Composites Science and Technology 164 (2018) 282–289

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Pressure-crystallized piezopolymer/ionomer/graphene quantum dot composites: A novel poling-free dynamic hybrid electret with enhanced energy harvesting properties

Chenwen Xu[a,1], Long Jin[a,1], Lei Zhang[a,1], Chuanfeng Wang[a], Xi Huang[a], Xuebing He[a], Yali Xu[a], Rui Huang[b], Chaoliang Zhang[c], Weiqing Yang[a,**], Jun Lu[a,*,2]

[a] Key Laboratory of Advanced Technologies of Materials, Ministry of Education, School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, Sichuan, China
[b] College of Polymer Materials Science and Engineering, Sichuan University, Chengdu 610065, Sichuan, China
[c] State Key Laboratory of Oral Diseases, West China Hospital of Stomatology, Sichuan University, Chengdu 610041, China

ARTICLE INFO

Keywords:
A. Polymer-matrix composites (PMCs)
A. Smart materials
B. Electrical properties

ABSTRACT

We report the design and fabrication of a novel self-powered poling-free dynamic electret by hybridizing a piezocomposite with graphene quantum dots (GQDs). The polymeric hybrid piezoelectret was prepared through the solution casting of a ternary poly (vinylidene fluoride) (PVDF)/Nafion/GQD composite followed by pressure crystallization. During the fabrication, Nafion ionomer filled PVDF cells, resulting in the formation of artificial macroscopic dipoles, and GQDs induced the self-assembly of macromolecular chains in PVDF cell walls, leading to the growth of piezoelectric nanowires. The synergistic action of the man-made macroscale dipoles of Nafion and the inherent molecular dipoles of PVDF cells, together with the deformation and relaxation of the in situ formed polar crystalline polymeric nanowires, enabled the PVDF/Nafion/GQD composites to convert kinetic mechanical energy into electricity with remarkably enhanced efficiency. Compared with its PVDF/Nafion counterpart, the electrical output of a developed PVDF/Nafion/GQD nanogenerator, without any treatment of electrical poling, achieved considerable increase in both short-circuit current and open-circuit voltage, and showed better stable and durable performance for more than 20000 continuous working cycles. Particularly, the PVDF/Nafion/GQD composite also exhibited more improved mechanical-to-electrical conversion even if it has endured a long-term brine disposal. The study presented herein may open a new avenue for the manufacturing of a new class of electret-transducer materials that permit applications in powering autonomous micro-/nano-systems with high operational and environmental stability.

1. Introduction

Mechanical energy, existing in different forms, such as human motion, vibration, water flowing, and so on, is prevalent and available everywhere we live. The development of new energy harvesting techniques, scavenging the renewable and ubiquitously distributed mechanical energy from ambient environment and then converting it into electricity, is of great significance for the sustainability of modern society [1–4]. Since the first zinc oxide nanowire-based generator was demonstrated [1], various nanogenerators, with different structures and functions, have been developed for efficient mechanical-to-electrical conversion, primarily through the utilization of two effects: piezoelectricity and triboelectricity [2,4–6]. Of the current materials in the assembling of piezoelectric generators, piezopolymers, including bulk piezopolymers, piezocomposites and voided charged polymers [6], have attracted a great amount of attention, mainly due to their adequate mechanical strength, easy processing, high chemical resistance and diverse flexibility for sophisticated design and integrated applications [2,5–18].

Voided charged polymers, also called piezoelectret or ferroelectret, are morphologically cellular-structured polymer films, and their piezoelectricity originates from dimensional changes of man-made

* Corresponding author.
** Corresponding author.
E-mail addresses: wqyang@swjtu.edu.cn (W. Yang), junluprc@hotmail.com (J. Lu).
[1] These authors equally contributed to this work.
[2] Other used names Jun Lv and Jun Lyu.

https://doi.org/10.1016/j.compscitech.2018.06.010
Received 9 April 2018; Received in revised form 4 June 2018; Accepted 9 June 2018
Available online 12 June 2018
0266-3538/

macroscopic dipoles, formed through the high-voltage-induced microplasma discharge of the gas in the inner voids [6–11]. Compared with other types of piezopolymers, the foamed piezoelectret exhibits a number of advantages, such as large piezoelectric d_{33} coefficient and low acoustic impedance, and has been demonstrated to be highly efficient as energy harvester materials [8–11]. However, the formation of the piezoelectret foams is relatively complex, involving a chemical/physical process in which biaxial stretching of polymers forms lens-like voids [6–11]. Also, the long-term stability of the piezoelectrets is of concern, especially for these operations in volatile harsh environments [6–11]. Another notable disadvantage for voided charged polymers, being the same with other state-of-the-art piezopolymers, is that achieving their piezoelectricity inevitably requires a rigorous high-voltage electrical poling, which results in substantial additional power consumption and sometimes electrical breakdown of the samples [2,6–11].

Graphene quantum dots (GQDs), nanometer-sized fragments of graphene, exhibit a myriad of alluring physiochemical properties, due mainly to their quantum confinement and edge effects [19–21]. The 2D GQDs are more environmental friendly if compared with conventional semiconductor QDs such as CdTe and PbS, and remain mechanically and chemically stable and highly conductive at the scale of a few benzene rings [19–21]. Being considered as the next big small things, GQDs have gained tremendous attention for their enormous potentials in bioimaging, optical sensing, micro/nano-electronics and energy storage/conversion [19–21]. Nevertheless, the research is still at the early stage, and developing advanced strategies in creating novel functional GQD-based nanomaterials persists as an important challenge for further applications [19–21].

To overcome the main shortcomings of voided charged polymers, we recently developed a void-filled piezoelectret by filling the holes of a piezopolymer, poly (vinylidene fluoride) (PVDF), with a solid perfluorosulfonate ionomer, Nafion [22]. The PVDF/Nafion based generator has demonstrated outstanding properties in kinetic energy harvesting. Its open-circuit voltage output density reached 14.6 V cm^{-2}, exceeding that of most of current piezoelectric polymers reported to date.

Herein, PVDF/Nafion composite was hybridized with GQDs. This leads to the design and fabrication of a novel poling-free dynamic hybrid electret, with further improved efficiency in mechanical-to-electrical conversion. Compared with the conventional voided charged polymers, the PVDF/Nafion/GQD based composite showed more advantages in its fabrication easiness, energy conversion efficiency and long-term operational stability and durability in complex environments. Particularly, its piezoelectric response was achieved without any electrical poling treatment.

Fig. 1 schematically describes the composite structure and working mechanism of the PVDF/Nafion/GQD based dynamic hybrid piezoelectret generator (PNGDPG). The piezoelectret composes of GQD hybridized cellular PVDF with its cells filled by Nafion, prepared through the solution casting of a PVDF/Nafion/GQD blend followed by high pressure crystallization. Nafion ionomer, with its proton transport enabled by the dissociation and separation of cations (protons) and anions (sulfonic anions), forms artificial macroscopic dipoles, and pressure crystallization promotes the yielding and orientation of β form crystallites in PVDF. Moreover, GQDs induce the high pressure self-assembly of molecular chains in PVDF cell walls, and lead to the growth of piezoelectric nanowires. Distinct from those traditional piezoelectrets, initially there is no charge on the surfaces of the PNGDPG. The man-made solid dipoles of Nafion remains dormant until activated in PVDF cells. They begins to work only when the polar crystalline PVDF cell networks, together with the in situ formed piezoelectric nanowires, deform and relax under the stimulus of a dynamic mechanical force. The mechanical stimulation initiates voltage creation and accumulation on both sides of PNGDPG, due mainly to the piezoelectric responses of PVDF, and then the generated potential enables the movement and distribution of the mobile ions in Nafion. Afterwards, the synergistic action of the active macroscale dipoles of Nafion and the inherent molecular dipoles of PVDF cells, together with the involvement of the PVDF nanowires by their deformation and relaxation, make the PNGDPG capable of converting kinetic mechanical energy into electricity stably and durably.

Compared with its PVDF/Nafion counterpart, the developed PVDF/Nafion/GQD nanogenerator, without any treatment of electrical poling, demonstrated more enhanced mechatronic efficiency. This is mainly attributed to the GQD induced nanowire structures that may exhibit flexibility and ability in mechanical-to-electrical conversion. Besides, PVDF/Nafion/GQD-based generator showed good durability, and its electrical output performance could be further improved by increasing the ion concentration in composite matrix.

2. Experimental part

Nafion® solution, 5 wt% Nafion® 117 in water and alcohol, was supplied by DuPont. PVDF powder, commercial-grade Solef 6010, was acquired from Solvay Co., Ltd, Belgium. GQDs, possessing 1–5 layers of graphene, 1–2 nm thickness and 5–15 nm lateral dimensions, with 80–90 at.% C and 10–20 at.% O/N, were provided by Shanghai Simbatt Energy Technology Co., Ltd, and used as received. An analytical grade N, N-dimethylformamide (DMF) was provided by Chengdu Kelong Chemical Co.,Ltd, and used as received. A schematic illustration for the mixing process of the composite components is shown in Fig. 2a. Nafion

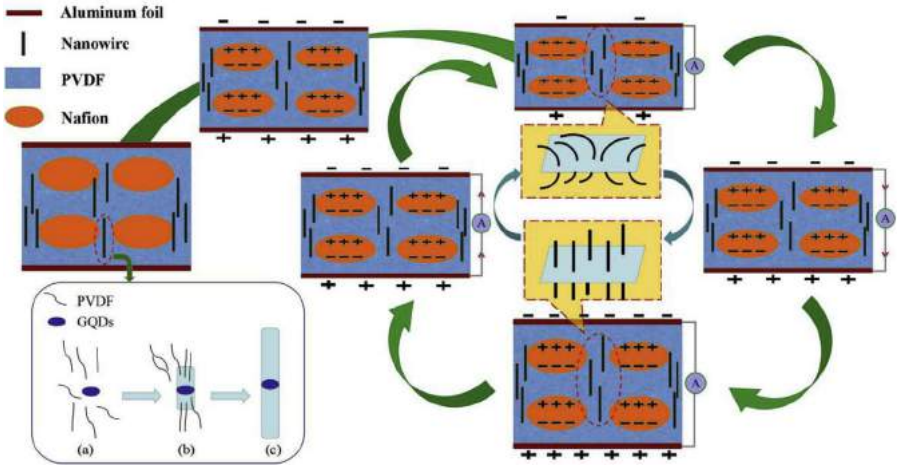

Fig. 1. Schematic drawing of the composite structure and working mechanism for a PVDF/Nafion/GQD dynamic piezoelectret generator (PNGDPG).

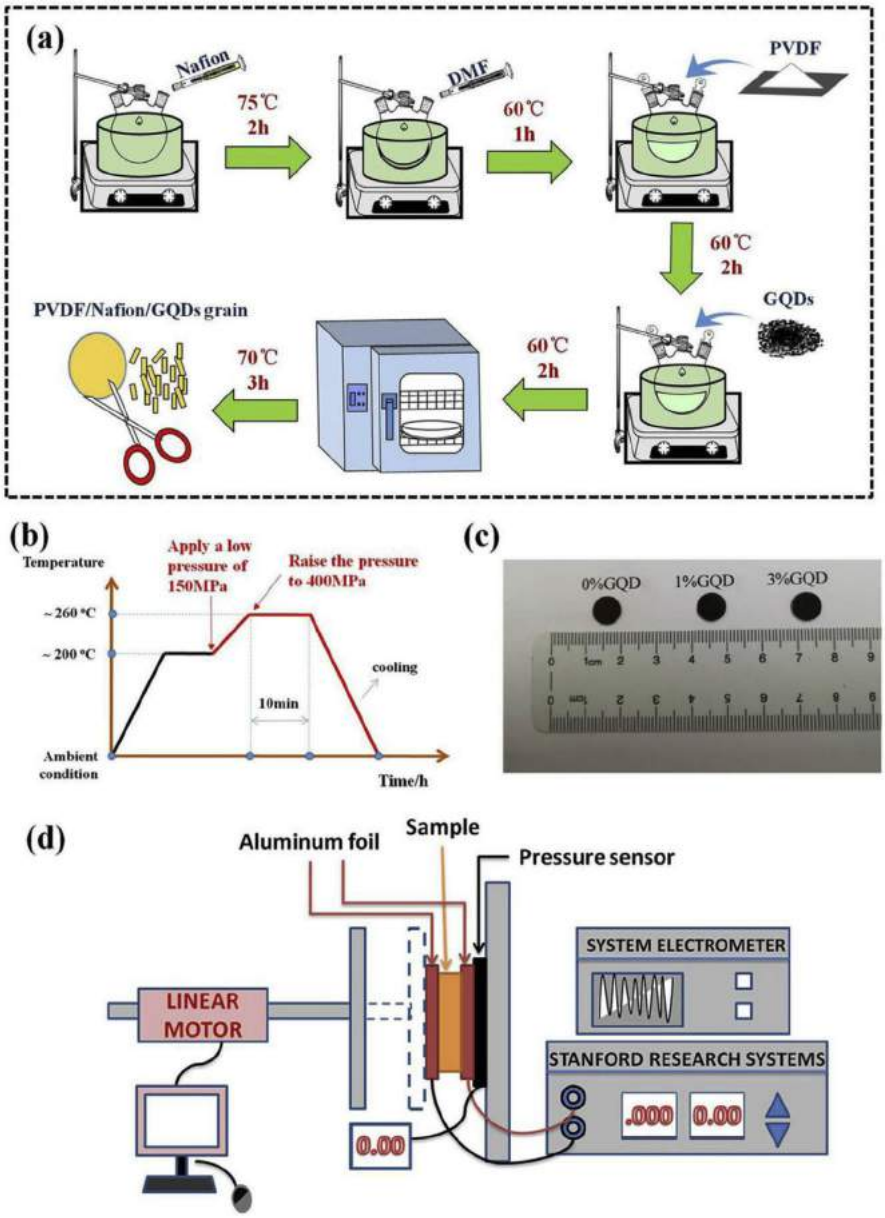

Fig. 2. Schematic diagram illustrating the mixing process of PVDF, Nafion and GQD (a), the experimental procedure in fabricating the PVDF/Nafion/GQD dynamic piezoelectret (PNGDP) with a piston-cylinder high-pressure apparatus (b), a digital picture showing the physical size and appearance of the as prepared PNGDP samples (c), and the schematic representation of the impact measurement system for concurrently collecting the generated electrical potential and current outputs (d).

solution was first heated up to evaporate solvent at 75 °C for 2 h, and then dissolved by DMF at 60 °C for 1 h. After that, PVDF and GQDs were respectively added in the reformed solution with mechanical stirring for 2 h. Subsequently, PVDF/Nafion/GQD solution were coated on glass substrates, and dried in a vacuum oven at 70 °C for 3 h to remove the DMF solvent. Finally, the dried PVDF/Nafion/GQD blend films were detached and pelletized for the following high pressure crystallization.

High-pressure experiments for the PVDF/Nafion/GQD composites were carried out with a self-made piston-cylinder apparatus [26], and the experimental procedure was schematically illustrated in Fig. 2b. Three specimens were prepared by varying GQDs concentration but with a fixed PVDF/Nafion composition, with a consistent column aspect, 8.04 mm in diameter and 0.50 mm in thickness, as shown in Fig. 2c.

Transmission electron microscopy (TEM) detections were performed with a JEOL JEM-2100F apparatus. Differential scanning calorimetry (DSC) measurements were conducted at atmospheric pressure by using a TA-Q20 instrument. Wide-angle X-ray diffraction (WAXD) results were obtained at room temperature with a DX-1000 diffractometer. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) data were obtained by using a Nicolet 5700 spectrometer. After the WAXD and ATR-FTIR characterizations, the sample surfaces were etched, and then coated with gold for scanning electron microscopy (SEM) observations with a JSM-6330F apparatus.

The energy harvesting performance of the developed hybrid piezoelectret nanogenerators were evaluated by a periodic impacting test, with an experimental setup schematically described in Fig. 2d. The generated open-circuit voltage and short-circuit current, were collected using a Keithley 6514 system electrometer and a Stanford Research SR570 low-noise current preamplifier, respectively, with a NTI AG HS01-37 × 166 linear motor as the impact source.

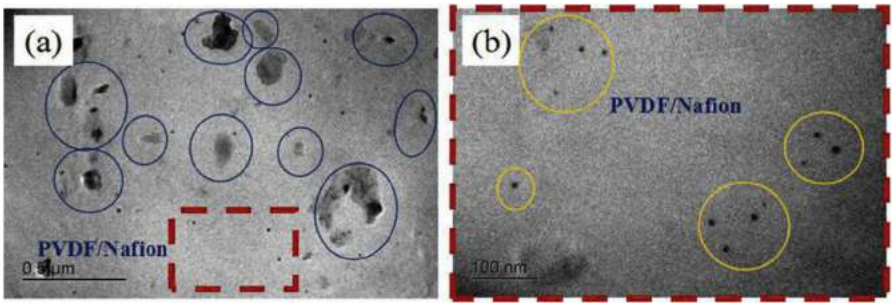

Fig. 3. TEM photographs of the as fabricated PVDF/Nafion/GQD composite sample with 3.0 wt-% GQD loading, just before the applied high-pressure treatment. (b) is a magnified view of the portion highlighted by the red frame in (a). PVDF/Nafion: 60/40, wt/wt. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3. Results and discussion

Fig. 3 gives out the typical TEM photographs of the as fabricated PVDF/Nafion/GQD composite with 3 wt.-% GQDs concentration, prior to the treatment by high pressure. As can be seen, the GQDs intrinsically tend to aggregate, and GQDs agglomerations, with size distributed from several tens of nanometers to a hundred nanometers, were formed during the composite fabrication (Fig. 3a). Nevertheless, still many GQDs were dispersed in the polymer matrix with their size less than ten nanometers (Fig. 3b).

Fig. 4a shows the DSC curves of the PVDF/Nafion/GQD samples with various GQD concentrations, crystallized at 400 MPa, 260 °C for 10min. Multiple melting peaks were observed for the composite samples, with and without GQDs incorporation, suggesting alterations of crystalline forms, morphologies and substructures occurred, tuned by the variation of the GQD loadings at high pressure. Particularly, the endotherms with higher melting points, emerging at around 200 °C, indicated polar extended-chain crystals of PVDF were formed in those samples [16]. WAXD and IR data, used for the identification of the crystalline phases of PVDF, are shown in Fig. 4b and c, respectively. The apparent single peak of orthorhombic β phase, at 2θ angle 20.4–21.1° (WAXD), coming from the superposition of the (110)β and (200)β reflections [16], were observed on the profiles of these pressure crystallized samples. The β-phase bands appear distinctly at peaks in 840 and 1280 cm^{-1} (IR), further confirmed large amounts of β phase crystals were formed in the samples.

Fig. 5 shows the typical SEM micrographs of the fractured cross sections of the high pressure crystallized PVDF/Nafion/GQD samples. The sample surfaces were etched before SEM observations, which removed Nafion, and subsequently revealed the PVDF cells, originally filled by this solid state ionomer (Fig. 5a, c and e). As shown by the high-magnification SEM images (Fig. 5b, d and f), extended-chain crystals with parallel striations were crystallized in the samples. Also, embedded in the PVDF cells, a few 1D β form nanowires of the polymer were observed in the sample with 1 wt.-% GQDs loading (Fig. 5d). More such piezoelectric nanowires were crystallized by increasing the GQDs loading to 3 wt.-% (Fig. 5f). In contrast, no nanowire was detected in the PVDF/Nafion sample without the introduction of GQDs (Fig. 5b). The growth of the PVDF nanowire structures may be attributed to a GQD-induced self-assembly at high pressure. The GQDs plays the role as a catalyst, and in situ catalyzed the assembly of the macromolecular chains in PVDF cells into nanowires [16–18].

The electrical outputs of the poling-free PNGDPG samples, developed with different GQDs concentrations, were measured under the stimulation of low frequency impacts. Herein, the different PNGDPGs are denoted as PNGDPG-0, 1 and 3, individually representing the samples without GQDs, with 1 wt.-% and 3 wt.-% GQDs loadings. Fig. 6 shows the generated open-circuit voltage and short-circuit current of the PNGDPGs at a stimulated frequency of 5 Hz and applied force of 60 N. The PNGDPG-0, 1 and 3 attained 50, 20 and 60 nA outputs for short-circuit current, and 3.2, 2.7 and 3.9 V output for open-circuit voltage, respectively. Compared with its PNGDPG-0 counterpart, although decreased electrical outputs were observed for PNGDPG-1, the PNGDPG-3 nanogenerator achieved 20% increase in current output and 25% increase in voltage output.

The variability in electrical outputs of the PNGDPGs should be ascribed to the GQDs controlled variation of the density, size, morphology, crystalline form and substructure of the PVDF cells as well as the dielectric performance of the composite matrices. For PNGDPG-1, piezoelectric nanowires were formed in situ (Fig. 5 c and d), and they further improved the piezoresponse of the nanogenerator. Nevertheless, the nanowires at the same time reinforced the PVDF cells, and increased their modulus. This subsequently reduced the dimensional changes of the inside artificial dipoles of Nafion during the composite deformation. Also, the introduced electrically conducting GQDs may change the dielectric properties of the composite [23]. It may become conductive at relatively low filler loading, and then electrostatic screening occurred, due mainly to its special foamed structure [23–25]. In this case, the piezoresponse enhanced by the limited amounts of nanowires was not strong enough to counteract the electrical output weakened by the modulus increase and electrostatic screening. As a result, PNGDPG-1 showed more decreased electrical output than PNGDPG-0. For PNGDPG-3, a large amounts of nanowires were crystallized in PVDF cells (Fig. 5 e and f), and the situation was completely different. The deformation and relaxation of sufficient piezo-nanowires, with their unique structures exhibiting high flexibility and sensitivity to

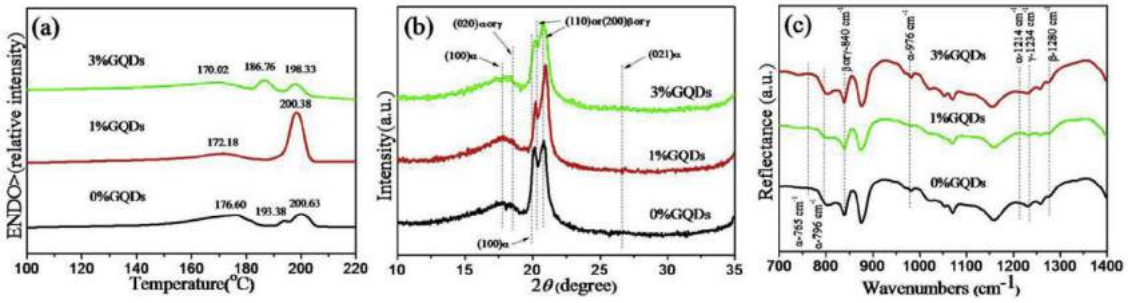

Fig. 4. DSC (a), WAXD (b) and ATR-FTIR (c) results of the PVDF/Nafion/GQD composite samples with different GQD concentrations, crystallized at 400 MPa, 260 °C for 10 min. PVDF/Nafion: 60/40, wt/wt.

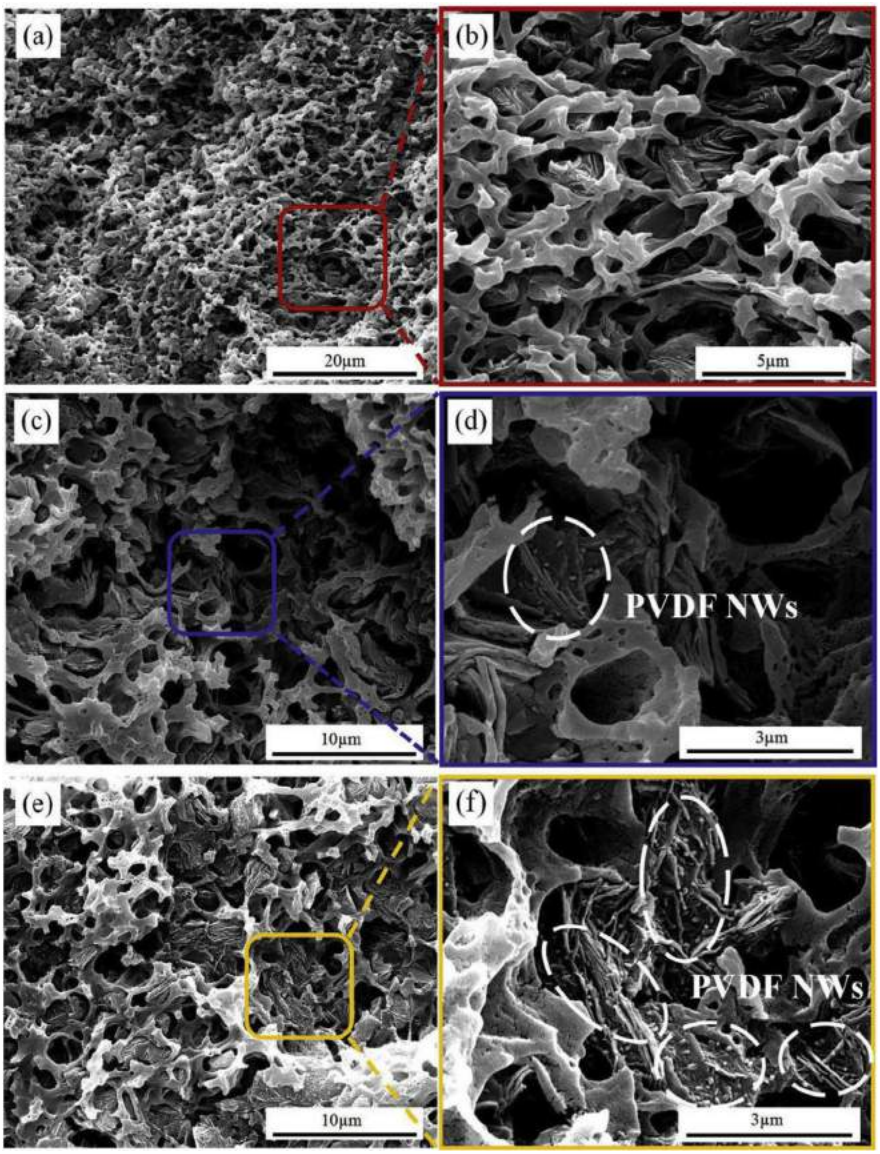

Fig. 5. Cross-sectional view of the SEM images of the PVDF/Nafion/GQD composite samples with 0 wt.-% (a–b), 1.0 wt.-% (c–d) and 3.0 wt.-% (e–f) GQD loadings, respectively, crystallized at 400 MPa, 260 °C for 10 min (b), (d) and (f) are magnified views of the portions highlighted by the square frames in (a), (c) and (e), respectively. PVDF/Nafion: 60/40, wt/wt.

mechanical stimuli, not only offset the negative effect from modulus increase and electrostatic screening, but also achieved a synergistic effect with the actions of the man-made macroscale dipoles of Nafion and the inherent molecular dipoles of PVDF cells, and then enabled PNGDPG-3 to convert mechanical energy into electricity with more enhanced efficiency.

The ionic conductivity of Nafion stems from the mobility of hydrated cations and water through the polymer matrix, and is directly related to the state of hydration [26]. The PNGDPGs were further soaked in a 10 wt.-% NaCl aqueous solution for 20 h, and then removed for the reevaluation of their energy harvesting performance. As shown in Fig. 7a and b, compared with their unsoaked counterparts, the electrical outputs of the NaCl-soaked PNGDPGs were much improved. The NaCl-soaked PNGDPG-0, 1 and 3 realized 60, 60 and 85 nA outputs for short-circuit current, and 3.9, 3.3 and 5.0 V output for open-circuit voltage, respectively. By a brine disposal process, all the PNGDPGs achieved more than 20% further increase for both current and voltage outputs. This may be attributed to the increase of ion content in the PNGDPG samples. During the NaCl disposal, more water and ions were permeated in the PNGDPGs, which increased the ionic conductivity in the Nafion fillers and subsequently accelerated the overall macroscopic dipole movements. The zoom-in views of one-cycle electrical curves of the brine-soaked PNGDPGs are similar to those of the unsoaked ones: a current pulse has positive and negative peaks, and a voltage pulse has large positive peak and negligible negative peak (Fig. 7c and d). This suggested ionic concentration increase in polymer matrix did not affect the capacitance characteristics of such GQDs hybridized piezoelectret.

Sustained operational performance is critically important for the real applications of piezoelectric nanogenerators. The long-term stability and durability of the PNGDPGs were confirmed for both original and brine disposed samples, and the results of the short-circuit current as a function of hitting cycles are illustrated in Fig. 8. All the PNGDPG samples were continuously hit for more than 20000 cycles at a stimulated force of 60 N and frequency of 1.4 Hz. In the beginning, the short-circuit current outputs of the PNGDPGs, whether untreated or treated with NaCl solution, decreased slightly with the increase of the hitting cycles. Nevertheless, as the tests went on, this downward trend was gradually diminished. After the periodic impacts exceeded 10000 cycles, The PNGDPGs showed excellent stability and durability in electrical outputs. The current outputs kept stable for the next 10000 cycles,

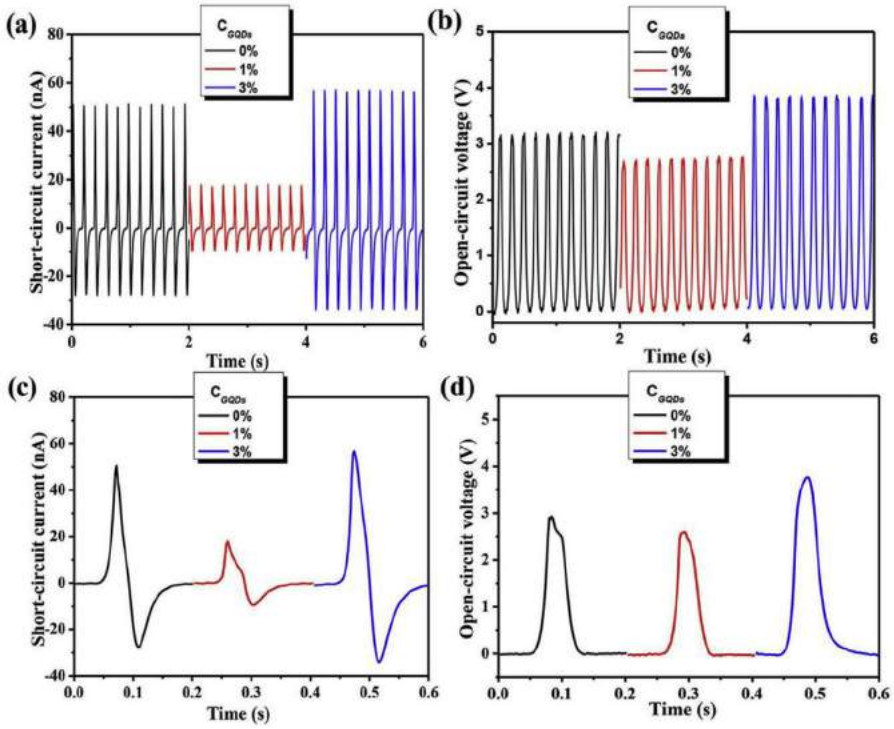

Fig. 6. Electrical outputs of the PNGDPGs with different concentration of GQD: (a) short-circuit current and (b) related open-circuit voltage, respectively, generated at a stimulated frequency of 5 Hz and applied force of 60 N; (c) short-circuit current and (d) corresponding open-circuit voltage output signals detected in a single press-and-release cycle.

and no performance degradation was observed when the tests were terminated. We noted that PNGDPG-3 exhibited better stable and durable performance, with its electrical output much higher than that of PNGDPG-0 in each testing cycle. The durability tests for the NaCl-soaked PNGDPGs also revealed that the GQDs hybridized piezoelectrets were actually with high environmental tolerance, as they demonstrated more improved mechanical-to-electrical conversion even if they have endured a long-term brine disposal.

4. Conclusion

In summary, we further improved the mechanical-to-electrical conversion efficiency of a voided-filled piezoelectret by introducing GQDs into PVDF/Nafion matrix, which also led to the design and fabrication of a novel poling-free dynamic hybrid electret. Compared to its PVDF/Nafion counterpart, the PVDF/Nafion/GQDs based nanogenerator, without any electrical poling treatment, achieved about 20% increase in short-circuit current output and 25% increase in open-circuit voltage output. The improvement was attributed to the GQD-

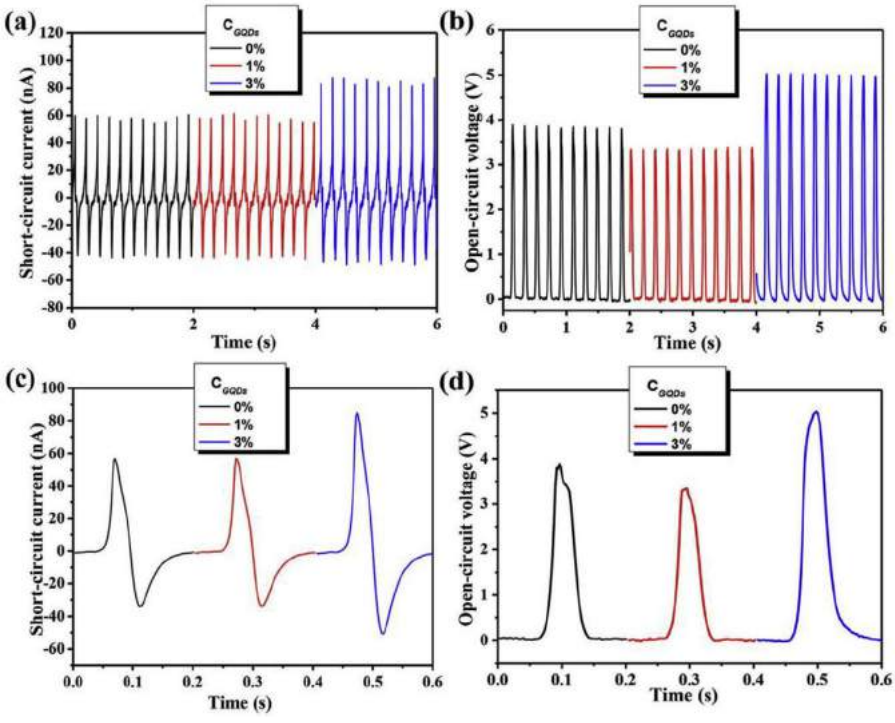

Fig. 7. Electrical outputs of the same PNGDPGs used in Fig. 6, just after being soaked in a 10 wt.-% NaCl aqueous solution for 20 h: (a) short-circuit current and (b) related open-circuit voltage, respectively, generated at a stimulated frequency of 5 Hz and applied force of 60 N; (c) short-circuit current and (d) corresponding open-circuit voltage output signals detected in a single press-and-release cycle.

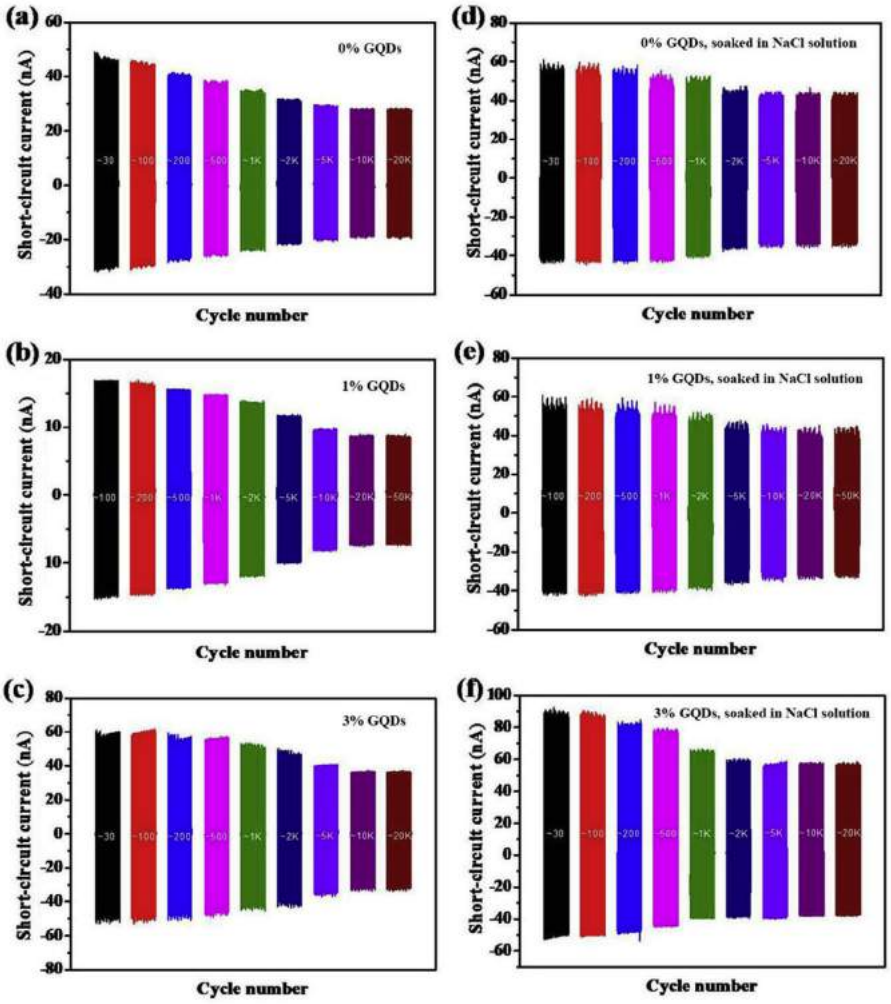

Fig. 8. Stability and durability test of the PNGDPGs with various GQD concentration: (a–c) output current-time curves for more than 20000 continuous working cycles just after the fabrication of the samples; (d–e) output current-time curves for more than 20000 extra continuous working cycles of the same samples, which has been soaked in a 10 wt.-% NaCl aqueous solution for 20 h since the test in (a) was performed; whole signal, stimulated by a 1.4 Hz 60 N impact.

induced piezoelectric nanowire structures in PVDF cells, which further realized a synergistic action with artificial macroscale dipoles of Nafion and inherent molecular dipoles of PVDF, and then exhibited excellent flexibility and ability to convert mechanical energy into electric energy. Besides, PVDF/Nafion/GQDs based nanogenerator showed better long-term stability and durability, and its electrical outputs were improved further by increasing the ionic concentration in composite matrix. Considering its simple fabrication, efficient energy conversion and high durability, we believe the as developed PVDF/Nafion/GQDs based hybrid piezoelectret, with a new working mechanism, may provide a promising and robust platform for self-powered applications that are able to efficiently harness kinetic energy from the all-pervading mechanical movements.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51373139), Sichuan Science and Technology Program (No. 2018JY0166) and Technological Projects for Distinguished Young Scholars of Sichuan Province (No.2015JQ0013). The authors extended their gratitude to Professor Yajiang Huang (Sichuan University) for valuable discussions.

References

[1] Z.L. Wang, J. Song, Piezoelectric nanogenerators based on zinc oxide nanowire arrays, Science 163 (2006) 242–246.
[2] F.R. Fan, W. Tang, Z.L. Wang, Flexible nanogenerators for energy harvesting and self-powered electronics, Adv. Mater. 28 (2016) 4283–4305.
[3] J. Chen, Y. Huang, N.N. Zhang, H.Y. Zou, R.Y. Liu, C.Y. Tao, X. Fan, Z.L. Wang, Micro-cable structured textile for simultaneously harvesting solar and mechanical energy, Nat. Energy 1 (2016) 16138.
[4] H.J. Kim, J.H. Kim, K.W. Jun, J.H. Kim, W.C. Seung, O.H. Kwon, J.Y. Park, S.W. Kim, I.K. Oh, Silk nanofiber-networked bio-triboelectric generator: silk bio-TEG, Adv. Energy Mater. 6 (2016) 1502329.
[5] M.M. Abolhasani, K. Shirvanimoghaddam, M. Naebe, PVDF/graphene composite nanofibers with enhanced piezoelectric performance for development of robust nanogenerators, Compos. Sci. Technol. 138 (2017) 49–56.
[6] K.S. Ramadan, D. Sameoto, S. Evoy, A review of piezoelectric polymers as functional materials for electromechanical transducers, Smart Mater. Struct. 23 (2014) 033001.
[7] W. Wirges, M. Wegener, O. Voronina, L. Zirkel, R. Gerhard-Multhaupt, Optimized preparation of elastically soft, highly piezoelectric, cellular ferroelectrets from nonvoided poly (ethylene terephthalate) films, Adv. Funct. Mater. 17 (2007) 324–329.
[8] N. Wu, X. Cheng, Q. Zhong, J. Zhong, W. Li, B. Wang, B. Hu, J. Zhou, Cellular polypropylene piezoelectret for human body energy harvesting and health monitoring, Adv. Funct. Mater. 25 (2015) 4788–4794.
[9] J. Hillenbrand, P. Pondrom, G.M. Sessler, Electret transducer for vibration-based energy harvesting, Appl. Phys. Lett. 106 (2015) 183902.
[10] J.W. Zhong, Q.Z. Zhong, X.N. Zang, N. Wu, W.B. Li, Y. Chu, L.W. Lin, Flexible PET/EVA-based piezoelectret generator for energy harvesting in harsh environments, Nano Energy 37 (2017) 268–274.
[11] X.C. Ma, X.Q. Zhang, P. Fang, Flexible film-transducers based on polypropylene piezoelectrets: fabrication, properties, and applications in wearable devices, Sensor

Actuat. A Phys. 256 (2017) 35–42.
[12] J. Lu, S.G. Kim, S. Lee, I.K. Oh, A biomimetic actuator based on an ionic networking membrane of poly (styrene-alt-maleimide)-incorporated poly (vinylidene fluoride), Adv. Funct. Mater. 18 (2008) 1290–1298.
[13] M.C. García-Gutiérrez, A. Linares, J.J. Hernández, D.R. Rueda, T.A. Ezquerra, P. Poza, R.J. Davies, Confinement-induced one-dimensional ferroelectric polymer arrays, Nano Lett. 10 (2010) 1472–1476.
[14] P. Martins, A.C. Lopes, S. Lanceros-Mendez, Electroactive phases of poly (vinylidene fluoride): determination, processing and applications, Prog. Polym. Sci. 39 (2014) 683–706.
[15] C.M. Wu, M.H. Chou, Polymorphism, piezoelectricity and sound absorption of electrospun PVDF membranes with and without carbon nanotubes, Compos. Sci. Technol. 127 (2016) 127–133.
[16] D.P. Zhang, P.F. Tian, X. Chen, J. Lu, Z.W. Zhou, X.M. Fan, R. Huang, Fullerene C60-induced growth of hollow piezoelectric nanowire arrays of poly (vinylidene fluoride) at high pressure, Compos. Sci. Technol. 77 (2013) 29–36.
[17] P. Tian, C. Xu, H. Huang, X. Chen, L. Zhao, J. Lyu, How about resurrecting the research of mechanically actuated robotic capsule endoscopy by designing novel pressure crystallised self-powering composite structures? Gut 65 (2016) A231.
[18] C. Lu, L. Zhang, C.W. Xu, Z.Z. Yin, S.B. Zhou, J.X. Wang, R. Huang, X.Q. Zhou, C.L. Zhang, W.Q. Yang, J. Lu, Self-powered graphene quantum dot/poly (vinylidene fluoride) composites with remarkably enhanced mechanical-to-electrical conversion, RSC Adv. 6 (2016) 67400–67408.
[19] L.A. Ponomarenko, F. Schedin, M.I. Katsnelson, R. Yang, E.W. Hill, K.S. Novoselov, A.K. Geim, Chaotic Dirac billiard in graphene quantum dots, Science 320 (2008) 356–358.
[20] S.J. Zhu, Y.B. Song, X.H. Zhao, J.R. Shao, J.H. Zhang, B. Yang, The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective, Nano Res 8 (2015) 355–381.
[21] X.T. Zheng, A. Ananthanarayanan, K.Q. Luo, P. Chen, Glowing graphene quantum dots and carbon dots: properties, syntheses, and biological applications, Small 11 (2015) 1620–1636.
[22] C.W. Xu, L. Zhang, Y.L. Xu, Z.Z. Yin, Q. Chen, S.Y. Ma, H.H. Zhang, R. Huang, C.L. Zhang, L. Jin, W.Q. Yang, J. Lu, Filling the holes in piezopolymers with a solid electrolyte: a new paradigm of poling-free dynamic electrets for energy harvesting, J. Mater. Chem. A 5 (2017) 189–200.
[23] J.C. Wang, J.L. Wu, W. Xu, Q. Zhang, Q. Fu, Preparation of poly(vinylidene fluoride) films with excellent electric property, improved dielectric property and dominant polar crystalline forms by adding a quaternary phosphorus salt functionalized graphene, Compos. Sci. Technol. 91 (2014) 1–7.
[24] Y.L. Yang, M.C. Gupta, K.L. Dudley, R.W. Lawrence, Novel carbon nanotube-polystyrene foam composites for electromagnetic interference shielding, Nano Lett. 5 (2005) 2131–2134.
[25] H. Pang, L. Xu, D.X. Yan, Z.M. Li, Conductive polymer composites with segregated structures, Prog. Polym. Sci. 39 (2014) 1908–1933.
[26] K.D. Kreuer, Ion conducting membranes for fuel cells and other electrochemical devices, Chem. Mater. 26 (2014) 361–380.