First Preparations and Characterization of Conductive Polymer Crystalline Nanoneedles[†]

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Summary: Single crystalline nanoneedles of three families of the most studied conductive organic polymers - polythiophene, polyaniline and polypyrrole - were synthesized for the first time using an interfacial polymerization process that takes place with simultaneous crystallization. As the crystal growth is concurrent with polymerization, more ordered crystal packing can be expected. Most of the bulk conducting-polymer systems studied contains regions that are inhomogeneous. Single nanocrystals of conducting polymers have not been reported, although needle-shaped bulk crystals of the quarterphenyl cation radical salt have previously been studied. The investigation of processes in a nanodomain of a single crystal is critical in ascertaining the *inherent* electronic properties of polymer nanoelements. The organic conductive nanoneedles were characterized using TEM, HRTEM, electron diffraction, EDS, and EPR to establish their crystal structure and composition. Scanning tunneling microscopy/spectroscopy (STM/STS) investigation were conducted to examine their electronic behaviors, leading to the discovery of a field-induced conductance switching with response times on the millisecond level. The switch voltages are in the range of 3 to 4 volts in STM experiments, consistent with the trend of the band gap of the three polymers. The organic conductive nanoneedles with nano-tip having high density of mobile electron may serve as interesting elements for nanoscale electronics.

Keywords: conjugated polymers; organic electronics; organic nanostructures

Introduction

While inorganic crystal in nanometer scale has been an area of intense investigation,[1,2] the subject of organic polymer nanocrystals in high purity is yet to be developed. We summarize here the first synthesis of conductive polymer nanocrystals with fast electronic conductance switching function developed in our laboratory. These systems, we believe, are of both fundamental as well as technological significance. Such novel nanoelectronic material can serve as elements for revolutionary nanoelectronic devices. For example, the nano-tip with high density of mobile electron in the conductive needle can serve as conductive nanoprobe.[3] These organic crystals are conjugated systems, which have been, in bulk state, applied successfully to electronics based on their tunable electronic properties and adaptability to conventional processing methods.[4–13] Polythiophene (PEDOT), polyaniline (PANI) and polypyrrole (PPY) nanoneedles are the focuses

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[†] This presentation is based on: Dr. Kai Su's Ph.D. dissertation (CUNY 2007); K. Su, N. Nuraje, L. Zhang, I. W. Chu, R. M. Peetz, H. Matsui, N. L. Yang, *Adv. Mater.* **2007**, *19*, 669; and N. Nuraje, K. Su, N.-l. Yang, H. Matsui, *ACS Nano* **2008**, *2*, 502.

of our current effort in interfacial polymerization process; To date, these three macromolecules represent the most important group of conducting polymers.[14]

Most bulk conducting polymer systems studied consist of crystalline as well as amorphous regions. Fundamental study of the processes in nano-domain is essential in ascertaining the inherent electronic properties of polymer nano-elements. Single nanocrystals of conductive polymer have not been reported; although needle-shaped bulk crystals of quarterphenyl cation radical salt were previously studied,[15,16] and highly ordered polymer structures were prepared by methods including electrochemical epitaxial polymerization,[13] solution spin-coating on functionalized surface,[17] and solid-state polymerization of monomer crystals.[18]

Applications of interface synthesis to prepare nanomaterials have been well-documented.[19,20] A general scheme of applying an interfacial polymerization-crystallization process to prepare single crystals of conductive conjugate polymer in nanoneedle form is as follows, using (PEDOT) system as an example.

The aqueous/organic interfacial system used was composed of 3, 4-ethylenedioxythiophene (EDOT) in an organic solvent and an oxidant, ferric chloride ($FeCl_3$), in DI water. The use of ferric chloride as oxidant in the precipitation polymerization of thiophenes has been documented.[21–23] In such cases, polymer chains are generally formed first, followed by precipitation formation of crystals. Our system represents the first use of ferric chloride in the interfacial polymerization of thiophenes. This polymerization proceeds with an attendant crystal growth, thus higher order of crystal packing can be expected. The process has been also extended to the polymerization of anilines and pyrroles.

Experimental and Results

Synthetic methodology was described elsewhere for the three monomers.[24,25] PEDOT is used here as an example of synthesis. In a typical synthesis, the monomer was dissolved in dichloromethane (DCM, 5 mL, 1 mg/mL) served as the lower organic layer and $FeCl_3$ dissolved in DI water (5 mL, 1 mg/mL) as the upper layer. After 2 days, the aqueous layer was then carefully collected for purification. To prevent the hydrolysis of $FeCl_3$, 5 drops of concentrated HCl solution (37%) were added into the collected suspension. The nanoneedle suspension was then centrifuged and re-suspended three times followed by a final dialysis process for 10 hours using a dialysis tubing (D9277, Sigma-Aldrich) in ultrapure water.

The oxidative coupling polymerization of EDOT involving an aqueous/organic interface was facilitated by $FeCl_3$,[26] representing a system of crystallization during polymerization in the nano-regime. This oxidative coupling of EDOT was much slower than the fabrication of polyaniline (PANI) nanofibers from a similar process.[27] The PEDOT nanoneedle samples were usually collected after 48 hours while the formation of PANI nanofibers using persulfate as the oxidant required at most 10 minutes. Unlike the usual solution polymerization followed by a formation of insoluble crystals, this slow coupling polymerization involved an interface mediating the formation of superior crystal packing in the product. The nanocrystals are composed of PEDOT from an ensemble of degrees of polymerization, as expected from their needle shape, with inner chains longer than the outer ones. The PEDOT products from our system show clearly nanoneedle structures having a width of about 15 nm and a length of about 50 nm with pointed tips (Figure 1a, b: transmission electron microscopic, TEM, images). Based on the 50 nm needle length, longest possible chain would have 126 thiophene rings. There may be more than one chain tip-to-tip. To our best knowledge, this is the first reported needle-shaped conducting polymer nanocrystalline structure.

The initial formation of PEDOT nanoneedles was most likely from the interface

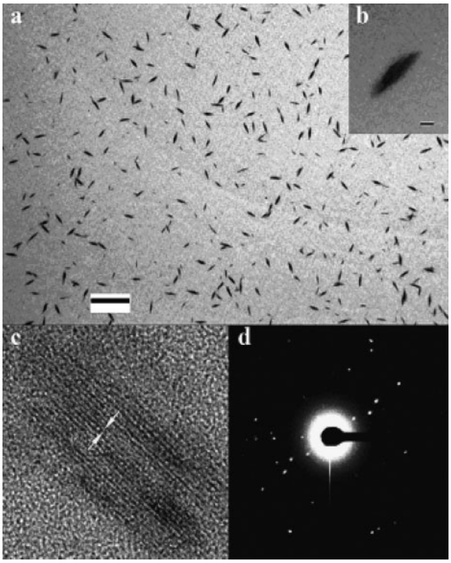

Figure 1.
PEDOT nanocrystals. a) TEM image. b) Single nanoneedle image. c) HRTEM. d) Electron diffraction. Scale bar = 200 nm in a, 20 nm in b) The arrows in c) show the chain spacing distance of 0.6 nm, which was confirmed by the electron diffraction results.[24]

with subsequent migration to the aqueous phase as polymer nanoneedles grow. To establish the general applicability of this interfacial system, pentane instead of DCM was also used as the organic layer for EDOT monomers (Figure 2). The organic pentane layer then served as the upper layer and the migration direction of nanoneedles was in the gravity direction.

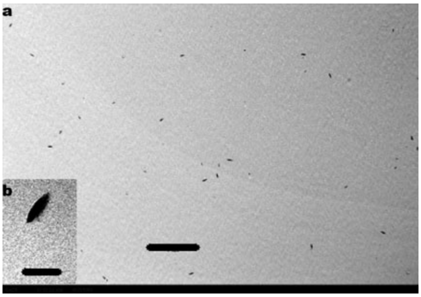

Figure 2.
TEM images of PEDOT nanoneedles synthesized using pentane as the organic upper layer. Scale bar = a) 1 μm, b) 100 nm.

Same sample as used in the TEM showed exceptionally high level of order in high-resolution transmission electron microscope (HRTEM) and electron diffraction studies. The HRTEM image (Figure 1c) gives a vivid lattice structure of the nanoneedle. Although different lattice dimensions were obtained for PEDOT from different syntheses, the polymorphs can be assigned as an orthorhombic lattice.[28,29] The lattice constants a, b, and c are designated as the lateral chain spacing, π-π stacking distance, and repeating unit length, respectively. The electron diffraction pattern (Figure 1d) shows well-defined diffraction spots, indicating the nanoneedles as highly ordered single crystals. The lattice units were assigned as $a = 0.584$ nm (confirmed by HRTEM, Figure 1c), $b = 0.494$ nm, and $c = 0.796$ nm. The π-π stacking distance, $b = 0.494$ nm, is on the low end of the reported range of 0.425 nm to 0.68 nm.[28–30] The lateral chain spacing, $a = 0.584$ nm, is a very close distance when compared with the range of 1.3 to 1.5 nm reported values for PEDOT with external dopants of different sizes and concentrations.[28,29] The contributing factors to this short π-π stacking and close lateral spacing include the expected favorable packing of the incoming monomers on the crystal template and the lack of high concentration large external dopants. Energy dispersive X-ray spectroscopy (EDS, Figure 3) supported a C/O/S ratio of 6/2/1 and on the average one Cl^- anion for 54 thiophene rings without observable iron. Since no external doping was applied, Cl^- anions served the role of charge compensation. The chains are likely composed of macroradical cations as well as neutral PEDOT depending on if oxidation or deprotonation as the last step of chain growth.[26] Therefore, the maximum average number of thiophene ring per PEDOT chain can be placed as 54, a number representing a low molecular weight polymer but larger than that of oligomers. With the present acidic environment of the polymerization system ($pH = 2.45$ in aqueous phase) and in the absence of proton

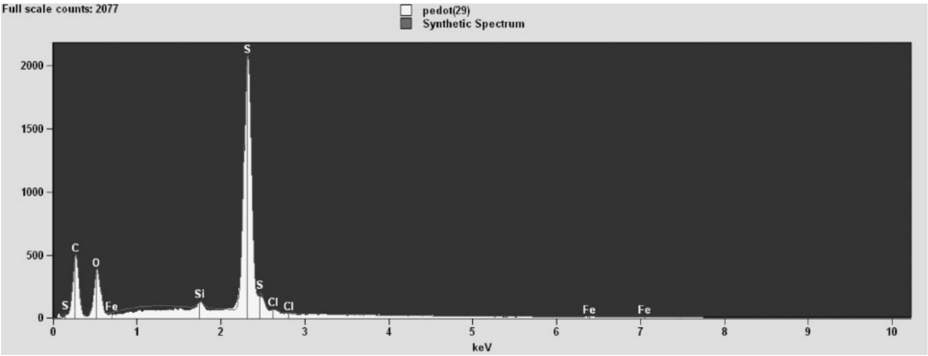

Figure 3.
EDS spectrum for PEDOT from interfacial crystallization-polymerization.

acceptor in the media, cation radical should represent most the charge state of the chains. Submicronic hematite needles were observed by aging $FeCl_3$ in NaH_2PO_4 buffer at 1000 °C for 3 days.[31] For our organic nanoneedles, the electron paramagnetic resonance, EPR, spectrum (Figure 4) clearly shows the characteristics of PEDOT (linewidth ~3.9 G, g-value ~2.0083) without observable hematite. The presence of hematite would be readily observable as a very intense EPR signal at g-value ~2.04 with broad linewidth ~500 G.[32]

A representation of typical STM/STS results is shown in Figure 5. STM images were obtained for individual nanoneedles (Figure 5b) followed by positioning the STM tip on the middle of a nanoneedle for STS at the completion of the scanning. The tunneling I-V curves (Figure 5a) were

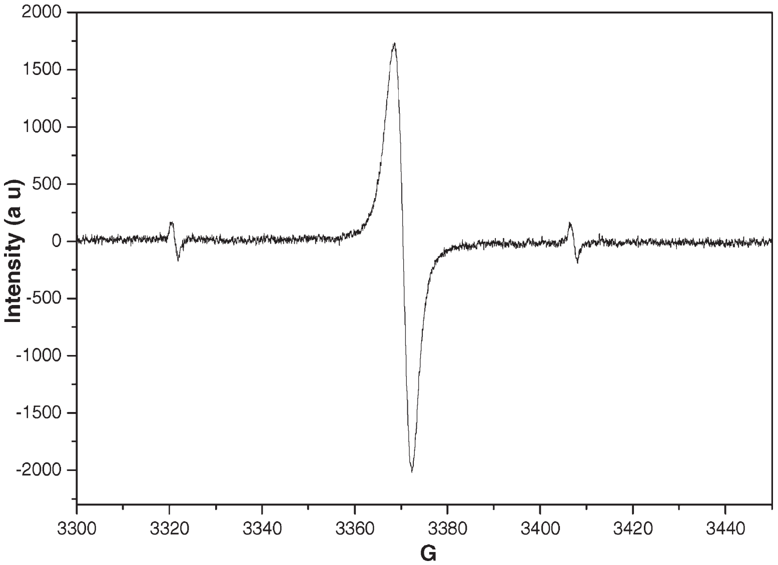

Figure 4.
First-derivative EPR spectrum of PEDOT nanoneedle at room temperature. (linewidth ~3.9 G; g-value ~2.0083); with Mn^{2+} marker signals, 3rd and 4th line signals.

recorded from −4 to 4 volts bias voltage range for both the PEDOT needles and the gold substrate. The gold-111 surface, as a reference, showed a typical metallic tunneling I-V behaviour. Unlike the gold surface, PEDOT nanoneedles showed abrupt switching behaviours at about −3 and 3 volts.

The conductance behaviour most likely involves the electron transport along the π-π stacking direction of the PEDOT nanoneedle. The plateau region from −3 to 3 volts can be assigned as *OFF* or insulating state (tunneling current < 0.04 nA) of the switch. When the bias voltage increased to 3 volts, the tunneling current abruptly jumped to a saturated amplitude (tunneling current > 10 nA). The two regions beyond −3 and +3 volts are the *ON* or highly conducting state of the switch. The switching process was in the millisecond scale, which is comparable to that of molecular switches. At low applied field (0–3 volts), the barrier was high enough to prevent the passage of tunneling current through PEDOT and the switching-off process took over. This non-contact measurement on nanocrystals without external dopant differs inherently from the contact measurement on highly doped and charged conjugate bulk systems in that tunneling current are being monitored in the present case.[11,30]

A comparison of the switch behaviors of PEDOT, polyaniline (PANI) and polypyrrole (PPY) is shown in Figure 6. Apparently, the conductance switch occurs at different bias voltage, ∼±3 volt for PEDOT, ∼±3.5 volt for PANI and ∼±4 volt for PPY, individually. PANI and PPY show similar behaviors with switching voltages relating to the respective polymer band gaps.

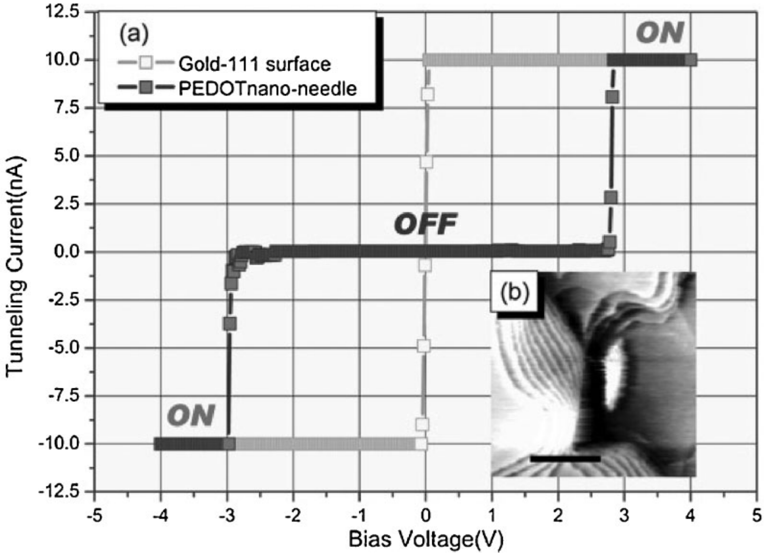

Figure 5.
Representative switching behavior of the nanoneedle. The STS experiments a) were conducted on STM scanner. The white square data points show a typical tunneling I-V curve of Gold-111. The grey square data points show the tunneling I-V curve of a PEDOT nanoneedle. The plateau between −3 and +3 volts was assigned as the OFF (low conductance) state and the two regions beyond ±3 volts were assigned as the ON (high conductance) states. The sweep time for both the curves was 10 seconds. Two hundred data points were collected for each curve. The I-V measurement on a single needle can be repeated many times. The switching response was estimated in the millisecond time scale. STM experiments were conducted on the same instrument using a constant current (100 pA) mode at a low servo level (servo gain %: I = 0.3, P = 0.1). b) A representative STM topological image was collected at the scanning rate of 0.5 Hz, 8.5 minutes per frame.[24]

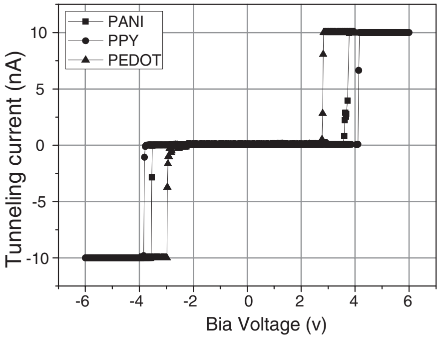

Figure 6.
Comparison of the conductance switch behavior of PEDOT, PANI and PPY nanoneedles.

Conclusions

Poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline and polypyrrole single crystalline nanoneedles with fast conductance switch properties were synthesized for the first time, using an interfacial polymerization process with attendant crystallization. Orthorhombic lattice units were assigned to the single nanocrystals with closer π-π stacking and lateral distances than most PEDOT systems. The absence of external large dopant and the crystallization during chain growth led to closely packed crystals, a condition contributing to electronic conduction. These nanoneedles show a novel switching behaviour with its response time in millisecond scale. The discovery of the new nanomaterial reported here can contribute to nanoelectronics in advancing fundamental understanding and developing novel organic nano-elements.

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