Supporting Materials:

Large Scale Synthesis of V-shaped Rutile Twinned Nanorods

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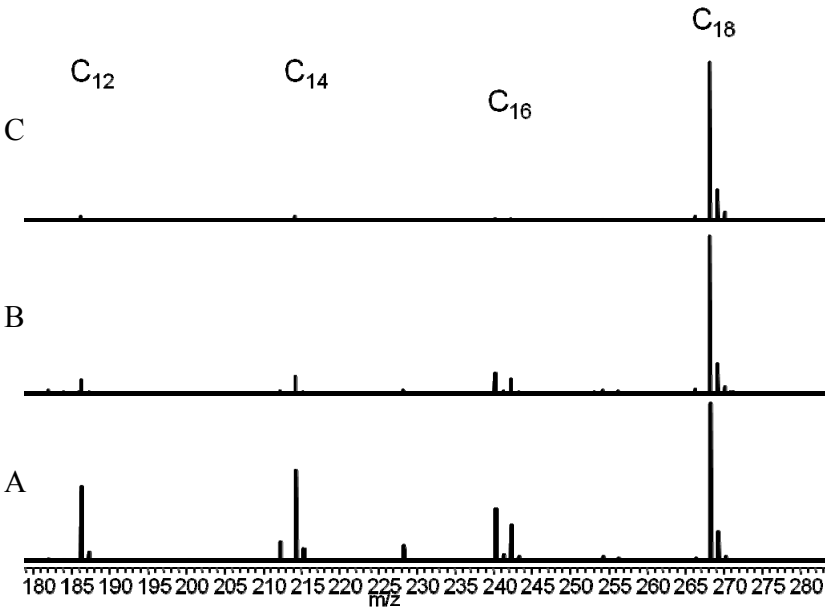
Supplemental S1 Mass spectra of oleylamine samples distilled at different time points.

Supplemental S2 XRD patterns from samples in Figure 3.

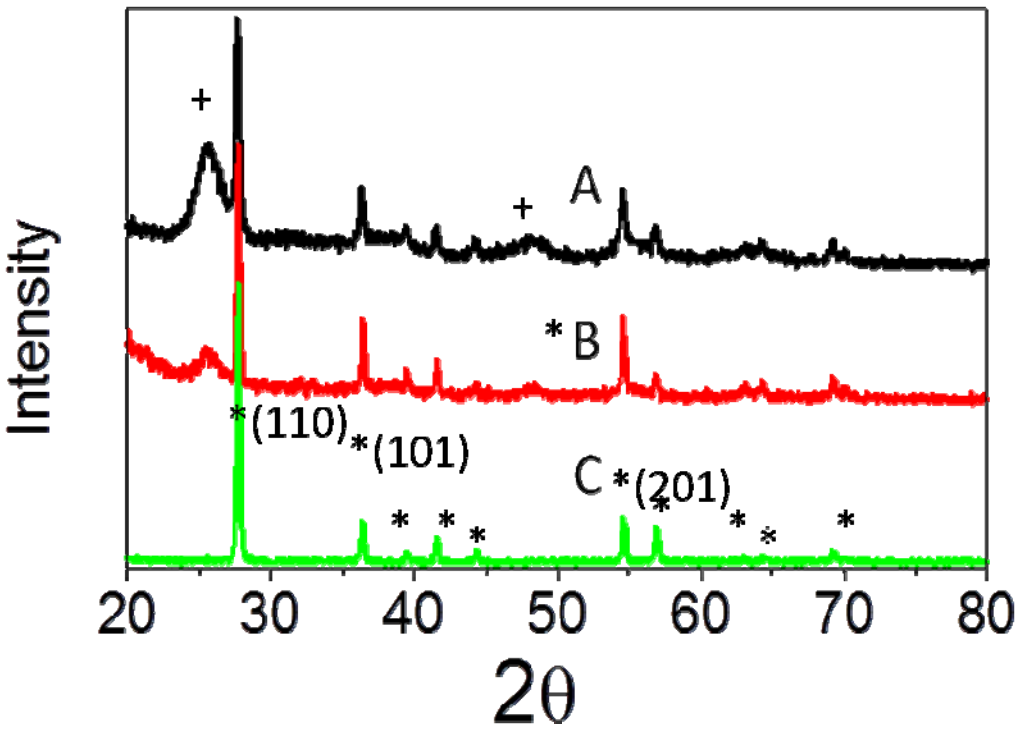
Supplemental S3 TEM of rutile nanotwins with broken brookite nanoparticles

Supplemental S4 Brookite nanorods with different aspect ratios synthesized at 290°C

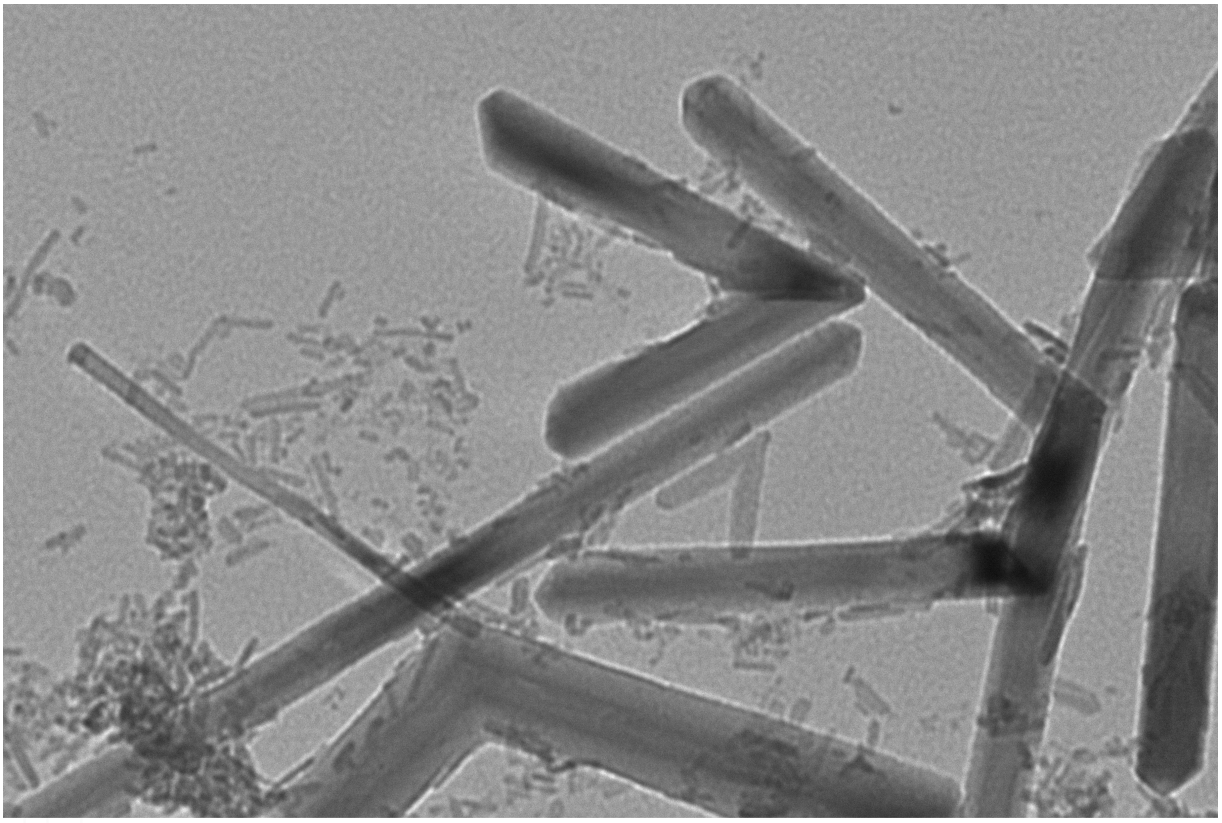
Supplemental S5 STEM images of brookite nanorods at different growth times at 290°C



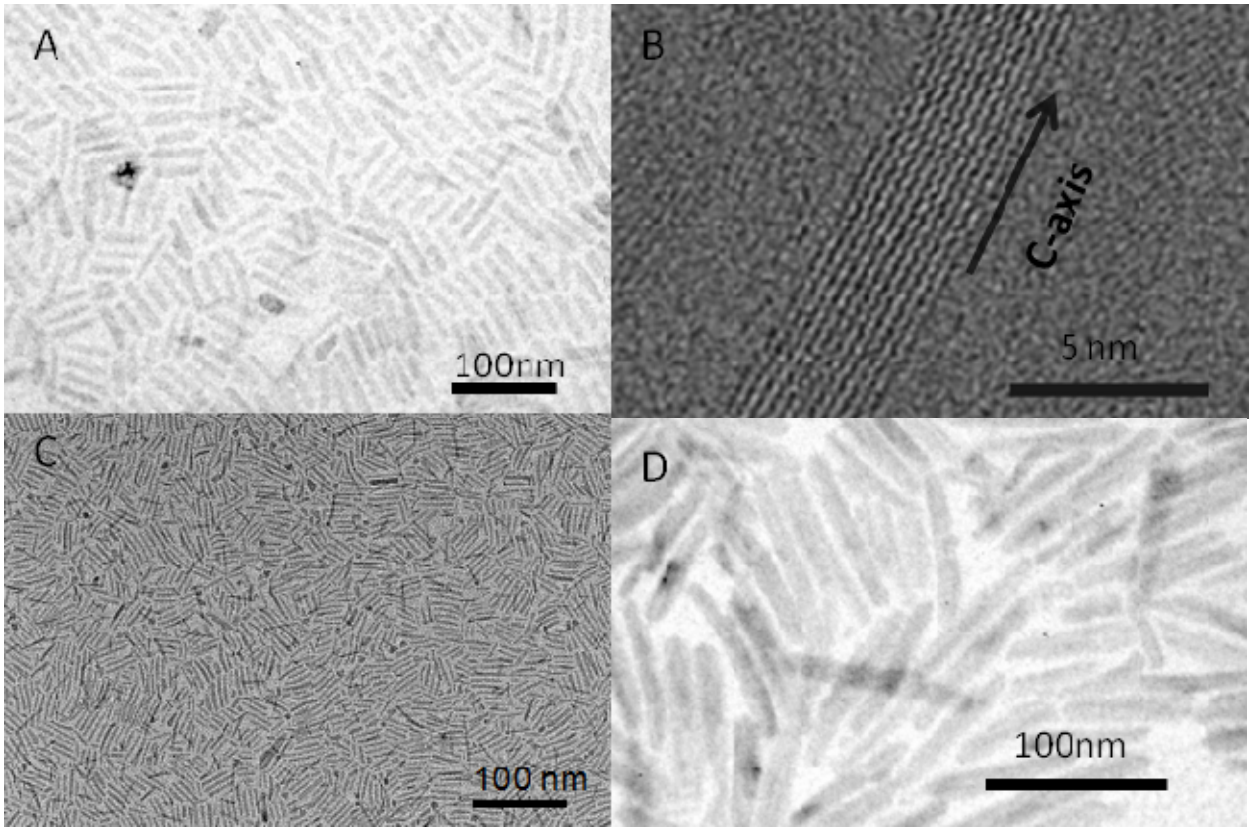
Supplemental S1. Mass spectra of distilled fractions of oleylamine. A) Oleylamine as received. B) After 10 min distillation. C) After 20 min distillation. As shown, most of low boiling point short chain amines were removed during distillation.



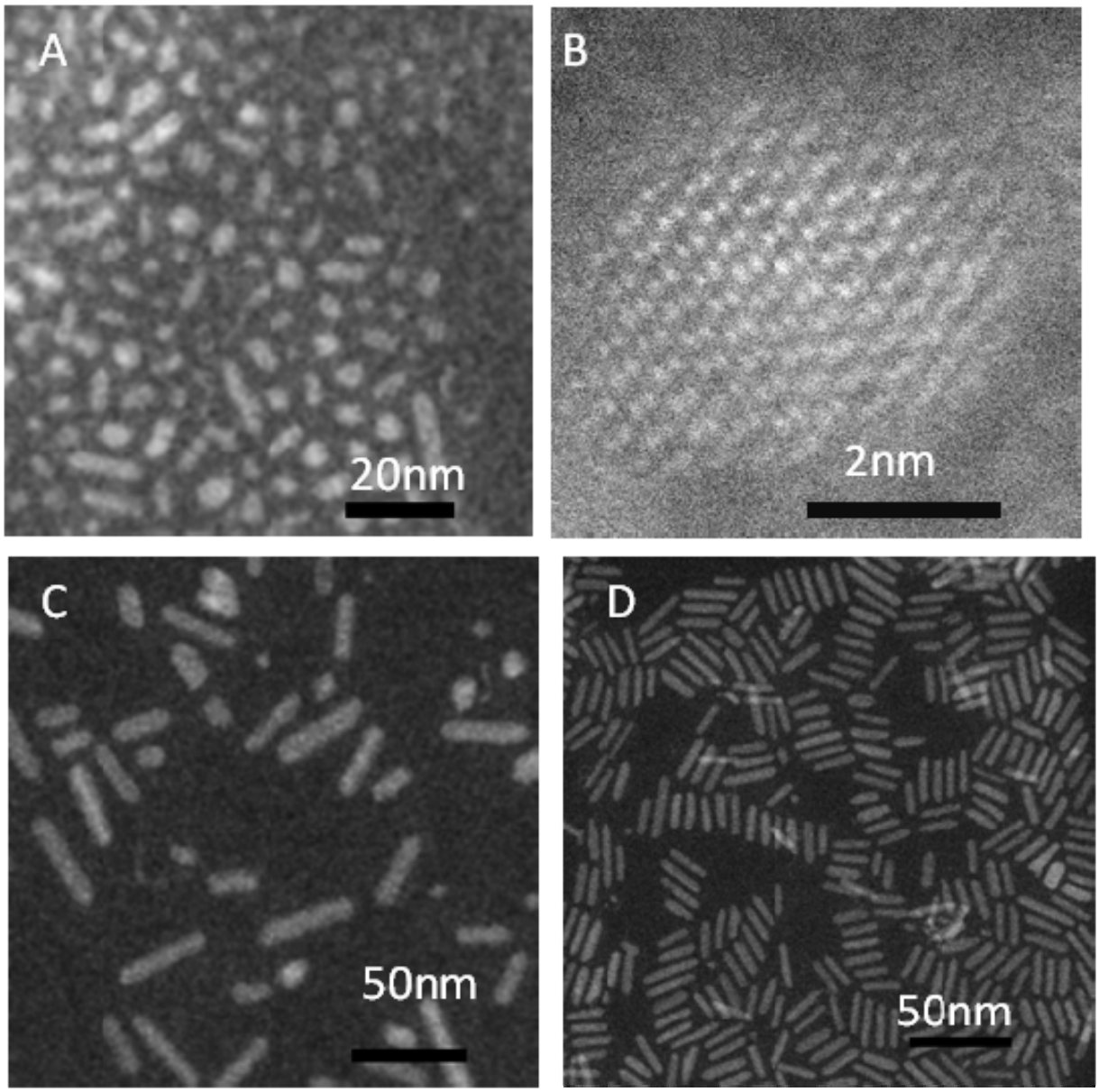
Supplemental S2. XRD patterns from samples in Figure 3. A) Same sample of Figure 3A. B) Same sample of Figure 3B. C) Same sample of Figure 3C. Peaks labeled with * were from rutile phase, the broad peaks labeled with + were from brookite phase.



Supplemental S3. TEM image of rutile nanotwins in presence of broken brookite nanoparticles, supporting the contention that brookite nanorod dissolution provides titania to support rutile nanotwins growth.



Supplemental S4. Brookite nanorods with different aspect ratios synthesized at 290°C. A) TEM image of brookite nanorods ~ 4 nm x 20 nm. B) A high resolution STEM image of a single brookite nanorod. C) A STEM image of brookite nanorods ~ 5 nm x 40 nm. D) A TEM image of nm brookite nanorods ~ 15 nm x 80 nm.



Supplemental S5. STEM images of brookite nanorods after different growth times at 290°C. A) after 1 min, appearance of nanorods with d ≤ 5 nm. B) An HAADF image of a particle after 1 min displays an anatase (100) surface; the bright features correspond to Ti rows. C) After 5 min, nanorods with d = ~ 5 nm. D) After 20 min, a more uniform population of nanorods with d = ~ 5 nm. The process is in consistent with the mechanism that anatase seeds catalyzed the anatase-to-brookite phase transition during brookite nanorods growth proposed by Buonsanti *et al* (R. Buonsanti, V. Grillo, E. Carlino, C. Giannini, T. Kipp, R. Cingolani, P. D. Cozzoli, **2008**, *J. Am. Chem. Soc., 130*, 11223.)