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Complementary Microscopy Techniques Applied for Characterizing the Localized Nanoscale Structure of Poly (Vinylidene Fluoride)

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Poly (vinylidenefluoride) (PVDF), a well-recognized electroactive polymer, has been studied extensively over many decades. Recently, there has been increasing interest in tuning the electrical properties of PVDF from ferroelectric to piezoelectric and to pyroelectric, which can be attained via controlling the microscale structure down to the nanoscale structure [1-2]. To optimize the preparation conditions of PVDF and its copolymers, as well as to improve the performance for many applications, comprehensive analytical techniques are of great importance. In this paper, we demonstrate complementary nanoscale characterization and measurement techniques, by conducting a systematic

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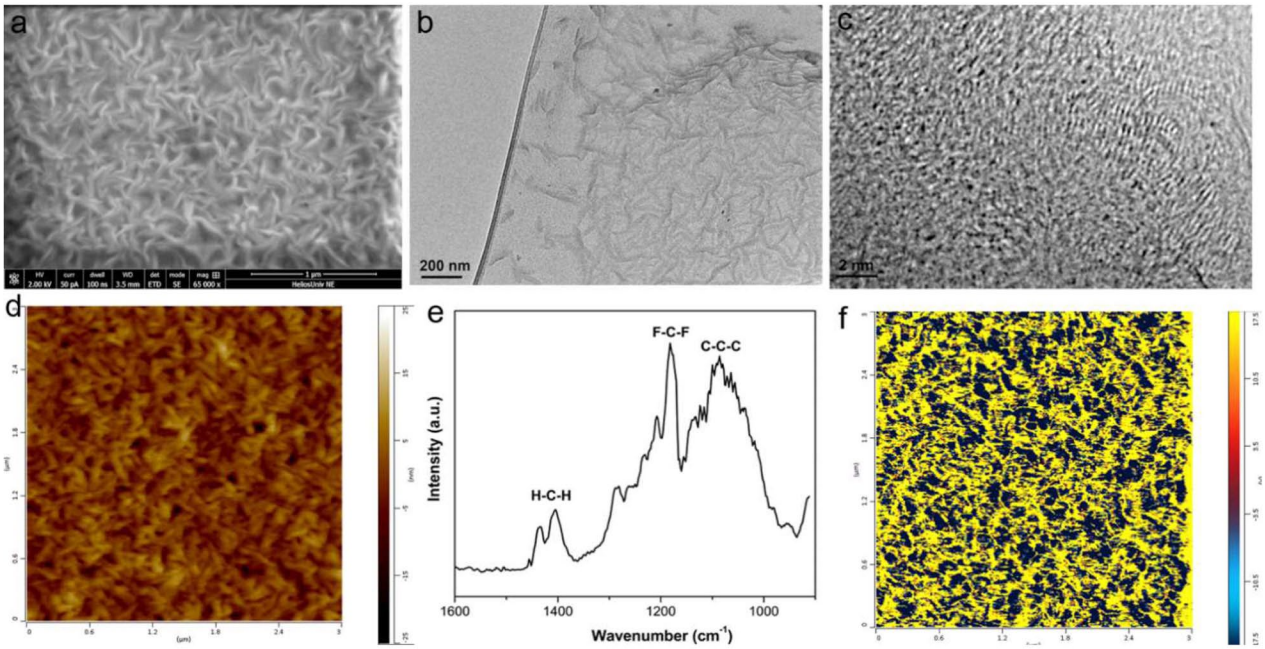

Figure 1. (a) SEM image of typical PVDF morphology; (b-c) Low magnification and high magnification TEM images of PVDF showing that the annealed PVDF film is partially crystallized and partially amorphous; (d) AFM topography image of PVDF with a scan area of 3 μm x 3 μm; (e) Localized nanoscale IR spectra; (f) Corresponding chemical mapping image at the wavelength of 1066 cm^{-1}, showing the map for the C-C antisymmetric stretching absorption band.

and coordinated study involving scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), nanoscale infrared (IR) spectroscopy, chemical mapping and force mapping, to probe the localized morphology, crystalline structure, molecular structure, chemical property and stiffness mapping at the nanoscale.

The thin PVDF film (80-100 nm in thickness) studied here was made of a copolymer of 70% vinylidine fluoride and 30% trifluoroethylene, P(VDF-TrFe). This film was spin-coated on a substrate of a p-type silicon wafer, followed by drying and annealing at 135 °C for 4h in a vacuum oven. Fig. 1a shows an SEM image of typical PVDF morphology which has a high density forming on the substrate. Figs. 1b-c show low magnification and high magnification TEM images, respectively, which confirm that the annealed PVDF film is partially crystallized and partially amorphous. Fig. 1d shows

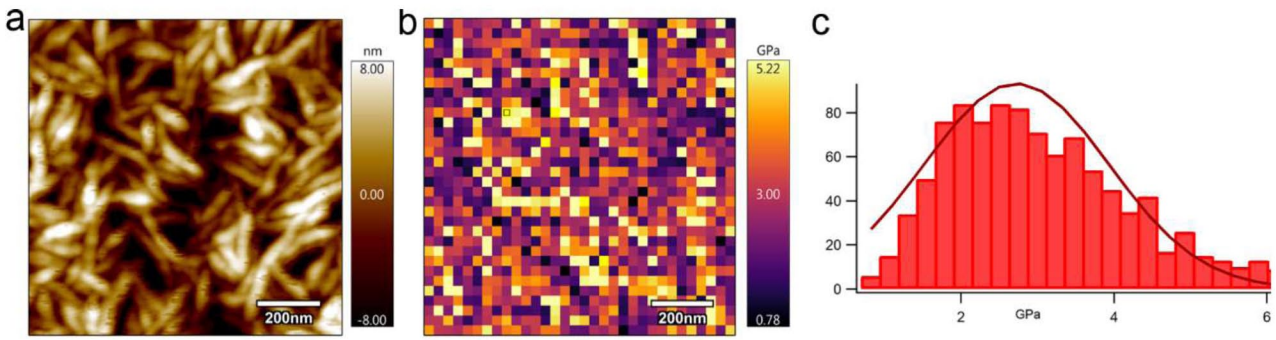

Figure 2. (a) AFM topography image of PVDF with a scan area of 1 µm x 1 µm; (b) Corresponding force map by making numerous load-displacement curves onto the scan area; (c) Histograms of elastic modulus obtained from the force map shows the measured modulus primarily ranges from 1.75-3.50 GPa.

an AFM topography image of PVDF with a scan area of 3 µm x 3 µm. By positioning the AFM probe to a specific location, we can acquire the localized IR spectrum with nanoscale resolution. Note that the probe tip radius is approximately 50 nm, which is far below the conventional optical diffraction limit [3]. As shown in Fig. 1d, the C-C antisymmetric stretching, CF2 antisymmetric stretching, CH2 wagging and CH2 bending stretch of all-trans (TT) chains structure at 1071 cm^{-1}, 1176 cm^{-1}, 1398 cm^{-1} and 1428 cm^{-1}, are the fingerprint for β-phase in the IR spectrum. Besides IR spectrum, we can also acquire the corresponding chemical map. We fixed the laser frequency at 1066 cm^{-1} and recorded the AFM cantilever deflection amplitude. Fig. 1e shows this map for the C-C antisymmetric stretching absorption band, which allows us to investigate the relationship between morphology and molecular structure of the same section.

Fig. 2a shows the AFM topography image of PVDF film with the scan area of 1µm x 1µm. Fig. 2b shows the corresponding force map, which was acquired by making numerous force curves onto the scan area. By analyzing the load-displacement curves, we calculated the local elastic modulus. A histogram obtained from the force map (Fig. 2c) shows the measured modulus primarily ranges from 1.75-3.50 GPa. Complementary techniques of SEM, HRTEM, AFM, nanoIR, and force mapping can provide comprehensive localized nanoscale morphology, structural, chemical, and mechanical analysis, which greatly enable the broader applications in sensors, actuators, and energy harvesting [4].

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