

A simple and convenient route to prepare poly(vinylidene fluoride trifluoroethylene) copolymer nanowires and nanotubes

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Poly(vinylidene fluoride trifluoroethylene) copolymer nanowires and nanotubes have been prepared for the first time *via* a high temperature (≤ 260 °C) vacuum infiltration method, which is a simple and convenient route for fabricating polymer nanowires and nanotubes when polymers, instead of monomers, are used as the starting materials.

In recent years, there has been tremendous interest in template-based synthesis of one-dimensional nanomaterials for nanotechnology applications. A range of materials, for example carbon, oxide ceramics, metals, III–V semiconductors, metal oxides, have been infiltrated into the pores of anodic alumina membrane (AAM) using a variety of preparation methods including chemical vapor deposition,¹ sol–gel,² electrochemical deposition,³ vapor–liquid–solid (VLS) growth⁴ and thermal evaporation.⁵ In contrast, there have been comparatively few reports on the preparation of polymer or copolymer nanowires, nanorods, and nanotubes, which may arise from the fact that most of the currently used preparation methods cannot be used to fabricate polymer nanowires, nanorods, and nanotubes. For example, the hydrothermal solution synthesis, chemical vapor deposition, thermal evaporation, and VLS growth methods have been used to prepare oxide ceramics, carbon, metal oxides, III–V semiconductor nanowires, nanorods, and nanotubes,^{1,4–6} but these methods cannot be applied to prepare polymer nanowires and nanotubes because they involve the use of very high temperature.

Recently, nanowires, nanorods, and nanotubes of several polymers have been synthesized. Martin *et al.*^{7–9} pioneered the preparation of electronically conductive polypyrrole, poly(3-methyl thiophene), and polyaniline nanowires, nanorods, and nanotubes by oxidative polymerization or electrochemical deposition of corresponding monomers inside the pores of AAM. Besides, poly(*p*-phenylene vinylene) nanorods and nanotubes,¹⁰ polyacetylene nanofibers,¹¹ polyacrylonitrile nanotubes,¹² poly(3,4-ethylene dioxythiophene) nanowires and nanotubes,¹³ polyferrocenylsilane nanorods,¹⁴ polypyrrole/poly(methyl methacrylate) coaxial nanowires,¹⁵ carbon nanotubes/polyacrylonitrile coaxial nanotubes,¹⁶ have also been prepared using AAM or polycarbonate membranes as templates. Whatever the preparation methods used, the starting material is a monomer and the polymerization occurs in the pores of AAM. It is clear that these methods cannot be applied to prepare polymer nanowires, nanorods, and nanotubes if the starting material is already polymerized.

Poly(vinylidene fluoride trifluoroethylene), P(VDF-TrFE), is an important ferroelectric copolymer which has been used for nearly

three decades in electromechanical and piezoelectric device applications.¹⁷ To our knowledge, there has been no report on the preparation of P(VDF-TrFE) nanowires and nanotubes which may have potential applications as sensors and actuators in microelectromechanical systems. In this communication, we report, for the first time, the preparation of P(VDF-TrFE) copolymer nanowires and nanotubes using a simple and convenient vacuum infiltration method.

Several circular pieces of AAM were used for the fabrication of the copolymer nanowires and nanotubes. Two piece of AAM of 21 mm diameter and 60 μm thickness and having a nominal pore size of 200 nm were purchased from Whatman. The remaining pieces of AAM of 10 mm diameter and 40 μm thickness and having pore sizes of about 35 nm and 90 nm, respectively, were prepared in our laboratory using a two-step anodizing process.³ 0.35 g of P(VDF-TrFE) copolymer pellets with a VDF/TrFE molar ratio of 70 : 30 was dissolved in 15 ml of methyl ethyl ketone (MEK) to form a solution. The solution was cast on a flat glass plate to form thin films with a thickness of about 30 μm which was then heated to 135 °C and kept at that temperature for 6 h to remove the residual MEK. Disk-shaped film samples of diameter similar to that of the AAM were placed on the surface of the AAM and heated to 230 °C–260 °C in a vacuum oven and kept at that temperature for 10 min. Then, the oven was evacuated to a pressure of 2.5 Pa for 15–30 min using a mechanical pump. After evacuating for an appropriate period of time the samples were slowly cooled to 135 °C *in situ* and kept at that temperature for 10 h to increase the crystallinity of the copolymer. Finally, the samples were cooled to room temperature at a rate of 1 °C min^{-1} . While some of the copolymer had infiltrated into the pores of the AAM, there was a layer of copolymer film remaining on the surface of the AAM. Before field-emission scanning electron microscope (FE-SEM) measurements the AAM was completely dissolved in a 4 M NaOH aqueous solution, and then thoroughly rinsed with distilled water, leaving the nanowires and nanotubes attached to the remaining copolymer film. The morphology of the copolymer nanowires and nanotubes was observed using a FE-SEM (JEOL JSM-6335F). X-ray diffraction measurements were made using a Bruker D8 Advance X-ray diffractometer equipped with Cu K α radiation of wavelength $\lambda = 1.5406$ Å. The capacitance of the nanowires and the bulk sample were measured using a HP 4194A impedance analyzer.

Fig. 1(a) shows the FE-SEM image of P(VDF-TrFE) copolymer nanowires prepared at 230 °C using a AAM with a pore size of about 35 nm. It can be seen that the diameter of the nanowires is about 35–40 nm, which is slightly larger than the pore size of the AAM. We have also successfully prepared nanowires

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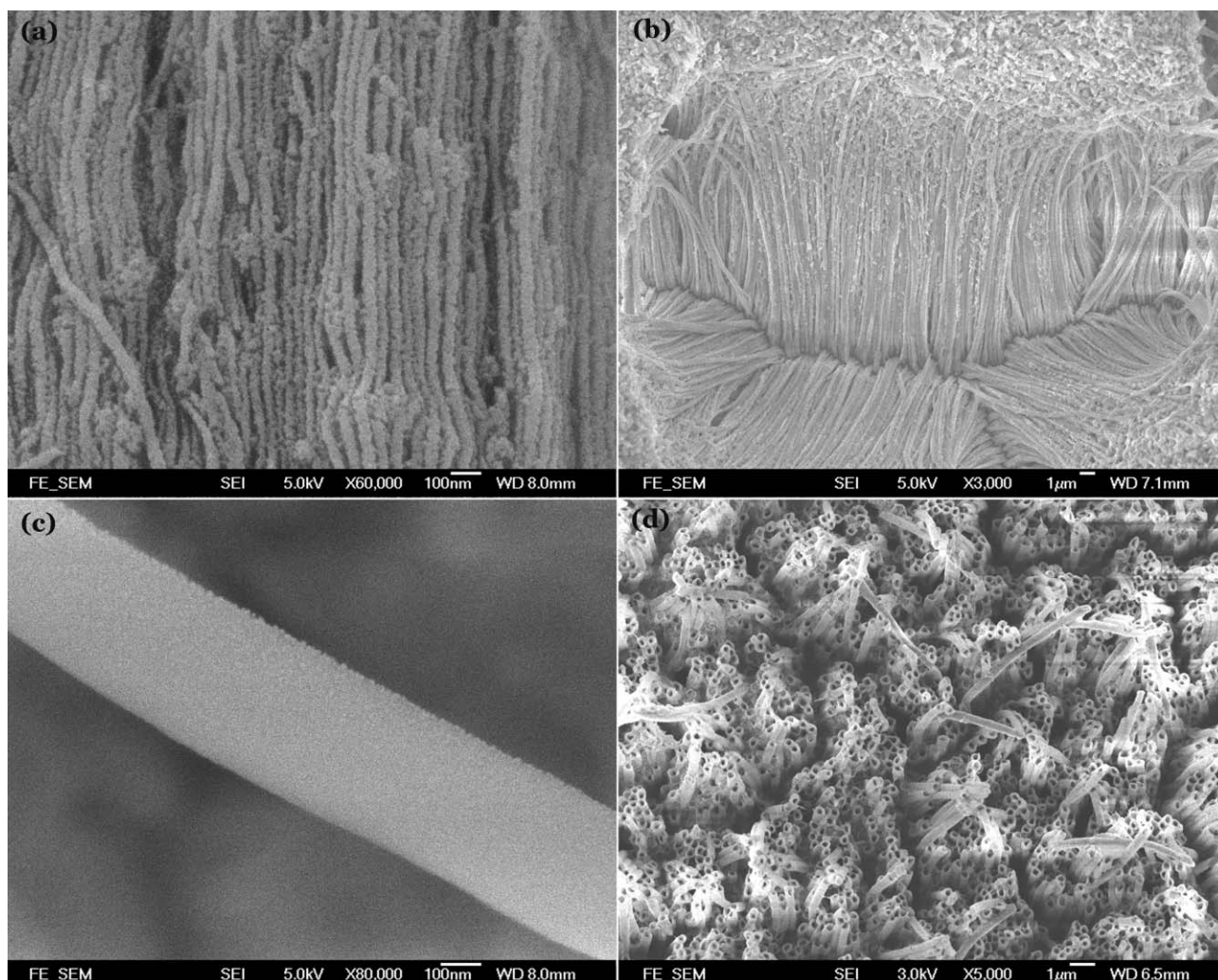


Fig. 1 FE-SEM images of the P(VDF-TrFE) nanowires and nanotubes.

with a diameter of about 110 nm under the same condition using a template with a pore size of about 90 nm. Fig. 1(b) shows the FE-SEM images of P(VDF-TrFE) nanowires prepared at 230 °C using a AAM with a nominal pore size of 200 nm. It is seen that the nanowires are arranged roughly parallel to one another. The diameter of the nanowires is about 350 nm [Fig. 1(c)], which is approximately 30–40% larger than the actual pore size of the AAM. We have observed that nanowires were formed in the pores of the AAM over a large fractional area of the AAM. Because the copolymer nanowires are very soft, some of the nanowires tangled together after the AAM had dissolved. Fig. 1(d) shows the FE-SEM images of P(VDF-TrFE) nanotubes prepared at a temperature of 260 °C using an AAM with a nominal pore size of 200 nm. Again, we have observed that the P(VDF-TrFE) copolymer has been infiltrated into the pores of the AAM over a large fractional area (FE-SEM images not shown here). The nanotubes produced had a wall thickness of about 40 nm and an outer diameter of about 350–380 nm, which is larger than the pore size of the AAM. Similar expansion in the diameter of polymer nanowires and nanotubes has been observed in electronically conductive polypyrrole nanotubes⁷ and poly(*p*-phenylene vinylene) nanorods and nanotubes.¹⁰ Whether nanowires or nanotubes were formed

depends on the temperature and pore size of the AAM. Higher temperature and larger pore size favor the formation of nanotubes. Moreover, it was found that the length of the nanowires and nanotubes ranges from about 25 μm to 60 μm, which depends on the temperature, evacuation time, and the thickness of the template.

To find out whether the nanowires and nanotubes have the same crystal structure as the bulk samples, X-ray diffraction measurements were made on the nanowires. Beforehand, the copolymer film on the surface of AAM was removed by mechanically polishing and then cleaning with acetone and ethanol. Fig. 2 shows the X-ray diffraction pattern of the nanowires. For comparison, the diffraction patterns of a AAM and P(VDF-TrFE) bulk sample are shown in the inset of Fig. 2. First, we note that there is no Bragg reflection in the 2θ range of 12–40° for the AAM (see inset), indicating that the AAM is amorphous. As is known, the P(VDF-TrFE) with a VDF/TrFE molar ratio of 70/30 is a semicrystalline copolymer which consists of a ferroelectric crystalline β -phase embedded in an amorphous matrix, and the β -phase has a quasi-hexagonal close packing with orthorhombic $mm2$ structure.¹⁷ As seen in the inset, the bulk copolymer sample exhibits an intense diffraction peak at $2\theta = 19.7^\circ$

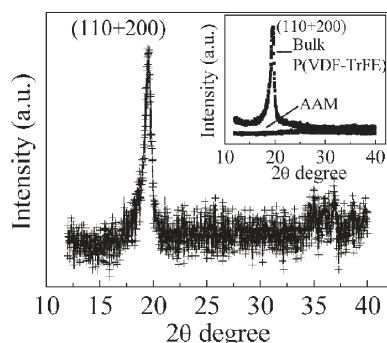


Fig. 2 X-Ray diffraction pattern of the P(VDF-TrFE) nanowires. The inset show the X-ray diffraction patterns of the bulk P(VDF-TrFE) and AAM.

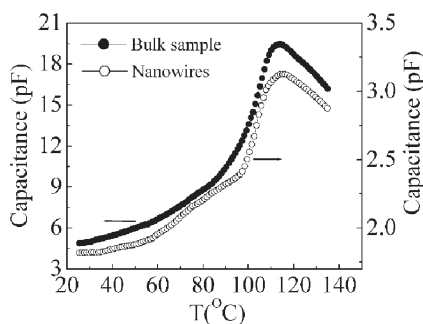


Fig. 3 Temperature dependence of the capacitance of the nanowires and the bulk samples.

which is a characteristic diffraction peak of the ferroelectric phase of P(VDF-TrFE) composed of the overlapping (110) and (200) reflections.¹⁸ Fig. 2 shows that there is a diffraction peak at $2\theta = 19.6^\circ$ for the copolymer nanowires, indicating that the nanowires have the same crystal structure as the bulk sample.

Fig. 3 shows the temperature dependence of the capacitance of the nanowires and the bulk sample, as measured at a frequency of 100 kHz. It is seen that the capacitance of the nanowires and the bulk sample exhibits a peak near 114°C , which corresponds to the paraelectric to ferroelectric phase transition. This implies that the nanowires are ferroelectric at room temperature.

In summary, this is the first report of template-based fabrication of P(VDF-TrFE) copolymer nanowires and nanotubes using a simple and convenient vacuum infiltration method at $230\text{--}260^\circ\text{C}$. X-ray diffraction measurements show that the nanowires have the

same crystal structure as that of the bulk material. The successful preparation of the P(VDF-TrFE) copolymer nanowires and nanotubes demonstrates that the high temperature vacuum infiltration method can be applied to prepare other polymer nanowires and nanotubes using polymers as starting materials. Further investigations on the dielectric and ferroelectric properties of the copolymer nanowires and nanotubes are in progress.

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