†Electronic supplementary information (ESI)

for

Topochemical Conversion of Protonated Titanate Single Crystal into Platelike $Ba_{0.5}Sr_{0.5}TiO_3$ Mesocrystals with Controllable Microstructures†

Dengwei Hu,[†,‡] Xin Luo,[‡] Xingang Kong,[§] Yan Wang,[†] Yasuhiro Tanaka,[‡] and Qi Feng*[,‡]

[†] *Department of Chemistry and Chemical Engineering, Baoji University of Arts and Science, 1 Gaoxin Road, Baoji, Shaanxi, 721013 PR China*

[‡] *Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20 Hayashi-cho, Takamatsu-shi, 761-0396 Japan*

[§] *School of Materials Science and Engineering, Shaanxi University of Science and Technology, Weiyang, Xi'an, Shaanxi, 710021 PR China*

† Electronic supplementary information (ESI) available.

* Corresponding author. E-mail: feng@eng.kagawa-u.ac.jp; Fax: +81 (0)87-864-2402; Tel: +81 (0)87-864-2402

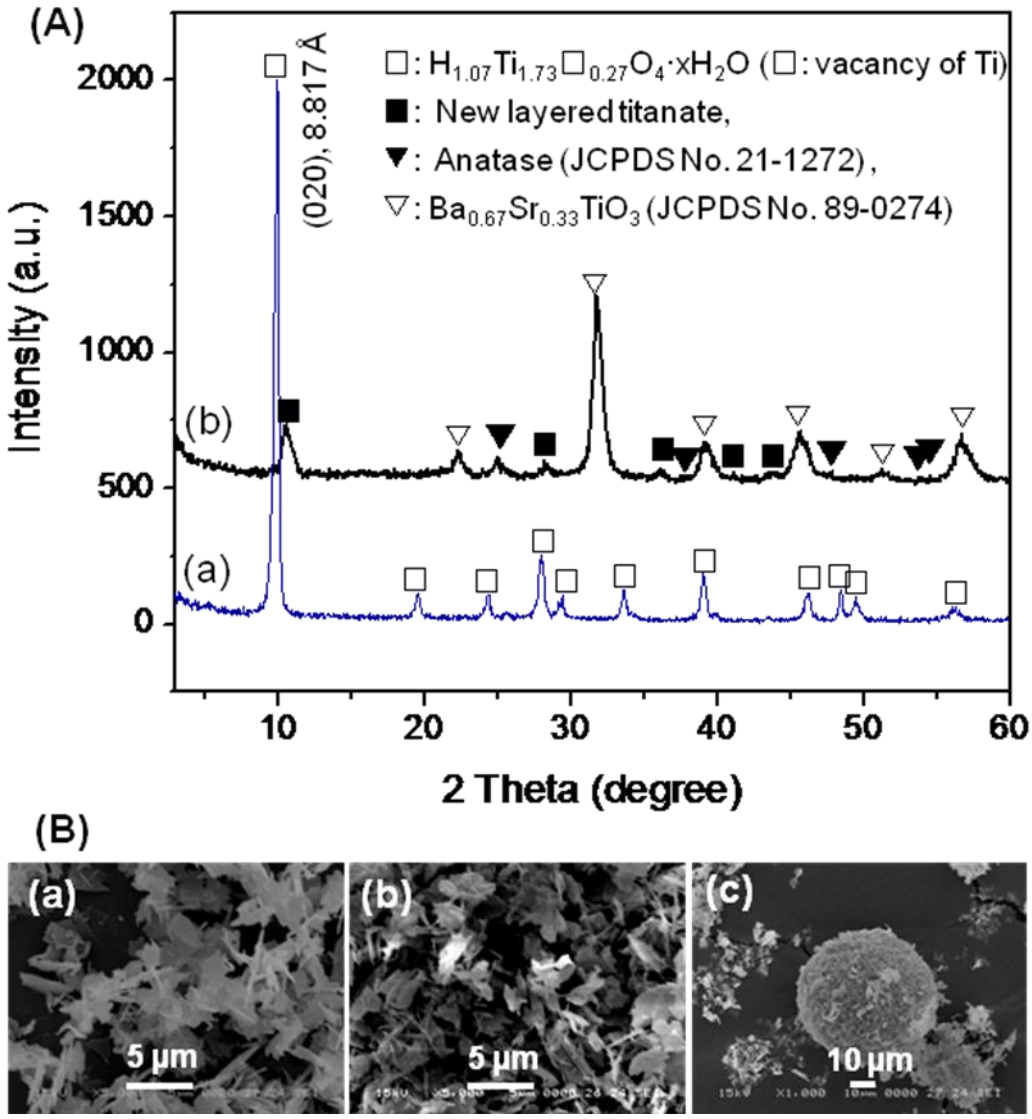

Fig. S1†. (A) XRD patterns and (B) SEM images of (a) $H_{1.07}Ti_{1.73}□_{0.27}O_4 \cdot xH_2O$ (□: vacancy of Ti) (HTO) crystals and (b, c) samples obtained by solvothermal treatments of HTO-$Ba(OH)_2$-$Sr(OH)_2$ (molar ratio of Ti/Ba/Sr = 1:0.5:0.75) mixture in water-ethanol mixed solvent (volume ratio = 5:25) at 200 °C for 12 h.

Platelike $H_{1.07}Ti_{1.73}□_{0.27}O_4 \cdot xH_2O$ (□: vacancy of Ti) (HTO) crystals can be prepared as reported by us previously.[1] 6.9 g of anatase TiO_2 nanoparticles, 5.1 g of KOH, 0.6

[S1] Wen, P. H.; Itoh, H.; Tang W. P.; Feng, Q. *Langmuir* **2007**, 23, 11782–11790.

g of $LiOH \cdot H_2O$, and 25 mL of distilled water were sealed into a Hastelloy-C-lined vessel with internal volume of 45 mL, and then heated at 250 °C for 24 h under stirring conditions. After the solvothermal treatment, the obtained sample was washed with distilled water and dried at room temperature to obtain $K_{0.80}Ti_{1.73}Li_{0.27}O_4$ (KTLO) crystals. The KTLO crystals (4.0 g) was treated with a 0.2 $mol \cdot L^{-1}$ HNO_3 solution (500 mL) for 24 h under stirring conditions to exchange K^+ and Li^+ in the layered structure with H^+, and then the sample was washed with distilled water. After the acid treatments were done twice, the layered protonated titanate HTO single crystals were obtained. The as-obtained crystals were collected and washed with distilled water and ethanol, before air-drying at 60 °C for 12 h, and then the HTO (3.2 g) single crystals were obtained.

For the synthesis of the platelike BST mesocrystal, one-step solvothermal process was firstly attempted. HTO (0.096g), $Ba(OH)_2 \cdot 8H_2O$, and $Sr(OH)_2 \cdot 8H_2O$ in a molar ratio of Ti/Ba/Sr＝1:0.5:0.75, and 30 ml of water-ethanol mixed solvent (volume ratio=5:25) were placed in a Teflon-lined, and then solvothermally treated at 200 °C for 12 h under stirring conditions. After the solvothermal-treatment, the product was filtered firstly, and then washed by 0.1 $mol \cdot L^{-1}$ acetic acid and distilled water in sequence, finally dried at room temperature. **Fig. S1†** shows the XRD patterns and SEM images of HTO single crystal before and after solvothermal treatment in alkali earth metal hydroxides mixed solution. After solvothermal treatment, a simple $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) cannot obtain but a mixture phase of new layered titanate, $Ba_{0.67}Sr_{0.33}TiO_3$, and anatase, suggesting that the composition of BST cannot control easily. In addition, sphere granular aggregate can be generated easily because of high concentration of alkali earth metal hydroxides (Fig. S1B-c). This result suggests that the platelike BST particles are difficult to be prepared using the on-step solvothermal process.

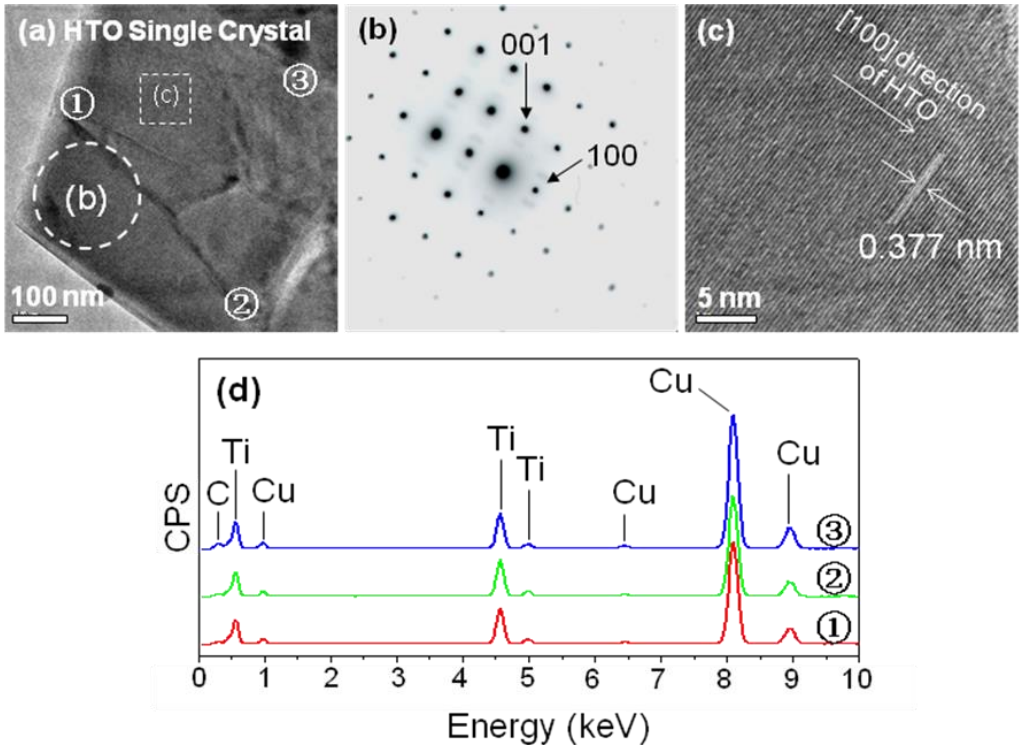

Fig. S2†. (a) TEM image, (b) SAED pattern, (c) HRTEM image, and (d) EDS spectra of HTO single crystal. EDS spectra ①, ②and ③correspond to those at the positions marked ①, ②, and ③ in (a) TEM image, respectively.

Fig. S2† shows TEM image, SAED pattern, HRTEM image, and EDS spectra of HTO single crystal. The TEM image reveals a platelike crystal morphology and smooth surface, which are consistent with FESEM image in Fig. 1B-a. In the SAED pattern of HTO, the clear and ordered diffraction spots can be easily assigned to the HTO phase with orthorhombic system located along the [010] zone axis (Fig. S2b). The [010] direction (*b*-axis direction) is perpendicular to the basal plane of the platelike HTO crystal. The clear lattice fringe of 0.377 nm in HRTEM image can be well assigned to for the (001) plane of the HTO phase (Fig. S2c). The direction of the (001) plane agrees with [001] direction in SAED pattern (Fig. S2b). The EDS analysis result reveals that Li^+ and K^+ were exchanged completely with H^+ after the acid-treatment of KTLO (Fig. S2d).

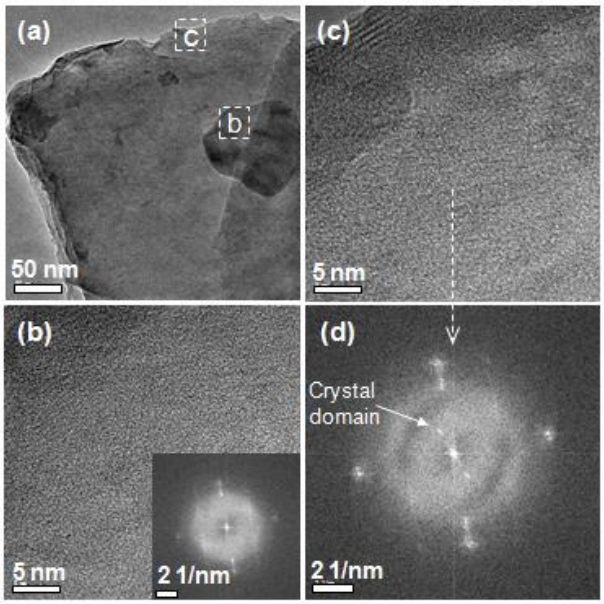

Fig. S3† (a) TEM image and (b, c) HRTEM images of BHA-30/0 sample obtained by solvothermal treatment of HTO single crystals and $Ba(OH)_2$ (molar ratio of Ti/Ba = 2) in water solvent at 150 °C for 12 h. (b, c) HRTEM images are derived from the (b, c) white panes in (a) TEM image, respectively. The inserted FFT pattern in (b) TEM image and (d) FFT pattern are derived from whole region of (b, c) HRTEM images by Fast Fourier Transformation, respectively.

Fig. S3† shows the TEM/HRTEM images and FFT patterns of the BHA-30/0 sample. The FFT patterns of the b and c are very similar, suggesting that the crystalline phase of small nanoparticles locating on the platelike particle surface in BHA-30/0 sample is same as the platelike particle rather than the BT simple phase.

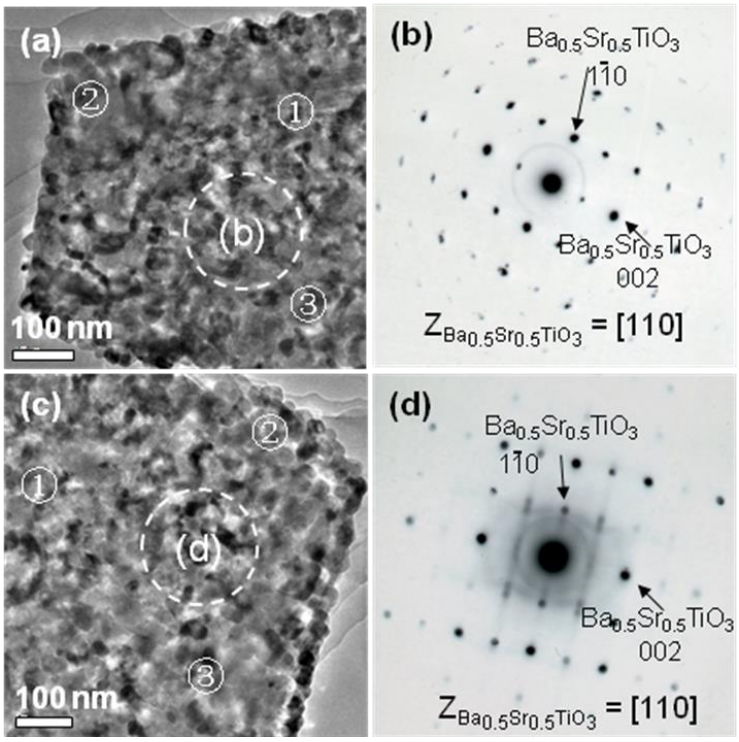

Fig. S4†. (a, c) TEM images and (b, d) SAED patterns of (a, b) BST-5/25-30/0 and (c, d) BST-30/0-10/20 samples obtained by solvothermal treatments of $Sr(OH)_2$ and BT/HTO nanocomposites at 200 °C for 12 h.

Fig. S4† shows that all the obtained particles present the platelike morphology and polycrystal structure constructed from nanocrystals. This result agrees with the FETEM images in Fig. 3B, respectively. All the SAED patterns show the single-crystal-like SAED spots which can be assigned to the BST phase with [110] zone axis located on the basal plane. These results imply that the platelike BST-5/25-30/0 and BST-30/0-10/20 samples are BST solid solution mesocrystals.

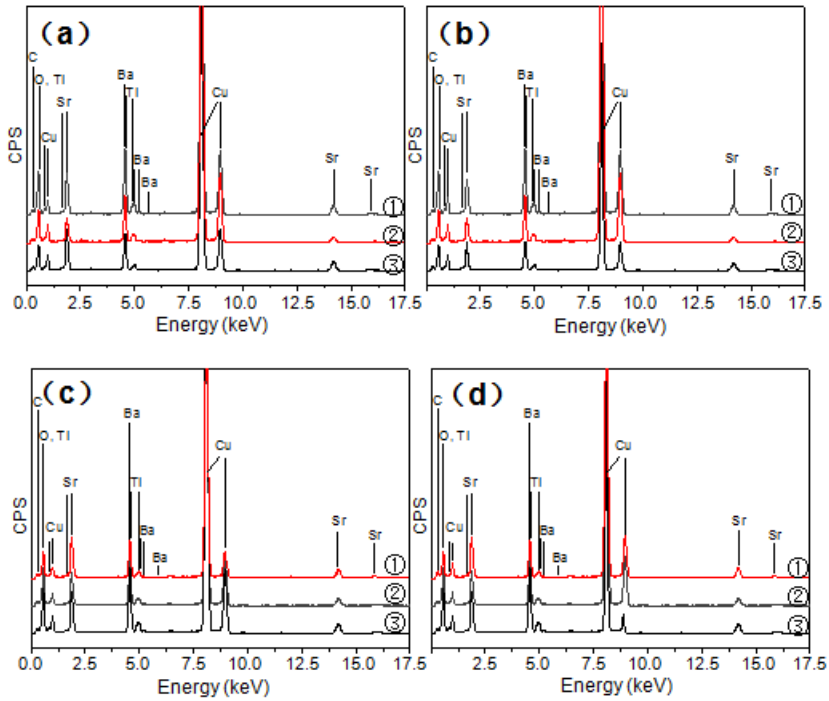

Fig. S5†. EDS spectra of (a) BST-30/0-30/0, (b) BST-5/25-30/0, (c) BST-30/0-10/20, and (d) BST-5/25-30/0 samples corresponding to the TEM images of Fig. 4a, S4a, S4c, 4c, respectively. EDS spectra of labeled "①", "②", and "③" symbol correspond to optionally selected positions in platelike particles shown in TEM images of Fig. 4a, S4a, S4c, 4c, respectively.

Fig. S5† shows the almost the same EDS spectra for same sample, suggesting uniform chemical composition distribution of Ba and Sr in the electron beam size of about 200 nm in the each platelike BST solid solution mesocrystal.

Table S1† Atom quantity ratio of Ti:Ba:Sr from corresponding EDS spectra in Fig. S5.

	(a) BST-30/0-30/0			(b) BST-5/25-30/0		
	Ti	Ba	Sr	Ti	Ba	Sr
①	1.00	0.50	0.50	1.00	0.49	0.49
②	1.00	0.49	0.49	1.00	0.50	0.48
③	1.00	0.51	0.50	1.00	0.48	0.49
Average ratio	1.00	0.50	0.50	1.00	0.49	0.49

	(c) BST-30/0-10/20			(d) BST-5/25-10/20		
	Ti	Ba	Sr	Ti	Ba	Sr
①	1.00	0.46	0.46	1.00	0.48	0.44
②	1.00	0.49	0.47	1.00	0.47	0.48
③	1.00	0.51	0.45	1.00	0.48	0.47
Average ratio	1.00	0.49	0.47	1.00	0.48	0.46

Table S1† shows the molar ratios of Ti:Ba:Sr from EDS analysis results in the platelike BST solid solution mesocrystals. Each investigating position of obtained platelike mesocrystal sample indicates almost same molar ratio of Ti:Ba:Sr, also revealing that the component contents are equally distributed.