ADVANCED ENERGY MATERIALS

Supporting Information

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Superior Energy-Storage Capacitors with Simultaneously Giant Energy Density and Efficiency Using Nanodomain Engineered $BiFeO_3$-$BaTiO_3$-$NaNbO_3$ Lead-Free Bulk Ferroelectrics

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Table S1 Refined structural parameters by using the Rietveld method for the *x*=0.1 ceramic measured at various temperatures.

T (°C)	Space group	Lattice parameters	V (Å^3)	R_{wp} (%)	R_p (%)	χ^2
-50	$Pm\bar{3}m$	a=b=c=3.9938(0) Å, α=β=γ=90°	63.704(3)	5.88	4.55	1.15
25	$Pm\bar{3}m$	a=b=c=3.9942(0) Å, α=β=γ=90°	63.723(2)	5.87	4.55	1.14
100	$Pm\bar{3}m$	a=b=c=3.9956(0) Å, α=β=γ=90°	63.791(3)	5.90	4.61	1.16
175	$Pm\bar{3}m$	a=b=c=3.9960(0) Å, α=β=γ=90°	63.810(2)	5.92	4.62	1.15
250	$Pm\bar{3}m$	a=b=c=3.9963(0) Å, α=β=γ=90°	63.827(2)	5.94	4.73	1.16

Table S2 Discharge properties of a few reported ceramics.

Composition	W_D (J/cm^3)	$t_{0.9}$ (ns)	E (kV/mm)	Ref.
$Na_{0.7}Bi_{0.1}NbO_3$	0.56	155	10	1
$Bi_{0.5}K_{0.5}TiO_3$-0.06La$(Mg_{0.5}Ti_{0.5})O_3$	0.76	200	14	2
$Sm_{0.03}Ag_{0.91}NbO_3$	4.2	20000	29	3
0.65$BiFeO_3$-0.3$BaTiO_3$-0.05Bi$(Zn_{2/3}Nb_{1/3})O_3$	0.09	100	7	4
0.91$NaNbO_3$-0.09Bi$(Zn_{0.5}Ti_{0.5})O_3$	0.77	50	12	5
0.9$(Sr_{0.7}Bi_{0.2})TiO_3$-0.1Bi$(Mg_{0.5}Hf_{0.5})O_3$	1	1250	16	6
0.65$Bi_{0.51}Na_{0.47}Ti_{0.9875}Nb_{0.01}O_3$-0.35Ba$(Ti_{0.7}Zr_{0.3})O_3$	1.23	1200	14	7
$(Na_{0.25}Bi_{0.25}Sr_{0.5})(Ti_{0.8}Sn_{0.2})O_3$	1.6	630	20	8
0.88$BaTiO_3$-0.12Bi$(Ni_{2/3}Nb_{1/3})O_3$	0.54	85	10	9
$Pb_{0.94}La_{0.02}Sr_{0.04}(Zr_{0.9}Sn_{0.1})_{0.995}$	8.6	185	39.5	10
x=0.1	2.4	97	20	This work

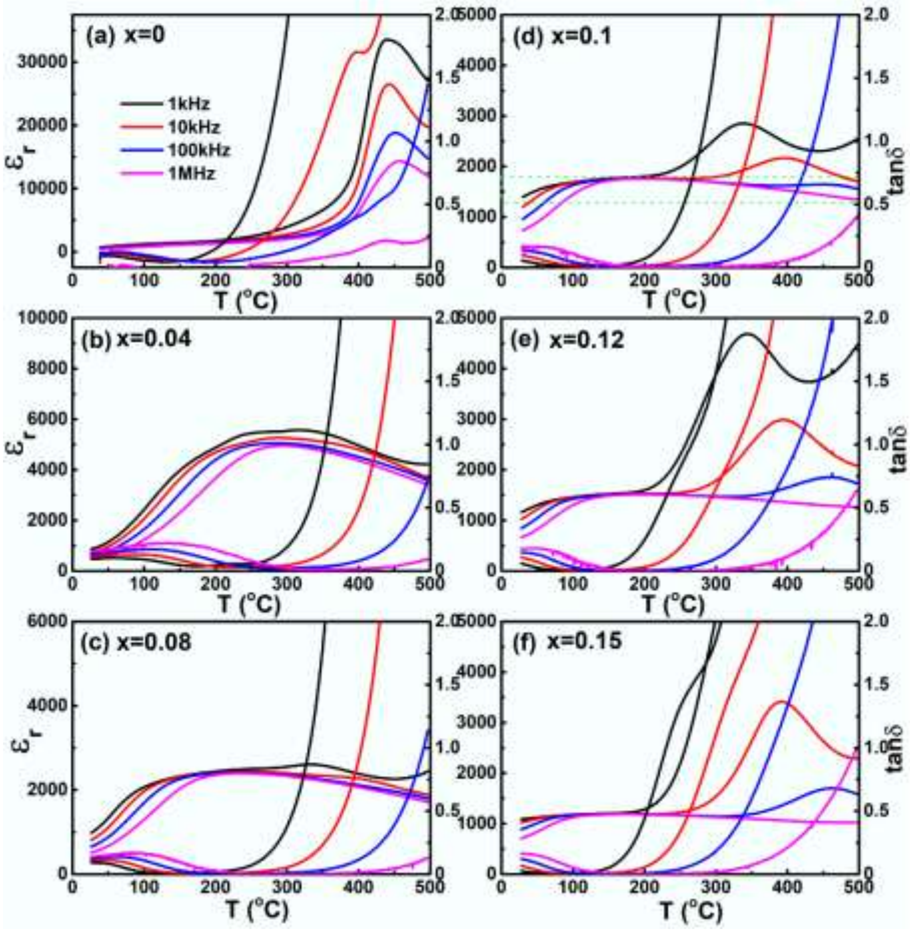

Figure S1. Temperature and frequency dependence of dielectric permittivity of (0.67-x)BF-0.33BT-xNN ceramics.

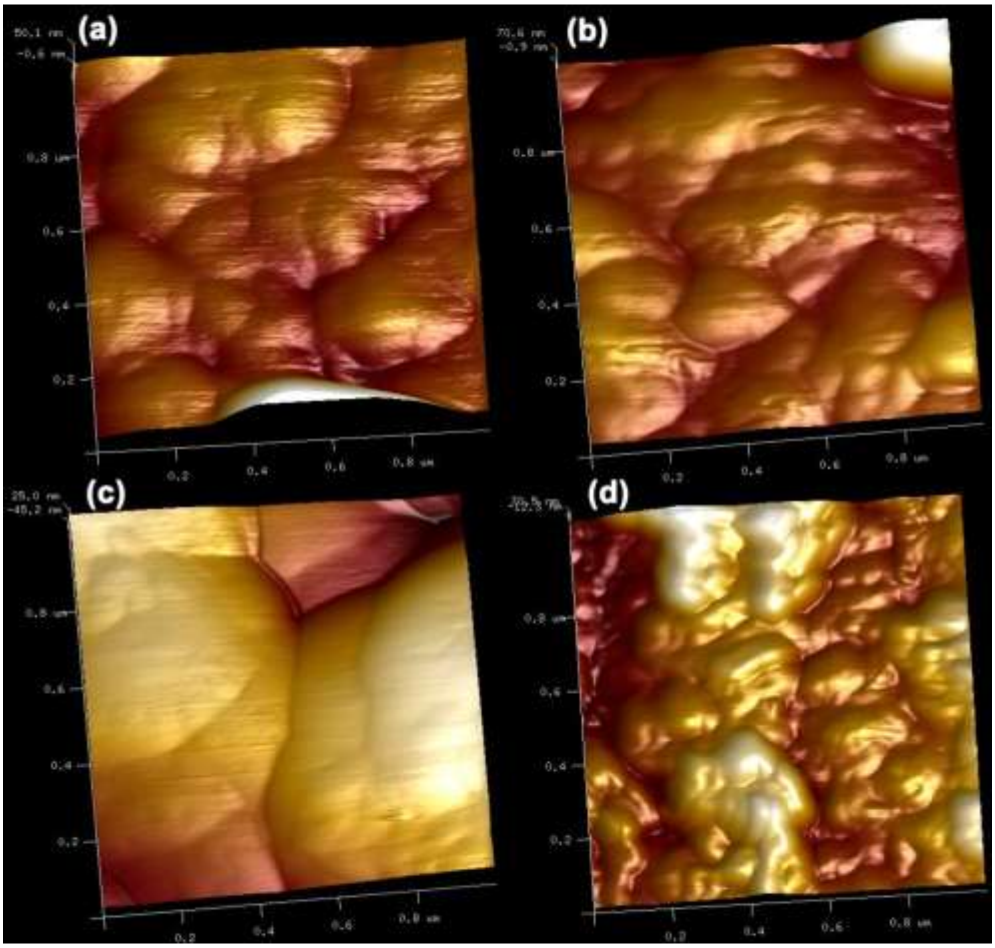

Figure S2. Surface morphology images of (0.67-x)BF-0.33BT-xNN ceramics: a) x=0, b) x=0.04, c) x=0.10 and d) x=0.15.

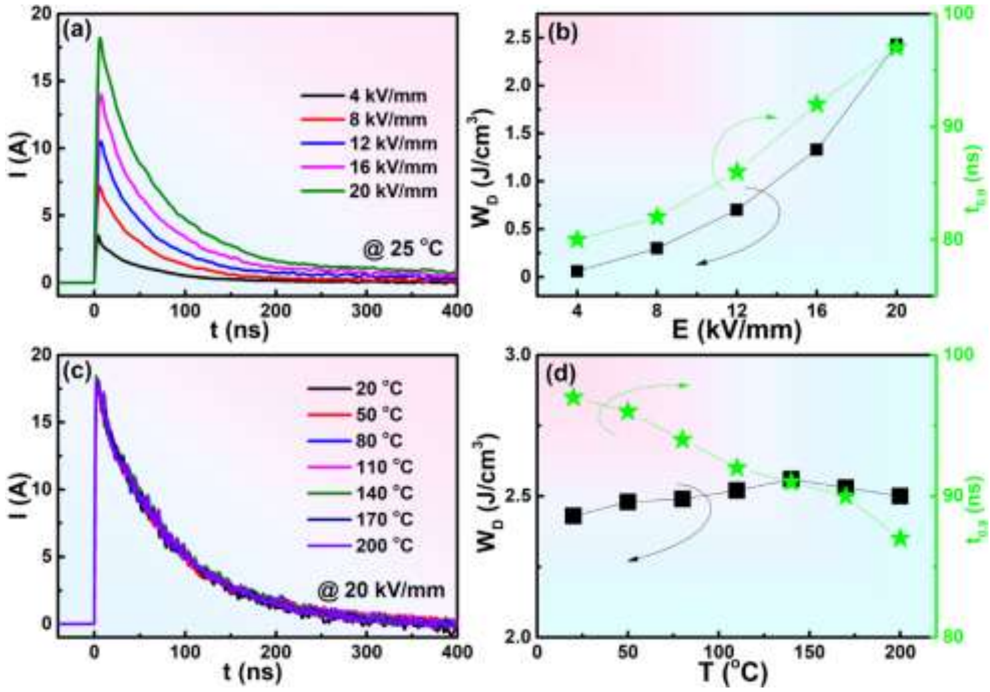

Figure S3. a) Room-temperature pulsed overdamped discharging current curves of the x=0.1 ceramic at a fixed load resistance of 200 Ω under various electric fields; b) the evolution of W_D and $t_{0.9}$ with changing electric field; c) The pulsed overdamped discharging current curves of the x=0.1 ceramic under 20 kV/mm at different measuring temperatures; d) the evolution of W_D and $t_{0.9}$ with changing temperature.

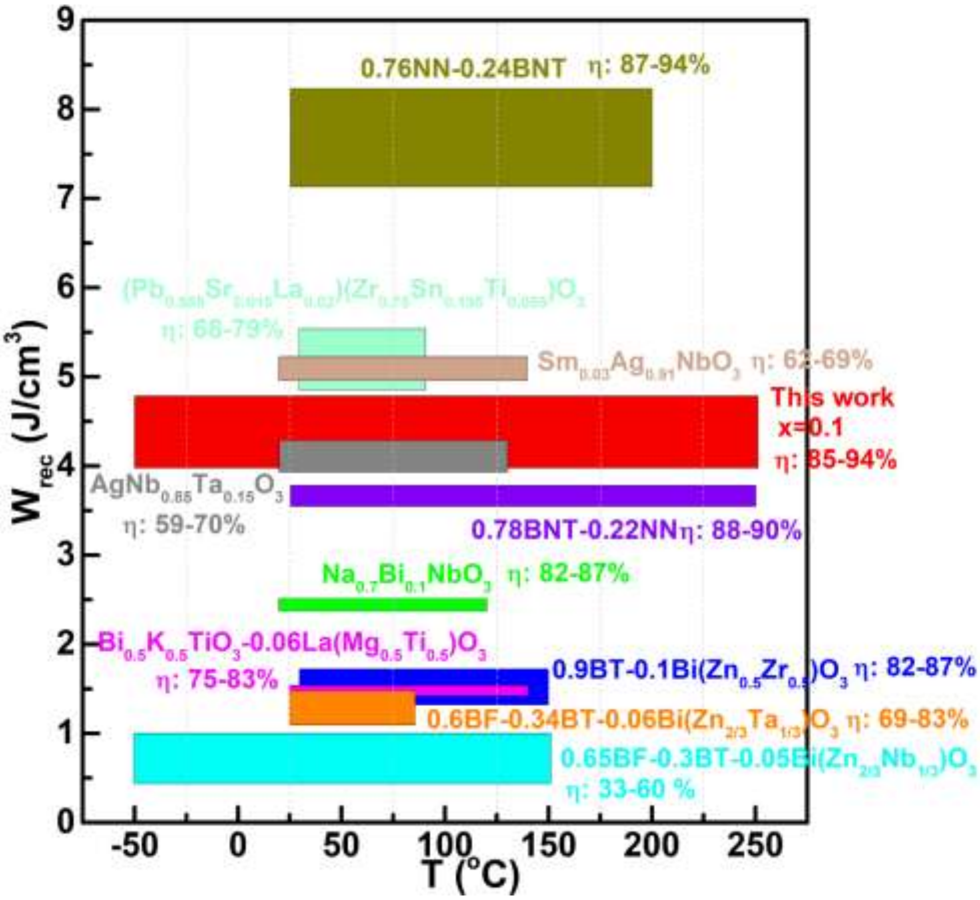

Figure S4. A comparison of temperature stability of W_{rec} and η among a few typical energy-storage bulk ceramics.[1-3,11-16]

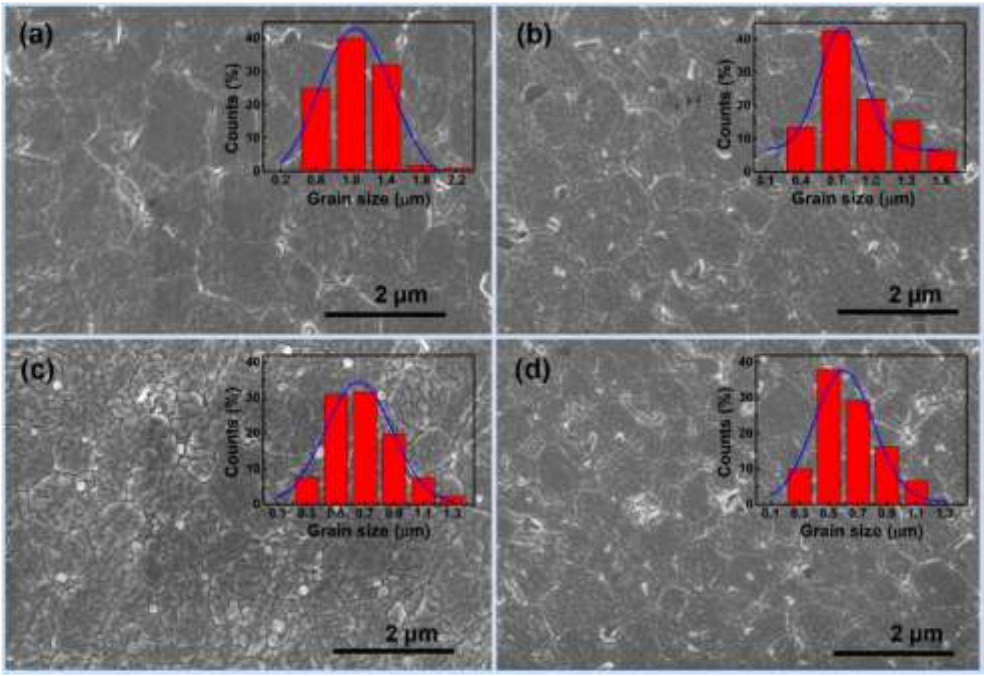

Figure S5. SEM micrographs on polished and thermally etched surfaces of (0.67-*x*)BF-0.33BT-*x*NN ceramics sintered at their optimum temperatures: a) x=0, b) x=0.04, c) x=0.1 and d) x=0.15.

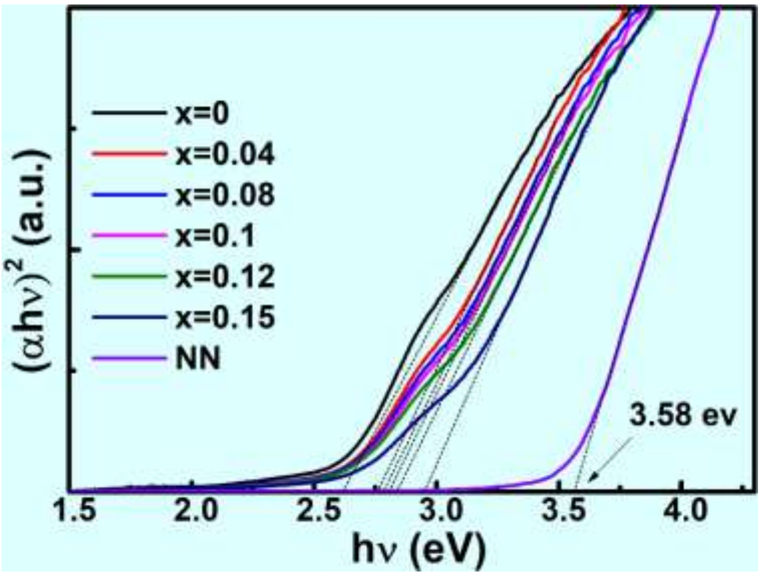

Figure S6. $(\alpha h\nu)^2$ versus hν plot of (0.67-*x*)BF-0.33BT-*x*NN and NN ceramics.

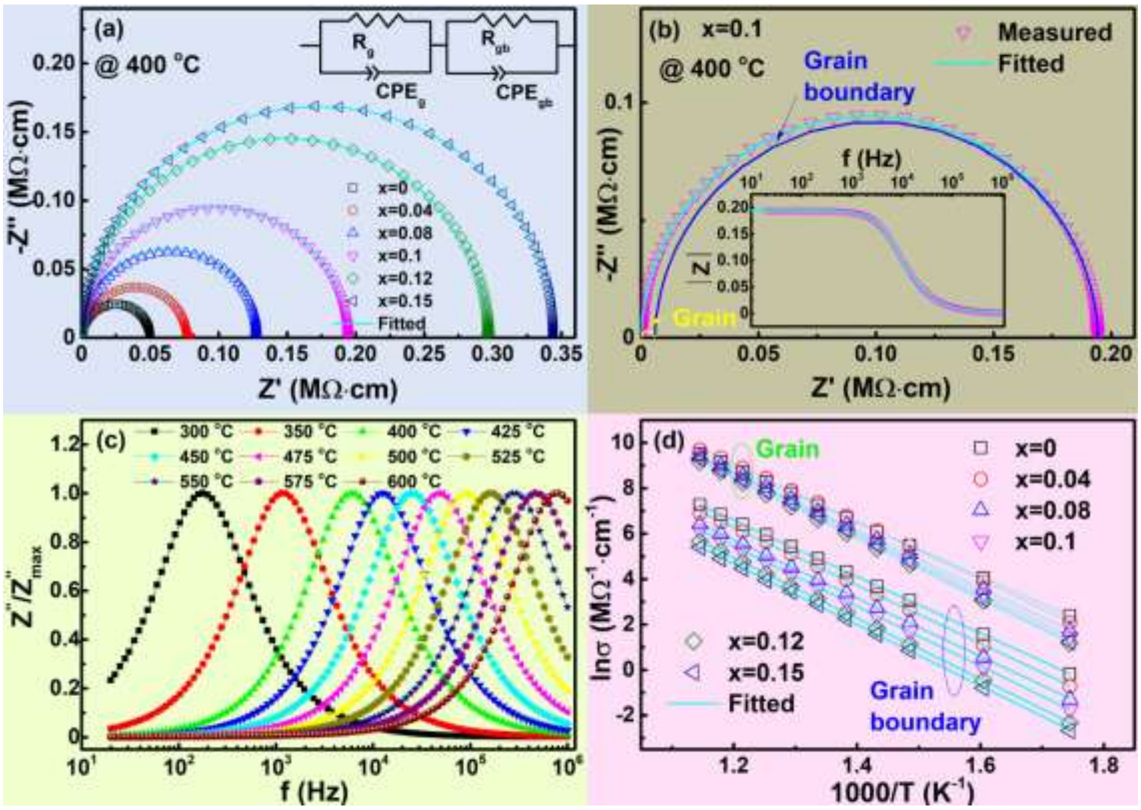

Figure S7. a) The complex AC impedance and fitting semicircles at 400 °C for the (0.67-*x*)BF-0.33BT-*x*NN ceramics; b) the fitted complex AC impedance including two semicircles corresponding to grain and grain boundary contributions, respectively, using the *x*=0.1 ceramic at 400 °C as an example via the equivalent circuit in the inset of a); c) plots of Z''/Z''_{max} versus frequency in the temperature range 300-600 °C for the *x*=0.1 ceramic; d) the Arrhenius-type plots of bulk conductivity for (0.67-*x*)BF-0.33BT-*x*NN ceramics.

References

[1] M. X. Zhou, R. L. Liang, Z. Y. Zhou, X. L. Dong, *J. Mater. Chem. A* **2018**, *6*, 17896.

[2] F. Li, T. Jiang, J. W. Zhai, B. Shen, H. R. Zeng, *J. Mater. Chem. C* **2018**, *6*, 7976.

[3] N. N. Luo, K. Han, F. P. Zhuo, C. Xu, G. Z. Zhang, L. J. Liu, X. Y. Chen, C. Z. Hu,

H. F. Zhou, Y. Z. Wei, *J. Mater. Chem. A* **2019**, *7*, 14118.

[4] D. W. Wang, Z. M. Fan, W. B. Li, D. Zhou, A. Feteira, G. Wang, S. Murakami, S. K. Sun, Q. L. Zhao, X. L. Tan, I. M. Reaney, *ACS Appl. Energy Mater.* **2018**, *1*, 4403.

[5] R. Shi, Y. P. Pu, W. Wang, X. Guo, J. W. Li, M. D. Yang, S. Y. Zhou, *J. Alloy. Compd.* **2020**, *815*, 152356.

[6] X. Kong, L. T. Yang, Z. X. Cheng, S. J. Zhang, *J. Am. Ceram. Soc.* **2019**, https://doi.org/10.1111/jace.16844.

[7] Y. Huang, Q. H. Guo, H. Hao, H. X. Liu, S. J. Zhang, *J. Eur. Ceram. Soc.* **2019**, *39*, 4752.

[8] L. T. Yang, X. Kong, Z. X. Cheng, S. J. Zhang, *J. Mater. Chem. A* **2019**, *7*, 8573.

[9] M. X. Zhou, R. H. Liang, Z. Y. Zhou, X. L. Dong, *Ceram. Int.* **2019**, *45*, 3582.

[10] X. H. Liu, Y. Li, X. H. Hao, *J. Mater. Chem. A* **2019**, *7*, 11858.

[11] H. Qi, R. Z. Zuo, A. W. Xie, A. Tian, J. Fu, Y. Zhang, S. J. Zhang, *Adv. Funct. Mater.* **2019**, 1903877.

[12] Q. B. Yuan, F. Z. Yao, Y. F. Wang, R. Ma, H. Wang, *J. Mater. Chem. C* **2017**, *5*, 9552.

[13] N. T. Liu, R. L. Liang, Z. Y. Zhou, X. L. Dong, *J. Mater. Chem. C* **2018**, *6*, 10211.

[14] Q. F. Zhang, H. F. Tong, J. Chen, Y. M. Lu, T. Q. Yang, X. Yao, Y. B. He, *Appl. Phys. Lett.* **2016**, *109*, 262901.

[15] L. Zhao, Q. Liu, J. Gao, S. J. Zhang, J. F. Li, *Adv. Mater.* **2017**, *29*, 1701824.

[16] H. Qi, R. Z. Zuo, *J. Mater. Chem. A* **2019**, *7*, 3971.