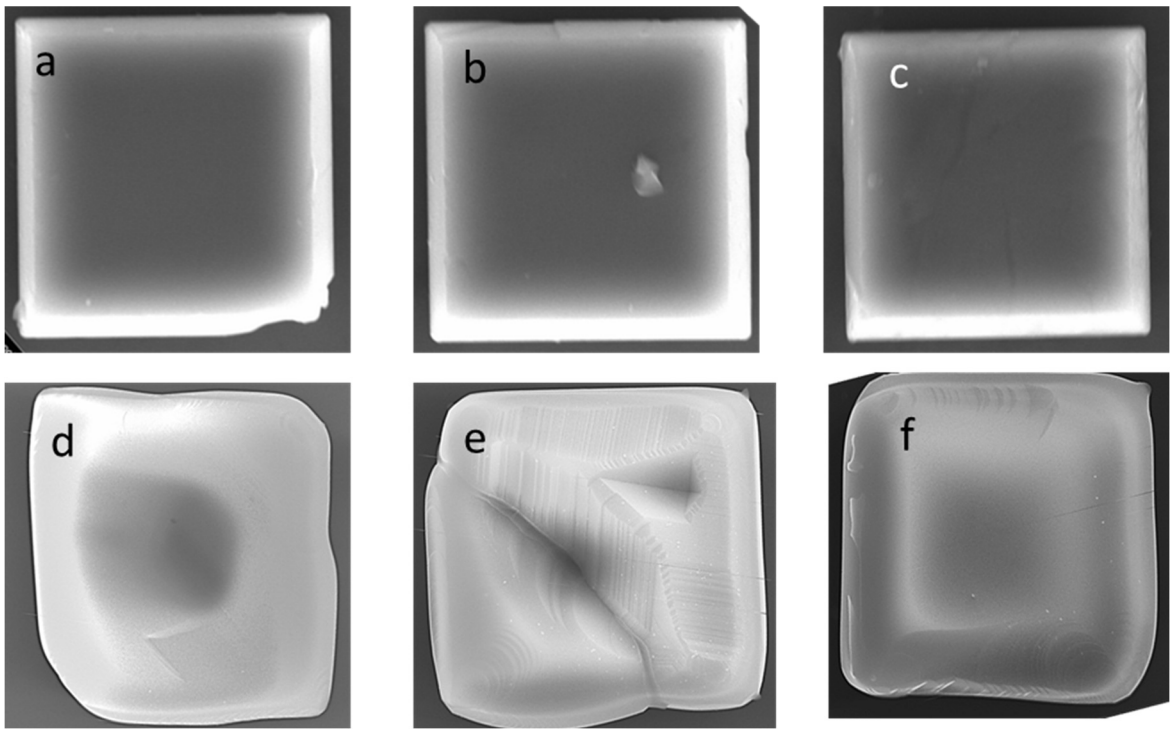

Figure S4. SEM images of anatase microcrystals before and after ART at 1075 ºC for 18 hours. a and d, b and e, c and f pairs are the same particles before and after annealing for 18 hours at 1075 ºC.

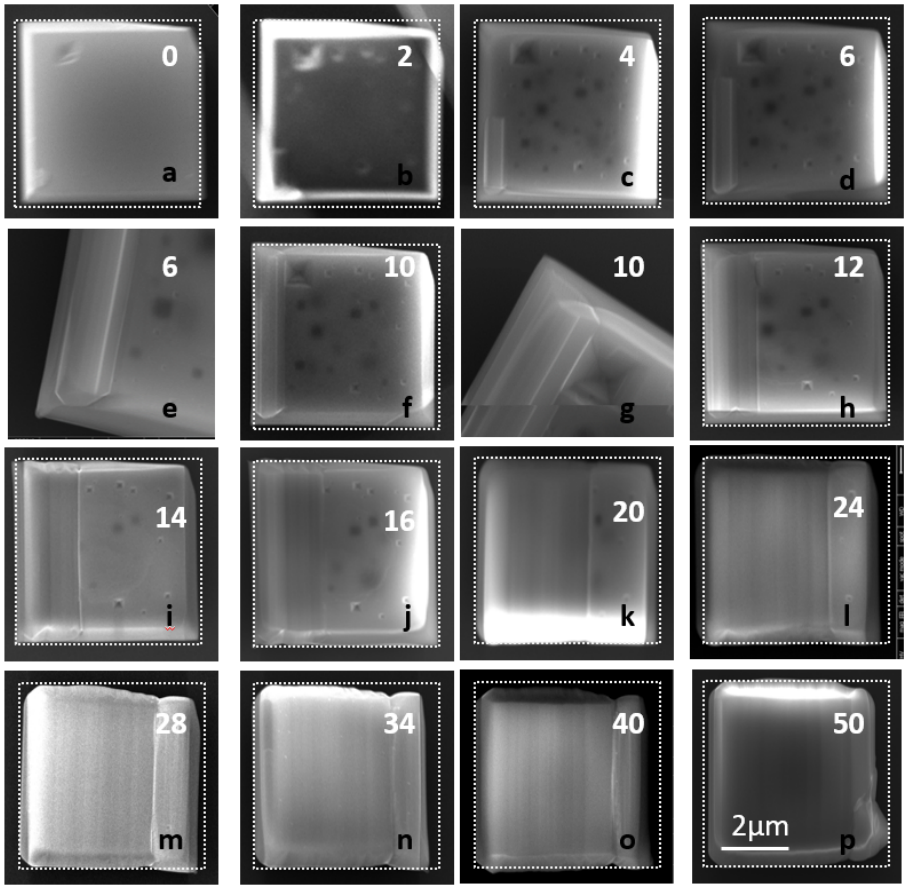

Figure S5. Sequential SEM images of Particle #5 at different annealing times. The numbers on the SEM images are the corresponding annealing time. The white dashed box represents the original size of the particle. Panels e and g are the zoom-in images of areas marked by the red dashed boxes in panels d and f.

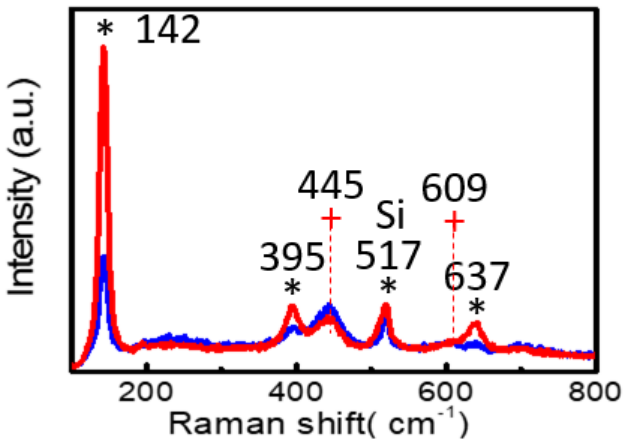

Figure S6. Full Raman spectra from 100 to 800 cm^{-1} of highlighted spots in Figure 3b for Particle #5 after annealing at 1050 ºC for 20 hours.

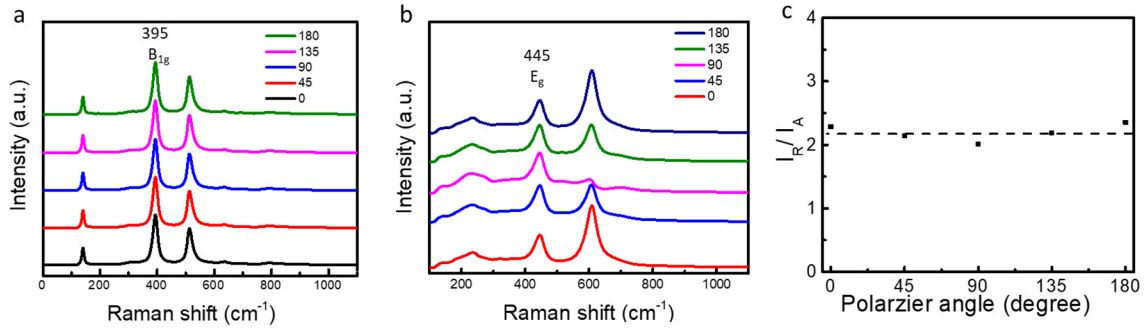

Figure S7. Raman spectra of commercial anatase (001) single crystal and rutile (110) single crystal with different polarizations. a: Anatase; b: Rutile; c: Area intensity ratio of anatase B_{1g} and rutile E_g (I_{B1g}/ I_{E1g}).

To quantitatively estimate the weight concentration of anatase/rutile phase of an unknown TiO_2 powder mixture by Raman spectroscopy, powders of pure anatase phase and pure rutile phase are generally mixed at different ratios to obtain a calibration curve because of the cross section differences in anatase and rutile phases.[3-6] In our approach, the intensity of anatase 395 cm^{-1} and rutile 445 cm^{-1} peak are adopted to estimate their weight percentages during ART. To calibrate, we measured the intensity of 395 cm^{-1} of a commercial pure anatase single crystal and that of 445 cm^{-1} of commercial pure rutile single crystal at different polarizations. The ratio (N) of I_{395}/I_{445} measured from commercial anatase and commercial rutile single crystal at the same laser power (Fig. S7) is 2.2.

The ART process starts with 100% anatase and is transformed to 100% rutile. TiO_2 microparticle will yield phase-depent signals proportional to their concentration under the same polarization during the ART process. Their signal intensities reflect their concentration ratio. The concentration of anatase can be estimated through this $C_a = {I_a}/{(I_{395} + N \times I_{445})}$, where C_a is anatase concentration, I_{395} is intensity of 395 cm^{-1} of anatase and I_{445} is the intensity of 445 cm^{1} of

rutile phase. The calculated concentration of anatase to rutile is 32% on the left (blue) and 63% on the right (red). The concentration analysis during the ART process in this paper is a semi-quantitative analysis because there are no calibration curves available for the two-phase spectra of known composition of single crystalline TiO_2 microparticles.

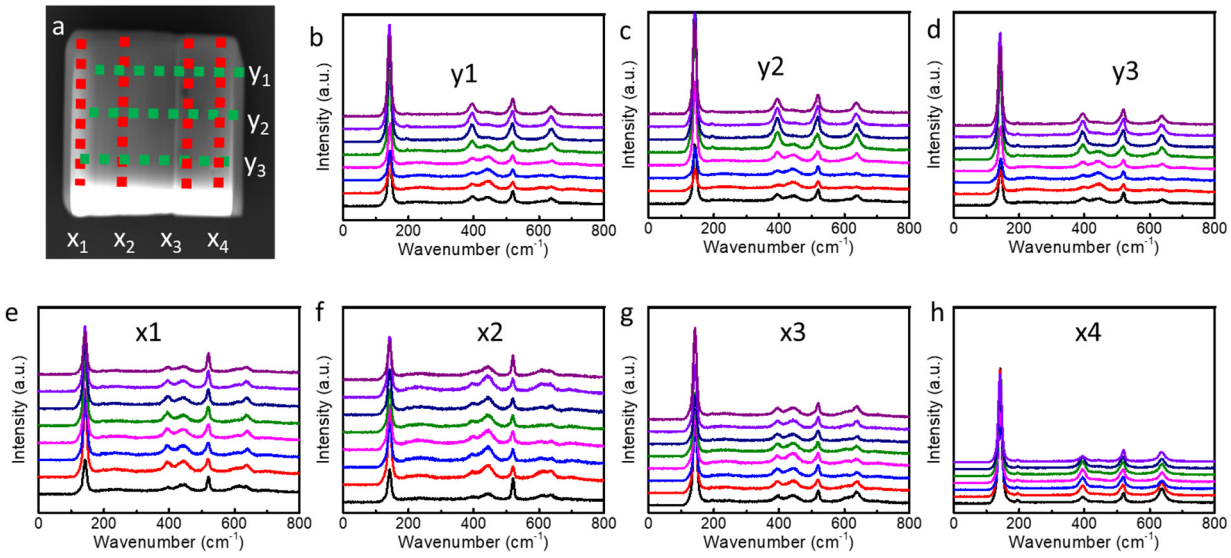

Figure S8. Spectra of Particle #5 at different positions. a: SEM and positions of the spectra; b: spectra from y1; c: from y2; d: from y3; e: from x1; f: from x2, g from x3; h: from x4.

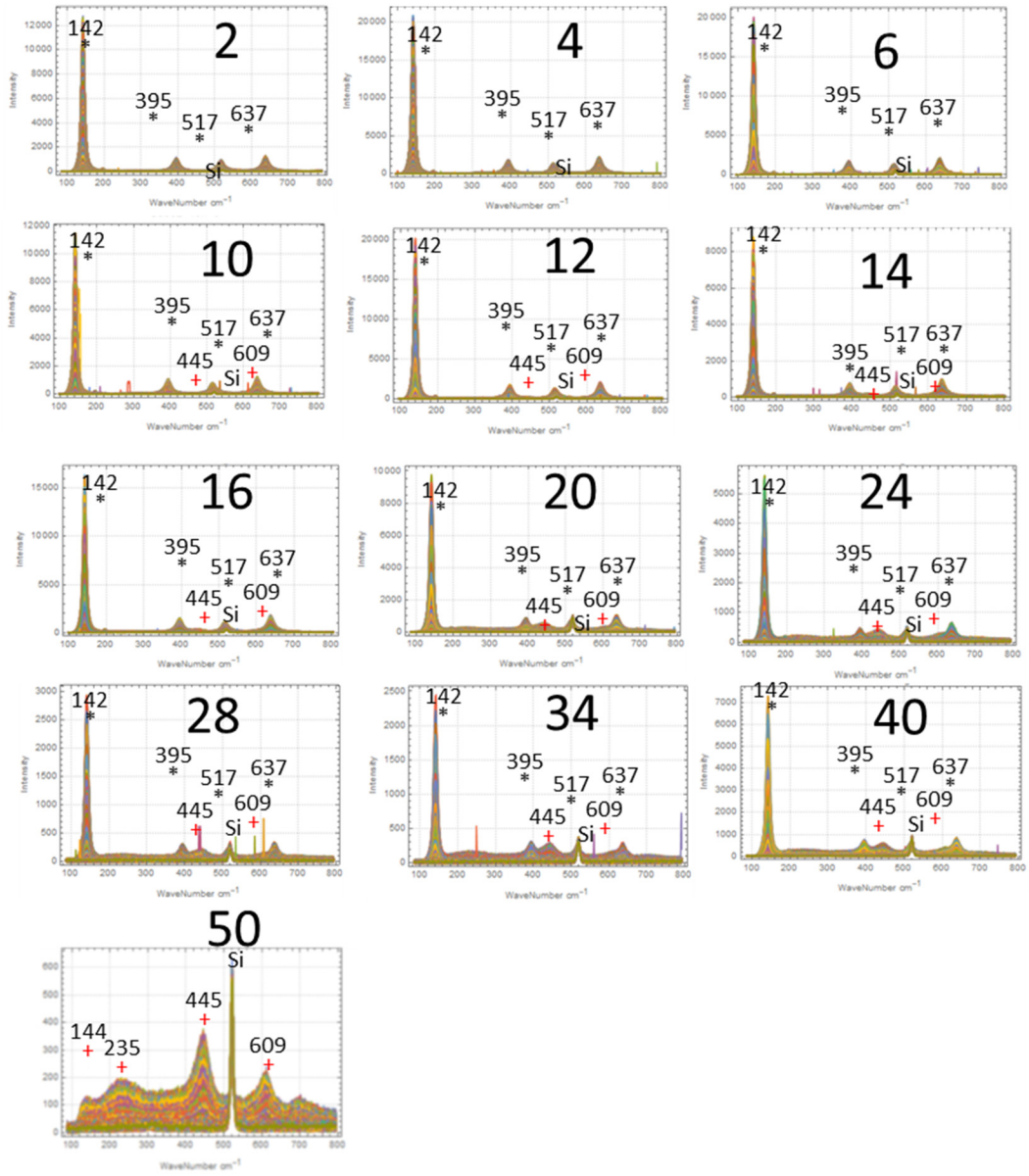

Figure S9. Complete Raman spectra of Particle #5 at different annealing times. The numbers on each picture are annealing hours.

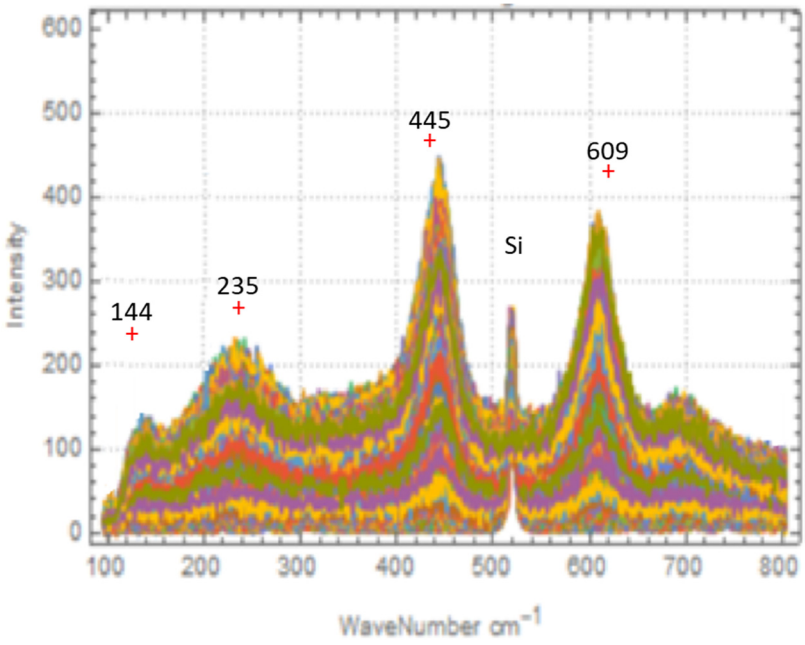

Figure S10. Raman Spectra of TiO_2 Particle #6 after 14 hours of annealing at 1050 ^{o}C.

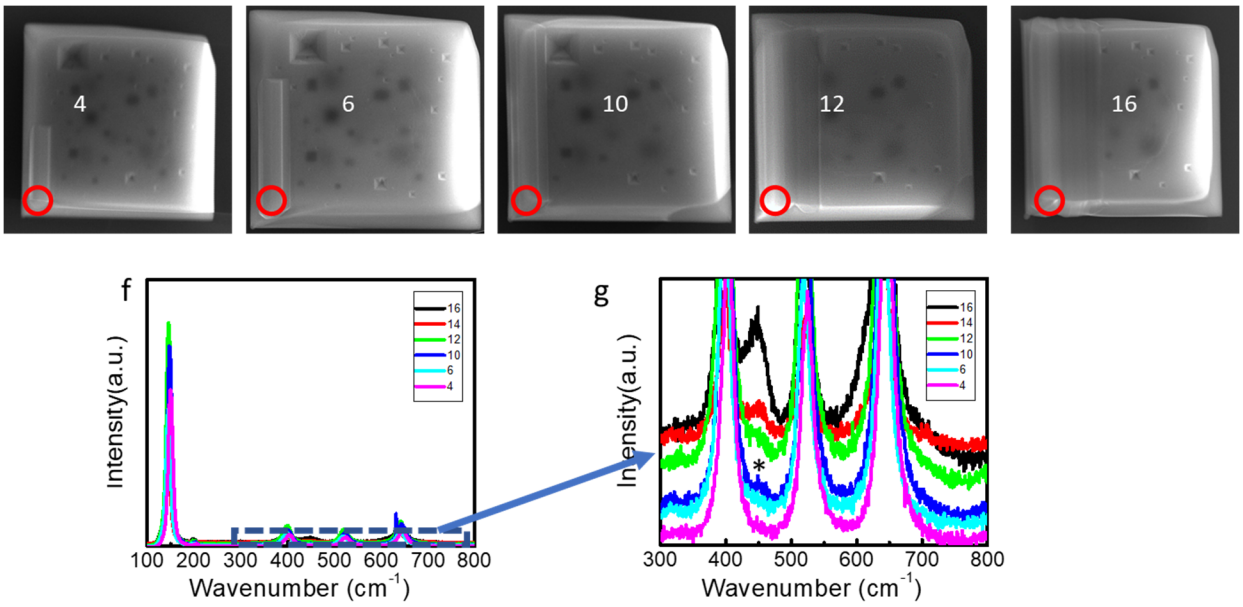

Figure S11. The temporal evolution of the nucleation site in Particle #5. a-e: SEM images of different annealing times. The number on each image is the annealing time. F: spectra of the nucleation site from 4 to 16 hours. g: magnified area from 300 cm^{-1} to 800 cm^{-1} in (g). (The peak of the rutile mode appeared at 10 hours, highlighted with *).

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