

Liquid/Liquid Interfacial Polymerization To Grow Single Crystalline Nanoneedles of Various Conducting Polymers

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ABSTRACT Single crystalline nanoneedles of polyaniline (PANI) and polypyrrole (PPY) were synthesized using an interfacial polymerization for the first time. The interfacial crystallization of conductive polymers at the liquid/liquid interface allowed PANI and PPY polymers to form single crystalline nanocrystals in a rice-like shape in the dimensions of 63 nm × 12 nm for PANI and 70 nm × 20 nm for PPY. Those crystalline nanoneedles displayed a fast conductance switching in the time scale of milliseconds. An important growth condition necessary to yield highly crystalline conductive polymers was the extended crystallization time at the liquid/liquid interfaces to increase the degree of crystallization. As compared to other interfacial polymerization methods, lower concentrations of monomer and oxidant solutions were employed to further extend the crystallization time. While other interfacial growth of conducting polymers yielded noncrystalline polymer fibers, our interfacial method produced single crystalline nanocrystals of conductive polymers. We recently reported the liquid/liquid interfacial synthesis of conducting PEDOT nanocrystals; however, this liquid/liquid interfacial method needs to be extended to other conductive polymer nanocrystal syntheses in order to demonstrate that our technique could be applied as the general fabrication procedure for the single crystalline conducting polymer growth. In this report, we showed that the liquid/liquid interfacial crystallization could yield PANI nanocrystals and PPY nanocrystals, other important conductive polymers, in addition to PEDOT nanocrystals. The resulting crystalline polymers have a fast conductance switching time between the insulating and conducting states on the order of milliseconds. This technique will be useful to synthesize conducting polymers *via* oxidative coupling processes in a single crystal state, which is extremely difficult to achieve by other synthetic methods.

KEYWORDS: interfacial crystallization · conductive polymers · single crystal · liquid–liquid interface.

The miniaturization of electronic devices becomes the main trend of the future semiconductor industry.¹ Development of building up nanoscale basic components for diverse logical functions is crucial to the next generation of microelectronics. Owing to their environmental stability, production cost, and electrochemical properties, conducting polymers have emerged as alternative materials to build electronic and optoelectronic devices.^{2,3} For example, conducting polymers have been successfully applied in light-emitting diodes,⁴ photovoltaic devices,⁵ and field effect transistors.⁶ However, the difficulty in obtaining highly crystalline nanometer-sized conducting polymers limited the ef-

forts to make high impact on industrial applications.^{7–9}

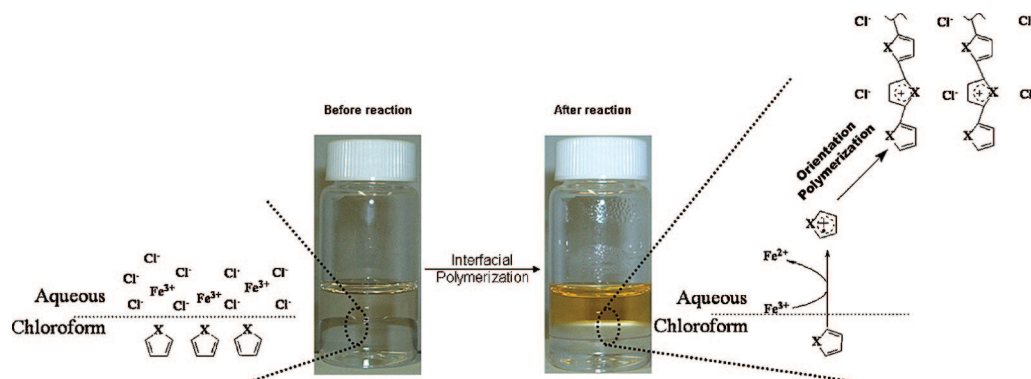
Because of these unique properties of conducting polymers in nanometer scale,^{10–12} they are of current interest in broad scientific areas. Furthermore, conducting polymer nanoparticles have characteristic electronic and optical properties^{10–12} owing to their size; the decrease in particle size can promote more effective doping¹³ and strengthen inter- and intrachain interactions to enhance the degree of crystallinity,¹⁴ which results in yielding the polymers with higher conductivity.^{15–21} Therefore, to obtain the highly crystalline polymer structure, techniques such as the coupling reaction of pre-organized monomers, solution spin-coating on functionalized surface, and electrochemical epitaxial polymerization have been applied.^{22–24} Recently, we reported the first synthesis of single crystalline conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), with the fast conductance switching property using an interfacial polymerization–crystallization process.²⁵ An important growth condition necessary to yield highly crystalline conductive polymers was the extended crystallization time at the liquid/liquid interfaces to increase the degree of crystallization. As compared to other interfacial polymerization methods, lower concentrations of monomer and oxidant solutions were employed to further extend the crystallization time.²⁶ While other interfacial growth of conducting polymers yielded noncrystalline polymer fibers, our interfacial method produced single crystalline PEDOT nanocrystals in the dimension of 15 nm × 50 nm. These nanocrystals displayed the conductance switching behavior between the insulating and conducting state

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Scheme 1. Slow polymerization through the oil/water interface.

as potentials were applied, and the abrupt changes of the conductivity occurred at ± 3.0 V.²⁵

To demonstrate that our technique could be applied as the general fabrication procedure for the single crystalline conducting polymer growth, this liquid/liquid interfacial method was extended to other conductive polymer nanocrystal syntheses. In this report, we demonstrated that the liquid/liquid interfacial crystallization could yield polyaniline (PANI) nanocrystals and polypyrrole (PPY) nanocrystals, other important conductive polymers, in addition to PEDOT nanocrystals. This liquid/liquid interfacial method yielded uniform and needle-shaped conductive polymers of PANI and PPY after 48 h and these conducting polymers had the single crystalline structure with the fast conductivity switching behavior within milliseconds. This technique will be useful to synthesize conducting polymers *via* oxidative coupling processes in a single crystal state, which is extremely difficult to achieve by other synthetic methods.

RESULTS AND DISCUSSION

Our aqueous/organic interfacial system was composed of water and DCM. The monomers of PANI and PPY were in the organic solvent while an oxidant, ferric chloride, was in the water phase. The oxidative coupling polymerization of the monomer was mediated at the aqueous/organic interface (Scheme 1). As compared to the experimental condition to synthesize PANI fibers at the interface,²⁶ our coupling polymerization was controlled to be much slower by reducing the concentration of the oxidant to 0.1 mg/mL to obtain their single crystals. The TEM image (Figure 1A) shows the nanoneedles of PANI with an average length and diameter of 63 and 12 nm. The average length and diameter of PPY are 70 and 20 nm as shown in Figure 2A. Single crystalline conducting polymers were first nucleated at the interface through oxidative coupling between PANI or PPY monomer from the organic layer and ferric chloride from the aqueous layer. These polymer nanocrystals were grown to the aqueous layer in the oriented direction and then they were dispersed into the aqueous layer in the nanoneedle form. The

high resolution TEM images of both PANI and PPY resolved their lattice fringes as shown in Figures 1B and 2B. In addition to these HRTEM images, electron diffraction patterns of PANI and PPY (Supporting Information) confirmed the single crystalline nature of the monodisperse nanoneedles.

We hypothesize that those single crystalline conducting polymers are grown by the interfacial polymerization–crystallization mechanism (Scheme 1). Previously it was reported that when polymerization of

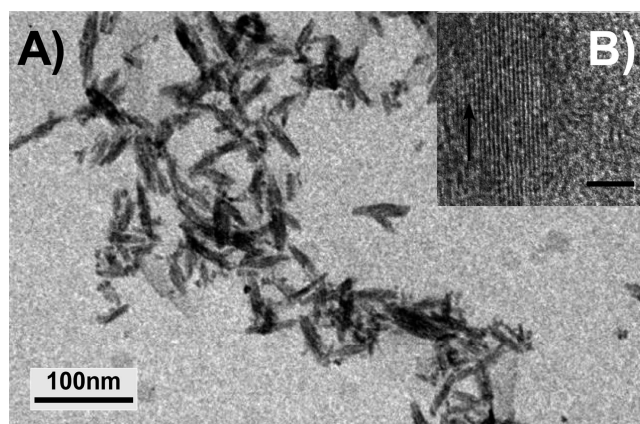


Figure 1. (A) TEM image of PANI nanoneedles; (B) HRTEM image of PANI nanoneedle. Scale bar = 3 nm. The arrow shows the direction of the long axis of [001].

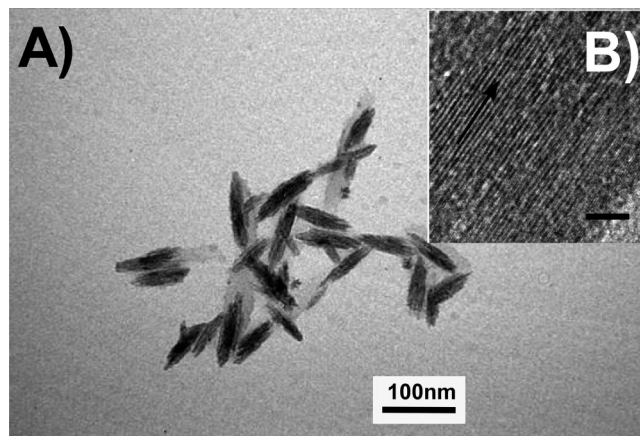


Figure 2. (A) TEM image of PPY nanoneedles; (B) HRTEM image of PPY nanoneedle. Scale bar = 3 nm. The arrow shows the direction of the long axis of [001].

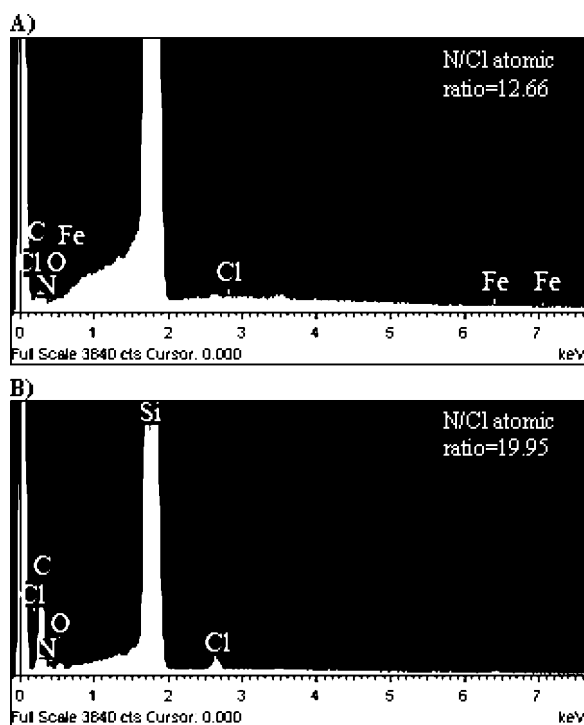


Figure 3. EDS spectra of polymer nanoneedles: (A) PANI, (B) PPY.

PANI occurs in two-phase matrix, these polymers grow in the noncrystalline fiber form at the interface and the polymerization terminates as polymers dispersed into aqueous phase because of the hydrophilic nature of the polymer.²⁷ When the monomer and the oxidant concentrations higher than those described in our experimental section were applied to polymerize PANI and PPY, the formation of amorphous nanofibers or granular particles were observed with fast growth kinetics, thus consistent with our hypothesis. To grow polymers in single crystalline structure at the interface, the interfacial reaction needs to be slowed significantly. We could achieve this condition by employing the low concentrations of the PANI/PPY monomer and the FeCl_3 oxidant. After attacked by the oxidant, the monomers

around the interfacial region are charged positively by losing electrons to Fe^{3+} ions. And then the counterions, Cl^- , bind these positive charges and bridge the repeated units as shown in the right illustration of Scheme 1. Because of the hydrophilic nature of these primary species, the polymerization proceeds along the normal of the interface followed by further coupling reactions. In our method, those oriented polymers could be aligned between positively charged repeated units and negatively charged Cl^- ions during the slow interfacial reaction (Scheme 1) to form elongated rice-like crystals as shown in Figures 1A and 2A. The polymerization with the disordered monomer alignment is also suppressed when freshly formed nanoneedles diffuse away from the reactive interface.²⁷ Since fewer monomers are attacked by radical cations, the oxidative coupling reaction could be terminated in a relatively short time scale, which also favors the formation of the shorter rice-shaped crystals rather than long fibers. The binding between the repeated units and Cl^- ions was confirmed by the energy dispersive spectroscopy (EDS) (Figure 3). The ratio between the counterion (Cl^-) and the monomer unit of PANI is 1:12 while the ratio for PPY is 1:20. The difference of the ion–monomer ratio between PANI and PPY reflects the difference in their ability to accommodate positive charges, in consistency with the lower ionization potential of PANI. It should be noted that these EDS spectra of PANI and PPY showed no iron traces in the resulting polymer nanocrystals.

These nanoneedles displayed interesting electronic properties due to their unique morphological and crystalline structure. We applied scanning tunneling spectroscopy (STS) to probe their electronic properties. In our STS studies for PANI and PPY nanoneedles, each suspension was collected from upper aqueous layer and dialyzed for 10 h in *nanowater* (resistivity 18.2 $\text{M}\Omega$ cm, total organic carbon level 10 ppb) to remove impurities. The purified suspension was then 10-fold diluted with *nanowater* and spin-coated on a gold (111) substrate surface. The tunneling I – V curves were recorded from -5 to 5 V scale for these polymers between the STM tip and Au substrate, and these STS spectra measured in this experimental setup were highly reproducible.²⁵ While bare Au substrate showed a typical metallic tunneling I – V behavior, the abrupt switching behaviors were observed for PANI at ± 3.5 V and PPY at ± 4 V as shown in Figure 4. The PANI nanoneedles were insulated in the range of -3.5 to *ca.* $+3.5$ V, and in the case of PPY nanoneedles the “OFF” state is between -4.0 and $+4.0$ V for PPY. Beyond these critical points, both PANI and PPY nanoneedles turned on the conducting state, and this switching process from the “OFF” to the “ON” states was in the millisecond scale. This result indicates that the barrier for electron injection is high in the range of “OFF” region to prevent the passage of tunneling electrons. Previously, the rapid

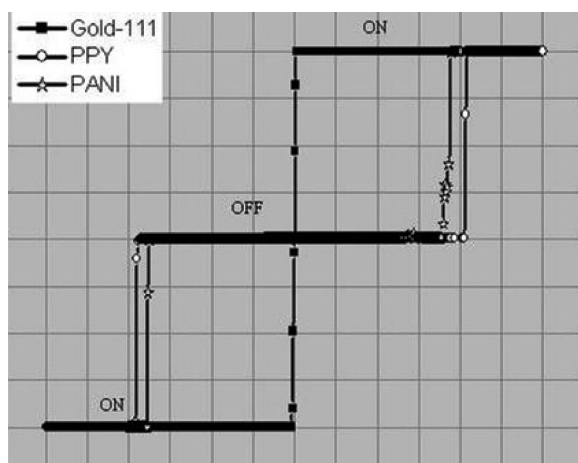


Figure 4. STS spectrum of PANI nanoneedles, PPY nanoneedles, and Au(111) substrate.

transition from the “OFF” to the “ON” states with the sharp raising slope in the $I-V$ curves was only observed in PANI in the molecular scale, grown electrochemically between electrodes in the length of 1 nm.²¹ Therefore, this is the first example to observe the fast conductance switching behavior in large conducting polymer crystalline domains.

Since the voltage range of “OFF” state is larger in PPY than PANI in Figure 4, this comparison indicates that the band gap for PPY nanoneedles is larger than the band gap for PANI nanoneedles. This is consistent with ultraviolet–visible (UV–vis) absorption spectra of PANI and PPY, as shown in Figure 5. From those spectra, the PPY nanoneedle has the higher band gap (2.5 eV) as compared to the PANI nanoneedles (2.21 eV).

CONCLUSION

Single crystalline nanoneedles of PANI and PPY were synthesized using an interfacial polymerization process for the first time. An interfacial polymerization–crystallization at the liquid/liquid interface allowed PANI and PPY polymers to form single crystalline nanocrystals in the rice-like shape in the dimensions of 63 nm × 12 nm for PANI and 70 nm × 20 nm for PPY. The conductance switching properties of

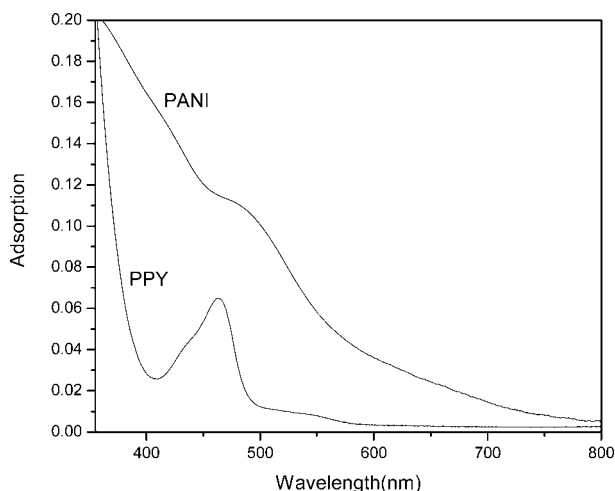


Figure 5. UV–vis spectra of PANI and PPY nanoneedles.

these crystalline polymers were observed in their $I-V$ curves, and the conductance switching was fast in the time scale of milliseconds. Since this liquid/liquid interfacial synthesis method yielded conducting polymers of PEDOT, PANI, and PPY in the single crystal state, our technique could be applied as the general fabrication process of single crystalline conducting polymers.

EXPERIMENTAL SECTION

Materials and Apparatus. Pyrrole, aniline, ferric chloride, dichloromethane, and dialysis tubing were purchased from Aldrich Chemical Co. Transmission electron microscopic (TEM) and high resolution transmission electron microscopic (HRTEM) studies were conducted on JEOL 1200 EX and Tecnai G2 F20 cryoelectron microscopes, respectively. The STM/STS processes were described in our previous publication on both PicoSPM II (Agilent) and Nanoscope IIIa MultiMode (Veeco) microscopes.²⁵ In STS tunneling spectra, each data point was measured in 10 ms.

Synthesis of Nanoneedle Shape Conducting Polymers. In a typical synthesis, aniline or pyrrole monomers were dissolved in dichloromethane (DCM, 5 mL, 1 mg/mL) to form the bottom organic layer, and the oxidant, ferric chloride (FeCl_3), was dissolved in deionized water (5 mL, 0.1 mg/mL) to form the upper water layer. After the interfacial system was established, the aqueous layer was collected after 48 h. The purification processes of resulting polymer nanocrystals were described elsewhere.²⁵

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Supporting Information Available: Electron diffraction patterns of PANI and PPY nanoneedles of these polymer nanoneedles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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