Agglomerated carbon nanotube-induced growth of piezoelectric 3D nanoarchitectures assembled from hollow 1D nanowires of poly (vinylidene fluoride) at high pressure

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Carbon nanotubes (CNTs) intrinsically tend to bundle and/or aggregate, and various techniques were explored to improve the dispersibility of CNTs in polymer matrices during the preparation of a variety of CNT/polymer based composites. However, herein we report the entangling nature of CNTs can be utilized for the rapid formation of unique piezoelectric three dimensional (3D) nanoarchitectures of poly (vinylidene fluoride) (PVDF). The controllable growth of the 3D nanostructures, assembled from hollow one dimensional (1D) PVDF nanowires, was achieved by the high-pressure crystallization of a binary CNT/PVDF based composite, in which CNT agglomerations were not destroyed during the fabrication process. This was attributed to the cooperation effect of the agglomerated CNTs served as hard-template and the physical interactions of macromolecular chains at high pressure as self-assembly driving forces. The present study provides a facile and effective approach to construct functional 3D nanostructures in situ, and the hybrid structures, consisting of CNTs and piezoelectric PVDF nanowires, may permit niche applications in a self-powering nanosystem that harvests its operating energy from the environment.

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1. Introduction

3D nanostructured materials, especially those assembled from 1D nanowires or two dimensional (2D) nanosheets, have received intense research interest because of their potential applications as functional materials with collective properties [1–4]. The properties of 3D nanoarchitectures depend not only on their chemical composition, but also on their structure, phase, shape, size, and size distribution [1]. Recently, a simple, low-cost approach was presented that converts low-frequency mechanical energy into electricity using piezoelectric zinc oxide nanowires grown radially around textile fibers [5,6]. Also, a novel hierarchical structure, integrating zinc oxide nanowire arrays on silicon micropyramids, was reported as an effective superhydrophobic antireflection coating for improving the energy-conversion efficiency of solar cells [7]. The approaches developed above are a new paradigm for the applications of 3D nanoarchitectures in nanotechnology and green energy, and are of critical importance for sensing, medical science, infrastructure/environmental monitoring, defense technology and personal electronics [5–7].

As a flexible soft material, polymeric 3D nanostructures show unique properties in organic-based electronic devices [8–11]. So far, polymeric 3D nanostructures have been prepared by using zeolite channels, track-etched polycarbonate, and porous alumina membranes as hard templates, or by using micelle, surfactant, liquid crystal and inverse micro-emulsion as soft-templates [4,8–10]. Moreover, a laser direct-writing technique employing multiphoton absorption processes has become a tool in the fabrication of micro-/nanometer-scale structures of polymers [11]. Among these, synergistic effect between the metal or inorganic materials and the incorporated polymeric matrix has been observed for the developed 3D hybrid nanoarchitectures, and very much interested by many researchers, such as 3D composite of...
poly (N-acetylaniline) nanorods/platinum nanoclusters [8], and 3D, arrayed, nanotubular architecture of polypyrrole/ruthenium dioxide [9].

Poly (vinylidene fluoride) (PVDF), exhibiting a pronounced polymorphism that transforms between several crystal forms under certain conditions, is one of the limited known piezoelectric class of polymers [12]. PVDF promises applicability in diverse field of technology because of its high piezoelectric activity and availability as flexible thin films [13–19]. Particularly, piezoelectric properties of the polymer have been utilized to harvest energy from ambient environments, and several nanogenerators, based on PVDF, were fabricated by direct-writing [14], hybrid [15], and lithography-free, template-assisted preparation methods [16], respectively. Nevertheless, the successful development of ferroelectric polymer devices depends on the effective fabrication of polar ferroelectric crystalline structures of PVDF, such as β and γ [13–16].

CNT, an excellent carbon material with a tubular morphology and a nanoscale diameter, intrinsically tends to bundle and/or aggregate [20]. This presents a major impediment that must be overcome prior to realizing applications of CNTs as reinforcement components in polymer based composites, and tremendous efforts has been devoted to improving the their dispersibility in matrices [20]. However, in this work, we show that the entangling nature of CNTs can be exploited to the rapid growth of unique piezoelectric 3D nanostructures of PVDF. This was achieved by the high-pressure crystallization of a CNT/PVDF composite, in which CNT agglomerations were not destroyed during the composite fabrication process. By controlling crystallization conditions, 3D nanoarchitectures, assembled from 1D β-form PVDF nanowires, with polygonal shape and hollow structures, were finally formed in situ in the composite samples.

2. Experimental part

Multi-wall carbon nanotubes (MWCNTs) (>95% wt/wt purity) was purchased from 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, Shanghai. The corresponding weight-average molecular weight, M_w, was 322,000 g/mol. CNTs and PVDF were pre-mixed at 23,000 rpm, room temperature for 10 min in a commercial Joyoung JYL-C012 blender. This was followed by melt compounding at 60 rpm, 200 °C for 15 min using a ZJL-300 torque rheometer.

High-pressure experiments for the CNT/PVDF composites were carried out with a self-made piston-cylinder apparatus [18]. 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 (150 MPa) was applied, and the temperature was raised to a predetermined level. After equilibrium was established, the pressure was further raised to the predetermined level. These samples were kept under these conditions for a scheduled time, and then quenched down to ambient condition with a cooling rate of 1.5 °C/min.

Transmission electron microscopy (TEM) detections were performed with a Tecnai G2 F20 S-TWIN apparatus, employing a Leica EMUC6/FC6 microtome for the preparation of ultrathin sections through room-temperature microtome. Differential scanning calorimetry (DSC) measurements were conducted at atmospheric pressure by using a TA-Q20 instrument. The weight of sample was around 5 mg. Melting behavior of the crystals was investigated through a heating scan with a heating rate of 10 °C/min at N2 atmosphere. 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 in the range of 700–4000 cm⁻¹, with 32 scans conducted at a resolution of 4 cm⁻¹. WAXD and ATR-FTIR data were collected at the fresh and smooth surfaces of the samples, which were obtained through fracture at liquid N2 temperature. After the WAXD and ATR-FTIR characterizations, the sample surfaces were etched by using a method modified from that developed by Vaughan [21], and then coated with gold for scanning electron microscopy (SEM) observations using a HITACHI S-3400 apparatus.

3. Results and discussion

Fig. 1 shows the TEM results of the as-fabricated CNT/PVDF (5/95, wt/wt) sample without being treated by high pressure. As can be seen, some CNTs achieved relatively good dispersion in PVDF matrix (Fig. b). Nevertheless, large CNT aggregations, with size around several hundreds of nanometers, were still observed (Fig. c). Although the adopted physical and mechanical route herein has been proven to be effective in the preparation of the well-dispersed binary composite of fullerene C60 and PVDF [18], the above observations suggested it was not so satisfactory for the dispersion of CNTs, a carbon material with a high aspect ratio.

The CNT/PVDF composite with 5.0 wt.% CNT loading was selected for the high pressure experiments by varying temperature, pressure and crystallization time. The crystallization conditions, as well as the results of DSC, WAXD and ATR-FTIR, are shown in

![Fig. 1. TEM photographs of the as-prepared CNT/PVDF (5/95, wt/wt) sample, just before the applied high-pressure treatment. (b and c) Are magnified views of the portions highlighted by the red and blue elliptical frames in (a), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
Figs. 2–4. Fig. 2a displays the DSC results of the CNT/PVDF samples crystallized at 500 MPa and different maximum crystallization temperatures. The results revealed that generally the melting temperatures of the high-pressure crystallized composite samples increased with the increase of crystallization temperature. Especially, the melting point of the sample crystallized at 280°C reached 202.7°C, almost 30°C higher than that of the sample crystallized at 230°C. The DSC data indicated that crystal form transforming occurred with the crystallization temperature increase [22,23]. Furthermore, the higher melting point for the sample crystallized at 280°C suggested a greater perfection for the obtained PVDF crystals, which may possibly be assigned to the formation of extended-chain crystals with β or γ form [22,23].

Commonly, the identification of the crystalline phases of PVDF was conducted by WAXD and FTIR measurements. To the X-ray diffraction data [22–24], the reflections of monoclinic α phase of the polymer at 2θ angles 17.7°, 18.5°, 19.9° and 26.5° are attributed to planes (100), (020), (110) and (021), respectively. The apparent single peak of orthorhombic β phase at 20.4°–21.1° actually comes from the superposition of (110) and (200) reflections, and the characteristic reflections of monoclinic γ phase are assigned to planes (020), (200) and (110), respectively [25]. As for IR bands, they are characteristic of α phase at 764, 796, 976 and 1214 cm⁻¹, β phase at 840 and 1280 cm⁻¹, and γ phase at 840 and 1234 cm⁻¹, respectively [26,27]. The IR band at 879 cm⁻¹, regarded as proportional to the thickness of the sample [28], is attributed to the amorphous phase of PVDF, and therefore cannot be used to identify any of the crystalline phases [29]. The relevant WAXD and ATR-FTIR spectra
of the composite samples crystallized at 500 MPa and variant maximum crystallization temperatures are shown in Fig. 2b and c, respectively. The intensity of the peaks characteristic of α phase decreased, while that of β phase increased, whether in WAXD or IR spectra, with the increase of crystallization temperature. The γ form crystals of PVDF began to emerge when crystallization temperature was above 245 °C. Particularly, no α phase was observed for both samples crystallized at 260 and 280 °C, respectively. Their crystal forms are totally a mixture of β and γ phase.

Fig. 3a shows the DSC data of the CNT/PVDF samples crystallized at 500 MPa, 260 °C for different times. Only single endotherms emerged on the DSC curves of the composite samples when crystallization time was above 10 min. Also, compared with that of the main peak of the sample crystallized at 260 °C maximum crystallization temperature, the melting point increased more than 10 °C, with the increase of crystallization time for just 10 min, and then it remained more or less the same when crystallization time was further prolonged. The relatively higher melting points still suggested that PVDF crystals with extended-chain lamellae as substructures were crystallized in the composite samples of this group [22,23]. The characteristic bands of WAXD and IR, shown in Fig. 3b and c, suggested that the content of both β and γ phase in the composite samples increased with the increase of crystallization time during 10–40 min. However, possibly due to high-temperature degradation, the reflection intensity of both β and γ phase decreased when crystallization time was increased to 60 min, though still no α phase was crystallized in the sample.

Among the previously pressure-crystallized samples, the composite sample crystallized at 500 MPa, 260 °C for 40 min was suggested the formation of β- or γ-form extended-chain crystals with the highest melting point. To investigate the pressure effect on the phase transition of the CNT/PVDF composite, three samples were also prepared at 300, 400, and 600 MPa, respectively, with other conditions being the same, and the characterization results are shown in Fig. 4a–c. Multiple melting behaviors were observed for all the samples of this group, and the melting point of the polymer was not further increased by varying pressure (Fig. 4a). Furthermore, in addition to β- and γ-form crystals, α phase was observed in both the composite samples crystallized at 300 and 400 MPa, respectively (Fig. 4b and c). These suggested that an appropriate higher pressure was required for the enrichment of more perfect piezoelectric crystals in CNT/PVDF composite system.

The above DSC, WAXD and IR data were further confirmed by SEM observations. For example, featured α spherulites were observed in the sample crystallized at 500 MPa and 245 °C maximum crystallization temperature (Fig. 5a). Also, a large amount of fiber-like structures corresponding to β crystals were revealed in the sample crystallized at 400 MPa, 260 °C for 40 min (Fig. 5b). With the pressure further increased to 600 MPa, the amount of β-form crystals increased, and no trace of α spherulites was observed. Furthermore, the pressure increase promoted the formation of a novel γ-phase spherulite (Fig. 5c). As disclosed by a zoom-in view, such γ-form spherulites were actually constructed by 2D nanosheet crystals (Fig. 5d).

Particularly, the direct morphologies of PVDF extended-chain crystals, with β or γ form, were given with SEM for certain samples with relative higher melting points. According to the previous investigations [30], striated appearance is the most characteristic feature for polymeric extended-chain crystals, and the striations should run parallel to the molecular chains. Fig. 6 shows the typical morphology of the extended-chain crystals in a CNT/PVDF sample, crystallized at 500 MPa and 280 °C maximum crystallization temperature. As can be seen, the γ-form extended-chain crystals, grown together with the β-form crystals, were clearly revealed (Fig. 6a). Moreover, a closed observation suggested the oriented β-form fibrils were also with extended-chain lamellae as substructures (Fig. 6b).

Recently, a template-free approach was developed for the fabrication of β-form crystalline PVDF nanowires with hollow structures, achieved through the high-pressure crystallization of well-dispersed nano-composites based on PVDF and fullerene C60 or C70 [21,31]. Fig. 7a shows the secondary electron image of the etched fracture surface of the CNT/PVDF sample crystallized at 500 MPa and 245 °C maximum crystallization temperature. Embedded in the polymer matrix, a 3D nanoarchitecture, assembled from such 1D nanowires, was observed, with size around several tens of micrometers. WAXD and IR data have suggested that the content of polar crystals with β phase increased significantly and no nonpolar α phase was formed when the crystallization temperature was increased to 260 °C at just the same pressure. Consistently, more such 3D nanoarchitectures were observed in this sample, as shown in Fig. 7b–d. The portions highlighted by
the red elliptical frames in Fig. 7a, c and d showed the polygonal shape and hollow structure of the assembled β-form 1D nanowires of the as-formed 3D nanoarchitecture. The 3D nanoarchitectures were observed only after the etching of the amorphous parts of the fracture surfaces. So they belong to a piezoelectric crystalline entity.

The morphology of the 1D nanowires was found to be very sensitive to the crystallization conditions. This resulted in the morphological change of the 3D nanoarchitectures that they constructed. The 3D nanoarchitecture shown in Fig. 7e was crystallized at 500 MPa, 260 °C for 20 min. Although the DSC data suggested that this 3D nanoarchitecture was with extended-chain lamellae as its substructures, inappropriate increasing of crystallization time resulted in the abnormal growth of the nanowires, and they lost their size uniformity. Also, crystallization at a relative higher temperature, especially for a longer time, may result in an undesirable degradation of the 3D nanoarchitectures, as shown in Fig. 7f.

The 3D polymeric nanoarchitectures, consisting of 1D nanowires, were obtained by the high-pressure crystallization of a CNT/PVDF (5/95, wt/wt) composite, for which the effective dispersion of CNTs was not achieved and large CNT agglomerations were formed during the composite preparation (Fig. 1c). For reference, another CNT/PVDF sample with 1.0 wt.% CNT loading, in which CNTs were better dispersed in the polymer matrix by the adopted physical and mechanical route, as shown in Fig. 8a, was crystallized exactly at 500 MPa and 260 °C maximum crystallization temperature. Treated with the same etching process, the fracture surface was mostly covered with polymeric spherulites, due to the predominant bulk crystallization of the polymer, and no trace of such 3D nanoarchitectures was observed (Fig. 8b). As for the sample of pristine PVDF, SEM only disclosed certain ordinary crystal structures of PVDF, after the same crystallization process at high pressure. Conclusively, CNT agglomerations, with large size, play a crucial role in the in situ growth of such 3D nanoarchitectures of PVDF.
The growth of the 3D nanoarchitectures may be attributed to the cooperation effect of the agglomerated CNTs, served as hard-template, and the physical interactions of molecular chains of PVDF at high pressure as self-assembly driving forces [21,32–34]. To summarize the growth process of the 3D nanostructures assembled from the 1D crystalline PVDF nanowires with hollow structures at high pressure, a schematic illustration is presented in Fig. 9. Starting from a mixture of PVDF molecules and CNT agglomerations (Fig. 9a), a molecular self-assembly is induced by CNTs at high pressure. By utilizing individual CNTs of the agglomerations as a hard template, PVDF molecules diffuse on the CNT surfaces, and then β-form lamellae are formed (Fig. 9b). The sensitivity of different phase transitions to pressure is known to be different, and pressure may shift the phase equilibrium so as to bring a new axis to the self-assembly space [30], especially with the introduction of CNTs. The continued growth and organization of the β-form lamellae of PVDF, templated by the CNTs, finally result in the large scale formation of the unique 3D piezoelectric nanoarchitectures under specific experimental conditions (Fig. 9c and d).

4. Conclusion

In summary, the entangling nature of CNTs was utilized for the controllable fast in situ growth of unique 3D polymeric nanoarchitectures, achieved by the high-pressure crystallization of a CNT/PVDF composite. The 3D nanostructures were assembled from 1D crystalline β-phase PVDF nanowires with hollow structures. Their large scale formation was attributed to the cooperation effect of the bundled CNTs, served as hard-template, and the physical interactions of molecular chains of PVDF at high pressure as self-assembly driving forces. We believe such piezoelectric 3D nanoarchitectures may diversify niche applications in self-powering nanodevices for energy scavenging from their working environments.

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References


