

The In-situ Observation and Investigation on the Formation Mechanism of Nanocavities in TiO₂ Nanofibers

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Supplementary: The TEM investigation on the initial stage of the phase transformation from TB to TA

We selected one nanofiber which calcinated at 500 °C for 1 hour to investigate the initial stage of the phase transition from TB to TA, as shown in Fig. S1 (a). The selected area electron diffraction pattern in Fig. S1(b) indicates that a small amount of anatase have formed at the surface of TB nanofiber which can be confirmed from the obvious $\{011\}_{TA}$ diffraction spots marked with yellow circles. The diffraction spots from TB and TA were both selected to obtain the dark-field images which are shown in Fig. S1(c) and 1(d). The results reveal that the newly-formed TA phase was distributed on the edge surface of the TB nanofiber. The high-resolution TEM image in Fig. S1(e) further proves the fact. Therefore, one conclusion can be drawn that the nanocavities preferentially formed on the edge surface of TB nanofiber. Because the TB to TA phase transformation is diffusion-type phase transformation, the nanocavities would spread from the edge to center at the surface of nanofiber during the process of the phase transformation.

In addition, our previous work confirms that the morphology of TB nanofiber grown by hydrothermal reaction is thin lath-shaped, as shown in Fig. S2(g) and 2(h). Fig. S2(e) and 2(f) also indicate that the mean thicknesses of the TB nanofibers is around 35-40 nm.¹ The depth of the nanocavities reported in this paper is around 20 nm according to the yellow thickness curve shown in Fig. 3(d). As it is speculated that both surface of the nanofibers contain the nanocavities after the phase transformation. The region inside the fiber do not have enough space to accommodate additional nanocavities. In this case, it can be concluded that the generation of nanocavities only happened at the surface of the fiber.

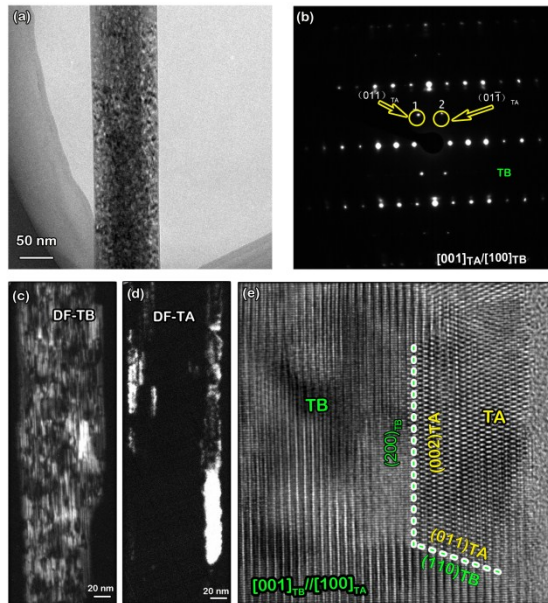


Fig. S1 The TEM investigation on the initial stage of the phase transformation from TB to TA. (a) the TEM BF image; (b) the SAED pattern; (c) the dark-field image from TB diffraction spot; (d) the dark-field image from TA diffraction spot; (e) the HRTEM image of the mixed-phase TB/TA nanofiber.

1. Jie Sun, Yimin Lei, Hongwei Liu, S. P. Ringer and Zongwen Liu. Single crystal forms induced diverse interface structures in TiO_2 (B)/anatase dual-phase nanocomposites. *Crystengcomm* 2016, **18**: 2089-2097.