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Communications to the Editor

Highly Oriented Nanowires from the Hierarchical Self-Assembly in Supramolecular Complex of Polyaniline with ω-Methoxypoly(ethylene oxide) Phosphates

Bhanu Nandan,[†] Jen-Yung Hsu,[†] Ayano Chiba,[‡]
Hsin-Lung Chen,*,[†] Chein-Shiun Liao,*,[§]
Show-An Chen,[†] and Hirokazu Hasegawa[‡]

Department of Chemical Engineering, National Tsing Hua University, Hsin-Chu 30013, Taiwan; Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 616-8510, Japan; and Department of Chemical Engineering and Material Science, Yuan Ze University, Nei-Li, Taoyuan 320, Taiwan

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π-Conjugated polymers are by far the most promising functional polymers for applications in less expensive and flexible electronic devices.[1] Polyaniline (PANI) is a conjugated polymer which has been widely studied for electronic and optical applications.[2] PANI has a simple and reversible acid/base doping/dedoping chemistry, enabling control over properties such as free volume,[3] solubility,[4] electrical conductivity,[5] and optical activity.[6] Recently, PANI nanostructures, especially nanowires, fibers, rods, and tubes, have received considerable attention since such materials are expected to possess the advantage of both low-dimensional systems and organic conductors.[7] These electrically conducting nanostructures have the potential to play an important role in optoelectronic nanodevices, ranging from single-molecular transistors and electron-emitting flat panel displays to chemical nanosensors and artificial actuators. However, a simple and effective process for obtaining these nanowires remains a scientific challenge.

PANI nanowires have been synthesized mainly by template-guided polymerization techniques. The template used was either "hard" and insoluble solid supports such as zeolite channels,[3,8] anodized alumina,[9] and controlled pore-size membranes[10] or "soft" structural directing molecules such as surfactants,[11] liquid crystals,[12] DNA,[13] thiolated cyclyodextrins,[14] and polyelectrolytes.[15] Recently, polyaniline nanowires/nanofibers were shown to form spontaneously during the chemical oxidative polymerization of aniline without template.[16] The nanofibrillar morphology appeared to be intrinsic to polyanline synthesized in water. Two approaches, namely, interfacial polymerization and rapidly mixed reactions, were developed to prepare pure PANI nanofibers. Furthermore, the diameters of the nanofibers could be tuned between 30 and 120 nm by changing the dopant acid. Efforts have also been made to synthesize conducting PANI nanofibers by seeded polymerization,[17] electrospinning,[18] and mechanical stretching.[19] Recently, polyaniline nanofibers were prepared by a novel polymer wrapping method using schizophyllan.[20] PANI nanowires have also been fabricated on inorganic material surfaces by combining self-assembly and template synthesis techniques.[21] However, in spite of many attempts using a variety of techniques, the synthesis of highly uniform and oriented PANI nanowires with diameters less than 50 nm remains a challenging task. The controlled orientation of electroactive polymer nanostructures is especially critical for applications such as light emitting and microelectronic devices.[21a]

Herein, we report a simple but effective method for preparing highly oriented PANI nanowires using a supramolecular self-assembly approach. The nanowires thus prepared have fairly uniform diameter of ca. 30 nm and length up to several micrometers. The nanowires are formed by a unique hierarchical self-assembly in the complexes of the emeraldine base form of PANI with a phosphoric acid-terminated poly(ethylene oxide) (PEO), i.e., ω-methoxypoly(ethylene oxide) phosphates (PEOPA). The synthetic procedures of these complexes conducted in the aqueous media have been described elsewhere[22] (see also Supporting Information). In the complex the acid head group of PEOPA acts as the protonic acid dopant for PANI (M_w = 65 149; M_n = 39 343 as measured by GPC using NMP as the

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* To whom correspondence should be addressed. E-mail: hslchen@mx.nthu.edu.tw; csliao@saturn.yzu.edu.tw.
[†] National Tsing Hua University.
[‡] Kyoto University.
[§] Yuan Ze University.

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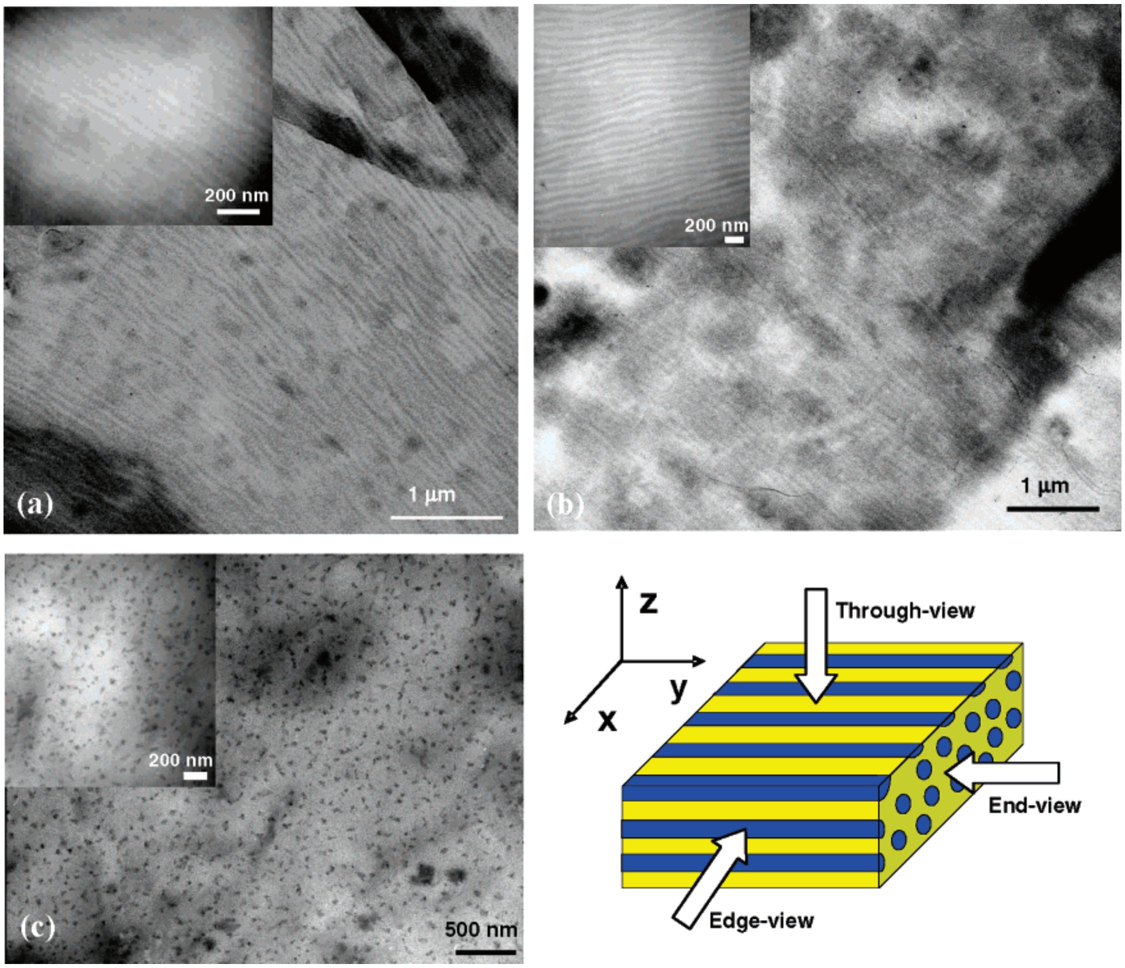

Figure 1. TEM images of PANI(PEOPA) nanowires in (a) through-view ($x-y$ plane), (b) edge-view ($y-z$ plane), and (c) end-view ($x-z$ plane). In-plane ($x-y$ plane) conductivity was measured along several directions and found to be highest along the y-axis and lowest along the x-axis. The out-of-plane conductivity measured along the z-axis was also very low (see text).

solvent) while the long hydrophilic PEO tails render it water-soluble. The overall complex composition is denoted by R, which expresses the average number of PEOPA molecules bound to one monomer unit of PANI prescribed by the feed ratio of the two components. Thin films of the PANI(PEOPA) complex with $R = 0.5$ were cast from the aqueous solution on a glass substrate for further analysis.

In a previous article, we had shown that due to the strong repulsion between the ionic PANI backbone and nonionic PEO side chains, the well-doped PANI in PANI(PEOPA) complexes formed a microphase-separated lamellar morphology consisting of alternating ionic (PANI backbone and phosphate group of PEOPA) and nonionic (PEO side chain) layers with the interlamellar distance of ca. 6 nm.[22] Our previous study was based only on results obtained in the reciprocal space using SAXS. However, on the basis of our recent results obtained in real space using TEM, we will show that apart from the small-scale assembly the system further self-organizes on a much larger length scale, leading to nanowires with ca. 30 nm in diameter.

Figure 1a−c shows the TEM micrographs obtained from the ultrathin sections of the PANI(PEOPA) complex stained by OsO_4. The TEM images in Figure 1a were obtained when viewed normal to the surface of the film (through-view), whereas those in Figure 1b,c were viewed parallel to the surface along two perpendicular directions (edge-view and end-view). In the through-view and edge-view, TEM micrographs show alternating bright and dark layers of uniform thickness which are oriented in one direction. The thickness of the dark and the bright layers is found to be ca. 30 and 40 nm, respectively, in both through- and edge-view, and the length of the nanostructures extends up to several micrometers. These 1-D aligned nanostructures spread nearly over the whole film. Furthermore, the TEM micrograph obtained in end-view (Figure 1c) reveals dark cross sections of rodlike structure, indicating that the characteristic morphological entity observed is in fact nanowire. Because OsO_4 is a preferential staining agent for PANI, the nanowires showing dark image in the micrographs should compose predominantly of the aggregates of poorly doped PANI chains. The bright regions, which form the matrix phase, should contain the smaller-scale lamellae formed by the well-doped PANI chains as PEOPA accounts for the main composition in this phase.[22] It is noted that the oriented nanowire morphology is also observable for other binding fractions; however, the level of orientation is best for $0.3 \leq R \leq 0.5$.

Figure 2a,b shows the 2-D SAXS patterns obtained when X-ray was passed along different directions through the as-cast film. In the through-view the SAXS pattern shows a weak and broad circular reflection at $q \sim 1.00$ nm^{-1} (Figure 2a). However, in the edge-view the SAXS pattern displays two bright arcs in the equatorial direction superimposing on the weak circular reflection (Figure 2b). The observed scattering feature is associated with the smaller-scale lamellar structure with the interlamellar distance of 6.28 nm organized by the well-doped PANI in the complex. The equatorial arcs in the edge-view pattern attest that a significant portion of the lamellae exhibits

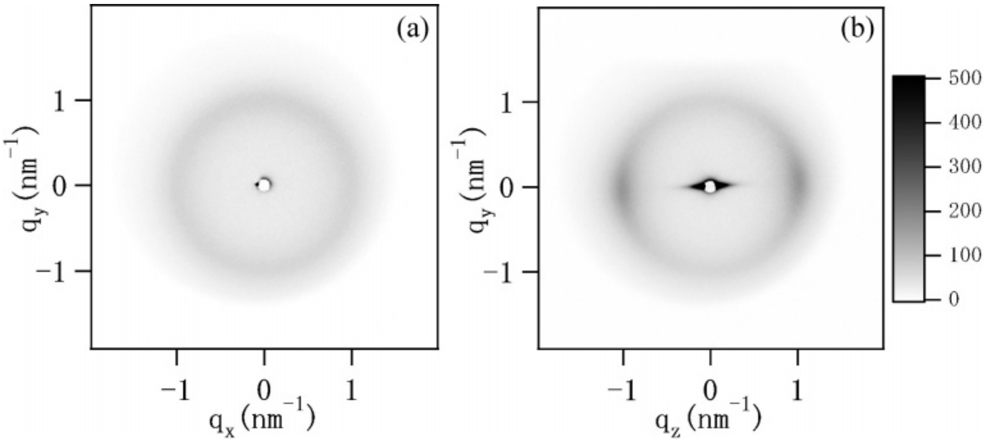

Figure 2. 2-D SAXS patterns obtained from the as-cast PANI(PEOPA) complex in (a) through-view and (b) edge-view.

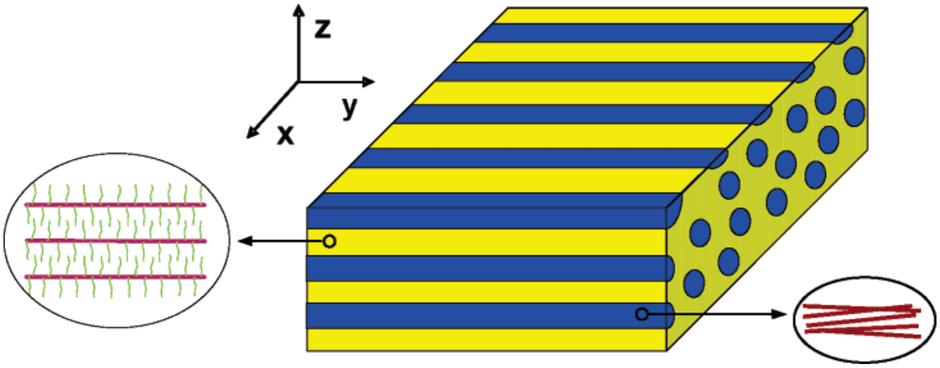

Figure 3. Schematic illustration of the hierarchical structure in PANI(PEOPA) complex.

large-scale orientation with the lamellar normal aligning along the *z*-axis. An intense reflection is also observed at low *q* as a bright streak along equatorial direction in the edge view; this is attributable to surface reflection. It must be mentioned here that the observed scattering pattern contains no contribution from the lamellar crystallites of PEO as the PEOPA is in melt state at room temperature due to low molecular weight.

Figure 3 schematically illustrates the proposed hierarchical structure of the PANI(PEOPA) complex. The figure illustrates the presence of uniform and oriented nanowires on the larger length scale. The nanowires are formed mainly by the poorly doped PANI aggregates and their orientations may be directed by the assembly of the smaller-scale lamellar structure (formed by well-doped PANI chains) in the matrix phase with the layers stacking perpendicular to the long axis of the rods. These well stacked lamellae gives rise to the bright arcs in the 2-D SAXS pattern.

The mechanism of the formation of the highly oriented nanowires is not clear at this point. We believe that the solid-state morphology is related to the dispersion state of the complex in the solution state.[23] As the PANI chains get doped by PEOPA in the aqueous medium, the well-doped chains gradually go to solution. A fraction of PANI chains (i.e., the poorly-doped PANI) may however still be in aggregate form, and these aggregates disperse relatively well in the aqueous medium due to the PEOPA doping at their surfaces. During solvent removal the well-doped and the poorly-doped PANI phase separate, where the well-doped PANI chains spontaneously self-assemble into the smaller-scale lamellae which subsequently direct the organization and orientation of the poorly-doped PANI aggregates forming the nanowires. We speculate that the large-scale orientation of the smaller-scale lamellar structure, which further directs the orientation of the nanowires, is probably driven by the highly directional hydrogen bonding between the hydroxyl and the ether groups or among the hydroxyl groups within the PEO layers in the lamellar structure.[24]

The PANI(PEOPA) film was found to display tridirectional anisotropy of macroscopic electrical conductivity, where the in-plane conductivity (*x*−*y* plane in Figure 3) of the film varied from 0.2 mS/cm (along the nanowire axis, *y*-axis) to 5 μS/cm (perpendicular to the nanowires, *x*-axis), and the out-of-plane conductivity was about 7 μS/cm. This anisotropic feature not only verifies the formation of highly oriented nanowire structure in the film but is also crucial for application of the material as one-dimensional optoelectronic nanodevices. We would like to note here that although the conductivity is not high, it is still in useful range for application. Moreover, the use of a processable polymeric dopant (i.e., PEOPA) for PANI, though leading to a somewhat low conductivity, will facilitate an easy fabrication of devices.

It is interesting that such a spontaneous self-organization occurs uniformly all over the film with a preferred orientation. Recently, we have also observed the formation of oriented and uniform nanowires in another conjugated polymer system which consists of poly(2-phenyl-3-phenyl-4-(3′,7″-dimethyloctyloxy)-1,4-phenylenevinylene) (DPO−PPV) hydrogen bonded with an amphiphile 4-dodecylresorcinol (DR) (cf. Supporting Information). This may imply a general tendency for such systems to self-organize on a large scale and with a proper mechanistic and theoretical understanding may provide a new strategy for the design of one-dimensional nanostructured materials with unique electronic and photonic functions.

In summary, we have demonstrated a self-assembly process in a complex of PANI with PEOPA that results in the formation of hierarchical nanostructures with two length scales. The smaller-scale lamellae formed by the well-doped PANI chains may direct the organization of the aggregates of poorly-doped PANI, leading to highly oriented nanowires of fairly uniform diameter in the sub-50 nm range. The synthetic procedure of the complex is easy; moreover, since the nanostructures are processed from aqueous solution, the procedure is environmentally friendly.

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Supporting Information Available: Synthetic procedure of the complex, characterization details, UV−vis data, enlarged TEM micrographs, and brief result showing the formation of oriented nanowire structure in the blend of poly(2-phenyl-3-phenyl-4-(3′,7″-dimethyloctyloxy)-1,4-phenylenevinylene) (DPO−PPV) with an amphiphile 4-dodecylresorcinol (DR). This material is available free of charge via the Internet at http://pubs.acs.org.

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