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Polyaniline nanowires by electropolymerization from liquid crystalline phases

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Conductive polyaniline nanowires in emeraldine form can be deposited by potentiodynamic electropolymerization from a reverse hexagonal liquid crystalline phase where one-dimensional (1D) aqueous channels can serve as space-confined reactors. Polyaniline nanowire bundles with single-wire diameter of 50–70 nm and length of several microns were obtained from surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse hexagonal liquid crystalline phase. Impedance measurement suggests improved ordering of the reverse hexagonal liquid crystal under external electric field during the electropolymerization process. This enhanced ordering appears essential for the nanowire growth. The nanowires obtained can be easily collected by a simple washing process.

Introduction

Nanowires of conductive polymers have been extensively studied because of their high electrical conductivity and high mechanical flexibility, their ability to be electrochemically switched between electronically insulating and conducting states, and their potential applications in nanodevices.[1–4] At present, conductive polymer nanowires are most commonly prepared by chemical or electrochemical oxidation of the corresponding monomers inside a "hard template" with cylindrical pores such as anodized alumina,[1] track-etched polycarbonate[1,2] and mesoporous silica.[4] These hard templates are effective, but they are sometimes tedious to fabricate and not easy to remove after wire deposition if separate nanowires are desired. Recently, conducting polyaniline nanowires have been grown on gold electrodes modified with a self-assembled monolayer (SAM) through a so-called molecular templating method.[5] Although the template is easy to remove, the process for preparing the molecular template is not simple. Template-free polymerization has been attempted, but only large tubular structures (hundreds of nanometres) were produced by using the protonic acid dopant $C_{60}(OSO_3H)_6$.[6]

Surfactant mesophase based synthesis for zeolite-like porous materials and inorganic nanoparticles and nanowires has been widely reported.[7–9] However, most of these preparations were carried out at low surfactant concentrations (*e.g.*, 0.1 M) where micelle formation or microemulsion dominates. In contrast, high surfactant concentration can lead to formation of a normal hexagonal liquid crystal or a reverse hexagonal liquid crystal that supplies 1D aqueous channels as microreactors for controlling material growth on the nanometre scale. At present, mesoporous silica and porous metal and semiconductor have been obtained by using normal hexagonal liquid crystals as templates.[10–12]

In this study, we attempt to demonstrate that polymer nanowires can be obtained by combining electropolymerization process (electrochemical oxidation) with lyotropic liquid crystalline phase (reverse hexagonal liquid crystal) at high surfactant concentrations. Electrodeposition is preferred here because it is easy to control and can operate at ambient conditions. We will also demonstrate that a high electric field gradient between two narrowly spaced electrodes may synergistically align the reverse hexagonal liquid crystal parallel to the electric field direction through electro-osmotic flows within the aqueous channels.[13,14] We use potentiodynamic growth by scanning electrode potential because it has been shown to be advantageous over galvanostatic deposition for producing stable and conductive polymers.[5,15–17]

Experimental

Reagents

Anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (98 wt%), oil phase *p*-xylene (99 wt%) and aniline (99.5+ wt%) were obtained from Aldrich Chemical Company. Sulfuric acid (96 wt%) was purchased from Fisher Scientific. All chemicals were used as received without further purification. Distilled water was passed through a Barnstead system until its resistivity reached 17 MΩ cm.

Preparation of reverse hexagonal liquid crystalline phases

Reverse hexagonal liquid crystalline phases were prepared according to a well-studied ternary phase diagram consisting of AOT, oil phase *p*-xylene, and water.[18] For growth of polyaniline nanowires, the water phase was substituted by aniline monomer acid solution (0.1 M aniline + 0.2 M H_2SO_4). Sulfuric acid was used to improve the solubility of aniline. A typical composition is 1.5 M AOT in *p*-xylene and $[H_2O]:[AOT]$ molar ratio of 10–20. The above mixture was rigorously stirred and was kept to equilibrate for at least 12 h before electropolymerization.

Potentiodynamic electropolymerization of polyaniline

Electrodeposition was conducted by using a Solartron 1287 potentiostat in a three-electrode configuration and the aforementioned reverse hexagonal liquid crystalline phase as electrolyte at 25 °C. A polished stainless steel plate (16 × 16 mm) was used as working electrode (anode) to collect nanowires. Another stainless steel plate (16 × 16 mm) was used as counter electrode (cathode) and a saturated calomel electrode (SCE) as reference electrode. Polyaniline nanowires were deposited potentiodynamically by scanning the working

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electrode potential between -0.2 V and $+0.12$ V (*vs.* SCE) at a rate of 40 mV s^{-1} for 30 cycles. After electrodeposition, the nanowire deposit on the working electrode was thoroughly washed with ethanol to remove the liquid crystalline phase.

Characterization

Liquid crystalline phases were examined by a Nikon Microphot-FXA polarizing microscope at room temperature. SEM images were obtained in a Philips XL30-FEG SEM operated at 20 kV with no additional gold sputtering on samples. Fourier transform infrared spectra were recorded on a Bruker Equinox 55 using KBr pressed pellets. Impedance measurement was performed on a Solartron 1260 Impedance Gain-Phase Analyzer at frequency range of 0.1 Hz to 1×10^5 Hz and AC amplitude between 10 mV and 1000 mV. Resistance values were taken at a low frequency of 0.1 Hz which reflected DC type resistivity. Resistivity (ρ) is calculated as $\rho = rs/l$ (r: resistance; s: electrode surface area; l: electrode distance).

Results and discussion

Polarized light micrograph patterns (Fig. 1) show characteristic birefringence of the AOT–*p*-xylene–H_2O reverse hexagonal liquid crystal before and after doping with aniline acid solution (0.1 M aniline and 0.2 M H_2SO_4).[19,20] This indicates that the controlled addition of aniline monomer and H_2SO_4 in the aqueous phase did not disrupt the liquid crystalline phase.

Stable and conductive polymers were usually electrochemically grown by scanning electrode potential.[15–17] Fig. 2 shows the first eight cycles of cyclic voltammograms for polyaniline electropolymerization from AOT–*p*-xylene–H_2O (0.1 M aniline + 0.2 M H_2SO_4) reverse hexagonal liquid crystalline phase (Fig. 2A) and aniline acid solution (0.1 M aniline + 0.2 M H_2SO_4) (Fig. 2B). All cycles are almost consistent and contain oxidation/reduction peaks that are relevant to the redox chemistry of polyaniline.[15–17] In Fig. 2A, the oxidation peak corresponding to polyaniline formation appears in the range 0.6–1.2 V. This is a little higher than the oxidation potential of 0.3–1.0 V for polyaniline directly deposited from aniline acid solution (surfactant-free) (Fig. 2B). On the other hand, the reduction potentials are almost the same (0.6–0.1 V). This suggests that aniline oxidation starts at higher anodic potential in the liquid crystalline phase with space-confined growth environment than in surfactant-free acid solution. No obvious oxidation peaks (-0.2 to 0.2 V) for stainless steel appear in the voltammograms, suggesting that stainless steel is stable as anode during the electrodeposition process.[15–17] Polished stainless steel was chosen as electrode here because it has a very flat surface so that the electrode distance can be controlled by simply using PTFE tape with measured thickness as spacer between working and counter electrode. The effect of electrode distance on polyaniline deposition will be discussed later.

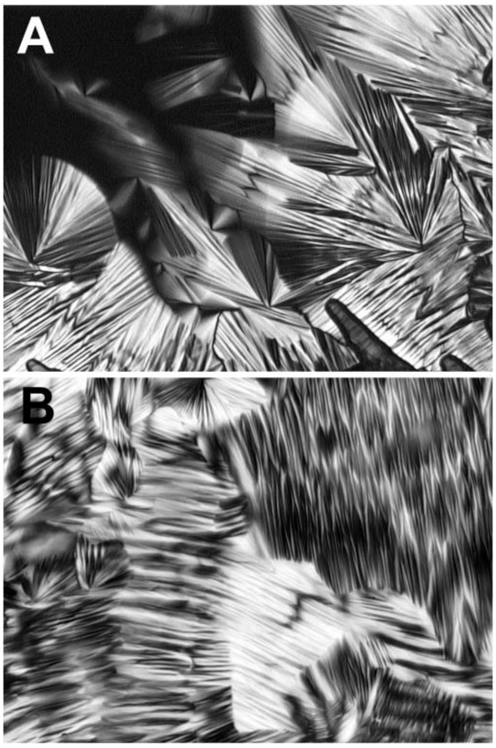


Fig. 1 Polarized light micrograph of AOT–*p*-xylene–H_2O reverse hexagonal liquid crystal before (A) and after (B) doping aniline acid solution (0.1 M aniline + 0.2 M H_2SO_4).

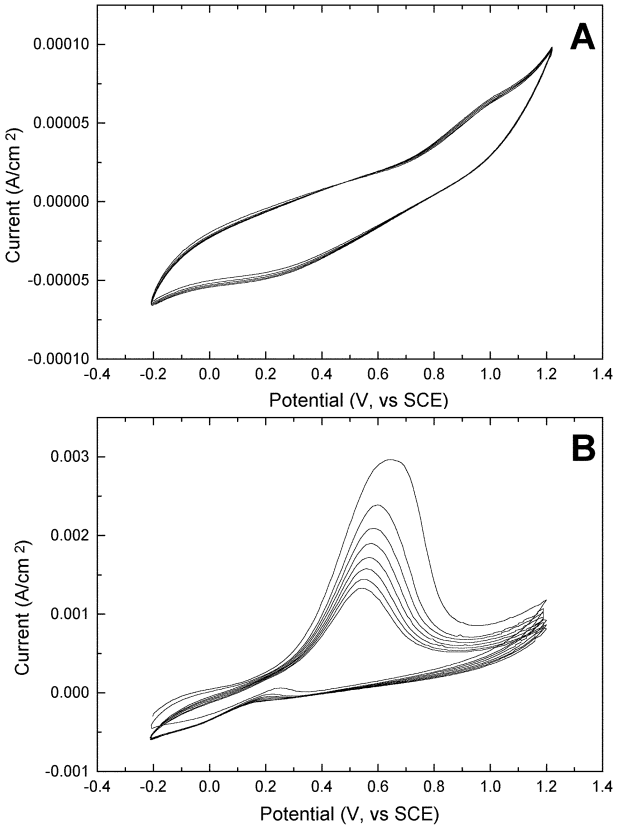


Fig. 2 Cyclic voltammograms for (A) AOT–*p*-xylene–H_2O (0.1 M aniline + 0.2 M H_2SO_4) reverse hexagonal liquid crystalline phase and (B) aniline acid solution. Scan rate = 40 mV s^{-1}. Number of cycles = 8.

Polyaniline nanowire arrays with light green color were grown from AOT–*p*-xylene–H_2O (0.1 M aniline + 0.2 M H_2SO_4) reverse hexagonal liquid crystalline phase (Fig. 3A, 3B). The nanowire arrays can reach several micrometres in length after 30 growth cycles. The nanowires are almost lying on the electrode surface probably due to washing, and this indicates that the polyaniline nanowires are highly flexible. After ultrasonication for 30 min, the nanowire bundles can be separated into many single nanowires (Fig. 3C). This suggests that the polyaniline nanowires may be used in the aggregated form (bundle) or as single wires for various potential applications. The diameter of an individual nanowire is approximately 50–70 nm (Fig. 3B, 3C), which is much larger than that of 1D aqueous channels (<10 nm) within the AOT liquid crystalline phase.[8] The size mismatch between template media and templated inorganic structures has been previously reported.[9] Although the exact cause is not clear, it is possible that these nanowires are formed through coalescence of nanowires with smaller diameters.[21]

The ordered aqueous channels in reverse hexagonal liquid

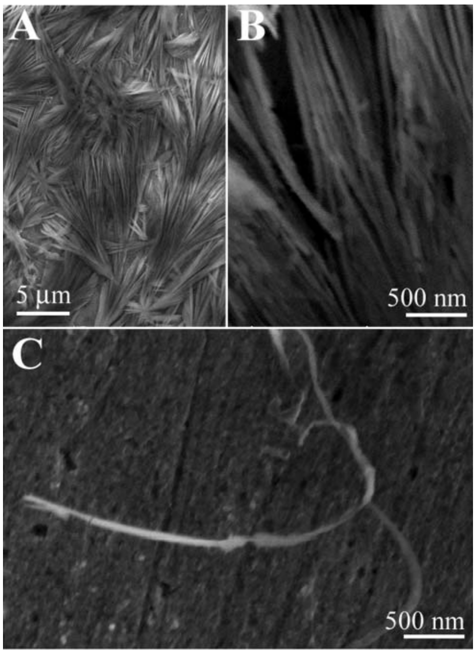


Fig. 3 Scanning electron micrographs of (A, B) polyaniline nanowire arrays electrodeposited from AOT–*p*-xylene–H_2O (0.1 M aniline + 0.2 M H_2SO_4) reverse hexagonal liquid crystal, at different magnifications, top view; (C) a separate nanowire from ultrasonic dispersion of sample A.

crystal are normally short (*e.g.*, hundreds of nanometres). The fact that nanowires in this study can be microns long (Fig. 3A) suggests enhanced ordering of the liquid crystal phase (*i.e.* larger ordered 1D aqueous channels within the liquid crystal) when the working electrode and counter electrode were narrowly spaced (within 1 mm apart). It was found that only irregular polyaniline structures were produced when the two electrodes were moved more than 3 mm apart possibly because of poor alignment and ordering of liquid crystals (Fig. 4A).[14] In addition, control experiments showed that only micron-sized particles were produced by electrodeposition directly from aniline acid solution (surfactant-free) (Fig. 4B).

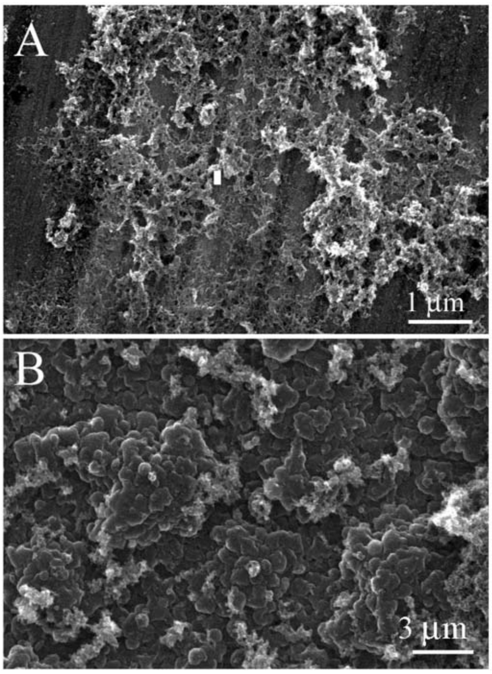


Fig. 4 Scanning electron micrographs of (A) polyaniline deposit from AOT reverse hexagonal liquid crystal with two electrodes 3 mm apart; (B) polyaniline particles electrodeposited from aniline acid solution (0.1 M aniline + 0.2 M H_2SO_4).

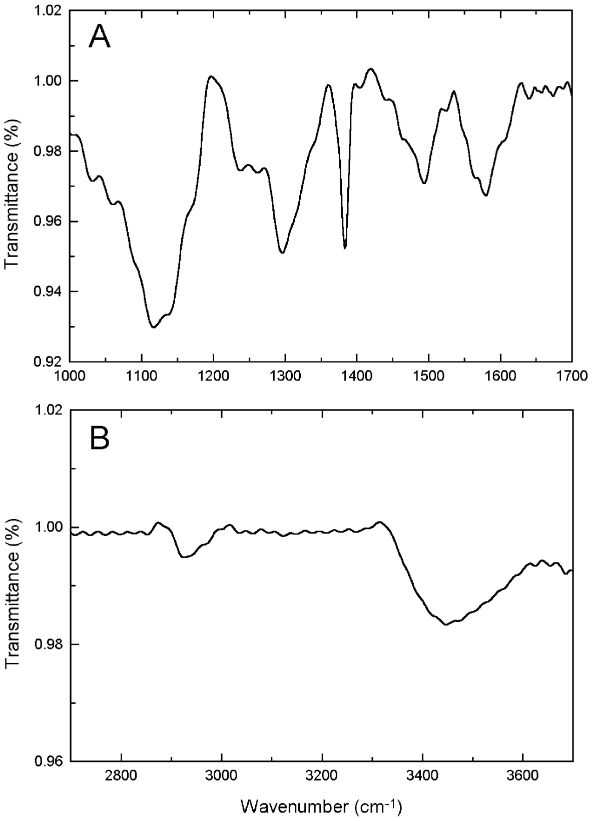
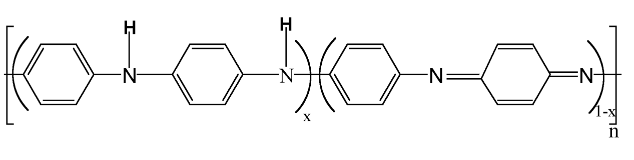


Fig. 5 Fourier transform infrared spectrum of polyaniline nanowires. (A) 1000–1700 cm^{-1}; (B) 2700–3700 cm^{-1}.

The infrared (IR) spectrum of polyaniline nanowires is shown in Fig. 5. The absorption in the frequency range 3300–3600 cm^{-1} is due to the N–H stretching mode. Bands at 1297 cm^{-1} and 1160 cm^{-1} correspond to the C–N stretching mode and bending mode, respectively. The groups N–B–N (B represents a benzenoid ring) and N=Q=N (Q represents a quinoid ring) absorb at 1493 and 1581 cm^{-1} respectively, with similar peak intensities, and this can be used to evaluate the oxidation state of polyaniline.[3,6,16,17] Polyaniline nanowires obtained in this study exist in the emeraldine form, which contains roughly equal amounts of benzenoid units (reduced form) and quinoid units (oxidized form) in polymer chains (Scheme 1).[3,16,17] The emeraldine form has been found to be conductive.[16] The results show that polyaniline nanowires grown from liquid crystalline phase have the same chemical structure as the polyaniline films electrodeposited from aqueous acid solution even though their morphologies are different.[17]

It is expected that nanowire formation is closely related to ordering of 1D aqueous channels within the reverse hexagonal liquid crystalline phase. Resistivity of the liquid crystal may reflect the continuity and ordering of aqueous channels. The conductivity is mainly from ion movements in the 1D aqueous channels. It was confirmed that high concentration anionic surfactant AOT in the oil phase (1.5 M) has poor conductivity (resistivity = 10^6 Ω m). Also, no deposit was found when



Scheme 1 Structure of conductive polyaniline nanowires (emeraldine form); $0 < x < 1$.

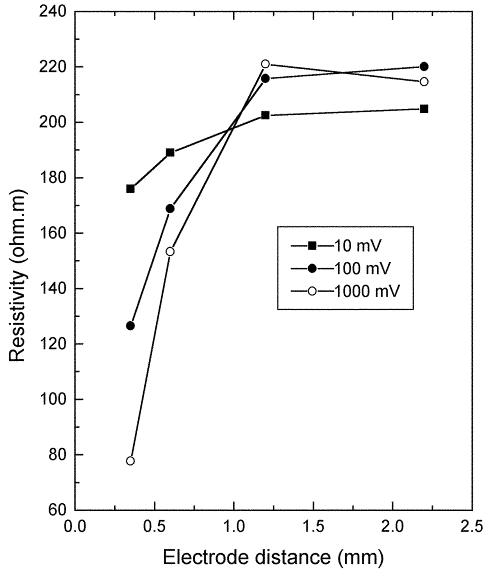


Fig. 6 Resistivity of reverse hexagonal liquid crystal AOT–*p*-xylene–H_2O (0.1 M aniline + 0.2 M H_2SO_4) as a function of electrode distance and AC amplitude.

electrodeposition was carried out from reverse micelles with a low concentration of surfactant AOT (0.2 M) because of the isolation of the aqueous phase. It is expected that resistivity decreases with better alignment of the 1D aqueous channels. Fig. 6 shows the change of resistivity of the reverse hexagonal liquid crystal *versus* the distance between the working electrode and counter electrode. When the electrode distance is lower than 1 mm, the resistivity decreases dramatically with the decrease of electrode distance for the AC amplitudes measured between 100–1000 mV. In addition, resistivity decreases with increase of the AC amplitude across the two electrodes (amplitude from 10 mV to 100 mV to 1000 mV). The reduction of resistivity suggests better alignment of 1D aqueous channels within the reverse hexagonal liquid crystalline phase with the decrease of electrode distance and the increase of amplitude. It is noted that the electrode potential during the AC impedance measurement is similar to the potential used during the potentiodynamic growth of polyaniline. Based on the above discussion, one possible mechanism for the growth of polymer nanowires from reverse hexagonal liquid crystalline phase is presented in Fig. 7. Although the exact template mechanism is not clear, it appears that the narrowly separated electrodes may have indeed created an electric field high enough (thus high current density) to help align the reverse hexagonal liquid crystal parallel to the electric field direction, which in turn facilitates the growth of long nanowires.

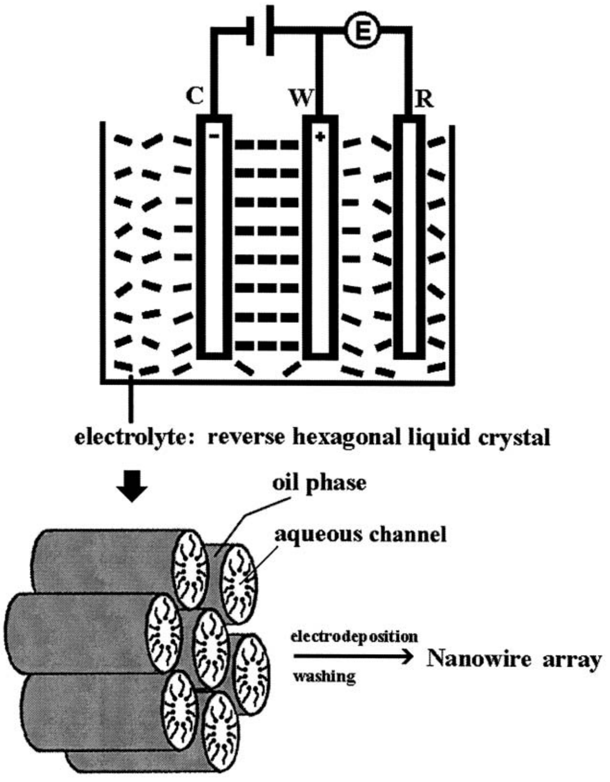


Fig. 7 Schematic of a proposed mechanism for nanowire electrodeposition from reverse hexagonal liquid crystalline phase. The electropolymerization was carried out in a three-electrode configuration (C—counter electrode; W—working electrode; R—reference electrode).

Conclusions

In summary, conductive polymer nanowires can be potentiodynamically electropolymerized by using a reverse liquid crystalline phase with 1D aqueous channels to control material growth on the nanometre scale. The nanowires can be easily collected by a simple washing process. The electrode distance appears important for deposition of high quality nanowires. This synthesis approach is fast, simple, and reproducible and a great variety of organized assemblies are potentially available by simply adjusting the surfactant type and liquid crystal composition.

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