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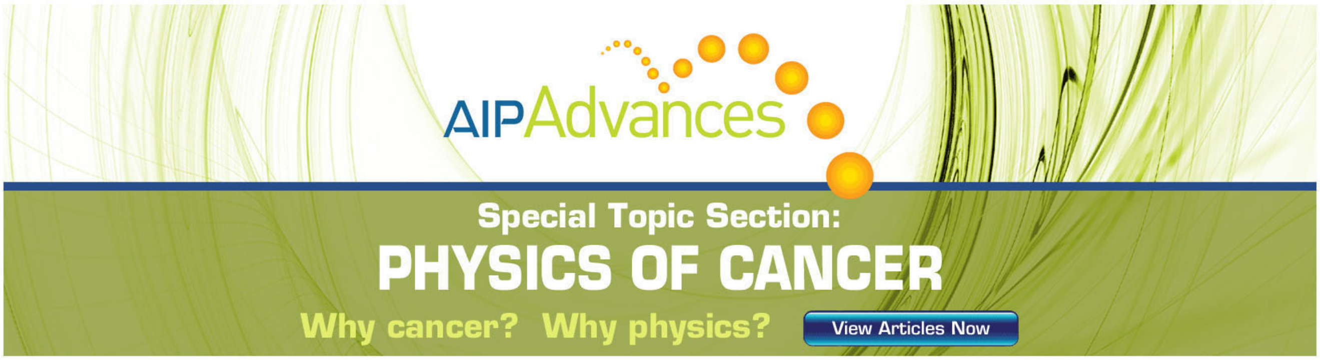

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APPLIED PHYSICS LETTERS **100**, 043702 (2012)

Evidence of ferroelectricity and phase transition in pressed diphenylalanine peptide nanotubes

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Self-assembled peptide nanotubes (PNT) are unique nanoscale objects having a great potential for a multitude of applications. Strong piezoactivity and polar properties in aromatic dipeptides were recently observed in stand-alone nanotubes using piezoresponse force microscopy and 2nd harmonic generation. In this work, we report macroscopic dielectric and polarization vs. field measurements on pressed PNTs before and after annealing at 150 °C. The results corroborate nanoscale study and present a clear evidence of ferroelectric-like behaviour and phase transition in this technologically important material. The dielectric constant of PNT pellets obeys apparent Curie-Weiss (CW) law with the CW constant $C \approx 230\,^{\circ}C$ and transition temperature at $T \approx 142\,^{\circ}C$. *© 2012 American Institute of Physics*. [doi:10.1063/1.3676417]

Ordering of molecular dipoles and ferroelectricity in organic materials are becoming increasingly important in view of promising opportunities offered in the fields of microelectronics and biosystems.[1–3] Many organic biomaterials including proteins, peptides, aminoacids, and polysaccharides have highly organized molecular dipole assemblies[3–5] and can be, in principle, switched by the external electric field, e.g., to be ferroelectric. Diphenylalanine (FF) peptide nanotubes (PNT) are example of such material and have been extensively studied in view of multiple applications as biocompatible templates, biosensors, tissue engineering components, etc.[6–9] They possess remarkable physical and chemical properties including high mechanical stiffness,[10] high crystallinity,[9] biofunctional interfaces,[11] etc. In particular, strong piezoelectric and polar properties in FF PNTs were observed by piezoresponse force microscopy (PFM)[12] and 2nd harmonic generation (SHG)[13] techniques. Piezoelectric coefficients were unexpectedly high, reaching 60-70 pm/V in shear mode,[12] thus being of the order of these in conventional ferroelectrics such as $LiNbO_3$. However, it was not possible to switch polarization along the tube axis due to geometrical constraints and extremely high coercive field as observed by switching spectroscopy PFM.[13] Temperature-dependent PFM and SHG studies revealed the existence of irreversible phase transition at about 140-150 °C from polar hexagonal to non-polar orthorhombic structure.[13] This study was undertaken in order to investigate this irreversible phase transition in PNTs by conventional dielectric method on macroscopic samples prepared by pressing of self-assembled PNTs into pellets and thus to confirm ferroelectric-like properties in aromatic peptides. Local piezoelectric properties were measured too in order to link current results to previous data on stand-alone tubes.

PNT pellets were prepared by dissolving the FF building blocks in lyophilized form in 1,1,1,3,3,3-hexafluoro-2-propanol at a concentration of 100 mg/ml. The stock solution was then diluted to a final concentration of 2 mg/ml in double-distilled water for the self-assembly process to occur. The diluted solution was dried onto a gold coated silicon surface (150 nm Au, 15 nm Cr). The PNT powder was made by scraping off the tubes and subsequent uniaxial cold pressing (50 MPa) into pellets of 10 mm in diameter and 0.1–0.2 mm in thickness. Silver electrodes were then deposited onto major faces by sputtering. The dielectric constant was measured using a HP 4284A Precision LCR meter as a function of temperature in a homemade furnace. Polarization vs. voltage measurements were performed using a conventional Sawyer-Tower method at room temperature. PFM characterization was done with a commercial atomic force microscope (Ntegra Prima, NT-MDT) equipped with external function generator and lock-in amplifier (see more details in Ref. 14). Doped Si cantilevers with the spring constants in the range 0.02-1 N/m driven at a frequency 5 kHz were used.

Figures 1(a)–1(c) show representative scanning electron microscopy (SEM) images of the investigated FF PNT samples in three different forms. As expected, as-grown PNTs demonstrate a variety of tubes of different lengths, diameters, and lateral orientations due to their spontaneous self-assembly on the substrate surface (Fig. 1(a)). After pressing, the microstructure looks much more uniform due to tube crashing and densification process (Fig. 1(b)). Sometimes, we could even observe the tube fragments embedded into dense matrix. Temperature treatment (at about 150 °C) led to "recrystallization" of some tubes and their reappearance on the surface of the pellet (Fig. 1(c)). The crystallographic structure was followed by conventional x-ray powder

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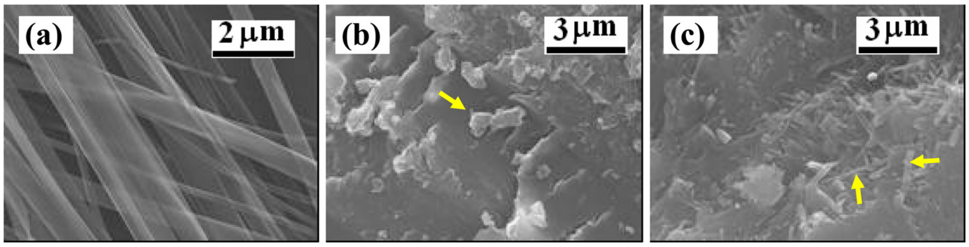

FIG. 1. (Color online) SEM images of (a) stand-alone tubes, (b) after cold pressing under 50 MPa, (c) after annealing at 150 °C. Yellow arrows show remaining tube fragments (abundant for annealed tubes).

diffraction method (see supplementary material for further details[31]). The positions of XRD peaks in pressed samples are very close to those of stand-alone tubes for both hexagonal (before annealing) and orthorhombic (after annealing) structures, respectively.[6,31] Different intensity of the peaks (and their suppression in some cases) could be satisfactorily explained by additional stresses and defects appeared due to pressing. Thus, it can be concluded that the pressed samples may adequately represent electrical properties of the original nanotubes taking into account the effects of mechanical stress and notable porosity.

In order to link our macroscopic data to nanoscale measurements performed on stand-alone tubes, we performed PFM imaging in order to reveal polarization distribution and possible switchability at the nm scale. The results are presented in Figs. 2(a) and 2(b) for pressed PNTs samples before and after heating at 150 °C. The observed clear out-of-plane (OOP) and in-plane (IP) PFM contrasts in virgin PNTs sample are compatible with their piezoelectricity in the axial direction (providing both longitudinal and shear deformations) and varies in the magnitude and phase because of the random orientation of the tube fragments in the pressed sample. The maximum effective vertical piezoelectric coefficient exceeds ≈7-8 pm/V judging by the comparison of PFM histogram peaks in Fig. 2(d) with those of triglycine sulphate (TGS) single crystals (not shown). This is comparable with the previous d_{33} estimation obtained for vertical PNT bundles.[13] On the other hand, no piezocontrast was seen in annealed tubes (Fig. 2(b)) due to their anti-polar arrangement.[13] Nanoscale poling of two stripes (±100 V, 10 lines) was then performed during the scanning of the 10 × 10 μm^2 area in the contact regime for pressed sample before and after annealing (Figs. 2(b) and 2(c)). As-pressed pellets (before annealing) did not show any switching behaviour even after high electrical bias applied to the surface. This is consistent with their poor switching properties in a full agreement with earlier PFM results.[12] Completely different switching properties were observed in annealed pellets (Fig. 2(c)) where strong polarization signal appears after poling.

Further, the samples were tested for the possible switching behavior using a modified Sawyer-Tower method at room temperature. Pressed (but not annealed) samples demonstrate almost linear polarization vs. field dependence up to 400 kV/cm (Fig. 3(a)). Weak hysteresis seen in this figure may come from the conductivity contribution to the switching current.[15] This behavior is expected in view of the extremely high coercive field and unfavorable (random) configuration of the tube fragments pressed into a dense pellet. On the contrary, annealed pellets show clear polarization hysteresis compatible with their nanoscale properties presented in Fig. 2(c). The maximum polarization value is about 0.2 μC/cm^2 but this is only a lower estimate as the polarization did not reach saturation. The molecular modeling predicts the saturation polarization value in the orthorhombic phase in the radial direction ~0.75 μC/cm^2.[16] If we assume that only radial polarization contributes to the total switching polarization, we should average all possible orientations of the tube fragments to calculate the mean value of the polarization under saturation:

$$P_{av} = \frac{\int_0^{\pi/2} \int_0^{\Phi} P_S(\cos\theta \sin\theta d\theta) \cos\varphi d\varphi}{\int_0^{\pi/2} \int_0^{\Phi} \sin\theta d\theta d\varphi}, \qquad (1)$$

where φ is the angle between the tube axis and electric field direction and θ describes the orientation of polarization in the radial direction. If we assume that the polarization can be radially switched between possible *a* and *b* directions in the orthorhombic structure, this equation is simply reduced to $P_{av} = \frac{\sqrt{2}P_S}{\pi} \approx 0.34\,\mu\mathrm{C/cm}^2$. This value is quite close to that observed in our work but is apparently lower because the hysteresis by far did not reach the saturation. Higher fields cause irreversible degradation of the investigated pellets.

It has been recently shown[13] that the structural transformation in peptide nanotubes occurs at about 150 °C. To prove the existence of phase transition, we undertook conventional dielectric permittivity measurements as a function of temperature (Fig. 3(b)). The measurement revealed the occurrence of the clear peak on heating at this temperature pertaining to the apparent phase transition from the polar hexagonal to non-

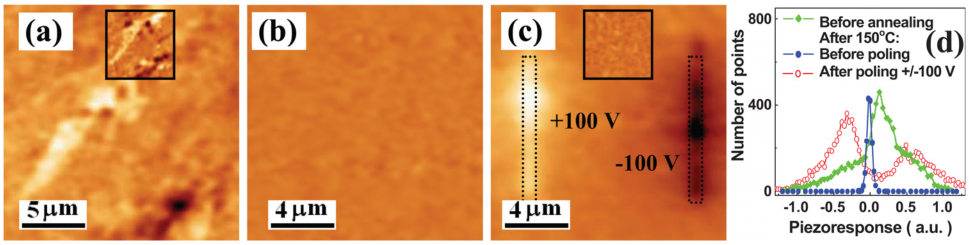

FIG. 2. (Color online) (a) OOP PFM image of PNT pellet (before annealing). (b) OOP PFM image of annealed (150 °C) pellet. (c) OOP after poling under +100 and −100 V for annealed sample. (d) Comparison of PFM histograms in PNT pellets. Insets to (a) and (c) are the corresponding IP images (horizontal scales 25 × 25 and 20 × 20 μm^2, respectively). Dotted lines delineate poling areas (10 passes of the cantilever).

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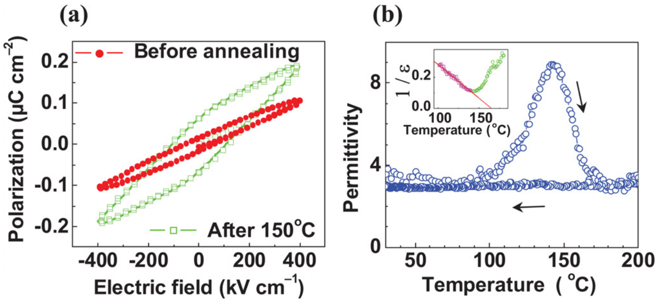

FIG. 3. (Color online) (a) Polarization hysteresis loops of PNT pellets before and after annealing. (b) Temperature dependence of the dielectric permittivity and inverse dielectric permittivity (inset) in as-pressed sample. Arrows indicate heating or cooling cycles.

polar orthorhombic phase with $T_{max} = T_C = 142\,°C$. Moreover, fitting of the temperature dependence of the inverse permittivity below T_{max} yields classical Curie-Weiss behavior: $1/\varepsilon = (T_{cw} - T)/C_W$ with the Curie-Weiss constant C_W of about 230 °C and $T_{cw} = 162\,°C$. It was not possible to extract the CW law above T_{max} due to the scattering of data points caused by irreversible disordering and possible degradation. The behavior is in full agreement with earlier results by PFM and SHG where irreversible changes of piezocontrast have been observed.[13] The value of CW constant is characteristic of the order-disorder phase transition and can be rationalized in terms of ordering of polar groups with permanent dipole moments as common in organic ferroelectric, for example, in squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione).[17] Large difference between T_{max} and T_{cw} hints to the first-order-like phase transition. However, we could not observe any temperature hysteresis as the transition was irreversible and possibly accompanied with the small water and phenylalanine loss.[18] The maximum value of effective dielectric permittivity ε of the pressed pellets at the maximum (that is apparently lower than that expected in stand-alone tubes) is about $\varepsilon \approx 10$, while at room temperature this value is $\varepsilon \approx 4$, in a good agreement with published results on similar biomaterials.[19] Again, these values are lower estimates of the dielectric constant in stand-alone tubes due to apparent porosity in pressed samples.

A possible explanation of the low Curie-Weiss constant values and mechanism of the weak ferroelectric-like behavior in pressed PNTs is based on the common for these organic molecular structures cooperative proton tautomerism[20] provided by ordering and stacking in sheets through N-H…O hydrogen bonding.[9,21] Peptide nanotubes are also prone to easy changes of the torsion angles and rotation of their dipole moments and thus are susceptible to polarization switching in the applied electric field (if the structure and internal inherent coercive field allow such changes as in the case of annealed samples[13]). We should note that the observed ferroelectric-like properties and switching in FF PNTs are intrinsically linked to other biomaterials based on proteins and peptides,[22] for example, to ion channels in biological membranes. It was suggested that PNTs could serve as artificial ion channels for such biologically significant ions as K^+ and Na^+.[23,24] Curie-Weiss behavior was shown to exist below phase transition in a natural ion channel, as was clearly demonstrated by Leuchtag.[25] Related studies based on *ab initio* modeling of proton transfer in the protein gating segments S4 of ion channels[26,27] have shown that, in order to be a ferroelectric, the coupling between the protons and protein would have to produce a two-minimum potential energy surface for the protons, thus making the type of transition found in macroscopic ferroelectrics possible in S4 segments of natural ion channel, too.[28]

In principle, piezoelectrictiy in compliant polymers can come from the well-known electret effect (as well as an apparent hysteresis under high electrical bias), and thus the observed effects could be due to the space-charge polarization as common to various polymers and composites on their base.[29] However, the fact that PNTs possess sufficiently high Young modulus ($E \approx 19\,GPa$)[30] and their inherent properties such as Curie-Weiss law, symmetry change with temperature and observed polarization hysteresis conjecture in favor of ferroelectricity. Evidently, further measurements and modeling efforts are needed to clear out the microscopic origin of the ferroelectric-like behavior in this material.

In conclusion, a strong evidence of ferroelectricity in pressed FF peptide nanotube samples is demonstrated in this work. Common to ferroelectrics, a classical Curie-Weiss behavior and permittivity peak are found in the as-prepared state of PNTs on heating. The polarization switching is hampered by the high coercive field and random orientation of the tube fragments in pressed pellets. However, the samples can be switched after annealing at about 150 °C due to the phase transition into the orthorhombic phase where electric field-induced rotation of the radial polarization component becomes possible.[16] The cooperative motion of protons is suggested as the mechanism of ferroelectric-like behavior in this technologically important material.

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