Electronic Supplementary Material (ESI) for *RSC Advances*

Topological Relations and Piezoelectric Responses of Crystal-axis-oriented $BaTiO_3/CaTiO_3$ Nanocomposites†

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(1) One-step Solvothermal Soft Chemical Process

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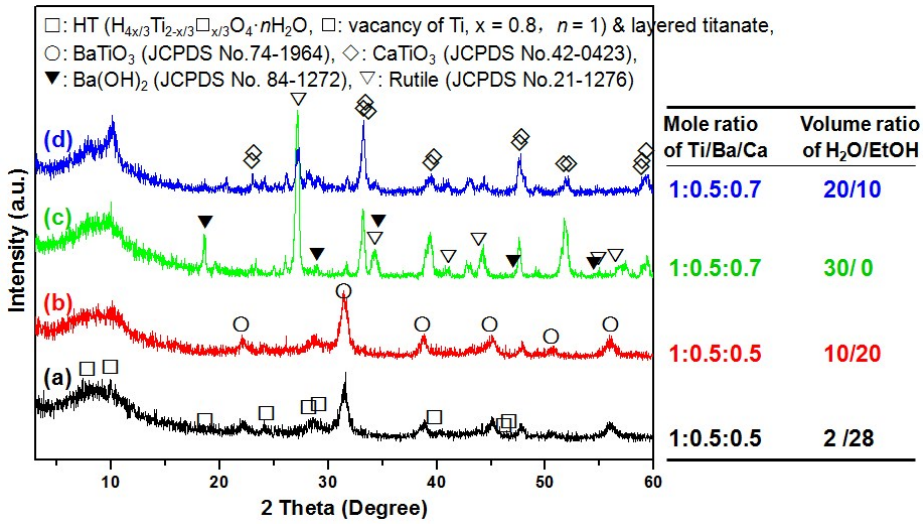

Fig. S1 XRD patterns of samples obtained by solvothermal treatments of mixed HT-$Ba(OH)_2$-$Ca(OH)_2$ powders with different mole ratios of Ti/Ba/Ca in water-ethanol mixed solvents with different volume ratios at 200 °C for 12 h.

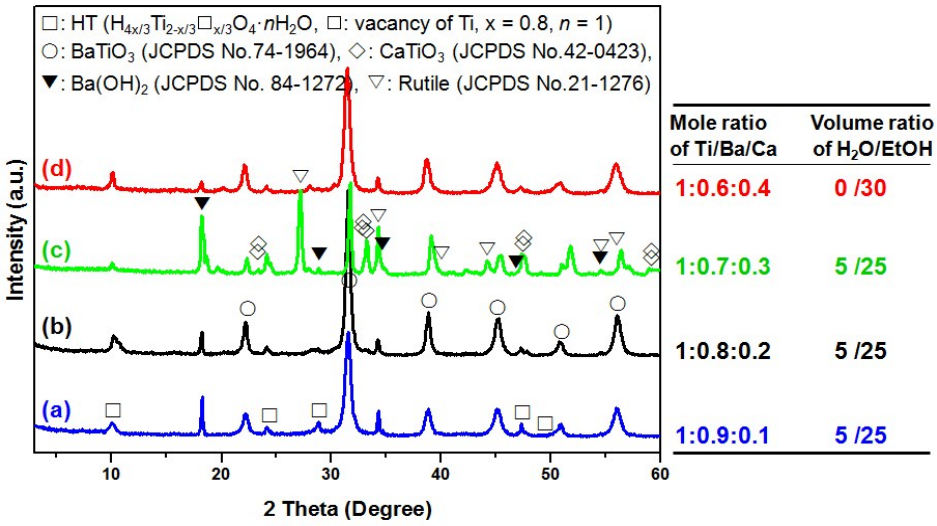

Fig. S2 XRD patterns of samples obtained by solvothermal treatments of mixed HT-$Ba(OH)_2$-$Ca(OH)_2$ powders with different mole ratios of Ti/Ba/Ca in water-ethanol mixed solvents with different volume ratios at 200 °C for 12 h.

Fig. S1 and **S2** show the samples obtained by one-step solvothermal process under different conditions. Pure BT and CT mixed phases cannot obtain but some mixed phases including new layered titanate, rutile, BT, and CT, and unreacted HT and $Ca(OH)_2$. These results suggest that the pure BT and CT composite are difficult to be prepared and the compositions of BT and CT cannot be controlled easily by using the one-step solvothermal process. The crystallinity of the generated products increases with increasing ethanol content in the reaction solvent of the one-step

process. This phenomenon can be explained by the different reactivities of $Ba(OH)_2$, $Ca(OH)_2$ and HT in the solvents with different polarity and solubility.

(2) Two-step Solvothermal Soft Chemical Process

We designed a two-step solvothermal soft chemistry process to form BT/CT nanocomposites. In the first step, the layered HT precursors were reacted partially with the different $Ba(OH)_2$ solutions to form the homogeneous $BaTiO_3$/HT (BT/HT) nanocomposites. Our previous studies indicate that the homogeneous BT/HT nanocomposites can be easily prepared and the formed BT phase can be indexed to a pseudocubic (ICDD no. 74-1964) unit cell because of the small tetragonal distortion.[1,2] The platelike BT/HT nanocomposite prepared in the water solvent, and the formed BT nanoparticles are distributed uniformly in the platelike particle bulk, while in that prepared in water-ethanol mixed solvent, the formed BT nanoparticles are preferentially distributed near the platelike particle surface.[1] In order to obtain BT/CT nanocomposite, a platelike BT/HT nanocomposite with uniformly distributed BT nanocrystal in the bulk is necessary. Hence, we selected the platelike homogeneous BT/HT nanocomposite obtained in water as precursor in the solvothermal process of the second step.

In the second step, the generated platelike homogeneous BT/HT nanocomposites were solvothermally treated in the $Ca(OH)_2$ suspension in water-ethanol mixed solvent to form the 2D mesocrystalline BT/CT nanocomposites. The SEM images in **Fig. S3** show the obtained samples with the irregularly platelike morphology. The thickness of the 2D mesocrystalline BT/CT nanocomposites is approximate 210 nm. And these irregularly platelike paticles show a size of $2 \sim 5$ μm. This result suggests that the platelike morphology can be maintained after the two-step solvothermal treatment from the HT single crystal. These results are consistent with the results of the FESEM and TEM images in **Fig. 2** and **3,** respectively.

[S1] D. W. Hu, H. Ma, Y. Tanaka, L. F. Zhao and Q. Feng, Ferroelectric mesocrystalline $BaTiO_3/SrTiO_3$ nanocomposites with enhanced dielectric and piezoelectric responses, *Chem. Mater.*, **2015**, 27, 4983–4994.

[S2] D. W. Hu, X. Luo, X. G. Kong, Y. Wang, Y. Tanaka and Q. Feng, Topochemical conversion of protonated titanate single crystals into platelike $Ba_{0.5}Sr_{0.5}TiO_3$ mesocrystals with controllable microstructures. *CrystEngComm.* **2015**, 17, 1758–1764.

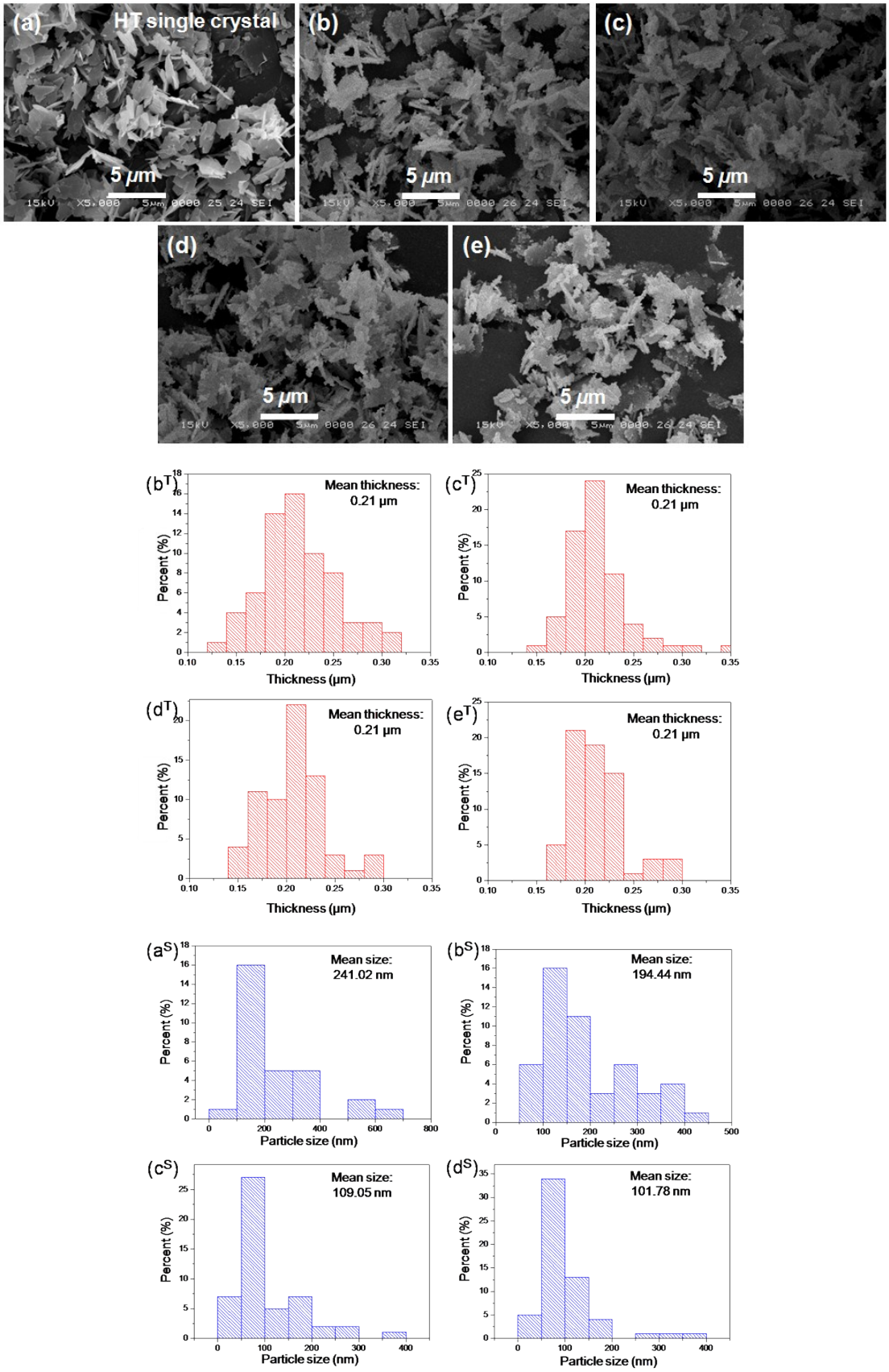

Fig. S3 SEM images of (a) HT crystals, and samples of (b) BT/CT-1/3, (c) BT/CT-1/1, (d) BT/CT-2/1, and (e) BT/CT-6/1 obtained by solvothermal treatments of different

BT/HT nanocomposites and $Ca(OH)_2$ in water-ethanol mixed solvent with volume ratio of 5:25 at 200 ^oC for 12 h, respectively. (b^T-e^T) thickness distributions of the samples shown in Fig. S3(b-e), respectively. (a^S-d^S) particle size distributions of the samples shown in Fig. 2(a-d), respectively. The thickness distributions and particle size distributions were investigated from the (Fig. S3(b-e)) SEM images and (Fig. 2(a-d)) FESEM images by a Nano Measurer software (by Fudan University) , respectively.

(3) Compositional Analysis

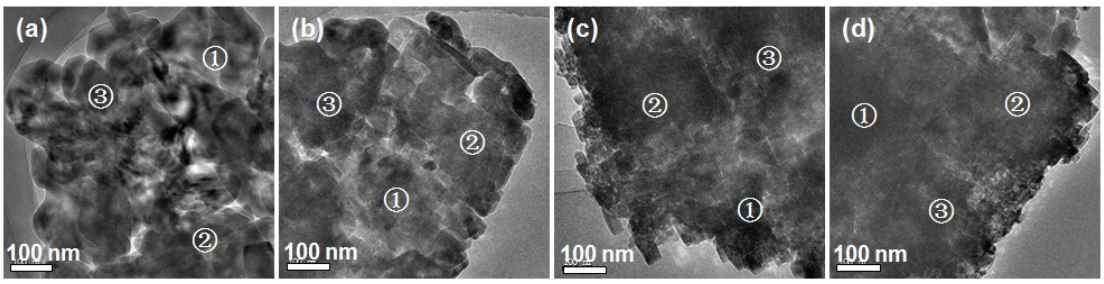

Fig. S4 TEM images of samples of (a) BT/CT-1/3, (b) BT/CT-1/1, (c) BT/CT-2/1, and (d) BT/CT-6/1 obtained by solvothermal treatments of different BT/HT nanocomposites and $Ca(OH)_2$ in water-ethanol mixed solvent with volume ratio of 5:25 at 200 ^oC for 12 h, respectively. The regions in TEM images marked "①", "②", and "③" correspond to the positions measured on the TEM system for obtaining EDS spectra and the quantitative atom ratios of Ti:Ba:Ca in **Table S1**. The selected EDS spectrum from three spectra for each sample is listed in the **Fig. 4(A)**.

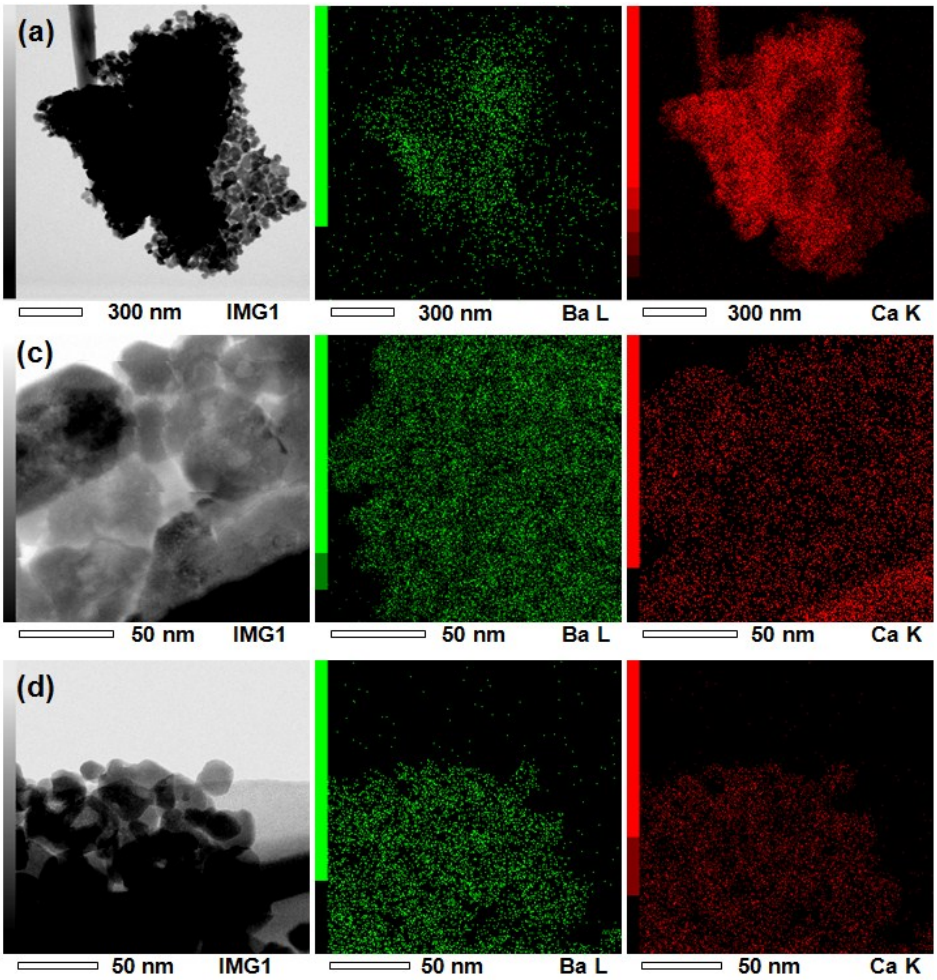

Fig. S5 EDS-mapping TEM images of samples of (a) BT/CT-1/3, (c) BT/CT-2/1, and (d) BT/CT-6/1 obtained by solvothermal treatments of different BT/HT nanocomposites and $Ca(OH)_2$ in water-ethanol mixed solvent with volume ratio of 5:25 at 200 ^oC for 12 h, respectively. The EDS-mapping TEM image of sample of (b) BT/CT-1/1 is illustrated in **Fig. 4(B)**.

Fig. S5 and **4(B)** show the EDS-mapping TEM images of the samples obtained by solvothermal treatments of BT/HT nanocomposites and $Ca(OH)_2$. The green and red colors are representing Ba and Ca, respectively. The EDS-mapping results indicate that the content of Ba increases with the decrease of the content of water in the reaction solvents. This result is consistent with atom ratio of Ti:Ba:Ca from EDS spectra in **Table S1** and **Fig. 4(A)**. These results suggest that the compositions of the BT and CT can be controlled by the feed of $Ba(OH)_2$ and $Ca(OH)_2$ in the generated samples.

(4) Piezoelectric Response

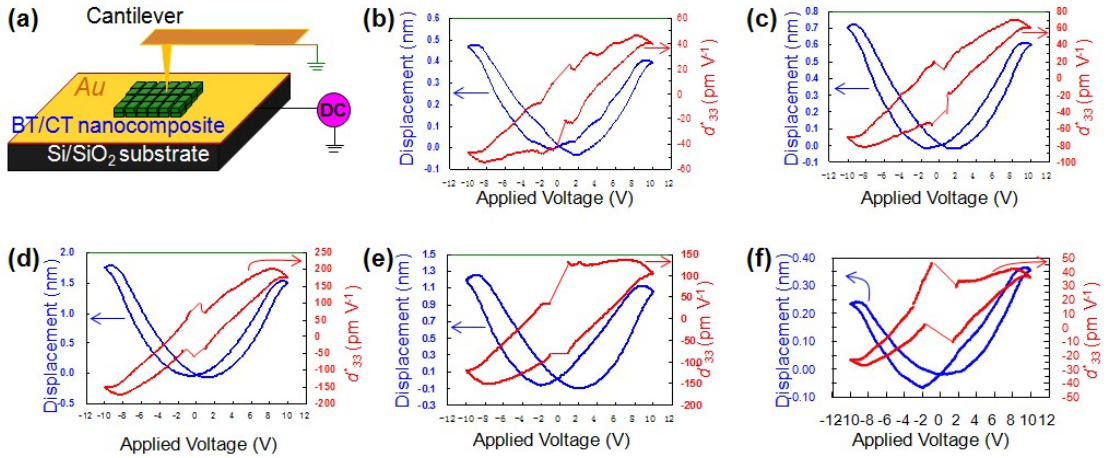

Fig. S6. (a) Schematic illustration of measurement of the piezoelectric response of an individual mesocrystal by SPM (scanning probe microscopy) system. Displacement-Voltage curve and calculated converse piezoelectric coefficient curve of (b) CT mesocrystal, (c) BT/CT-1/3, (d) BT/CT-2/1, (e) BT/CT-6/1 samples, and (f) BT mesocrystal. The displacement-Voltage curve and calculated converse piezoelectric coefficient curve of BT/CT-1/1 is illustrated in **Fig. 6** (a).

Fig. S6 illustrates that the typical butterfly loops of electric-field-induced displacement obtained for some individual titanate crystals, and the converse piezoelectric coefficient were also calculated and labeled to the right axis. The loops of CT and BT mesocrystals can give the average d^*_{33} values of (**Fig. S6b**) 40.9 and (**Fig. S6f**) 35 pm V^{-1}, respectively. The loops of mesocrystalline BT/CT mesocrystals can reach the average d^*_{33} values of 62.2 (**Fig. S6c**, BT/CT-1-3), 184 (**Fig. S6d**, BT/CT-2-1), and 112 (**Fig. S6e**, BT/CT-6-1) pm V^{-1}, respectively. Then, the average d^*_{33} value increases significantly to ~208 pm V^{-1} for the mesocrystalline BT/CT-1-1 mesocrystals (**Fig. 6a**).

Table S1. Quantitative atom ratios of Ti:Ba:Ca in mesocrystalline BT/CT nanocomposites evaluated from EDS spectra. No. "①", "②", and "③" correspond to the positions marked ①, ②, and ③ in TEM images (**Fig. S4**), respectively.

	(a) BT/CT-1/3			(b) BT/CT-1/1			(c) BT/CT-2/1			(c) BT/CT-6/1		
	Ti	Ba	Ca	Ti	Ba	Ca	Ti	Ba	Ca	Ti	Ba	Ca
①	2.00	0.50	1.48	2.00	0.92	1.06	2.00	1.27	0.71	2.00	1.69	0.25
②	2.00	0.52	1.47	2.00	0.89	1.06	2.00	1.28	0.69	2.00	1.70	0.26
③	2.00	0.48	1.52	2.00	0.92	1.05	2.00	1.25	0.71	2.00	1.71	0.24
Average ratio	2.00	0.50	1.49	2.00	0.91	1.06	2.00	1.27	0.70	2.00	1.70	0.25
Ba/Ca of average ratio		1:2.98			1:1.16			1:0.56			1:0.15	
$BaTiO_3$ (mol%)		25.2			46.2			64.2			87.0	

The molar ratios of Ti:Ba:Ca from EDS analysis results in BT/CT nanocomposites are listed in **Table S1**. The average molar ratio results indicate that the Ca content decreases and Ba content increases in an order of BT/CT-1/3<BT/CT-1/1< BT/CT-2/1< BT/CT-6/1. This result is also well consistent with the peak intensity change of XRD (**Fig. 1**). These results suggest that the BT/CT ratio can be adjusted by controlling the feed of $Ba(OH)_2$ and $Ca(OH)_2$. It is a good approach for the configuration of the heteroepitaxial interface with a high density.