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Roles of carbon nanotube and $BaTiO_3$ nanofiber in the electrical, dielectric and piezoelectric properties of flexible nanocomposite generators

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ABSTRACT

We report the electrical, dielectric and piezoelectric properties of flexible PDMS-based nanocomposite generators, which are tunable by different contents of multi-walled carbon nanotube (MWCNT, 0.0–5.0 wt%) and $BaTiO_3$ nanofiber (10–50 wt%). The $BaTiO_3$ nanofiber with tetragonal structure was manufactured by an electrospinning and following calcination process. For the first series of nanocomposite generators with 30 wt% $BaTiO_3$ nanofiber and 0.0–5.0 wt% MWCNT, both electrical and dielectric properties were dramatically enhanced at a critical MWCNT content of 0.47 wt% owing to the formation of percolating networks of MWCNT in the presence of $BaTiO_3$ nanofibers, as verified by SEM analysis. Accordingly, the nanocomposite generator with 30 wt% $BaTiO_3$ and 5.0 wt% MWCNT achieved the highest conductivity of 0.12 S/cm and dielectric constant of 4474 at 1 kHz, whereas the nanocomposite generator with 30 wt% $BaTiO_3$ and 2.0 wt% MWCNT attained the best piezoelectric performance by harvesting average output voltage of ~3.00 V, current of ~0.82 μA, and power of ~0.14 μW. In cases of the second series of nanocomposite generators with 2.0 wt% MWCNT and 10–50 wt% $BaTiO_3$ nanofiber, the electrical conductivity and dielectric constant increased with the increment of $BaTiO_3$ content up to 40 wt%. Overall, the nanocomposite generator with 2.0 wt% MWCNT and 40 wt% $BaTiO_3$ nanofiber generated the highest average output voltage of ~3.73 V, current of ~1.37 μA, and power of ~0.33 μW, which was feasible to light up commercial LEDs and to charge a capacitor after rectification, revealing the potentiality in powering self-sufficient nanodevices and wireless electronics.

1. Introduction

Piezoelectric nanocomposite generators (PNGs) have gained tremendous attention from both industry and academia because they can harvest energy from mechanical actions to power electric devices instantly, which thus alleviates the energy crisis and environmental problems [1,2]. Nowadays, the widely known piezoelectric materials include lead zirconate titanate (PZT), barium titanate ($BaTiO_3$), zinc oxide (ZnO), zinc sulfide (ZnS), poly(vinylidene fluoride) (PVDF), etc. Among the piezoelectric materials, $BaTiO_3$ with high piezoelectric coefficient (149 pC/N) and dielectric constant (100–11000) is one of the most promising lead-free perovskite-structured materials [1,3–10].

To improve the piezoelectric property of PNGs, intensive efforts have been made by introducing nanofillers. Carbon nanotubes (CNTs) with excellent electrical and physical properties have been used abundantly as reinforcing fillers in composite materials to evaluate the effect of its content on various properties for a number of advanced applications [11,12]. The incorporation of CNTs in PNGs also plays an important role in the piezoelectric property for different reasons. Park et al. reported that a nanocomposite including 12 wt% $BaTiO_3$ nanoparticle and 1 wt% multi-walled carbon nanotube (MWCNT) achieved an increase of output voltage from 0.17 to 3.2 V under bending deformation due to better distribution of nanoparticles and stress enhancement by adding MWCNT [2]. Sun et al. reported that a nanocomposite containing 12 wt% ZnO nanoparticles and 1 wt% MWCNT exhibited significantly enhanced output voltage of 7.5 V owing to the presence of MWCNT serving as “nano-electrical bridge” between ZnO nanoparticles, compared with a nanocomposite with only ZnO nanoparticle (0.8 V) [13]. Ahn et al. and Hao et al. have investigated the

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effect of the MWCNT content on the piezoelectric properties of PVDF/MWCNT nanocomposites manufactured by an electrospinning process and have found that a dramatic increase in the β-phase crystal formation with higher MWCNT loadings due to the intense stretching of PVDF during the electrospinning [14,15]. It is thus considered that MWCNT serves as a nucleating agent for developing β-phase PVDF crystals during the electrospinning process as well as an electrical bridge among the piezoelectric PVDF crystals in the nanocomposites.

The amount of the piezoelectric materials is also an important factor influencing the piezoelectric performance of PNGs. Mahadeva et al. fabricated hybrid piezoelectric papers by attaching $BaTiO_3$ nanoparticles to the positively charged wood cellulose fibers via a strong electrostatic interaction prior to the process of making paper sheets [16]. Piezoelectric response of the hybrid paper was found to increase significantly with increment of $BaTiO_3$ loading. The effective piezoelectric coefficient, d_{33}, increased from 1.02 pC/N for the paper with 11 wt% $BaTiO_3$ to 4.8 pC/N for the paper with the highest nanoparticle loading of 48 wt% $BaTiO_3$. In case of P(VDF-TrFE)/$BaTiO_3$ composites, d_{33} also increased with the increment of the $BaTiO_3$ content, reaching a highest value of 32 pC/N at the $BaTiO_3$ content of 60 wt% [17].

In this study, the roles of $BaTiO_3$ nanofiber and MWCNT in the electrical, dielectric and piezoelectric properties of flexible nanocomposite generators were investigated. The $BaTiO_3$ nanofiber with tetragonal structure was manufactured via an electrospinning and following calcination process. Because $BaTiO_3$ nanofibers are brittle and they cannot be used solely, polydimethylsiloxane (PDMS) as a highly flexible silicone-based elastomer was adopted as the nanocomposite matrix. For the purpose, PDMS-based flexible PNGs with different contents of MWCNT (0.0–5.0 wt%) and $BaTiO_3$ nanofiber (10–50 wt%) were fabricated. The electrical, dielectric and piezoelectric properties of the flexible PNGs were then investigated systematically by taking into account the roles and contents of MWCNT and $BaTiO_3$ nanofiber in the PNGs. The harvested piezoelectric energy was also evaluated to light up commercial light-emitting diodes (LEDs) and to charge a capacitor after rectification.

2. Experimental

2.1. Preparation of $BaTiO_3$ nanofiber and piezoelectric nanocomposite generators (PNGs)

$BaTiO_3$ nanofibers were prepared by electrospinning a sol-gel precursor and following calcination process as described in literature [6,18]. Barium acetate (2.55 g, Sigma-Aldrich Com.), titanium butoxide (3.4 g, Sigma-Aldrich Com.), and 2,4-pentanedione (2.0 g, Samchun Pure Chemical Com.) were dissolved in acetic acid (6 ml, Samchun Pure Chemical Com.) by magnetic stirring for 24 h to form a homogeneous sol-gel precursor. Poly(vinyl pyrrolidone) (PVP, 1.0 g, Sigma-Aldrich Com.) was added into the solution to control the viscosity and stirred magnetically for 12 h. To fabricate precursor nanofibers, the sol-gel precursor solution was electrospun at a condition of voltage of 15 kV, tip-to-collector distance of 18 cm, extrusion rate of 1 ml/h, and collector rotating speed of 800 RPM. The fabricated precursor nanofibers were calcined to form $BaTiO_3$ ceramic nanofibers by increasing temperature stepwise to 1000 °C and finally holding at 1000 °C for 6 h.

To manufacture flexible PNGs with various $BaTiO_3$ nanofiber and MWCNT contents, predetermined amounts of MWCNT (CM-95, diameter of 10–15 nm, length of 10–20 μm, Hanwha Chemical) (0.0–5.0 wt%) and $BaTiO_3$ nanofiber (10–50 wt%) were dispersed ultrasonically in ethyl acetate for 1 h using a bath-type ultrasonicator (50–60 Hz). After adding PDMS (Sylgard 184 Silicone Elastomer Kit, Dow Corning) into ethyl acetate solutions, another ultrasonication was applied for 1 h. Subsequently, a curing agent (weight ratio of 1:10 to base paste) was added into the solutions, which were then poured into glass petri-dishes. After evaporating the solvent totally, composite pastes were casted on Scotch tape-coated glass substrates to be ~250 μm thick by a doctor-blade. Finally, the composites were cured on a hot plate at 100 °C for 12 h. The fabricated specimens were named as PDMS/$BaTiO_3$(X)/MWCNT(Y), where X and Y denote the relative contents of $BaTiO_3$ nanofiber and MWCNT in the PNGs by wt%, respectively, as summarized in Table 1. For an electric poling process, the PNGs were sandwiched by Aluminum foil-attached cover slides and poled under an electric field of 5 kV/mm for 12 h in a bath containing silicone oil (KF-96, Shin-Etsu Silicone Korea Co., Ltd) at ambient temperature. Then, electrically poled specimens were rinsed with ethanol to remove the silicone oil and Aluminum foil as an electrode was attached on the top and bottom sides of the PNGs.

2.2. Characterization

The morphological features of $BaTiO_3$ nanofiber and flexible PNGs were characterized by using a cold type field emission scanning electron microscope (SEM, S-4800, Hitachi). To obtain the SEM images, the fracture surfaces of the PNGs were coated with osmium conductive metal. The crystal structure of $BaTiO_3$ nanofiber was identified by a high performance X-ray diffractometer using Cu-Kα radiation (D/MAX-2200 Ultima/PC, Rigaku). The electrical current of the PNGs was measured as a function of applied voltage by using an electrometer (2400, Keithley Instruments). The frequency-dependent electrical and dielectric properties of the PNGs were measured by using a precision LCR meter (4980A, Agilent). The piezoelectric performance of the PNGs under a periodically applied finger pressure of 2 kPa was evaluated with aid of 7½-digit graphical sampling multimeter (Keithley Instruments).

3. Results and discussion

3.1. Structures of $BaTiO_3$ nanofiber

$BaTiO_3$ nanofibers were fabricated by an electrospinning of the precursor solution and following calcination process [19]. The SEM image and XRD pattern of Fig. 1(a)-(b) reveal that $BaTiO_3$ nanofibers with a tetragonal crystal phase, which are evident by the appearance of (002) and (200) reflections separated at $2\theta = \sim 45^\circ$, are well manufactured by the electrospinning and calcination process. To apply $BaTiO_3$ nanofibers into PDMS for manufacturing the flexible PNGs, an ultrasonication technique was adopted to disperse $BaTiO_3$ nanofibers in ethyl acetate initially, in which case $BaTiO_3$ nanofibers were broken randomly into short nanofibers as shown in the SEM image of Fig. 1(c). It was found that $BaTiO_3$ nanofibers have an average length of ~33.7 μm and an average diameter of ~354.1 nm, as represented in Fig. 1(d) and (e), respectively.

3.2. Role of MWCNT on structures and properties of PNGs

The cross-sectional SEM images (× 1000) of PNGs with 30 wt% $BaTiO_3$ nanofiber and different MWCNT contents of 0.0–5.0 wt% are shown in Fig. 2. Some pores detected in the images were formed by the pulling-out of $BaTiO_3$ nanofibers from the PDMS matrix, because the PNGs were fractured for SEM test. From the magnified cross-sectional SEM images (× 5000) of the PNGs. MWCNTs are found to be dispersed uniformly and randomly in the PDMS matrix