Self-powered heat-resistant polymeric 1D nanowires and 3D micro/nanowire assemblies in a pressure-crystallized size-distributed graphene oxide/poly (vinylidene fluoride) composite

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Abstract. Piezoelectric one- (1D) and three-dimensional (3D) hybrid micro/nanostructured materials have received intense research interest because of their ability in capturing trace amounts of energy and transforming it into electrical energy. In this work, a size-distributed graphene oxide (GO) was utilized for the concurrent growth of both the 1D nanowires and 3D micro/nanowire architectures of poly (vinylidene fluoride) (PVDF) with piezoelectricity. The in situ formation of the polymeric micro/nanostructures, with crystalline beta phase, was achieved by the high-pressure crystalization of a well dispersed GO/PVDF composite, fabricated by an environmentally friendly physical approach. Particularly, by controlling the crystallization conditions of the binary composite at high pressure, the melting point of the polymeric micro/nanowires, which further constructed the 3D micro/nanoarchitectures, was nearly 30°C higher than that of the original PVDF. The large scale simultaneous formation of the 1D and 3D micro/nanostructures was attributed to a size-dependent catalysis of the GOs in the pressure-treated composite system. The as-fabricated heat-resistant hybrid micro/nanoarchitectures, consisting of GOs and piezoelectric PVDF micro/nanowires, may permit niche applications in self-powered micro/nanodevices for energy scavenging from their working environments.

1. Introduction
Effective mechanical-to-electrical conversion is of great importance in powering small electronic devices and systems using the vibrational energy available in their working environments [1-3]. Of the current developed energy scavenging techniques, piezoelectric transduction, based on self-powered 1D micro/nanowires or their 3D assemblies, has received the largest attention, and already shown exciting application potentials in electronics, optoelectronics, sensors and biological science [1, 2]. Compared
with their inorganic counterparts, such as ZnO, PZT and BaTiO$_3$ [3], the lightweight and conformable micro/nano-structured piezoelectric polymeric materials have more advantages in the realization of all-organic-based self-powered electronic devices [4-6].

Figure 1. Typical TEM micrographs of the as fabricated GO/PVDF (0.5/99.5, wt/wt) composite.

PVDF is one of the limited known polymers with large piezoelectric coefficients, exhibiting a pronounced polymorphism that transforms between several crystal forms under specified conditions, and successful development of piezoelectric devices with the polymer depends on the effective fabrication of polar crystalline structures, such as $\beta$ and $\gamma$ [4-6]. Recently, nanostructured carbon allotropes, such as fullerenes [7, 8], carbon nanotubes [9, 10], graphene and its nanoplatelet [11], and graphene quantum dots [12], were utilized to induce the high-pressure self-assembly of PVDF molecules into polymeric micro/nano-architectures with piezoelectric crystalline $\beta$ phase. In this study, GO, a 2D carbon-based nanomaterial, with carboxylic acid moieties on the basal planes and edges of its sheets [13], was used in achieving control over the size, morphology and molecular ordering of PVDF micro/nanostructures. By the crystallization of a well dispersed binary GO/PVDF composite at high pressure, a large scale formation of the self-powered GO-based hybrid 3D micro/nanowire assemblies was realized with remarkably improved heat resistance.

2. Experimental

GO (>99% wt/wt purity), with 0.55-1.2nm thickness, was supplied by Chengdu Organic Chemicals Co., Ltd, Chinese Academy of Science, and used as received. PVDF powder, commercial-grade Solef 6010, was supplied by Solvay Co., Ltd, Belgium. The corresponding weight-average molecular weight, Mw, was 322000g/mol. GO and PVDF were pre-mixed at 23000rpm and room temperature in a commercial Joyoung JYL-C012 blender. This was followed by melt compounding at 60rpm, 200°C for 15min using a ZJL-300 torque rheometer.

Figure 2. DSC (a), WAXD (b) and ATR-FTIR (c) results of the original neat PVDF and GQ/PVDF (0.5/99.5, wt/wt) composite samples prior to the high pressure treatment, respectively.

High-pressure experiments for the GO/PVDF composite were carried out with a self-made piston-cylinder apparatus [7]. The following procedure for crystallization was used. After loading the samples, the temperature was increased to 200°C to allow them to be melted. Then a low pressure (150MPa) was applied, and the temperature was raised to a predetermined level. After equilibrium was
established, the pressure was further raised to the predetermined value. These samples were kept under these conditions for a scheduled time, and then quenched down to ambient condition.

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 PANalytical X’pert PRO diffractometer. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) data were obtained 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 using a JSM-6330F apparatus.

3. Results and discussion
Figure 1 shows the typical TEM micrographs of the as fabricated size-distributed GO/PVDF (0.5/99.5, wt/wt) composite, just before the applied treatment by pressure. As can be seen, an overall good dispersion of the GOs, with lateral dimensions from a few nanometers to several hundreds of nanometers, was achieved in PVDF matrix by the used easy physical and mechanical route.

A comparison experiment was conducted for the original pristine PVDF and the GO/PVDF composite samples, prior to the high pressure crystallization, and the results are shown in Figure 2. Although a slight increase of the melting point and melting enthalpy was observed by the introduction of GOs, no crystalline β form, essential in the creation of piezoelectricity of the polymer, was crystallized in the GO/PVDF composite. The characteristic bands of IR and WAXD were almost the
same, for the PVDF and its GO composite, which should be attributed to the reflections of monoclinic $\alpha$ phase.

Figure 4. SEM micrographs of the etched fracture surfaces of the GO/PVDF (0.5/99.5, wt/wt) composite samples, crystallized at 400MPa and different maximum quenching temperature: (a) 230°C; (b) 275°C.

Figure 3 gives out the DSC, WAXD and IR results of the GO/PVDF (0.5/99.5, wt/wt) composite samples after the high pressure treatment by varying temperature, pressure and crystallization time. With the increase of crystallization temperature, the melting point at high-temperature side increased, as revealed by the DSC data (Figure 3a, top). Also, the WAXD (Figure 3b, top) and IR (Figure 3c, top) reflections suggested that the content of $\alpha$ and $\beta$ phase in GO/PVDF decreased and increased, respectively, and $\gamma$ phase began to appear when the maximum quenching temperature reached 275°C. Multiple melting behaviors were observed for the composite samples crystallized at the same pressure and temperature for an increased time (Figure 3a, middle). Particularly, the main-peak melting point of the GO/PVDF sample crystallized at 400MPa, 260°C for 30min attained 203.72°C, which is around 30°C higher than that of the original PVDF. No $\alpha$ phase was detected for the composite samples crystallized for more than 30min, and their crystalline structures were totally with $\beta$ and $\gamma$ phase lamellae (Figure 3b and c, middle). The inappropriate increase of pressure hindered the melting point from further increasing (Figure 3a, bottom). However, $\alpha$ phase crystals were completely removed from the GO/PVDF simply by the pressure increase (Figure 3b and c, bottom). We noted that GO/PVDF composite samples with melting points above 200°C, corresponding to the formation of polar extended-chain crystals of the polymer, could be obtained through an appropriate combination of crystallization conditions.

The above DSC, WAXD and IR data were further confirmed by the morphological observation of the high pressure crystallized GO/PVDF samples. For example, featured $\alpha$ form spherulites covered the etched surface of the sample crystallized at 400MPa and 230°C, and no trace of $\gamma$ phase crystallite was observed (Figure 4a). Moreover, the number of fiber-like structures of $\beta$ crystals increased with the increase of crystallization temperature. Especially, $\beta$-form fibrils with striated appearance, the most characteristic feature for polymer extended-chain crystals, were clearly observed in the sample crystallized at 275°C (Figure 4b).

Piezoelectric $\beta$ form crystalline 1D nanowires of PVDF were formed in the high pressure crystallized size-distributed GQ/PVDF (0.5/99.5, wt/wt) composite, and the typical morphology of such nanowires is represented in Figure 5. The nanowires, embedded in the polymer matrix, were observed only by the etching of the amorphous part of the fracture surface, and they totally belong to a crystalline entity. Furthermore, the diameter, length and morphology of the PVDF nanowires were found to be very sensitive to the crystallization conditions. Sometimes the abnormal growth of the nanowires was observed, and they lost their size uniformity. Nevertheless, the polygonal shaped
nanowires, with uniform size and morphology, could be crystallized by an appropriate pressure treatment.

Figure 5. Typical SEM micrographs of the 1D polymeric nanowires in the GO/PVDF (0.5/99.5, wt/wt) composite samples, crystallized at different pressure, 260°C for 30min: (a) 500MPa; (b) 300MPa.

Figure 6. SEM micrographs of the 3D polymeric micro/nanowire architectures in the GO/PVDF (0.5/99.5, wt/wt) composite samples, crystallized at 400MPa and 245°C (a and b), 260°C (c and d) and 275°C (e) maximum quenching temperature, and 400MPa, 260°C for 10min (f), 30min (g) and 60min (h), respectively.

Figure 6 shows the representative SEM micrographs of the piezoelectric 1D micro/nanowire-assembled 3D architectures in the high-pressure crystallized GO/PVDF composite. The 3D micro/nanowire assemblies, with crystalline β form, were obtained with diversified morphologies and substructures by the variation of crystallization parameters. The DSC, WAXD and IR suggested that the melting point of such micro/nanowire architectures, as well as their molecular ordering, could be increased by the appropriate increase of crystallization temperature and time at the same pressure. Consistently, the substructures of the 3D assemblies were transformed from folded-chain lamellae into extended-chain lamellae. This finally resulted in the growth of the unique heat-resistant 3D micro/nanowire assemblies, as shown in Figure 6e, g and h.

The concurrent growth of the piezoelectric 1D and 3D polymeric micro/nanostructures, with super heat resistance, should be attributed to the self-assembly of PVDF macromolecular chains, induced by
a size-dependent catalysis of the GOs in the pressure-treated composite system [12, 14]. The GOs with smaller lateral dimension catalyzed the assembly of the polymer into micro/nanowires, and these with larger size induced the simultaneous formation of numerous 1D micro/nanowires that finally evolved into the 3D assemblies. Moreover, the existence of carboxylic acid groups in GOs may enhance the interactions of GOs with PVDF molecules in the growth of the GO-based hybrid micro/nanostructures with piezoelectricity.

4. Conclusion
In summary, concurrent in situ growth of 1D nanowires and 3D micro/nanowire assemblies, with crystalline β form, was achieved by the high-pressure crystallization of a well dispersed size-distributed GO/PVDF composite. The size, morphology and substructures of the micro/nanoarchitectures were controllable by the variation of crystallization conditions, which finally resulted in a large scale formation of piezoelectric polymeric 1D and 3D micro/nanostructures with remarkably improved heat resistance. The simultaneous formation of the 1D and 3D micro/nanostructures was attributed to a size-dependent catalysis effect of the GOs, enhanced further by the multiple interactions between GO and PVDF. The as fabricated GO-based hybrid micro/nanoarchitectures, with excellent thermal stability of their piezoelectric activity, may diversify niche applications in self-powered micro/nanodevices for energy harvesting, especially for those working in higher temperature environments.

Acknowledgements
This project was supported by the National Natural Science Foundation of China (51373139).

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