Nano Energy 32 (2017) 42–49

Contents lists available at ScienceDirect

Nano Energy

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

Ultrasensitive cellular fluorocarbon piezoelectret pressure sensor for self-powered human physiological monitoring

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ARTICLE INFO

Keywords:
Self-powered
Pressure sensor
Cellular
Piezoelectret
Physiological monitor

ABSTRACT

Flexible and wearable pressure sensors are of essential importance in developing artificial electronic skin (e-skin) for areas such as healthcare monitoring and clinical diagnosis. Here, we report an ultrasensitive cellular fluorocarbon piezoelectret pressure sensor (FPS) *via* a three-step hot-pressing method. By constructing micron-sized voids in the inner cell, and combination with outstanding charge storage ability of the fluorocarbon electrets, tremendous piezoelectric activity can be obtained. The flexible FPS showed advantages of remarkable sensitivity (7380 pC N^{-1}) in the subtle-pressure regime (< 1 kPa), fast response time (50 ms), very low limit of detection (5 Pa) as well as high stability (30,000 cycles). In addition, the flexible and self-powered FPS owns the capability for detecting human motions such as wrist stretching, cheek motion from open-bite-open, eyes blinking and chest respiration, respectively. It can be also used for monitoring human physiological signals such as radial artery pulse wave. By virtue of easy processability in large scale, light weight, and low cost, the FPS is especially suitable for mass production and flexible electronics, indicating their promising applications in artificial intelligence and mobile healthcare monitoring systems.

1. Introduction

Flexible and wearable pressure sensors are of essential importance for artificial electronic skin (e-skin) owing to the unique superiorities such as low-cost, light-weight, mechanical flexibility, and ultrasensitive capability to detect subtle pressure changes [1–7]. To meet the urgent demand for continuously personalized health/wellness monitoring, assessment and clinical diagnosis, additional requirements of skin compatibility, excellent stability, as well as low power consumption should be endowed to various intelligent sensing devices [8–14]. To date, pressure sensors based on various sensitive materials, such as micro/nanostructured polydimethylsiloxane (PDMS) [2], single-walled carbon nanotubes (SWCNTs) [4], Ge/Si nanowires [8], vertically aligned ZnO nanowire (NW) arrays [9], reduced graphene oxide (rGO) foam [15], polypyrrole (PPy) [16], polyvinylidene fluoride (PVDF) and its co-polymers [17,18], cellular polypropylene (PP) [19,20], and fluorocarbon polymers [21], *et al.*, have been successfully demonstrated in the last two decades. The basic working mechanisms of aforementioned pressure sensors include capacitance [4,22,23], organic field effect transistor (OFET)/thin film transistor (OTFT) [2,7,8,24], piezoresistivity [15,16,25–27], triboelectricity [28–31], and piezoelectricity [9,18,32]. It is noteworthy that most of the traditional pressure sensors are powered by batteries, which will lead to complex device structure and hinder their further applications for e-skin. Traditional piezoelectric materials with intrinsic polarity like ZnO NWs, lead zirconate titanate (PZT), prestigious PVDF and its co-polymers, suffer from some drawbacks including lower longitudinal piezoelectric coefficient (d_{33}), fragility, stiffness and high cost [33,34]. Recent emerging triboelectric pressure sensors based on the combination of triboelectric electrification and electrostatic induction may require sophisticated structural design to physically separate two different electron affinity materials [28–31].

Strikingly, space charged electret polymer with a cellular structure, also called piezoelectret or ferroelectret, which is a nonpolar material without any molecular dipoles, has been demonstrated to be highly efficient in charge storage and unexpected piezoelectricity when its inner voids were charged under a high electric field [35]. These novel piezoelectrets possess internal voids due to the cellular structure, which serve not only to reduce the polymer's Young modulus and hardness, but also to form macroscopic dipoles when charged to opposite

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http://dx.doi.org/10.1016/j.nanoen.2016.12.025
Received 6 November 2016; Received in revised form 13 December 2016; Accepted 13 December 2016
Available online 14 December 2016

polarities on their upper and lower internal surfaces. Once external pressure is exerted normal to its surface, these engineered internal dipoles are easily deformed, and large changes of their dipole moments may therefore be expected, which is the origin of the ultrahigh sensitivity [36,37]. Fluorocarbon polymers like polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP) with cellular structures are considered as new types of piezoelectrets, and have been proved to possess extraordinarily remarkable piezoelectric properties [38]. However, cellular structures are not easy to mediate due to their chemical inertness and insoluble characteristic. Although it is reported that multi-air voids can be introduced by fusing the films at high temperature upon application of mechanical pressure, additional vacuum process or structural nonuniformity is a major limitation [38,39]. Recently, we developed a hot-pressing method to fabricate composite electret using fibrous PTFE (f-PTFE) and compact FEP [21]. The two films were established easy to be cohesive by hot-pressing process as they both contain fluorine chemical bonds. In addition, low Young modulus of f-PTFE make it more sensitive to external stimulus.

Herein, we further demonstrated an ultrasensitive cellular fluorocarbon piezoelectret pressure sensor (FPS) *via* a simple three-step hot-pressing method. By constructing micron-sized voids in the inner cell, and combination with outstanding charge storage ability of the fluorocarbon electrets, tremendous piezoelectric activity can be obtained. The flexible FPS shows remarkable sensitivity (7380 pC N^{-1}) in the subtle-pressure regime (< 1 kPa), fast response time (50 ms), very low limit of detection (5 Pa) as well as high stability (30,000 cycles). In addition, the flexible FPS owns the capability for detecting human motions such as wrist stretching, cheek motion from open-bite-open, eyes blinking and chest respiration. It can be also used for monitoring human physiological signals such as radial artery pulse wave. By virtue of easy processability in large scale, light weight, and low cost, the FPS is especially suitable for mass production and flexible electronics, indicating their promising applications in artificial intelligence and mobile healthcare monitoring systems.

2. Material and methods

2.1. Fabrication of the Cellular FPS

In the first hot-pressing step, two layers of electrets, compact FEP (thickness of 50 μm, DuPont FEP50) and fibrous PTFE (f-PTFE, thickness of 25 μm, Shenzhen Gorest Technology Co. Ltd., porosity 60%), were stacked and hot pressed (120 °C, 10 MPa, 1–3 min) between two stainless steel plates (area 5×5 cm^2) to get the two-layer structured FEP/f-PTFE composite polymers. In the second hot-pressing step, the composite polymers were sandwiched between two patterned metal templates (area 5×5 cm^2) using a PDMS rubber (thickness of ~500 μm) as a buffer layer and hot-pressed (100 °C, 10 MPa, 1–3 min). In the third hot-pressing step, smaller pressure of 1 MPa and higher temperature of 280 °C were applied on the sandwiched FEP/f-PTFE, FEP, and FEP/f-PTFE films for ~5 min to make cellular structured composite fluorocarbon polymer. Then, negative corona charging was applied to generate macroscopic dipoles inside the cellular fluorocarbon polymer. Specifically, Samples were placed 5 cm beneath the corona needle under a high voltage −15 kV for 3 min. At last, a homogeneous FPS was obtained by metallizing silver electrodes onto both surfaces of the film using radio frequency magnetron sputtering method.

2.2. Measurement of quasistatic d_{33} Value

To study the quasistatic d_{33} of the FPS, a set of home-made device was designed, which consisted of an iron support stand, a weight (50 g, 0.49 N), and a computer-controlled Stanford low-noise current preamplifier (SR570). In our test, a force was applied on the sample by the weight and compressed the corresponding areas, resulting in transferred charges accumulation on both sides of the FPS. The quasistatic d_{33} can be obtained by using the transferred charges divided by the applied force.

2.3. Characterization

The morphology of samples was probed by a high-resolution field emission scanning electron microscope (FEI Nova NanoSEM 450). The corona charging system made up of a negative voltage DC power supply (DW-N503-4ACDE, Tianjin) and a corona needle. Silver electrodes onto both surfaces of the samples were fabricated by radio frequency magnetron sputtering method (JCP-600M4, Beijing, Technol).

2.4. Measurement

The electrical performance of the cellular FPS was measured using a SR570 and a NI PCI-6259. In the test, cellular FPS was mount vertically onto the fixed platform of a linear motor (RCH41×30D05A, Renishaw, Gloucestershire, U.K.), then a circular metal plate as the contact object was mount on the IMADA digital force gauge (Model ZPS-DPU-50N) to the other end of the linear motor controlled by PC for reciprocating motion.

3. Results and discussion

Fig. 1 shows the schematic illustration of the fabrication process of FPS, which can be summarized as a simple three-step hot-pressing method. Firstly, two layers of electrets, FEP and f-PTFE, were stacked together and hot pressed to get close adhesion (Fig. 1a and Fig. S1a). As well known, f-PTFE has superior charge storage ability due to the local defects such as chain breaks, double bonds, and free radicals in the fibrous structure [40]. However, the inner open holes will result in electrons migrating when electrodes are deposited on its surface [41]. Our two-layer FEP/f-PTFE composite polymers own an outer charge-impenetrable FEP layer, thus it can effectively capture positive or negative charges/ions in the interfaces between the compact FEP and f-PTFE. As illustrated in Fig. 1b and c, a second hot-pressing process with two patterned metal templates (size of 5×5 cm^2, Fig. S1b) and a PDMS rubber as a buffer layer was used to form concave structures on the composite polymers (Fig. 1d). From the digital image in Fig. S1c, it can be seen clearly that the composite polymers with concave structures were flexible and opalescent. The relatively high temperature of 100 °C was used for perpetual shaping the concave structures, which is vitally important in the fabrication of FPS. In the third hot-pressing step (Fig. 1e), smaller pressure was applied on the sandwiched FEP/f-PTFE, FEP, and FEP/f-PTFE films, to ensure the FFP/f-PTFE and FEP films strongly bonding without breaking the cellular structure [21]. Fig. 1i and j shows the cross-sectional scanning electron microscope (SEM) and digital image of the cellular structure, respectively. Macroscopic lens-shaped voids with thickness ~200 μm were formed inside the sandwiched cellular structure, which will result in low Young modulus and excellent piezoelectricity [37,40,42]. Moreover, negatively charged areas appeared brighter than the neutral background due to secondary electron emission in the SEM micrography, which is a clear evidence of the microdischarge phenomena inside the voids [37].

Then, the cellular fluorocarbon polymer was corona charged under a high voltage of 15 kV for 3 min (Fig. 1g). At this moment, the air inside the lens-shaped voids was broken down to generate positive and negative charges/ions. The charges/ions were then captured by the inside interface of the voids, forming the macroscopic dipoles. Finally, a homogeneous FPS was obtained *via* metallizing silver electrodes on both sides of the film by using radio frequency magnetron sputtering, as illustrated in Fig. 1k. Such a simple three-step hot-pressing fabrication process to prepare patterned cellular structure should be favorable for large-scale manufacturing.

To illustrate the working mechanism of the FPS, a finite-element