Electronic supplementary information for

Mesocrystal precursor transformation strategy synthesizing ordered hierarchical hollow TiO_2 nanobricks with enhanced photocatalytic property

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1. Experimental results

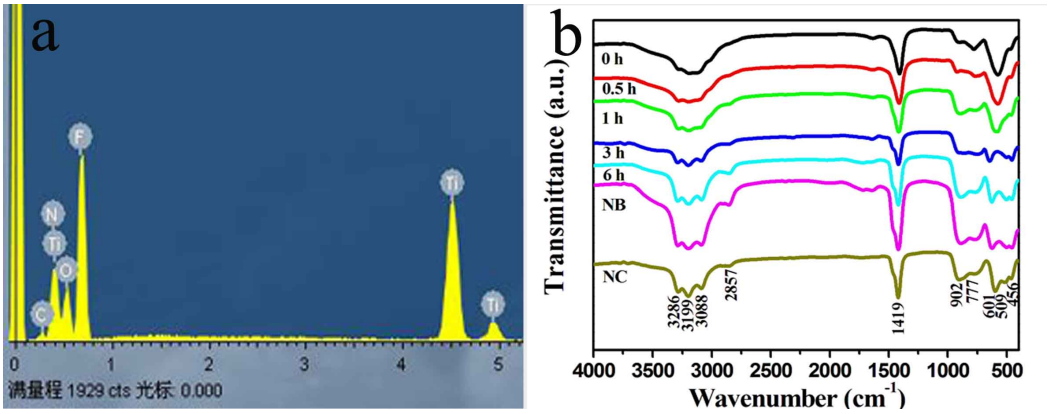

Fig. S1 (a) EDS spectrum of NB (b) FTIR spectra of NB as well as the precipitate obtained at different time in synthesizing NB.

FT-IR absorption bands at wavenumbers of 3286, 3199, and 3088 cm^{-1} for the samples are ascribed to the stretching modes of NH_4^+. The signals at 1419 and 2857 cm^{-1} are ascribed to the bending mode of NH_4^+ and its overtone band. The signal at 902 cm^{-1} is indicative stretching mode of

Ti=O (terminal oxygen). The signal at 601 cm^{-1} is ascribed to the stretching modes of Ti−F, and signals at 509 cm^{-1} and 456 cm^{-1} are ascribed to Ti−O. The signal of 777 cm^{-1} is due to a combination of lattice modes of Ti−O and Ti−F.[1-3]

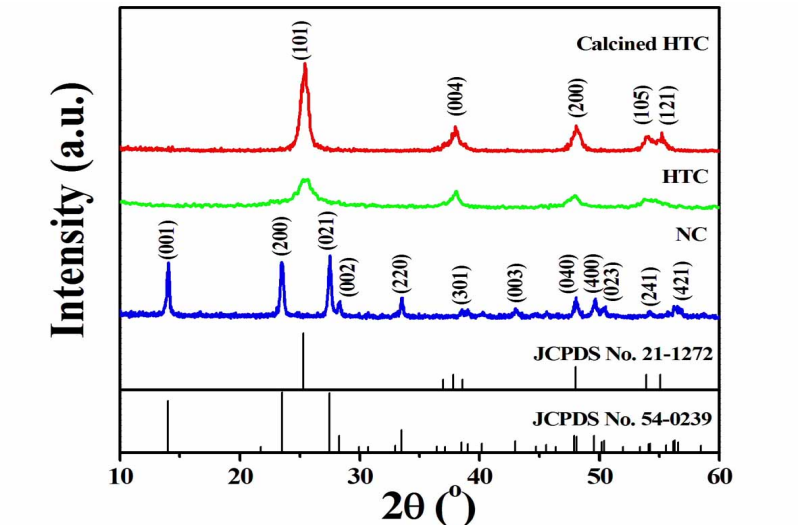

Fig. S2 XRD patterns of NC, HTC and calcined HTC.

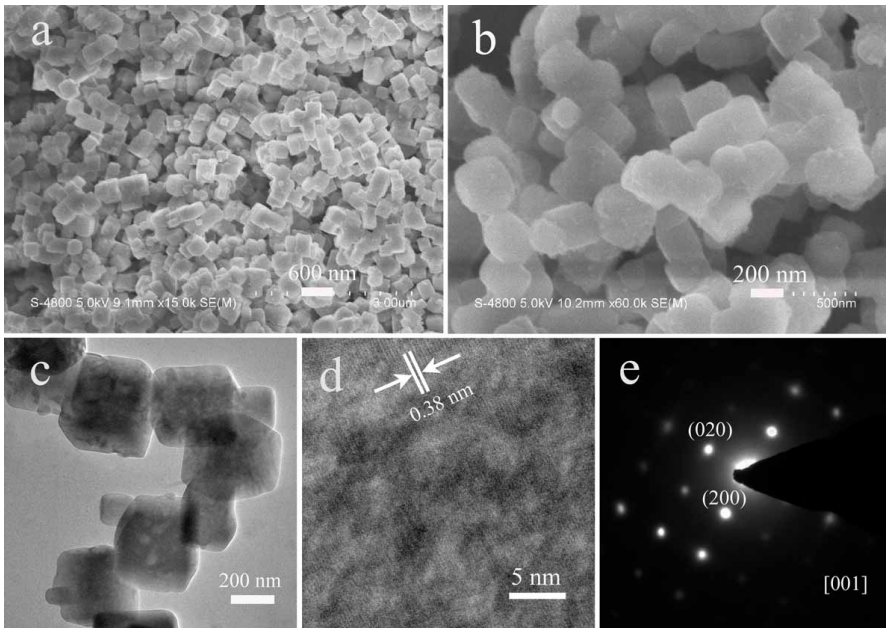

Fig. S3 (a) SEM and (b) high magnification SEM images of mesocrystal NH_4TiOF_3 NC, (c) TEM image, (d) HRTEM image and (e) SAED pattern of the mesocrystal NH_4TiOF_3 nanocubes.

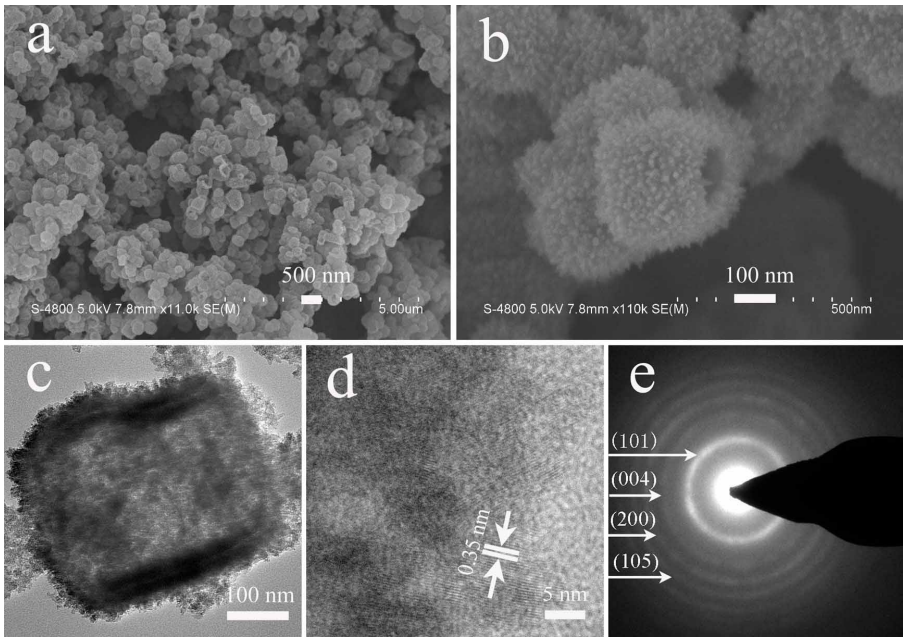

Fig. S4 (a) SEM, (b) high magnification SEM images and (c) TEM image of HTC, (d) HRTEM image of the nanothorns of HTC. (e) SAED pattern of the hollow TiO_2 nanocubes (HTC).

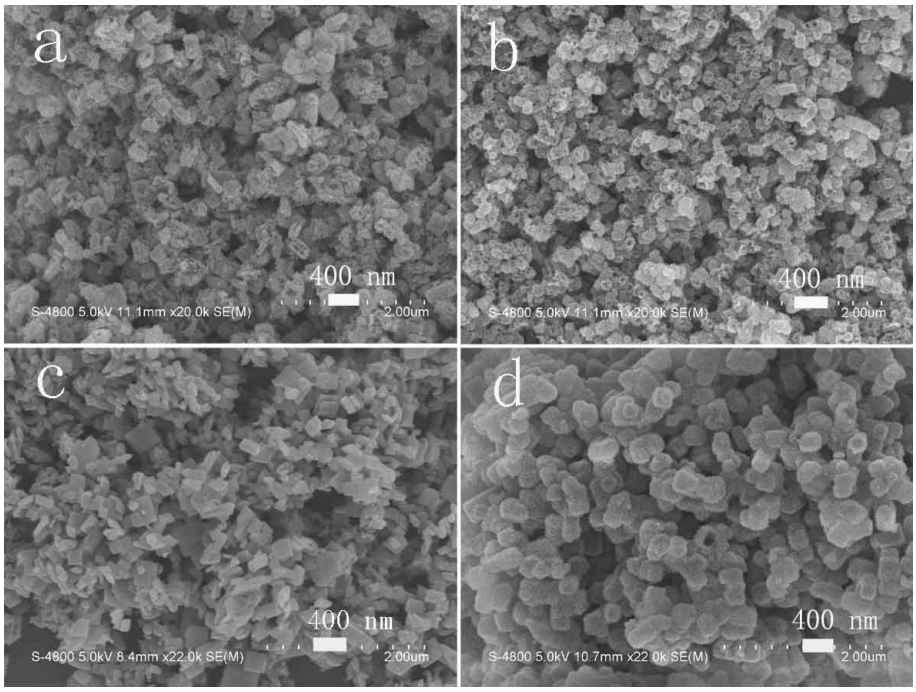

Fig. S5 SEM images of different anatase TiO_2 samples (a) the calcined HTB (b) the calcined HTC (c) STB (d) HTC.

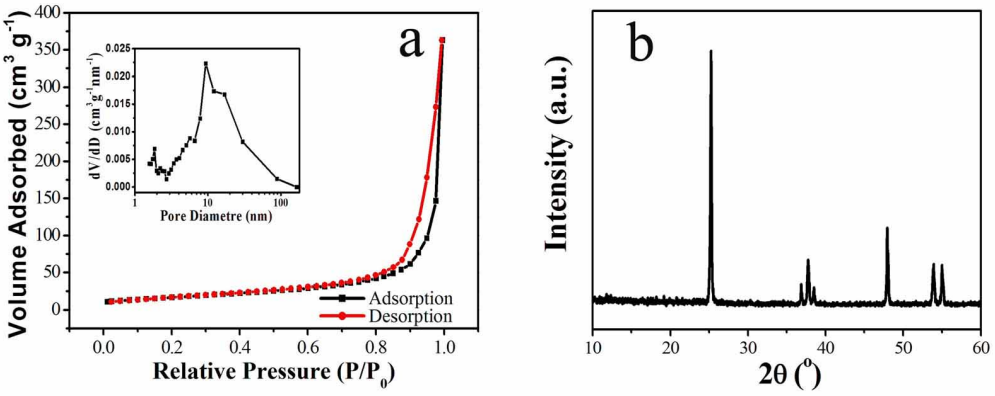

Fig. S6 (a) N_2 sorption isotherm and the corresponding pore size distribution (inset) of the calcined HTC. (b) XRD pattern of solid TiO_2 nanobrick (STB). (JCPDS No. 21-1272)

Table S1 BET results of the different synthesized samples.

Sample	Pore diameter (nm)	Pore volume ($cm^3 g^{-1}$)	Specific surface area ($m^2 g^{-1}$)
NC	1-3	0.043	5.56
NB	1-3	0.056	8.75
STB	1-4	0.108	22.74
HTC	7.0	0.422	54.75
HTB	16.4	0.466	67.42
Calcined HTC	10.2	0.562	60.37
Calcined HTB	17.8	1.640	68.20

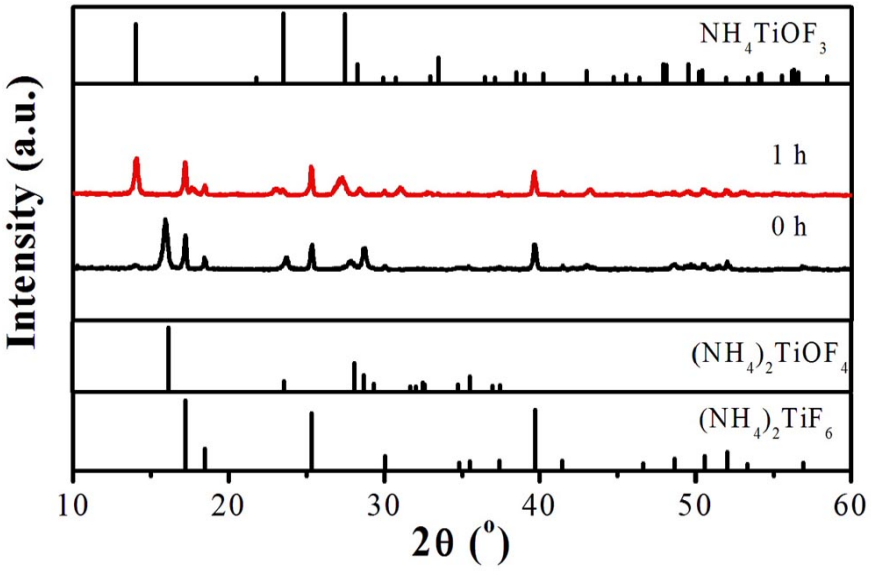

Fig. S7 XRD patterns of samples collected at different time in synthesizing mesocrystal NH_4TiOF_3 nanocube (0 h and 1 h)

At 0 h, the main phase of product is $(NH_4)_2TiOF_4$, accompanied with some amounts of $(NH_4)_2TiF_6$, and the least NH_4TiOF_3. When time increased to 1 h, only two phases existed containing $(NH_4)_2TiF_6$ and NH_4TiOF_3, and the NH_4TiOF_3 became the main phase. While at 0 h and 1 h in synthesizing NH_4TiOF_3 nanobrick, the main phase is both $(NH_4)_2TiF_6$.

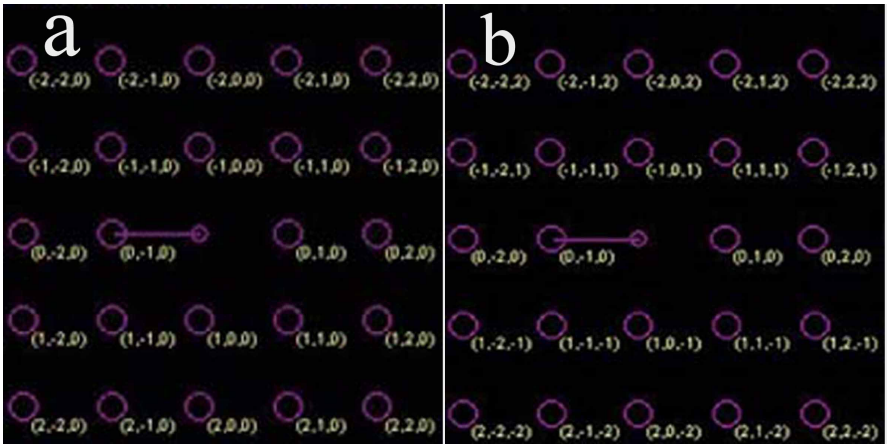

Fig. S8 Simulated electronic diffraction pattern of (a) NH_4TiOF_3 [001] direction (Orthorhombic, cell parameters: a = 7.5521, b = 7.5845, c = 6.3038 <90.0 x 90.0 x 90.0>) and (b) TiO_2 [010] direction (Tetragonal, cell parameters: a = 3.7852, b = 3.7852, c = 9.5139 <90.0 x 90.0 x 90.0>)

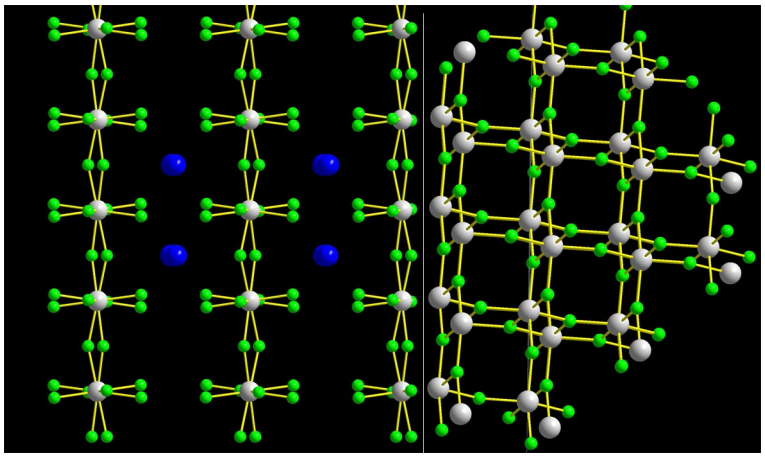

Fig. S9 Simulated crystal structure of the growth interface.(white spheres: Ti, green spheres: O/F, blue spheres: N)

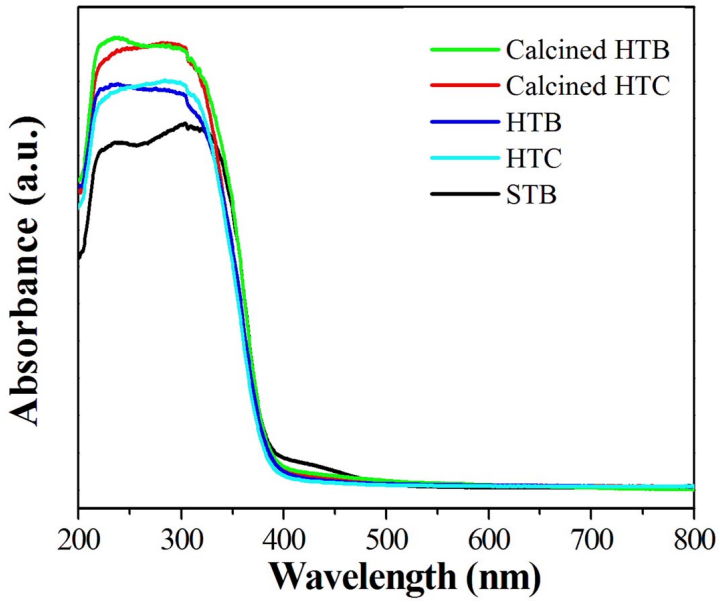

Fig. S10 UV-vis diffuse reflectance spectra of different prepared samples of TiO_2

References

1. L. Zhou, D. S. Boyle, P. O'Brien, *Chem. Commun.*, 2007, 144-146.

2. G. S. Shao, X. J. Zhang, Z. Y. Yuan, *Appl. Catal. B*, 2008, **82**, 208-218.

3. Y. Q. Liu, Y. Zhang, H. Li, and J. Wang, *Cryst. Growth Des.*, 2012, **12**, 2625-2633.