Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2019

Electronic Supplementary Information (ESI) for

Designing All-Inorganic Flexible Na_{0.5}Bi_{0.5}TiO₃-Based Film Capacitor with Giant and Stable Energy Storage Performance

Changhong Yang*ab, Jin Qianb, Yajie Hanb, Panpan Lva, Shifeng Huang, Xin Chenga and Zhenxiang Cheng*c

^a Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, China.

^b. School of Materials Science and Engineering, University of Jinan, Jinan 250022, China.

^cInstitute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, Innovation Campus, North Wollongong, NSW 2500, Australia.

*Corresponding Authors:

<u>mse_yangch@ujn.edu.cn</u> (Changhong Yang) cheng@uow.edu.au (Zhenxiang Cheng)



Figure S1. X-ray diffraction patterns of the mica substrate, and Mn:NBT-BT-xST/Pt/mica heterostructures (x=0.30, 0.45, 0.60, 0.75).



Figure S2. Weibull distributions and the fitting lines for the dielectric breakdown strengths of Mn:NBT-BT-xST (x=0.30, 0.45, 0.60, 0.75) film capacitors.

The characteristic dielectric breakdown strength (E_b) of Mn:NBT-BT-xST thin films were studied by Weibull distribution according to the following equations:

$$X_i = Ln(E_i) \tag{1}$$

$$Y_i = Ln\left(-\ln\left(1 - \frac{i}{n+1}\right)\right) \tag{2}$$

where E_i is breakdown electric field for each specimen arranged in an ascending order of $E_1 \le E_2 \le ... \ E_i \ ... \le E_n$, *i* is serial number of specimens, and *n* is the total number of specimens. Based on the Weibull distribution function, there should be a linear relationship between X_i and Y_i . The average E_b for each film can be extracted from the intersect points of the fitting lines and the horizontal line. As displayed in Figure S2, the slope parameter β , related to the scatter of E_b data, increases from 8.11 at x=0.3 to 12.92 at x=0.75, indicating an enhancement in dielectric reliability by ST incorporation. The E_b are calculated to be 2540, 2820, 3131 and 3441 kV cm⁻¹ for the x=0.30, 0.45, 0.60, and 0.75 films, respectively.



Figure S3. The bipolar *P*-*E* loops measured from low electric field to E_b , and corresponding P_r and P_m as functions of applied electric field for the Mn:NBT-BT-xST film capacitors: a) & e) x=0.30; b) and f) x=0.45; c) & g) x=0.60; d) & h) x=0.75.



Figure S4. a) The ε_r and tan δ as functions of temperature measured at frequencies from 1 kHz to 1 MHz for the Mn:NBT-BT film capacitor. b) Characterization of γ using the modified Curie-Weiss equation. The depolarization temperature T_d for Mn:NBT-BT film is ~90 °C, and the maximum ε_r occurs at ~280 °C (T_m). Using the modified Curie-Weiss relationship, the diffuseness parameter γ of the Mn:NBT-BT film is estimated to be 1.31, indicating a certain degree of relaxor state in film.



Figure S5. The unipolar *P-E* loops of the Mn:NBT-BT-0.45ST film capacitor measured under 1875 kV cm⁻¹ from 500 Hz to 20 kHz at room temperature.



Figure S6. The unipolar *P-E* loops of the Mn:NBT-BT-0.45ST film capacitor measured under 1875 kV cm⁻¹ &10 kHz at intervals of 25 °C in the temperature range of -100-200 °C.



Figure S7. The plots of leakage current density-electric field for the Mn:NBT-BT-0.45ST film capacitor at -100-200 °C.



Figure S8. a) The unipolar *P*-*E* loops, and b) corresponding P_r and P_m as functions of switching cycle during the 10⁸ charging-discharging cycles of the Mn:NBT-BT-0.45ST film capacitor at room temperature.



Figure S9. a) The room-temperature unipolar *P*-*E* loops, and b) corresponding P_r and P_m as functions of time during the 10³ s retention for the Mn:NBT-BT-0.45ST film capacitor.



Figure S10. The discharged voltage to a loading resistor (R_L) as a function of time of the Mn:NBT-BT-0.45ST film capacitor, which was measured by a specially designed resistance-capacitance (RC) circuit with R_L of 100 k Ω .



Figure S11. The leakage current density-electric field plots of the flexible Mn:NBT-BT-0.45ST film capacitor measured with various compressive and tensile bending radii.



Figure S12. The time-dependent discharged voltage at various radius of curvatures of the flexible Mn:NBT-BT-0.45ST film capacitor at 1875 kV cm⁻¹ and room temperature.



Figure S13. The leakage current density-electric field plots of the flexible Mn:NBT-BT-0.45ST film capacitor measured in its original flat state, and reflattened after various compressive/tensile bending cycles at 4 mm radius.

materials	E (kV/cm)	$P_{max}-P_r$ (μ C/cm ²)	W_{rec} (J/cm ³)	η (%)	Т (°С)	Bending test	Ref
VDF/PVDF	8200	~14.2	27.3	67	<85	-	[1,2]
P(VDF-TrFE-CTFE)	4000	~10	9	-	<150	-	[3,4]
P(VDF-TrFE-CTFE)/ P(VDF-HFP)	6000		21.9	~65			[5]
BT@BN/PVDF	6000	~6	17.6	~53			[6]
Mn:NBT-BT-0.45ST	2813	69.3	76.1	80.0	-100~200	r=2mm or 10 ⁴ at r=4mm	This work

Table S1. Comparisons of the energy storage property for the Mn:NBT-BT-0.45ST film capacitor and some reported representative organic capacitors.

[1] Z. B. Shen, X. H. Wang, B. C. Luo, L. T. Li, J. Mater. Chem. A, 2015, 3, 18146-18153.

[2] S. M. Yang, T. H. Kim, J. Yoon, T. W. Noh, Adv. Funct. Mater., 2012, 22, 2310-2317.

- [3] B. J. Chu, X. Zhou, K. L. Ren, B. Neese, M. R. Lin, Q. Wang, F. Bauer, Q. M. Zhang, *Science*, 2006, **313**, 334.
- [4] W. L. Warren, K. Vanheusden, D. Dimos, G. E. Pike, B. A. Tuttle, J. Am. Ceram. Soc., 1996, 79, 536-538.

[5] X. T. Ren, N. Meng, H. X. Yan, E. Bilotti, M. J. Reece, Polymer, 2019, 168, 246-254.

[6] S. B. Luo, J. Y. Yu, S. H. Yu, R. Sun, L. Q. Cao, W.-H. Liao, C.-P. Wong, Adv. Energy Mater., 2019, 9, 1803204.