

Facile Synthesis of Straight Polyaniline Nanostick in Hydrogel

Linghui Meng,[†] Yan Lu,[‡] Xudong Wang,^{*,†} Jian Zhang,[†] Yueqin Duan,[‡] and Chenxi Li^{*,†}

Key Laboratory of Functional Polymer Materials, Ministry of Education, Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China, and Institute of Material Physics, Tianjin University of Technology, Tianjin 300191, China

Received October 16, 2006

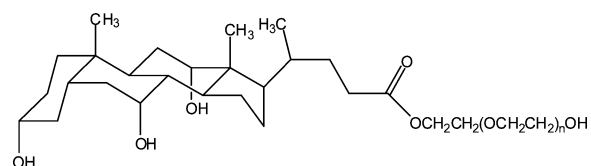
Revised Manuscript Received March 20, 2007

In recent years, conducting polymer nanostructures, such as nanotubes,^{1,2} nanobelts,³ nanofibers,^{4–8} etc., have received growing interest because of their novel physical properties and potential applications in hi-tech aspects, such as neuron devices,⁹ polymeric conducting molecular wires,¹⁰ chemical sensors or actuators,^{11–13} and gas-separation membranes.^{14,15} In the family of conducting polymers, polyaniline is unique due to its electronic, thermoelectric, and optical properties as well as its good environmental stability. Considerable efforts have been made on the synthesis of polyaniline one-dimensional nanostructures by polymerizing the monomer with the aid of either a “hard”^{10,16} or a “soft”^{6–8} template. Recently, Huang et al. have used two approaches—interfacial polymerization⁴ and rapidly mixed reactions⁵—to make pure polyaniline nanofibers. However, the synthesis of straight polyaniline nanosticks has rarely been reported. Moreover, although gels have been employed in the preparation of inorganic nanomaterials,^{17,18} there are few reports about the direct synthesis of polymer nanomaterials within hydrogel phase, especially low molecular weight hydrogels. In this paper, we report a novel method for facile synthesis of uniform straight polyaniline nanosticks by polymerizing aniline hydrochloric salt using ammonium peroxydisulfate (APS) as oxidant in a hydrogel system at ambient temperature.

In a typical process, 20 mg of low-molecular-weight hydrogelator, CA-PEG400 (Scheme 1), which was synthesized by conjugating of cholic acid (CA) and poly(ethylene glycol) 400 (PEG400),¹⁹ was dissolved in 0.8 mL of dilute hydrochloric acid (pH = 4–5) and mixed with 0.1 mL of 0.1 M aniline hydrochloric salt solution. Then, 0.1 mL of 0.1 M aqueous solution of APS was added with shaking. After the mixture was ultrasonically stirred, a transparent gel was formed immediately. During the oxidation process at room temperature, a color change from transparent to yellow and finally to dark brown was observed, as shown in Figure S1 (Supporting Information). After 1 day, the oxidation was completed, and the gel was well maintained. 0.1 mL of ethanol was added with shaking to break the network of hydrogel. The resulting precipitate was separated by centrifugation and washed with deionized water and ethanol several times to remove the residual gelator and salt. Finally, the pure dark brown powder was obtained after being dried in a vacuum oven.

The representative SEM and TEM images of PANI synthesized in hydrogel are shown in Figure 1. It is clear that nanosized PANI synthesized in hydrogel are almost regular sticks. The lower magnification image (Figure 1a) indicates that the sample consists of a large quantity of uniform one-dimensional struc-

Scheme 1. Molecular Structure of CA-PEG400



tures. The higher magnification image (Figure 1b) reveals that these structures are uniform nanosticks. The length of nanosticks ranges from 300 to 800 nm, and the average length is about 500 nm, as shown in Figure S2 (Supporting Information). The diameter slightly differs between nanosticks, in the range 50–70 nm, and within a single nanostick it is really constant. It should be noticed that all these nanosticks are very straight and isolated from each other, which are also confirmed by TEM image shown in Figure 1c. A typical selected area electron diffraction (SAED) measurement is also reported in Figure 1c. The broad Debye–Scherrer rings indicate that the nanosticks are poorly ordered, if not completely amorphous.

Polyaniline nanosticks were characterized with X-ray diffraction (XRD) and Fourier transform infrared spectroscopy

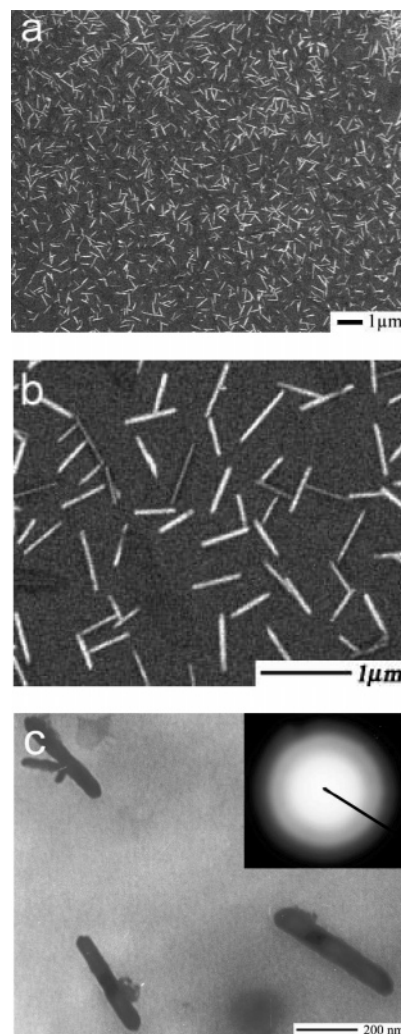


Figure 1. Typical SEM and TEM images of PANI synthesized in hydrogel: (a) SEM image at low magnification; (b) SEM image at high magnification; (c) TEM image and SAED pattern (inset) of typical PANI nanosticks.

[†] Nankai University.

[‡] Tianjin University of Technology.

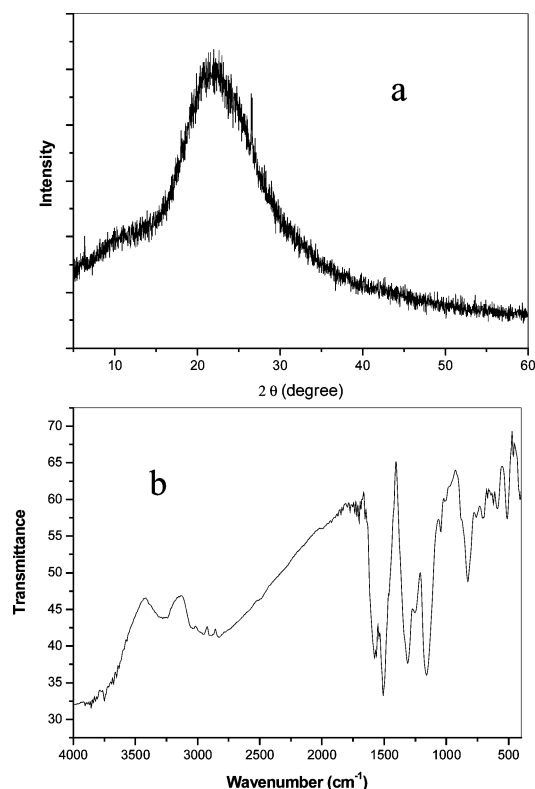


Figure 2. (a) X-ray diffraction pattern and (b) FTIR spectrum of PANI nanosticks synthesized in hydrogel.

(FTIR), as shown in Figure 2. The XRD result (Figure 2a) proves the primarily amorphous character of the sticks. The broad peak centered at $2\theta = 22.07^\circ$ ($d = 4.26 \text{ \AA}$) may be ascribed to the periodicity parallel to the polymer chain.²⁰ As Figure 2b shows, in the FTIR spectrum of PANI nanosticks, the adsorption peaks at 3277 and 1308 cm^{-1} correspond to the N–H and C–N stretching modes of the leucoemeraldine component, respectively. The peak at 1157 cm^{-1} is due to the C–H in-plane bending mode, and that at 1250 cm^{-1} is attributed to the protonated C–N group. The characteristic peaks at 1505 and 1574 cm^{-1} are assigned to the C=C stretching modes of the benzenoid ring and the quinoid ring,²¹ respectively, and the peak at 1574 cm^{-1} is lower than the peak at 1505 cm^{-1} , indicating that the state of the polyaniline nanosticks tend to be a kind of the leucoemeraldine form, which is consistent with the dark brown color²² of PANI powder synthesized in hydrogel.

Additional insight into the nanostick formation mechanism was provided by a series of experiments in which the morphology of the polymer was studied as a function of the acidity conditions at the beginning of the reaction. When the pH of the solution falls to 3 or lower, the resultant PANI particles are almost granular, as shown in Figure 3. This result is similar to that of Konyushenko.²³ Since aniline oligomers produced in the early stages of the polymerization are hydrophobic, they may aggregate on the framework of hydrogel and align themselves to constitute a template-like structure, which further predetermines the directional growth of PANI. However, once oligomers become protonated at low pH, they are likely soluble in the reaction medium due to the decreasing of hydrophobicity. This may alter the procedure for oligomer aggregation and, consequently, change the produced morphology. We also investigated the effects of the concentration of CA-PEG400 and APS on the morphologies of PANI, and these results are shown in Figures S3–S5 (Supporting Information). The more precise

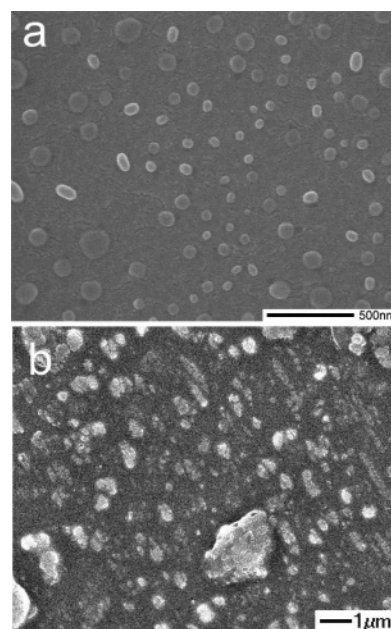


Figure 3. SEM images of PANI nanoparticles synthesized in hydrogel with the pH 3 (a) and 1 (b).

characteristics and formation mechanism of PANI nanosticks synthesized in hydrogel are currently being studied.

In conclusion, we have reported a novel procedure for the facile synthesis of straight uniform polyaniline nanosticks in a hydrogel. The approach here is simple, economical, and environmentally benign and may be applicable for the synthesis of other polymer or inorganic nanomaterials. The possible mechanism of formation of the nanosticks may be related to the aggregation and growth of aniline oligomers on the framework of the hydrogel. The straight uniform polyaniline nanosticks may provide potential applications such as nanodevices, chemical sensors or actuators and molecular probes, etc.

Experimental Notes. SEM images were obtained on a JSM-6700F field-emission scanning electron microscope, using an accelerating voltage of 10.0 kV. TEM and SAED images were obtained on a JEM-100CXII microscope with an accelerating voltage of 100.0 kV. XRD was carried out on a Rigaku D/max-2500 X-ray diffractionmeter using Cu (40 kV, 100 mA) radiation. The FTIR spectrum was measured by using a Bio-Rad FTS 6000 spectrophotometer.

Acknowledgment. This work was supported by National Natural Science Foundation of China (20604018) and Scientific Developing Foundation of Tianjin Education Commission (20050520).

Supporting Information Available: Figure S1, snapshots showing color change of PANI synthesized in hydrogel from transparent to dark brown; Figure S2, length distribution analysis of PANI nanosticks; Figure S3, SEM image of PANI bulks synthesized under similar reaction conditions only without hydrogelator; Figure S4, SEM images of PANI synthesized using 10 and 30 mg of CA-PEG400; Figure S5, SEM images of PANI synthesized using 0.05 and 0.2 M aqueous solution of APS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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MA062366N