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Tailoring the nanoscale boundary cavities in rutile TiO_2 hierarchical microspheres for giant dielectric performance

Wanbiao Hu,[a] Liping Li,[b] Wenming Tong,[a] Guangshe Li[a]*, Tingjiang Yan[a]

[a]State Key Laboratory of Structural Chemistry and [b] Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter and Graduate School of Chinese Academy of Sciences, Fuzhou 350002 (P. R. China),

Fax: (+) 86-591-83714946;

E-mail: guangshe@fjirsm.ac.cn.

Supporting Online Materials

S1. XRD pattern of rutile TiO_2 prepared under hydrothermal conditions: 2.3 M, 160 ^oC, 2h.

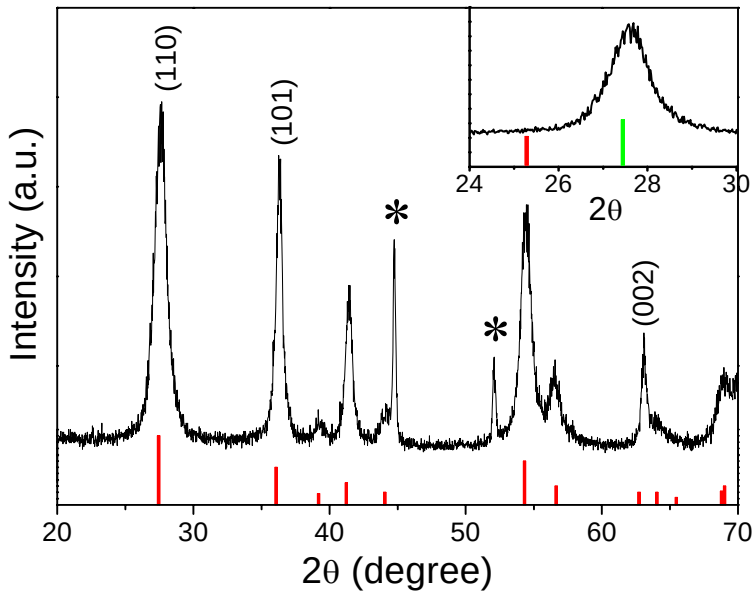
S2. XPS spectra of the as-prepared rutile TiO_2 microspheres.

S3. TG analysis of as-prepared TiO_2 microspheres.

S4. TEM images of as-prepared TiO_2 microspheres.

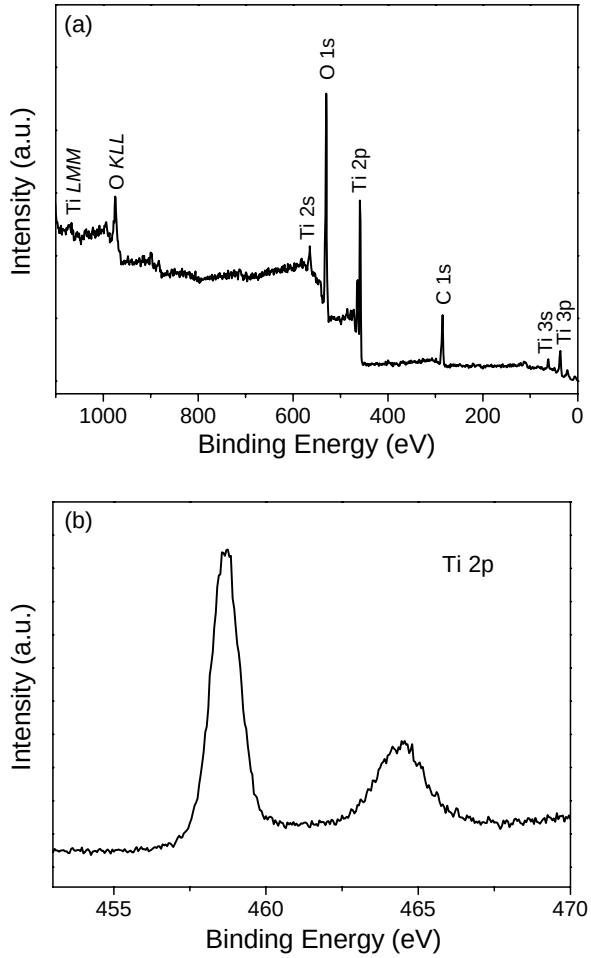
S5. TEM image and SAED pattern of the microspheres after annealing at 900 ^oC for 2 h.

(1) XRD



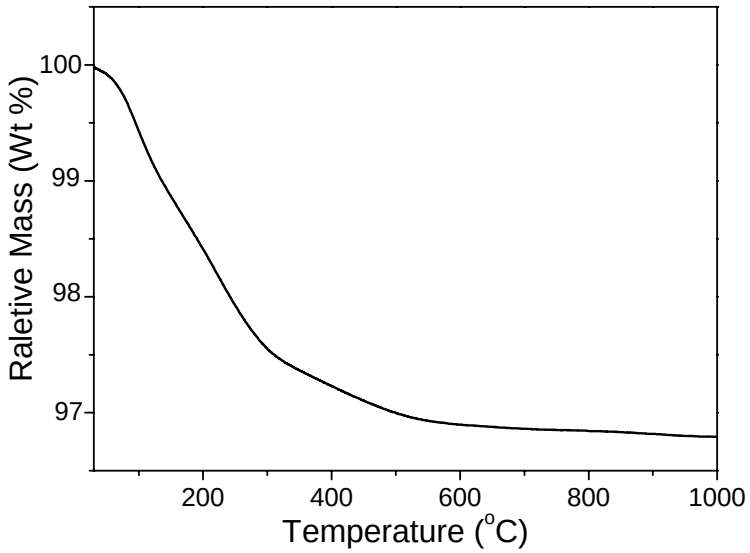
S1. XRD pattern of the sample prepared under an optimum condition of 2.3 M [$TiCl_4$] at 160 ^oC for 2h. Vertical bars denote the standard diffraction data of rutile TiO_2 (JCPDS, No. 76-1940). Inset is the enlarged pattern in a narrow 2θ range. Vertical bars denote the standard diffraction data of anatase (left) and rutile (right) TiO_2, respectively. All diffraction data matched well the vertical bars below the pattern, the standard data for rutile TiO_2, confirming the formation of single phase. The intense diffraction lines like (110) and (101) indicate the high crystallinity. It is also noted that both lines (101) and (002) were significantly narrowed, relative to the line (110), which indicate a preferential orientation of the primary particles.

(2) XPS



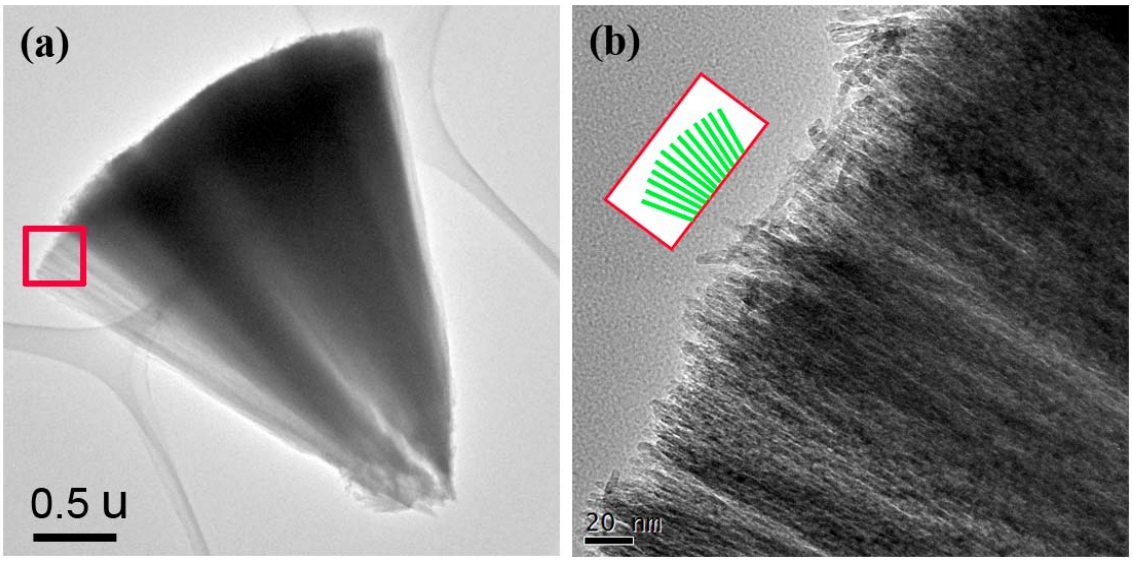
S2. XPS survey (a) and high-resolution (b) spectra of the as-prepared rutile TiO2 microspheres. The XPS survey spectrum reveals that the peak contains only Ti, O, and C atoms. The carbon peak is attributed to the residual carbon from XPS instrument itself. No peak of Cl signal from reagent was detected. Ti 2p spectrum consists of the distinct Ti $2p_{1/2}$ and Ti $2p_{3/2}$ photoelectron signals that are located at 464.4 and 458.6 eV, respectively. The spin-orbital splitting between these peaks is 5.8 eV, which is comparable with that of 5.74 eV reported previously. Both Ti 2p signals are highly symmetric, and no shoulders were observed on the lower energy sides of Ti $2p_{3/2}$ signal, which indicate that the rutile TiO_2 nanocrystals are stoichiometric and the concentration of lattice defects is extremely low.

(3) TG



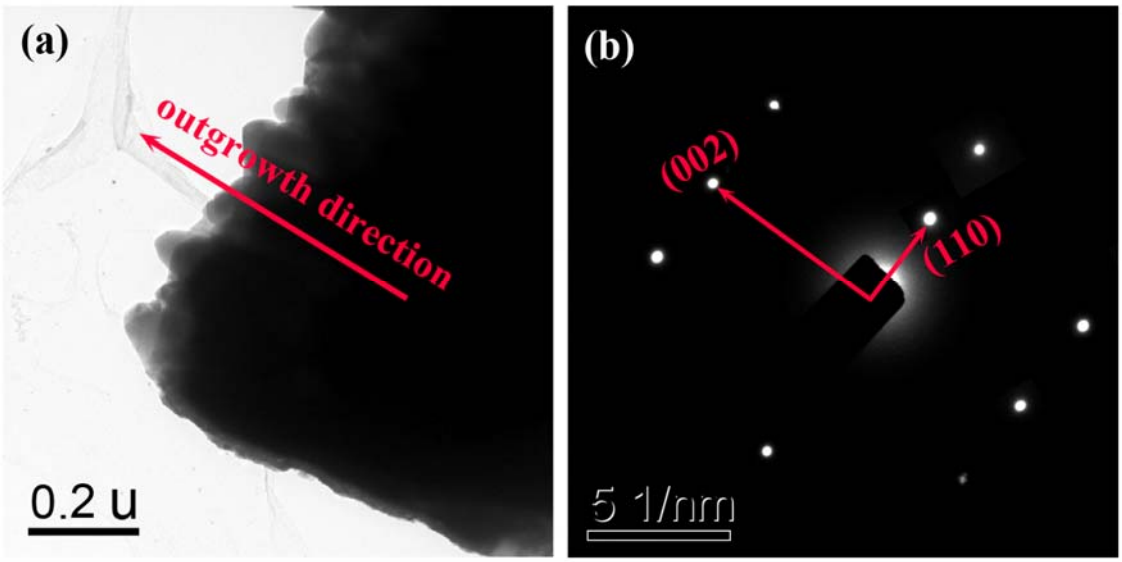
S3. TG analysis of as-prepared TiO_2 microspheres. It is indicated that water molecules adsorbed on the surfaces of the microspheres. The amount is estimated to be about 3.2 wt%, which would make a few contributions to the proton conductivity.

(4) TEM



S4. TEM images of as-prepared TiO_2 microspheres: (a) overall morphology, and (b) a selected portion highlighted in (a). From images, it is observed that boundary cavities exist in between the nanowires, as distinctly described in inset of (b).

(5) TEM and SAED



S5. (a) TEM image and (b) SAED pattern of the microspheres after annealing at 900 ^{o}C for 2 h. It can be seen that the nanowires have grown into nanorods. Meanwhile, the electron diffraction pattern consists of 2-dimension array dots of regularly round shape. These observations indicate that the nanoscale boundary cavites disappeared after annealing.