Rapid Forming of Nanowire Array on Polyvinylidene Fluoride Polymer Surfaces at Room Temperature by Ultrasonic Loading

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Forming nanostructures on a substrate have been an effective approach to regulating surface properties without changing material chemical compositions. However, such nano-forming processes are generally based on thermal plastic forming that needs to heat substrate material to its melting point, which is timeconsuming and induces a risk of oxidation, aging, or phase transition, especially when the material is a polymer. This research work develops a novel method to rapidly form nanowire arrays on polyvinylidene fluoride (PVDF) polymer at room temperature. Assisted by ultrasonic vibration, nanowires with a diameter of 200 nm are formed on PVDF surface within 0.7 s, while the highest forming temperature is 124 °C only, which is much lower than the melting point. In addition, the original β phase of PVDF can be retained after nano-forming by adjusting ultrasonic loading time. The agglomeration mechanism of the formed nanowires on the surface was also proposed based on the transverse flow and residual stress release during ultrasonic forming process. The water contact angle measurement showed that nanowire arrays altered the surface wettability of PVDF from hydrophilic to hydrophobic. This ultrasonic-assisted processing provides a new approach for functional surface design of PVDF and rapid nanostructure forming for various applications.

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1. Introduction

The design and fabrication of functional surfaces on different substrate materials have been a research hotspot in multidisciplinary fields involving, e.g., material science, advanced manufacturing, and interfacial science. The chemical surface modification and geometric surface patterning are the two commonly used methods to regulate surface free energy and morphology to achieve various surface functions, such as wettability, anti-bacteria, catalysis, electricity, and optical properties.^[1-3] In practical applications, micro/nanosurface patterning is highly desirable for special service conditions rather than chemical modification, considering the better durability without chemical composition changes of functional surfaces.^[4] Therefore, a variety of processes have been developed to form micro/nanostructures on structural and functional materials.

Polyvinylidene fluoride (PVDF) as a kind of polymer with high mechanical strength,

excellent corrosion resistance, and piezoelectric property has been extensively used in the products of various industries,^[5-8] such as battery anode binder, tactile sensor, pipeline system for chemical engineering, ultrafiltration membrane for water treatment, biomedical membrane for bio-separation, as well as nanogenerators. To enhance the performance and achieve functional surfaces, micro/nanostructures have been fabricated on PVDF surfaces mainly by spraying, coating, or thermal plastic forming. A micro-patterned PVDF membrane with anti-fouling behavior was prepared by sprayed non-solvent induced phase separation (NIPS), and the rectangular and triangular patterns with a feature size of 500-5000 µm were obtained by spraying and casting of PVDF-based solutions.^[9,10] Similarly, the diamond spacer was used as a template to form patterns on the films synthesized from the NIPS process of PVDF solutions. The obtained patterned PVDF membrane significantly increased the effective surface area and flux, and exhibited superhydrophobicity after chemical modification.^[11] However, this patterning process involved complex steps and required a long processing time of over 4 h. A simplified way was carried out to directly pour hot PVDF solutions on a polydimethylsiloxane (PDMS) template along with a quenching to obtain a membrane surface with sharkskin features to enhance its water-repellent property and



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water flux.^[12] The soft lithography-based process combining spin coating with hot stamping has also been developed for PVDF microstructures with lateral dimensions down to 1 um.^[13] In this process, the PVDF solution was spin-coated on the PDMS stamps and annealed under 100 °C for 5 min to obtain PVDF micro-pillars arrays at the diameters of 5 µm and 10 µm to increase the sensitivity of the acoustic pressure sensor.^[14] In addition, the micropatterns of 30 µm hexagons and 2 µm wide lines were formed on PVDF/PMMA blend films by transferring printing at 200°Cto achieve unique micro-capacitors.^[15] A series of PVDF micropillar arrays were fabricated by dip-coating along with hot imprinting by PDMS stamps to get a much higher piezoelectric coefficient after calcination and poling.^[16] In addition to the microstructures formed by the processes above, PVDF nanowire arrays with a diameter of 200 nm were prepared for flexible piezoelectric tactile sensor by hot embossing at 185 °C using the anodic aluminum oxide (AAO) template.^[17] The ultrasonic forming process was adopted for the nanowire fabrication on PVDF to improve the performance of the triboelectric nanogenerator,^[18] but the formed structures exhibited quite an irregular arrangement and low fidelity, due to the lack of control of loading heat and parameters. Subtractive process such as laser ablation has also been explored to fabricate features on PVDF,^[19,20] whereas the thermal defects need to be more effectively suppressed. It can be seen that PVDF integrated with micro/nano-features exhibits superior properties and can be widely used for diverse applications. However, most of the current structural forming methods are based on the manipulation of PVDF solutions with complex processing steps, which is time-consuming and limited to micro-scale structure forming. Thermal plastic forming can obtain nanostructures on PVDF surface, but the forming temperature generally needed is higher than the melting point of PVDF (\approx 170 °C), which may cause a risk of aging and phase transition. Therefore, novel approaches need to be explored for regular nanostructure forming.

Ultrasonic-assisted processing technology has been widely utilized for polymer welding and metal deforming. This research work will develop a facile nano-forming method assisted by ultrasonic loading for regular nanowire arrays on PVDF surfaces at room temperature, inspired by the viscoelastic heating behavior of polymers during ultrasonic welding,^[21,22] as well as the acoustic softening effect^[23–27] and activation effect of ultrasonic vibration on metals.^[28-30] However, the rapid nano-forming process developed in this work is quite different from ultrasonic welding in terms of critical factors, feature size, and processing mechanism. In the ultrasonic welding process, the interface bonding temperature needs to be increased to the glass transition point (T_g) or melting point (T_m) for amorphous or semi-crystalline polymers, and the higher bonding temperature below the thermal degradation point is generally pursued to facilitate the thermoplastic flow, molecular diffusion and fusion on the interface to achieve more reliable bonding.^[31,32] Thus, the temperature control for avoiding the phase transition has barely been considered in ultrasonic plastic welding. In contrast, for the ultrasonic nano-forming process in this work, the maximum forming temperature has been controlled to 124 °C below the melting point, which retained the β phase of PVDF. Besides, in the ultrasonic welding process, the plastic flow and fusion on the welding spots and welding seams in millimeters to centimeters scale are the

critical factors.^[33,34] While, in the ultrasonic nano-forming process in this work, the flow behavior and filling capability of thermoplastic material into AAO template in the nanoscale are considered to form a regular nanowire array on PVDF surface, and the surface morphology of the formed nanowire array also undergoes unique agglomerating evolution after dissolving template. Some researchers have explored the nanostructures forming on metals assisted by ultrasonic loading. For the crystalline metals, Ge et al. utilized the ultrasonic loading for $20 \approx 30$ s to fabricate nanowires on metallic simple substances including Ag, Au, Cu, Al, Ni, Sn, and Bi under a loading force of ≈ 1000 N.^[35] This process produced the alternating dislocations generation and recovery, which facilitated the plastic deformation of crystalline metals,^[23,24] and thus significantly reduced the nano-forming force. While, for the amorphous metals without dislocations and grain boundaries, the nano-forming mechanism under ultrasonic vibration is different. Ma et al. conducted ultrasonic assisted forming on a Zr-based amorphous alloy and obtained nanowires on the surface in a sub-second.^[36] The ultrasonic loading rapidly increased the temperature to 377 °C reaching the glass transition point (T_g) of the amorphous alloy, achieving superplastic flow behavior to form into nanowires. In addition to the thermal effect, it was also found that the high-frequency loading can significantly activate the surface atomic motion and homogeneous viscous flow of amorphous alloy,^[28,29] and thus enhance the plastic forming capability even under a temperature below T_g . Therefore, the effect mechanisms of ultrasonic vibration on different kinds of materials are distinct during nano-forming. In this work, the nanowires array forming process assisted by ultrasonic vibration for PVDF polymer with β phase will be explored, especially the dynamic loading stress, thermal response, and loading time are firstly considered to avoid the phase transition during nano-forming. Nanowires with a diameter of 200 nm are patterned on PVDF within 0.7 s. Also, a new evolution mechanism of nano-patterned surface morphology is proposed based on the transverse flow and residual stress release on the nanoscale during the ultrasonic forming process. The water contact angles of both the original and the patterned PVDF are compared to demonstrate the change in surface wettability.

2. Experimental Section

2.1. Sample Preparation

PVDF ($T_{\rm m} = \approx 170$ °C) polymer with β crystalline phase was selected for the present nanopatterning due to its wide applications in various fields. The PVDF samples with a thickness of 500 µm were cut into a circular shape with a diameter of 10 mm. The samples were first cleaned in absolute ethyl alcohol and deionized water by ultrasonic cleaning, and then dried by nitrogen blow to keep pristine surface for subsequent patterning.

2.2. Nanowire Array Forming Assisted by Ultrasonic Loading

The nanopatterning experiments of PVDF were conducted on an ultrasonic loading system with a resonant frequency of 20 kHz, which consisted of a pneumatic piston, a transducer, a horn, a worktable, and a power supply. The pneumatic piston was to



convert air pressure to mechanical stress on the horn which then exerted compression loading to a sample. Meanwhile, when turning on the ultrasonic power supply, the piezoelectric ceramics of the transducer would convert the alternating current to high-frequency (20 kHz) mechanical vibration with the maximum amplitude of 60 µm on the horn to achieve the ultrasonic loading on the PVDF sample. Porous anode aluminum oxide (AAO) templates with a diameter of 5 mm, which were synthesized by an anodic oxidation process^[37,38] were utilized in the forming process. And the size of nanoholes of the AAO template can be regulated by adjusting electrochemical parameters.^[39,40] As schematically shown in Figure 1, the ordered hole arrays with a diameter of 200 nm and pitch size of 450 nm were distributed on the AAO template, the scanning electron microscope (SEM) images were shown in Figure S3, Supporting Information, and the template was stacked with a PVDF sample. In addition, the copper film with a thickness of 200 µm was placed between the ultrasonic horn and AAO template as a buffer layer to uniformly transfer the loading stress. Under ultrasonic compression loading at room temperature, the softened PVDF surface material will fill in the nanoholes of the AAO template, which was induced by the thermo-mechanical stress. Then, the AAO template embedded in the sample surface was dissolved in the 15% wt NaOH solution within 10 min. Therefore, the nanowire array was rapidly patterned on the PVDF surface.

2.3. Dynamic Force Measurement and Thermal Imaging

The stacked PVDF sample, AAO template, and copper film were placed on a dynamometer mounted on the worktable of the ultrasonic loading system to record the real-time stress exerted on the PVDF sample in nanopatterning. The stress data were collected and processed by a data-acquisition card (National Instruments NI-9237) at the frequency of 2000 Hz. At the same time, the infrared thermal images and the corresponding temperature of the PVDF sample during the ultrasonic loading were captured from a side view by an infrared imaging camera (Fotric 280 d). This experimental scheme can effectively evaluate the dynamic stress and thermal characteristics of PVDF during ultrasonic loading.

2.4. Phase Transition Identification

The phase transition of the PVDF sample with the β phase used in the patterning experiments may occur under certain

thermo-mechanical stresses. Thus, the PVDF phase was detected by an X-ray diffraction (XRD) instrument (Rigaku MiniFlex 600) using the Cu K α radiation at the wavelength of 0.154 nm. The XRD pattern was acquired in a scanning angle 2θ range of 10° – 90° at the scanning rate of 4° per minute and the scanning interval of 0.02°.

2.5. Surface Chemistry Detection

The Fourier transform infrared (FTIR) spectrum tests by an equipment of Nicolet iS50, and the X-ray photoelectron spectroscopy (XPS) tests by an equipment of PHI 5000 Versaprobe III have been conducted for the original PVDF and the nanopatterned PVDF with nanowires obtained by ultrasonic forming, which is to clarify the surface chemistry changes after ultrasonic processing. The test results are shown in Figures S1 and S2, Supporting Information.

2.6. Surface Structure and Wettability Characterization

The nanostructures on the PVDF surfaces formed by ultrasonic loading were examined at different patterning areas under an SEM,(FEI Quanta 450FEG) after spray gold treatment. The surface wettability of both the original and patterned PVDF was characterized by water contact angle (WCA) which was measured by a droplet shape analyzer (DSA100S, Krüss) with a 1 μ L volume of water droplets.

3. Results and Discussion

The stacked layers of the PVDF sample, AAO template, and copper film were subjected to the compression loading of the ultrasonic horn as demonstrated in Figure 1. The loading process can be divided into two steps as shown in **Figure 2**a, the quasi-static loading was first applied on the stacked layers to eliminate interface gaps and to achieve a tight contact. It has been widely proved that higher pressure can improve the filling capability of thermoplastic materials into the nanoholes, thus achieving longer nanowires during the template forming processes,^[41,42] while the nanowire diameter is mainly determined by the hole diameter of the AAO template. In this research, the ultrasonic loading was utilized to fabricate a nanowire array on a PVDF surface, and the dynamic loading pressure was measured as shown in Figure 2a, it can be found that the instantaneous loading







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Figure 2. Dynamic stress and thermal behavior of the PVDF during ultrasonic assisted nano forming. a) Dynamic stress in different loading steps along with loading time. b) Temperature variation of the loading area of PVDF during the ultrasonic loading. c) The X-ray diffraction (XRD) patterns of the original sample and that after ultrasonic loading (UL) with different periods of time. (d) Thermal infrared images of PVDF at different loading steps.

pressure fluctuated significantly when applying the ultrasonic loading which caused surface waves and vibration of PVDF. This dynamic contact behavior between AAO template and sample surface induced the nonuniform stress and heat distribution on the forming area of PVDF surface, which will influence the filling capability of different areas during structural forming, especially, the nonuniform structural forming can be observed in the nanoscale forming process. As shown in **Figure 3**, the nanowires with different lengths were formed randomly on the PVDF surface due to the dynamic thermo-mechanical load under ultrasonic forming. Thus, it's difficult to quantitatively characterize the corresponding relation between the applied dynamic pressure and the formed nanowire length. While based on the previous experiments, it can be found that high loading pressure may break the brittle AAO template with a thickness of $50 \,\mu$ m, and also produce high temperature due to the viscoelastic



Figure 3. Scanning electron microscope (SEM) images of the nanowire array surface of the PVDF obtained by ultrasonic assisted forming. a) Surface morphology of the patterned PVDF. b) Short nanowire array area corresponding to region R1 in (a). c) Long nanowire array area corresponding to region R2 in (a). d) The mixed area of nanowires with different aspect ratios. e,f) The enlarged images of the vertically aligned nanowires and those agglomerated.



heating behavior, which reduced the forming performance and caused phase transition of PVDF. Therefore, considering these factors, a maximum initial loading pressure was optimized and selected as 1.27 MPa corresponding to 100 N (Figure 2a) to facilitate the nanowires forming while retaining the original β phase of PVDF. When the loading force reached up corresponding to 1.27 MPa, the ultrasonic vibration of the horn along the loading direction was triggered with the frequency of 20 kHz and the maximum amplitude of 60 µm, with which the ultrasonic loading (UL) was exerted on the stacked layers in ≈ 0.3 s, inducing stress fluctuation causing the relative sliding and clearance between stacked layers, especially during the half cycle period that the ultrasonic horn vibrated backward. The peak stress was about 4 MPa, while the general stress was less than 2 MPa during ultrasonic loading. Due to the vibratory friction and elastic-plastic deformation, a part of the ultrasonic vibration energy was dissipated into heat in the loading area, making the temperature of the PVDF rise rapidly from room temperature to the highest of 124 °C along with the ultrasonic loading (Figure 2b). The thermal infrared images clearly demonstrated the continuous thermal variation of the PVDF under different loading steps including pre-loading (period 1), quasi-static loading (period 2), ultrasonic loading (period 3), and unloading (period 4) (Figure 2d).

The comparison of the XRD peaks of the original and processed samples showed that the patterned PVDF after the ultrasonic loading (UL) of 0.3 s retained the original β phase (Figure 2c) which can be considered as 100% β phase content, while part of the β phase tended to change to the α phase after the UL of 0.8 s, because a combination XRD peaks of both the phases appeared. Thus, the PVDF exhibited a phase transition due to the excessive thermo-mechanical load, and the β phase content decreased to \approx 62.8%. This is because the ultrasonic loading after a sufficiently long period of time would increase the thermo-mechanical stress, and hence make the molecule bonds break and rearrange. By regulating the ultrasonic loading time, such as 0.3 s, the β phase of the patterned PVDF can be fully retained. And the FTIR and XPS tests for the original PVDF and the nano-patterned PVDF with nanowires showed no significant surface chemistry changes after ultrasonic loading, as shown in Figures S1 and S2, Supporting Information. In addition, the patterning process from the smooth PVDF surface into the nanowire arrays can be considered as a small plane stretching, which is a benefit to generating and preserving the β phase of the PVDF.^[43,44] Therefore, this nano-forming process including quasi-static loading and ultrasonic loading can be rapidly accomplished in 0.7 s at ambient temperature without undesirable phase transition.

The rapid nano-forming mechanism can be explained based on the viscoelastic heating behavior of PVDF and the stress wave effect under ultrasonic loading. Due to the intermolecular friction, PVDF will dissipate part of the input energy into heat when subjected to the high-frequency alternating strain induced by ultrasonic vibration.^[45,46] The strain energy of the PVDF under ultrasonic loading involves two parts including the elastic energy (W_e) related to the storage modulus (E_e) and the dissipation energy (W_d) related to the loss modulus (E_i). The dynamic strain of PVDF subjected to ultrasonic loading can be simplified to FNGINFFRING

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where ε_0 is the maximum elastic strain of the material with a sinusoidal strain, *f* is the ultrasonic frequency, *A* is the amplitude of the ultrasonic vibration, and *h* is the initial thickness of the original PVDF sample. The corresponding dynamic stress can be expressed as

$$\sigma = E_e \varepsilon_0 \sin 2\pi f t + E_l \varepsilon_0 \cos 2\pi f t \tag{2}$$

By substituting Equation (1) and (2) into Equation (3), the total energy input into the sample material per unit volume during one ultrasonic vibration cycle can be given by

$$W = \int_0^{1/f} \sigma d\varepsilon = \pi E_l (A/h)^2 \tag{3}$$

Thus, the mechanical energy of ultrasonic vibration is transformed into heat by viscoelastic dissipation, mainly due to the material's loss modulus (E_i). The temperature of the PVDF sample after the ultrasonic loading of time Δt can be estimated as

$$T = T_0 + \alpha W \Delta t f / \rho c = T_0 + \alpha \pi E_l A^2 \Delta t f / \rho c h^2$$
(4)

where T_0 is room temperature, α is the thermal conversion coefficient, ρ and c are the material density and specific heat capacity, respectively. It can be seen that the temperature of the PVDF sample during the ultrasonic loading has a significant positive correlation with the ultrasonic frequency, amplitude, and loading time. Also, the high temperature rising rate can be achieved under the loading with a high frequency.

Therefore, after 0.3 s of ultrasonic loading, the sample temperature rapidly increased to 124 °C, which induced the thermal softening and enhanced flowability of PVDF though this temperature was below its melting point (\approx 170 °C), which is a benefit to the plastic forming of surface structures. Such highfrequency cyclic loading brought about a high instantaneous strain rate,^[23] and produced dynamic stress waves in the PVDF sample. The AAO template can be considered as rigid compared with the PVDF. Thus the dynamic stress will intensively act on the sample surface due to the stress wave reflection and superposition at the template-PVDF interface with different acoustic resistance.^[47] It is well known that the pronounced capillary resistance and interfacial friction are the main barriers in nanoscale forming, which can dramatically increase the required forming force to an infeasible level to overcome.^[48] Thus, this stress concentration on the sample surface during ultrasonic loading can significantly improve the filling capacity of the thermally-softened PVDF into the nanoholes of the AAO template. In addition, the high instantaneous strain rate exerted by ultrasonic loading can effectively reduce the viscosity of the thermoplastic materials.^[49] and the instantaneous strain rate that the ultrasonic vibration introduced in the forming can also decrease the interfacial friction during the nanofilling process,^[50] making the flow more homogeneous and facilitating the nano-forming.

Because of such mechanisms, the nanowire array with a diameter of 200 nm was enabled rapidly on the PVDF surfaces without phase transition. The nanowire surface morphology was shown in Figure 3 after the AAO template was completely dissolved. It can be seen from the SEM images that the formed



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nanostructures contained two types of nanowires with different lengths (Figure 3a). One reason is that the ultrasonic vibration produces sinusoidal strain and surface waves on PVDF, inducing dynamic fluctuating contact between the AAO template and the PVDF surface, such as a relative sliding and clearance between the forming interface. Another reason is due to the original surface morphology of the AAO template, as shown in Figure S4, Supporting Information, the surface morphology measured by white light interferometer showed that the AAO template obtained by electrochemical oxidation was not an ideal flat surface. Though the synthetic process has been optimized to decrease the surface roughness to \approx 300 nm, it will still influence the uniformity of interface contact in the nanoscale during forming. This nonuniformity of dynamic contact can induce uneven heat and stress distribution on different surface regions under ultrasonic loading, thus accordingly forming different types of nanowires. The higher thermo-mechanical stress facilitates the filling process of the PVDF into the nanoholes of the template, forming longer nanowires on the surface. The regions of short nanowires with a length of $\approx 0.5 \,\mu m$ and the long nanowires with a length of $\approx 1 \,\mu m$ were shown in Figures 3b,c, respectively.

The shapes of the two types of nanowires were quite different as shown in the mixed region (Figure 3d). The short nanowires were vertically well aligned (Figure 3e), whereas the long nanowires tended to locally form into bundles due to agglomeration (Figure 3f). This indicated that the nanowires with different aspect ratios have undergone different evolutions after dissolving the AAO template. Similar phenomena have also been observed in the thermoplastic forming of nanowires of metallic glasses,^[48] which also involves the AAO template dissolution after forming. An explanation was that when the formed sample was immersed in acid or alkali solution for etching template, the liquid tension could produce a relatively large capillary force and a menisci interaction force between the nanowire arrays, which made the originally vertically-aligned nanowires tend to bend, especially when the liquid tension induced force exceeded the elastic restoring force of the nanowires.^[51] However, if the original nanowire arrays are distributed uniformly on the patterned sample surface, the liquid tension force around the nanowires should offset each other, which should not significantly influence the morphology of the nanowire. Thus, there should be other factors that affected the evolution from individual vertical nanowires into nanowire bundles.

Here, a new evolution mechanism of patterned surface morphology is proposed based on the transverse flow and residual stress release during the ultrasonic forming process. As shown schematically in Figure 4, the ultrasonic loading perpendicular to the sample surface generates thermos-mechanical stress, causing plastic deformation and transverse viscous flow of the PVDF sample. The sinusoidal strain and surface waves under ultrasonic vibration cause the dynamic fluctuating contact between the AAO template and PVDF surface. In addition, the surface morphology with peaks and valleys in the nanoscale of the AAO template (Figure S4, Supporting Information) also induces nonuniform interface contact. Thus, this nonuniform feature produces uneven heat and stress distribution as well as localized flow in different surface areas under ultrasonic loading. The simulation research also confirmed that the distribution of the heat generated in the loading zone was nonuniform due to the viscoelastic dissipation behavior of polymers under cyclic deformation of ultrasonic loading.^[46,52] The regions with larger thermo-mechanical stress would preferentially appear local transverse flow and fill into nanoholes in addition to the transverse flow of the whole surface, because of the better flowability at a higher temperature. Such regions will also exhibit better filling capacity and can form longer nanowires, as shown in Figure 3. As a result, the softened and viscous PVDF in each of these local transverse flow regions will bear the vertical stress along the nanoholes to fill in the AAO template, as well as the tangential force due to the local transverse flow, as illustrated in Figure 4. Therefore, a bending moment towards the center of the local region was produced on each nanowire. Nevertheless, due to the constraint of the nanoholes wall, the residual bending stress after the solidification of nanowires under room temperature will be released after dissolving the AAO template, causing the high-aspect-ratio nanowires to bend and form agglomeration in each local transverse flow regions, as shown in Figure 3.

The rapidly formed nanowire arrays assisted by ultrasonic loading have significantly changed the surface properties of the PVDF, despite the nanoscale evolution of surface morphology after dissolving the template. To compare the change, the surface wettability of both the original surface and the nanowire patterned surface has been evaluated, as shown in **Figure 5**, which is commonly concerned in various application scenarios.^[53] It can be seen that the original hydrophilic surface with the WCA of 69° was converted to the hydrophobic surface (WCA = 104°) after nano-forming. The wettability transition is due to the reason that the intensive nanowire arrays have effectively increased the area of the water–air contact interface



Figure 4. Nanowire agglomeration mechanism of PVDF after ultrasonic assisted forming.





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Figure 5. Surface wettability of the original and nano patterned PVDF surfaces.

between the water droplet and solid surface, which significantly alters the contact state. This comparison demonstrated the feasibility of the present rapid fabrication method for nanofunctional surfaces assisted by ultrasonic loading.

4. Conclusions

This research has developed a novel method to rapidly form regular nanostructures on PVDF surfaces assisted by ultrasonic vibration, which can also be extended to other thermoplastic materials. Nanowire arrays with a diameter of 200 nm have been successfully patterned on PVDF surfaces within 0.7 s by using an AAO template under ultrasonic loading at ambient temperature. The undesired phase transition of PVDF during nano-forming can be avoided, owing to the short forming time and low forming temperature below melting point under ultrasonic loading. The high instantaneous strain rate and high-frequency cyclic loading energy can be converted rapidly into heat and can produce intensive stress waves on the surface to enhance the filling capacity of the thermal softened PVDF. A new nano-evolution mechanism of the patterned surface morphology has also been proposed, based on the transverse flow of local regions during nanoforming, as well as the residual stress release after template dissolving. The nanowire patterned surface exhibits a hydrophobic property in contrast to the original hydrophilic surface, demonstrating that the present novel nano-forming method assisted by ultrasonic vibration can be used for functional surface fabrication on multiple scales.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

nanowires, PVDF, rapid forming, ultrasonic loading

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