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Communication

Graphene enabled percolative nanocomposites with large electrocaloric efficient under low electric fields over a broad temperature range

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ABSTRACT

For practical electrocaloric (EC) cooling devices, besides a large electrocaloric effect (ECE), the EC coefficients, e.g., $\Delta T/\Delta E$ and $\Delta S/\Delta E$, where ΔT is the adiabatic temperature change, ΔE is the applied field change, and ΔS is the isothermal entropy change, are equally or even more important. An EC material with a large ECE and large EC coefficients will lead to practical EC cooling devices with high reliability. Here, we investigate a graphene enabled percolative relaxor polymer nanocomposite in order to address the challenge of how to generate a practically usable electrocaloric effect (ECE) under low electric field. We show that, through a proper fabrication process, the nanocomposites can reach a $\Delta T=5.2$ K and $\Delta S=24.8\ \mathrm{J\,kg^{-1}\,K^{-1}}$ under $40\ \mathrm{MV\,m^{-1}}$, generating a large electrocaloric coefficients of $\Delta T/\Delta E=0.13\times10^{-6}\ \mathrm{km\,V^{-1}}$ and $\Delta S/\Delta E=0.62\times10^{-6}\ \mathrm{J\,m\,kg^{-1}\,K^{-1}\,V^{-1}}$. The work here indicates the promise of the percolative nanocomposite approach with graphene nanofillers to achieve a highly efficient and large ECE in the EC polymers for practical EC cooling.

1. Introduction

When an electric field is applied to a dielectric material, it induces a change in the dipolar ordering. As a result, the temperature and/or entropy of the dielectric material will change, which is known as the electrocaloric effect (ECE) [1,2]. Recent advances in the polar-dielectrics that exhibit giant ECE, i.e., a large adiabatic temperature change (ΔT) and a large isothermal entropy change (ΔS), have attracted great interest in the electrocaloric (EC) solid state cooling technologies which are environmentally benign and have potential to reach higher energy efficiency compared with the traditional vapor compression based cooling technologies [3–6]. However, in developing EC materials with giant ECE, most efforts in the past several years have been devoted to the EC materials which can generate large ΔT and ΔS under high electric fields. This has led to several EC materials exhibiting so called giant ECE, however, requiring very high electric fields, not far from the dielectric breakdown of the materials. For example, in the EC polymers, $\Delta T>15$ K was obtained under high electric fields ($>150\ \mathrm{MV\,m^{-1}}$) [7]. In EC ceramics, similar level of ECE can only be obtained at very thin films ($<1\ \mu\mathrm{m}$) [8,9]. As a result, it is still a great challenge to develop practical EC cooling devices from these EC materials due to very high field required.

In contrast, a team consisting of BASF, Astraunautics, and Haier demonstrated recently a commercially magnetocaloric cooler, using magnetocaloric materials with $\Delta T=4$ K induced using permanent magnet and running in a regenerative refrigeration cycle [10]. Hence, in order to demonstrate practical EC cooling devices, besides a large ECE, it is equally or even more important to develop approaches for the EC materials to have large EC coefficients, e.g., large $\Delta T/\Delta E$ and $\Delta S/\Delta E$ [11–13]. For practical applications, an EC material with a good EC response (>4 K) induced under low electric fields will enable the realization of first practical EC cooling devices, reduce the device fabrication cost, and improve the device reliability. Moreover, the large EC coefficients also impact on the efficiency of EC cooling devices, which is directly related to Q/U_e of the EC material where $Q=T\Delta S$ and U_e is the total charging electric energy to the EC material.

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From the thermodynamic Landau–Devonshire (L–D) theory of a ferroelectric material, the isothermal entropy change ΔS and adiabatic temperature change ΔT due to ECE are,

$$\Delta S = -\frac{1}{2}\beta P^2 \tag{1a}$$

$$\Delta T = \frac{1}{2}T\beta P^2/C_E \tag{1b}$$

where P is the electric polarization and β is a coefficient, Eq. (1b) is from $C_E T = T\Delta S$, where C_E is specific heat [14–16]. Since ΔT and ΔS of an EC material is directly proportional to the square of the polarization change P, to achieve large EC coefficients $\Delta T/\Delta E$ and $\Delta S/\Delta E$ requires that a large polarization change be induced under a low electric field. This paper reports a nanocomposite approach, exploiting the percolation effect of graphene nanofillers, to significantly increase the polarization level under low electric fields in the relaxor ferroelectric poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) (P(VDF–TrFE–CFE)) terpolymer, thus generating an highly efficient and large ECE in the nanocomposites.

Percolative composites, composed of electrically conducting fillers and insulating matrix, are well known for raising the dielectric constant K markedly above that of the matrix K_m, at low nanofiller contents ($f < f_c$), see Eq. (2),

$$K = K_m f_c/(f_c - f)^q \tag{2}$$

where f is the filler content, f_c is the percolation threshold, and q is a critical exponent ($\sim$1 for a 3-dimensional composite) [17–19]. Earlier studies further show that besides the regular percolative effect enhanced dielectric response, the large dielectric contrast between the conductive nanofillers and polymer matrix generates interfacial effects [20–22]. Besides the dielectric response, the enhanced local fields at the interfacial regions in the matrix are also responsible for the large material responses such as the electromechanical (EM) response in several polymer nanocomposites [20–22]. Hence, in order to maximize the interfacial effects, nanofillers with large specific surface areas are desired. Graphene, structurally monolayer of carbon atoms arranged in two-dimensional honeycomb lattice [23–25], possesses extremely large specific surface area and is attractive as the nanofillers in percolative nanocomposites for significantly enhancing the ECE in the EC polymers.

As a promising EC material, the relaxor P(VDF–TrFE–CFE) terpolymers exhibit a giant ECE where a $\Delta T = 16$ K was induced under 150 MV m^{-1} near room temperature [26]. However at low electric fields, ΔT is small (for example, $\Delta T < 1$ K under 40 MV m^{-1}) and consequently $\Delta T/\Delta E$ is also low ($< 0.02 \times 10^{-6}$ km V^{-1} at 40 MV m^{-1}). A nanocomposites strategy, which involves the combination of ferroelectric ceramic nanofillers ($BaTiSrO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$) and P(VDF–TrFE–CFE), has been proposed recently to enhance the ECE response [27,28]. However, the ECE enhancement is more pronounced at modest and high electric fields (above 75 MV m^{-1}). The ECE of these nanocomposites is not high at low electric fields, for example, $\Delta T = 2.5$ K under 50 MV m^{-1} for the $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$/P(VDF–TrFE–CFE) nanocomposites [28]. In this paper we show that a class of nanocomposites, employing the relaxor terpolymer/P(VDF–TrFE) copolymer blend as the matrix to form nanocomposites with graphene nanofillers and through a proper fabrication process, can reach a $\Delta T = 5.2$ K and $\Delta S = 24.8$ J kg^{-1} K^{-1} under a low electric field of 40 MV m^{-1}. As a result, the nanocomposites generate a large electrocaloric coefficients of $\Delta T/\Delta E = 0.13 \times 10^{-6}$ km V^{-1} and $\Delta S/\Delta E = 0.62 \times 10^{-6}$ J m kg^{-1} K^{-1} V^{-1}. The work here indicates the promise of nanocomposite approach with graphene nanofillers to achieve a highly efficient and giant ECE for the EC polymers.

2. Experimental section

2.1. Graphene fabrication

The graphene used in the experiment was derived from graphene oxide sheets (GO), according to a modified Hummer's method as described in a recently work [29], followed by a thermal expansion process. In this method, concentrated aqueous GO dispersion was freeze-dried. After complete removal of solvent, dried GO was placed in a temperature controlled furnace (Nabertherm), where the temperature was increased up to 1000 °C with the increasing rate of 10 °C min^{-1} and remained constant (1000 °C) for 1 h in the inert condition. Afterwards, the sample was allowed to cool down to room temperature and the obtained graphene (or thermally reduced graphene oxide) powder was collected. Throughout the procedure, nitrogen gas was kept flowing into furnace to make the inert condition. The final graphene was functionalized with fluorinated silane molecules (trichloro[1H-,1H-,2H-,2H-per-fluorooctyl] silane, Aldrich) through a silanization reaction.

2.2. Nanocomposites fabrication

P(VDF–TrFE–CFE) terpolymer (62.8/29.7/7.5 mol%) was synthesized using a suspension polymerization method by Piezotech (France), and P(VDF–TrFE) copolymer (65/35 mol%) was provided by Solvay (Belgium). The P(VDF–TrFE–CFE) terpolymer/P(VDF–TrFE) copolymer blends were prepared by dissolving the polymer power with 90/10 weight ratio of the two components in N,N-dimethylformamide (DMF, Aldrich) at room temperature. The functionalized graphene was dispersed in DMF by ultrasonication (VWR Scientific Aquasonic Cleaner 75 T) for 4 h with the gradual addition of polymer solution. The final solution was dropwise added into deionized water, and the resultant precipitate was dried at 90 °C under vacuum for 24 h, followed by a molding process at 180 °C. The resultant composites films were then uniaxially stretched to four times of their original length at room temperature. The final film thickness is ~11 μm. For electric characterization, gold electrodes with a thickness of 40 nm and diameter of 6 mm were sputtered on both surfaces of the nanocomposites films.

3. Characterization

The morphology of functionalized graphene was examined by a transmission electron microscope (Jeol 2010 LaB6). A Scanning Electronic Microscopy (SEM) FEI Nano 630 was adopted to characterize the cross-sectional morphology of nanocomposites. Two-dimensional (2D) wide-angle X-ray diffraction (WAXD) experiments were carried out on an Oxford Xcalibur diffractometer equipped with an ONYX CCD area detector. The X-ray wavelength was Cu Kα 0.1542 nm. FTIR spectra were obtained using a Bruker V70 infrared spectrometer equipped with a diamond ATR accessory. A differential scanning calorimeter (DSC) (TA Q 100) was used to observe the thermal behaviors of nanocomposites films from 0 °C to 200 °C with a heating and cooling rate of 10 °C min^{-1}. A precision LCR meter (4284 A) equipped with a temperature chamber (Delta 9023) was employed to characterize the dielectric properties of nanocomposites films. Polarization–electric filed (P–E) loops were measured using a Sawyer-Tower circuit.