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

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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

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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

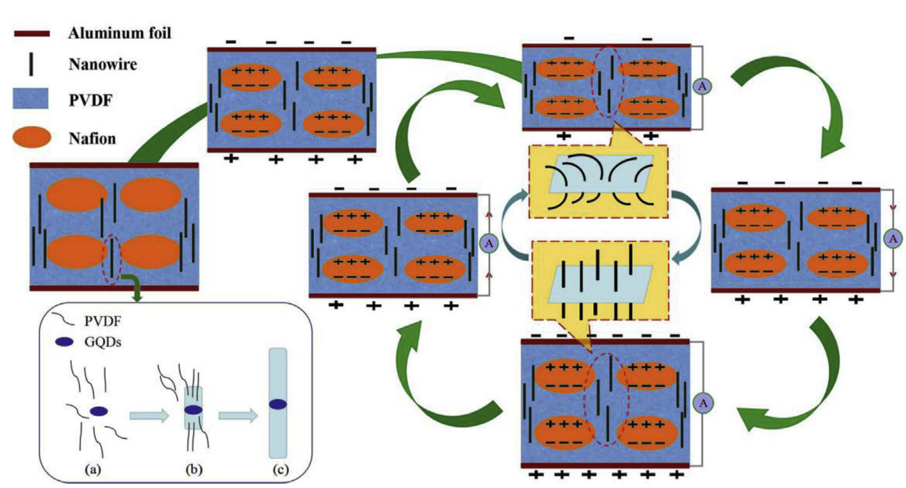


**Fig. 1.** Schematic drawing of the composite structure and working mechanism for a PVDF/Nafion/GQD dynamic piezoelectret generator (PNGDPG).