Exploring Surface and Tunneling Properties of Defect-Oriented Quasi-Graphene/Poly(vinylidene fluoride) Nanocomposite Films as Flexible 2D Materials for Electronic Applications

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Supporting Information

ABSTRACT: Here, we demonstrate the promising tunneling property of electrons across quasi-graphene/poly(vinylidene fluoride) (PVDF) through the Coulomb blockade region. The melt-mixing technique is used to prepare such a nanocomposite by mixing a nanofiller into the polymer matrix. The structure and surface morphology are studied using X-ray diffraction and field-emission scanning electron microscopy measurements, which show defects oriented in the sample while the binding of matrix with the nanofiller remains highly conductive even upon its binding with the insulating matrix. Tunneling properties of quasi-graphene/PVDF are studied using scanning tunneling microscopy measurements, which indicate high resistance in the Coulomb blockade region. Potential aspects of quasi-graphene/PVDF as a flexible material for device applications are also discussed.

1. INTRODUCTION

The last couple of decades have witnessed a great leap in transistor technology from the rapid development of microelectronics to the birth of present-day nanoelectronics with apparent deviations from Moore’s scaling trend followed by substantial size reduction.¹⁻¹⁴ Indeed, chemistry and materials science, in particular, have played a pivotal role in the evolution of integrated circuits by enabling the development of active devices with distinct and reliable properties.⁵⁻⁷ Of late, much attention has also been drawn into what is known as flexible electronics because of its portability, lightweight, and cost efficiency. Such unique features make it suitable for a wide range of applications, including robotics, sensors, displays, and tunable regulators.⁸ Nevertheless, developing a material with high flexibility and better dielectric strength to make it useful for flexible electronics remains still somewhat challenging, though a lot of progress has been made in this direction.

Nanocomposites are often regarded as potential materials for harvesting superior dielectric strength and conductivity. Mechanical, electrical, and also, thermal properties may often require improvement for materials that build circuit components regarding polymer electronics and other future technologies.⁶ In recent years, the high-k fillers along with polymers such as multiwalled carbon nanotubes (MWCNTs)/poly(vinylidene fluoride) (PVDF), graphene/PVDF, carbon nanotubes (CNTs)/PVDF, graphene/polyaniline (PANI), and MWCNT/PANI have been part of active research⁵⁻¹⁷ related to sensors, electromagnetic interference shielding, flexible electronics, etc. The high permittivity of a nanocapacitor is seen to be unevenly disseminated as the dielectric host due to

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the nanofillers conducts along with insulating polymer thin films between the matrices. It may be noted that graphene oxides (GOs) are popularly exploited as nanofillers for fiber-reinforced polymer composites.\textsuperscript{7–11,18–21} GOs can be chemically coated onto the surfaces of either carbon fibers or carbon fabric to augment the interfacial bonding properties through the surrounding polymer matrix of the composites.\textsuperscript{12–17,22–27} On the other hand, poly(vinylidene fluoride) (PVDF) is known for displaying ferroelectric behavior below 150 °C while pyroelectric and piezoelectric properties at room temperature.\textsuperscript{18,29} It also exhibits low dissipation and good permittivity.\textsuperscript{20} Besides, PVDF possesses the ability to get polarize quickly,\textsuperscript{20} which is harnessed in micro capacitors\textsuperscript{24–38} for electrostriction of muscles. However, as regards the preparation methods for CNT or graphene/PVDF composites by various processing and mechanical techniques, not much effort has been made to observe or control the distribution of graphene or CNT with PVDF.\textsuperscript{2,9,13,14,18,22} The reason is that CNT or graphene gets often randomly dispersed with the polymer PVDF matrix. Consequently, this makes easy conductive network between the filler and the matrix. Further, the dielectric, charge storage, and switching properties can be studied conveniently because of the presence of graphene nanofillers in the matrix.\textsuperscript{17,39} Such nanofillers can also be put into a hybrid matrix as graphene is a promising conductive material.\textsuperscript{39}

This work reports the preparation of quasi-graphene/PVDF using the solvent casting technique. The as-prepared quasi-graphene/PVDF films are characterized using X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), energy-dispersive spectroscopy (EDS), and Raman spectroscopy to study their structural and surface morphologies. The electronic structure of a quasi-graphene/PVDF film was examined using scanning tunneling microscopy (STM) and broadband dielectric spectroscopy (BDS) measurements. The as-prepared nanocomposites showed a conduction path, which was subsequently exploited in the device building.

2. RESULTS AND DISCUSSION

2.1. Structural Analysis. The XRD pattern in Figure 1 shows several peaks at 2θ ~ 18, 20, and 40° for PVDF and 2θ ~ 26° (JCPDS card no. 00-41-1487) for graphene. All of the above peaks are confirmed in the graphene/PVDF sample with their average grain size being close to 11 nm. Nevertheless, the increasing content of graphene nanofiller makes the amount of the α-phase (2θ ~ 18°) decrease somewhat (as the α-peak gets suppressed), while that of the β-phase (2θ ~ 20°) increases marginally. The β-phase of PVDF has better piezoelectric properties, which assures that the graphene/PVDF sample with slight upsurge in the β-phase of PVDF could be favorable for developing electronic devices.\textsuperscript{22}

2.2. Surface and Morphological Analysis. FESEM images in Figure 2a,b portray surface morphology of graphene, which appears as fine sheets of carbon. Figure 2c,d shows the FESEM images of PVDF, appearing as fine small spherical balls. Subsequently, the FESEM pattern of the graphene/PVDF nanocomposite is displayed in Figure 2e,f, in which the superior bonding is imaged. This is owing to the mixing of graphene as a nanofiller with PVDF. The brighter part in the image corresponds to the presence of graphene (as graphene is a well-known highly conductive material), exhibiting a typical two-dimensional (2D) structure (since small wrinkles and boundaries are visible) in nature. From Figure 2e,f, one can perceive that the distribution of graphene is well defined having PVDF throughout the matrix. Energy dispersion in the quasi-graphene/PVDF film is confirmed by the EDS pattern, as shown in Supporting Information Figure S2.

According to the Raman spectrum of quasi-graphene/PVDF (Figure 3), the G band due to the E\textsubscript{2g} mode of graphite at the Γ point is observed at 1592.4 cm\textsuperscript{-1}, while the D band due to the A\textsubscript{1g} breathing mode of the wrinkled graphite lies at 1298.3 cm\textsuperscript{-1}. The former represents the in-plane C=C bond-stretching mode of sp\textsuperscript{2}-hybridized carbon atoms, while the latter embodies the vibration from k-point phonons of carbon atoms with dangling bonds.\textsuperscript{27} We observe that the intensity ratio of the quasi-graphene/PVDF film (I\textsubscript{G}/I\textsubscript{D}) is found to be 1.24, implying that the excessive oxidation brings about many defects and a higher level of disorder. Furthermore, graphene can also be aligned well with an electric field.\textsuperscript{27}

2.3. Electrical Measurements. As shown in Figure S3, the conductivity plot of quasi-graphene/PVDF was taken from 1 to 10\textsuperscript{4} Hz frequency in the x-axis while its conductivity (σ) was measured from 10\textsuperscript{-11} to 10\textsuperscript{-4} S/cm, respectively. The extrapolated conductivity at σ(f) → 0 for quasi-graphene/PVDF lies close to 10\textsuperscript{-11} S/cm, which increases generally with the concentration of graphene nanofillers. Conductivity depends typically on the concentration of graphene. In our electrical investigation, both conductivity and capacitance analyses were focused on exploring the electrical applications. As reported in the literature, PVDF at σ(f) → 0 shows an almost insulating nature.\textsuperscript{40} However, upon incorporating a nanofiller, its conductivity surges quite significantly depending on the weight ratio of the nanofillers. It starts decreasing at a certain point, where the percolation threshold can be achieved. This increasing trend in the conductivity of the quasi-graphene/PVDF may be due to the transport of charge carriers with the aid of especially the filler content.

The frequency-dependent conductivity σ(f) is observed to obey the power law model

\[
\sigma(f) = \sigma_0 + A f^{n_1} + B f^{n_2} \text{ for } 0 \leq n_1 \leq 1 \text{ and } 0 < n_2 < 2
\]

leading to \[
\sigma(f) = \sigma_0 + A f^{n_1} \text{ for } n_2 = 0
\]

where \(\sigma_0\) refers to the dc conductivity (frequency-independent), A and B are the temperature-dependent

![Figure 1. XRD patterns and structural images of graphene, PVDF, and the graphene/PVDF nanocomposite.](Image)
parameters, and $f$ is the frequency. Additionally, $n$ indicates the power law exponent, representing thereby the degree of interaction and transport nature of the charge carrier, as expounded by Funke et al. For $0 \leq n_1 \leq 1$, the grain boundary conductivity refers to the low-frequency region, i.e., the hopping motion will involve translation motion with the sudden hopping, while for $0 < n_2 < 1$, the grain boundary conductivity refers to the high-frequency region, i.e., hopping motion will involve localized hopping without the species leaving the neighborhood.

According to Figure S3, quasi-graphene/PVDF obeys the power law, as given by eq 2, to display the single frequency as an activated region (i.e., only one region is observed). It may be noted that other than the lower-frequency region, most of the hops are ineffective. As the frequency increases, chances for the hops to be unsuccessful become more. It leads to the dispersive conductivity in the graphene/PVDF nanocomposite.

The tunneling nature of the nanocomposite is discussed in the following section. This excellent nature of perfect conductivity makes it suitable for electrical applications.

Figure 4 shows the scanning tunneling microscopy (STM) image of quasi-graphene/PVDF, which is imaged at 400 nm scale (Figure S4). The gold tip was held at one position of the quasi-graphene/PVDF film where voltage was varied from $-0.5$ to $0.5$ V. Correspondingly, the current variations were
measured from −10 to +10 nA and a nonlinear $I$–$V$ curve, as shown in Figure 4, was obtained, which make it suitable to be used in nonlinear devices. The nonlinearity found in the nanocomposite also makes it possible to use it in memory devices for the ON or OFF operation, i.e., for switching in devices as it also proves to be a better candidate for memory storage (Figure 4). The extinction ratio between ON and OFF operations is obtained as 48.5 dB. This nanocomposite provides a high tunnel current and allows biases as large as possible without any electrical breakdown. These nanocomposites provide a high tunnel current and also allow biases as large as possible without electrical tunneling. All of these convincingly reiterate that conduction in quasi-graphene/PVDF can potentially take place through quantum tunneling, which further suggests that such nanocomposites can be used in making some electronic devices of interest.

Figure 4 indicates the region identified for the Coulomb blockade, since there is no current flow in the said region between −0.1 and 0.1 V. This shows that there exists an increased resistance (i.e., resistances are not constant in this region) at small bias voltage, which comprises a tunnel junction. By applying a static magnetic field and allowing only few electrons to tunnel, the Coulomb blockade provides a region for the Pauli blockade. It results in the possibility of spin and orbital interactions to be occurred between the electrons. This is because it satisfies the energy-scale conditions $E = \frac{e^2}{2C}$, while electrons move onto the charging or discharging stage.

Capacitance along the Coulomb blockade region is 0.5 nF for quasi-graphene/PVDF at 1 Hz, as shown in Figure 5. There is a sharp rise in the capacitance for quasi-graphene/PVDF nanocomposites in the low-frequency region. As the weight ratio of the nanofiller increases, it can readily act as parallel plates for the formation of the conducting path to display the piezoelectric effect (Figures S5 and S6). This phenomenon will result in the charge storage inside the nanocomposites. At about 3 nF, the highest capacitive nature is observed for the as-prepared nanocomposites. As we know, before attaining the percolation threshold, there exists a tunneling current between any two nearby carbon bonds, depending upon the applied energy. As observed in Figure 5, after reaching the highest point, they are readily discharged, tending to attend its initial stage. This charging and discharging states of the nanocomposites make them suitable for the storage applications.

Figure 5 shows the $I$–$V$ plot of the device, as designed (Figure S7) using the quasi-graphene/PVDF nanocomposite.

$I$–$V$ measurements were carried out at various temperature stages to study how much temperature such nanocomposites can withstand. As shown in Figure 6, the current increases with the rise in temperature, thus demonstrating a good resistive path for quasi-graphene/PVDF. Such nanocomposites are capable of withstanding a certain limit of temperature, beyond which they may break down. One should hence be careful while handling such a kind of nanocomposite especially when it is exposed to excess heat or temperature.

3. CONCLUSIONS

In this work, we have successfully prepared the quasi-graphene/PVDF nanocomposite by a mere solvent casting technique. The as-prepared nanocomposites are mostly homogeneous in nature. The presence of both graphene and PVDF, as evident from the FESEM images where the bright regions stem from the large secondary electron emission, can be well associated with the conductivity plot. The charge storage capability as observed here demonstrates that such nanocomposites can be quite efficient for switching and storage applications. STM measurements subsequently affirm that quasi-graphene/PVDF can exhibit good tunneling behavior without any electrical breakdown even through the Coulomb blockade region. The electrical nature of the as-designed device was found to be efficient and thus can be potentially suitable for flexible electronics, for the possibility of providing high biasing without any breakdown in the circuit.

4. EXPERIMENTAL SECTION

4.1. Materials. Pristine poly(vinylidene fluoride) (PVDF) powder with $M_w \sim 530$ 000 g/mol and dimethylformamide (DMF) solution with 99.5% purity and of laboratory grade were purchased from Kevin Chemicals. Pristine graphene flake was purchased from Ad Nano Technologies with 99% purity and of 2–4 layers.

4.2. Preparation Methods. The melt-mixing technique (i.e., ultrasonication-assisted solution mixing) followed by melt compression was used to prepare the quasi-graphene/PVDF,
as shown in Supporting Information Figure S1. PVDF (25 g) was dissolved in 200 mL of DMF solution, and the predetermined amount of pristine graphene flakes was added to the solution. As-prepared graphene/PVDF with DMF solution was mixed mechanically for 1 h followed by probe-type ultrasonication for another 1 h. Graphene/PVDF/DMF solution was magnetically stirred for 1 h by maintaining the temperature between 50 and 70 °C to achieve proper dispersion in the solution. Finally, the solution was hot-pressed for about 6–8 h at a constant temperature of 80 °C and then it was allowed to cool to room temperature.

4.3. Characterization. An X’pert powder XRD system was used to analyze the crystalline structure of the pristine graphene, PVDF, and quasi-graphene/PVDF, which uses Cu Kα radiation (λ = 0.1540 nm). An FEI Quanta FEG 200 high-resolution field-emission microscope was used to image the surface and dispersion state of graphene flakes in quasi-graphene/PVDF.

4.4. STM Measurements. Quasi-graphene/PVDF was cut into pieces of 1 × 1 cm² diameter for the STM measurements using pA-STM (APE Research) and was connected to a spectrometer using special cables.

4.5. BDS Measurements. The as-prepared quasi-graphene/PVDF was cut into the circumference of 1 cm (i.e., cut in a circular or coin shape) and was connected using special cables to the spectrometer for the ac measurements using a Novocontrol broadband dielectric/impedance α analyzer.

# ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01151.

Schematic representation of quasi-graphene/PVDF, EDS pattern of quasi-graphene/PVDF, conductivity plot of quasi-graphene/PVDF, STM image and line profile for the graphene/PVDF nanocomposite, pictorial depiction of conducting path formation in the graphene/PVDF nanocomposite, measurement scheme for piezo responses from the device along with the piezoelectric effect under loading conditions for the graphene/PVDF nanocomposite, circuit design for a solid-based resistor as well as graphene/PVDF-based resistor (PDF).

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Author Contributions
A.S. and P.S. conceived the idea; P.S. analyzed the data; and P.S. and S.A. conducted the experiments under the supervision of A.S. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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# REFERENCES

(1) Thakre, A.; Borkar, H.; Singh, B. P.; Kumar, A. Electroforming free high resistance resistive switching of graphene oxide modified polar-PVDF. RSC Adv. 2015, 5, 57406–57413.
(2) Sen, A.; Kaun, C.-C. Effect of Electrode Orientations on Charge Transport in Alkanedithiol Single-Molecule Junctions. ACS Nano 2010, 4, 6404–6408.
(3) Amutha, S.; Sen, A. Asymmetric Coulomb oscillation and giant anisotropic magnetoresistance in doped graphene nanojunctions. Appl. Surf. Sci. 2018, 449, 384–388.
(4) Kumar, N.; Bhauunik, S.; Sen, A.; Shukla, P.; Pathak, S. D. One-pot synthesis and first-principles elasticity analysis of polymorphic MnO2 nanorods for tribological assessment as friction modifiers. RSC Adv. 2017, 7, 34349–34418.
(5) Stadlober, B.; Zirkl, M.; Irimia-Vladu, M. Route toward sustainable smart sensors: ferroelectric polyvinylidene fluoride-based materials and their integration in flexible electronics. Chem. Soc. Rev. 2019, 48, 1787–1825.
(6) Gao, S.; Wu, X.; Ma, H.; Robertson, J.; Nathan, A. Ultrathin Multi-functional Graphene-PVDF Layers for Multidimensional Touch Interactivity for Flexible Displays. ACS Appl. Mater. Interfaces 2017, 9, 18410–18416.
(7) Singh, V.; Joung, D.; Zhai, L.; Das, S.; Khondaker, S. I.; Seal, S. Graphene based materials: Past, present and future. Prog. Mater. Sci. 2011, 56, 1178–1271.
(8) Choi, W.; Lahiri, I.; Seelaboyina, R.; Kang, Y. S. Synthesis of Graphene and Its Applications: A Review. Crit. Rev. Solid State Mater. Sci. 2010, 35, 52–71.
(9) Avouris, P.; Dimitrakopoulos, C. Graphene: synthesis and applications. Mater. Today 2012, 15, 86–97.
(10) Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, J. R.; Ruoff, R. S. Graphene and graphene oxide: synthesis, properties, and applications. Adv. Mater. 2010, 22, 3906–3924.
(11) Cooper, D. R.; D’Anjou, B.; Ghattamaneni, N.; Harack, B.; Hilke, M.; Horth, A.; Majlis, N.; Massicotte, M.; Vandsburger, L.; Whiteway, E.; Yu, V. Experimental review of graphene. J. Phys. Condens. Matter Phys. 2012, 1, 1–56.
(12) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-dimensional gas of massless Dirac fermions in graphene. Nature 2005, 438, 197–200.
(13) Li, X.; Zhu, Y.; Cai, W.; Borysiak, M.; Han, B.; Chen, D.; Piner, R. D.; Colombo, L.; Ruoff, R. S. Transfer of large-area graphene films for high-performance transparent conductive electrodes. Nano Lett. 2009, 9, 4359–4363.
(14) Weiss, N. O.; Zhou, H.; Liao, L.; Liu, Y.; Jiang, S.; Huang, Y.; Duan, X. Graphene: An Emerging Electronic Material. Adv. Mater. 2012, 24, 5782–5825.
(15) Shukla, P.; Amutha, S.; Sen, A. Exploring Functionalized Graphene Nanocomposites for Nanoscale Switching. Int. J. ChemTech Research 2015, 7, 874–877.
(16) Deepak, A.; Shukla, P.; Ganesan, V.; Shankar, P. Scrutinizing the properties of functionalized graphene based polymer nanocomposites for electronic devices. Mater. Today: Proc. 2016, 3, 2352–2357.
(17) Arjmand, M.; Sadeghi, S.; Khajehpour, M.; Sundararaj, U. Carbon Nanotube/Graphene Nanoribbon/Polyvinylidene Fluoride Hybrid Nanocomposites: Rheological and Dielectric Properties. J. Phys. Chem. C 2017, 121, 169–181.
(18) Whitener, K. E.; Sheehan, P. E. Graphene synthesis. Diamond Relat. Mater. 2014, 46, 25–34.
(19) Zhang, Y.; Zhang, L.; Zhou, C. Review of Chemical Vapor Deposition of Graphene and Related Applications. *Acc. Chem. Res.* 2013, 46, 2329–2339.

(20) Chua, C. K.; Pumera, M. Chemical reduction of graphene oxide: a synthetic chemistry viewpoint. *Chem. Soc. Rev.* 2014, 43, 291–312.

(21) Them, F. T.; Moloto, M. J.; Dikio, E. D.; Nyangiwe, N. N.; Kotsedi, L.; Maaza, M.; Khenfough, M. Synthesis and Characterization of Graphene Thin Films by Chemical Reduction of Exfoliated and InterCalated Graphite Oxide. *J. Chem.* 2013, 2013, 1–6.

(22) Guermoune, A.; Charri, T.; Popescu, F.; Sabri, S. S.; Guillemette, J.; Skulason, H. S.; Szkopek, T.; Siaj, M. Chemical vapor deposition synthesis of graphene on copper with ethanol, ethanol, and propanol precursors. *Carbon* 2011, 49, 4204–4210.

(23) Yao, Y.; Li, Z.; Lin, Z.; Moon, K. S.; Agar, J.; Wong, C. Controlled growth of multilayer, few-layer, and single-layer graphene on metal substrates. *J. Phys. Chem. C* 2011, 115, 5232–5238.

(24) Campos-Delgado, J.; Botello-Méndez, A. R.; Algarra-Siller, G.; Hackens, B.; Pardoen, T.; Kaiser, U.; Dresselhaus, M. S.; Charlier, J. C.; Raskin, J.-P. CVD synthesis of mono- and few-layer graphene using alcohols at low hydrogen concentration and atmospheric pressure. *Chem. Phys. Lett.* 2013, 584, 142–146.

(25) De Arco, L. G.; Zhang, Y.; Kumar, A.; Zhou, C. Synthesis, transfer, and devices of single- and few-layer graphene by chemical vapor deposition. *IEEE Trans. Nanotechnol.* 2009, 8, 135–138.

(26) Chen, Z.; Ren, W.; Liu, B.; Gao, L.; Pei, S.; Wu, Z.-S.; Zhao, J.; Cheng, H.-M. Bulk growth of mono- to few-layer graphene on nickel particles by chemical vapor deposition from methane. *Carbon* 2010, 48, 3543–3550.

(27) Zhong, X. Functionalization of Graphene and Dielectric Property Relationships in PVDF/graphene Nanosheets Composites. *Int. J. Electrochem. Sci.* 2018, 13, 1–13.

(28) Broadhurst, M. G.; Davis, G. T. Physical basis for piezoelectricity in PVDF. *Ferroelectrics* 1984, 60, 3–13.

(29) Kawai, H. The Piezoelectricity of Poly (vinylidene Fluoride). *Jpn. J. Appl. Phys.* 1969, 8, No. 975.

(30) Lovinger, A. J. Ferroelectric polymers. *Science* 1983, 220, 1115–1121.

(31) Wang, M.; Shi, J. H.; Pramoda, K. P.; Goh, S. H. Microstructure, crystallization and dynamic mechanical behaviour of poly(vinylidene fluoride) composites containing poly(methyl methacrylate)-grafted multiwalled carbon nanotubes. *Nanotechnology* 2007, 18, No. 235701.

(32) Yee, W. A.; Kotaki, M.; Liu, Y.; Lu, X. Morphology, polymorphism behavior and molecular orientation of electrospun poly(vinylidene fluoride) fibers. *Polymer* 2007, 48, 512–521.

(33) Thomas, P.; Satapathy, S.; Dwarakanath, K.; Varma, K. B. R. Dielectric properties of poly(vinylidene fluoride)/CaCu3Ti4O12 nanocrystal composite thick films. *EXPRESS Polym. Lett.* 2010, 4, 632–643.

(34) Wang, J.; Li, H.; Liu, J.; Duan, Y.; Jiang, S.; Yan, S. On the $\alpha \rightarrow \beta$ Transition of Carbon-Coated Highly Oriented PVDF Ultrathin Film Induced by Melt Recrystallization. *J. Am. Chem. Soc.* 2003, 125, 1496–1497.

(35) Ohigashi, H.; Koga, K. Ferroelectric Copolymers of Vinylidenefluoride and Trifluoroethylene with a Large Electromechanical Coupling Factor. *Jpn. J. Appl. Phys.* 1982, 21, L455–457.

(36) Nandi, A. K.; Mandelkern, L. The influence of chain structure on the equilibrium melting temperature of poly(vinylidene fluoride). *J. Polym. Sci., Part B: Polym. Phys.* 1991, 29, 1287–1297.

(37) Lovinger, A. J. Ferroelectric Polymers. *Science* 1983, 220, 1115–1121.

(38) Fujisaki, S.; Ishihara, H.; Fujisaki, Y. Low-Voltage Operation of Ferroelectric Poly(vinylidene fluoride-trifluoroethylene) Copolymer Capacitors and Metal-Ferroelectric-Insulator-Semiconductor Diodes. *Appl. Phys. Lett.* 2007, 90, No. 162902.

(39) Fan, P.; Wang, L.; Yang, J.; Chen, F.; Zhong, M. Graphene/ poly (vinylidene fluoride) composite with high dielectric constant and low percolation threshold. *Nanotechnology* 2012, 23, No. 365702.