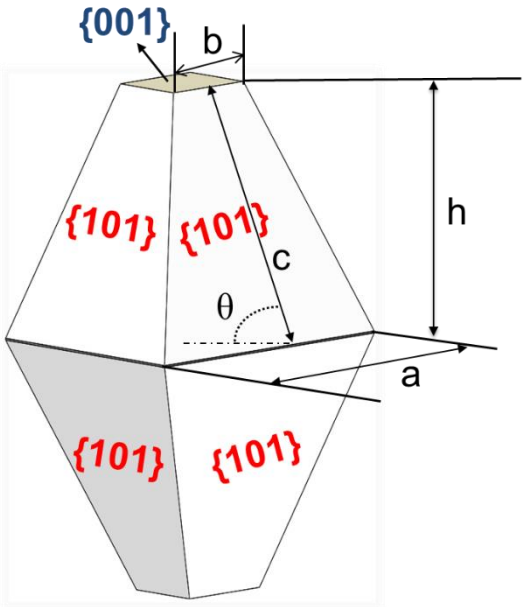
Supporting Information

Based on representative TEM and HRTEM images of as-synthesized anatase TiO_2 as shown in Figure 2 and assuming particle shapes expected from the Wulff shapes, we calculated the contributions from different facet orientations for the different types of TiO_2 nanocrystals through statistical analysis of TEM images. [1-3]

TiO_2-{101} nanocrystals



a=13.5nm

b=3.5nm

h=12.5nm

θ=68.3°

c=h/sinθ

There are two kinds of crystal planes exposed in TiO_2-{101} sample:{101} and {001}. We can figure out the percentages of {101} and {100} in TiO_2-{101} nanocrystals as follows:

$$S_{001}=2\times b^2$$

$$S_{101}= 8\times 1/2(a+b) \times c$$

$$P_{001}= S_{001}/ (S_{001+} S_{101}) =2\%$$

$$P_{101}= S_{101}/ (S_{001+} S_{101}) =98\%$$

We can figure out the percentages of {101} and {001} in TiO_2-{001} sample as follows:

$$S_{101}= 8\times 1/2(a+b) \times c$$

$$S_{001}=2\times b^2$$

$$P_{101}= S_{101}/ (S_{001+} S_{101}) =20\%$$

$$P_{001}= S_{001}/ (S_{001+} S_{101}) =80\%$$

References about the Wullf construction and related calculations:

(1) M. M. Maitani, K. Tanaka, D. Mochizuki, Y. Wada, *J. Phys. Chem. Lett.* **2011**, 2, 2655-2659.

(2) A. S. Barnard, L. A. Curtiss, *Nano Lett.* **2005**, 5, 1261-1266.

(3) S. Chen, A. M. Abdel-Mageed, L. Dan, J. Bansmann, S. Cisneros, J. Biskupek, W. Huang, R. J. Behm, *Angew. Chem. Int. Ed.* **2019**, 58, 10732-10736.

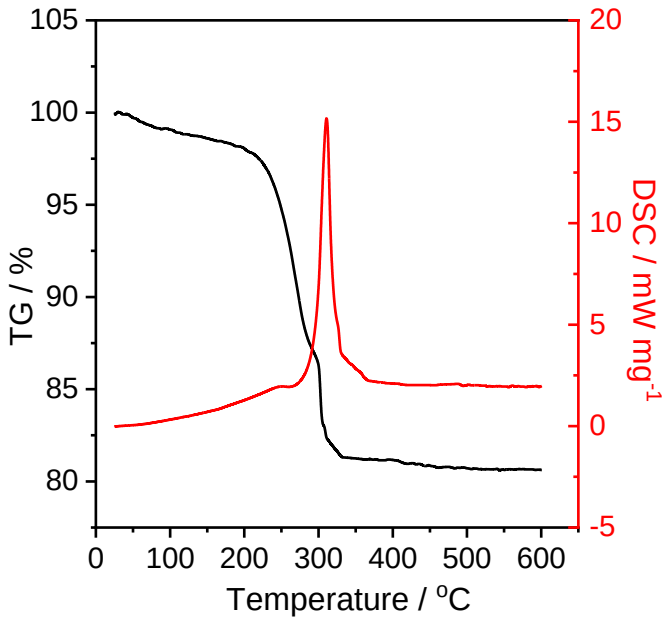


Figure S1. TG/DSC profiles for $Ir(acac)_3$.