CHEMISTRY OF MATERIALS

VOLUME 19, NUMBER 19 SEPTEMBER 18, 2007

Communications

Gram-Scale, Low-Cost, Rapid Fabrication of High-Quality Width-Controlled One-Dimensional Conducting Polymer Nanobelts

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Received May 17, 2007
Revised Manuscript Received July 25, 2007

Since the discovery of semiconducting oxide nanobelts in 2001,[1] beltlike nanomaterials have been the focus of intense research because they present a good system for examining dimensionally confined and structurally well-defined physical and chemical phenomena[1,2] and potential applications in numerous areas such as field-effect transistors,[3] nanometer-sized ultrasensitive gas sensors,[4] resonators,[5] and cantilevers.[6]

At the present time, one-dimensional (1D) nanostructured conducting polymers have attracted increasing interests because of their highly conjugated molecular structure, metal-like conductivity, and promising applications including nanosensor,[7] electrochromic devices,[8] integrated circuits,[9] batteries,[10] and photodetectors.[11] Basically, 1D conducting polymer nanostructures can be obtained chemically or electrochemically using hard- and soft-template methods. Although the hard-template[12] method is an effective route for fabricating diameter-controlled conducting polymer nanostructures, the preparation of the template is tedious and postsynthetic treatments are needed to remove them from the products, which might destroy as-prepared nanostructured materials. Soft-template approaches including use of surfactants,[13] seeding,[14] interfacial polymerization,[15,16] and oligomer-assisted polymerization[17] have been well-developed by several groups; however, part of reagents used are poisonous, resulting in a waste stream that must be treated. More recently, our group has reported that uniform poly-(*o*-phenylenediamine) (PPD) nanobelts could be synthesized from an *o*-phenylenediamine−$HAuCl_4$ aqueous solution at room temperature without using any template or surfactant.[18] However, the resulting precipitates are not "pure", and there are some Au nanoparticles in the final product. Also, because of the use of expensive reagent ($HAuCl_4$), industrialization of these nanobelts is unpractical.

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10.1021/cm071331e CCC: $37.00
Published on Web 08/21/2007

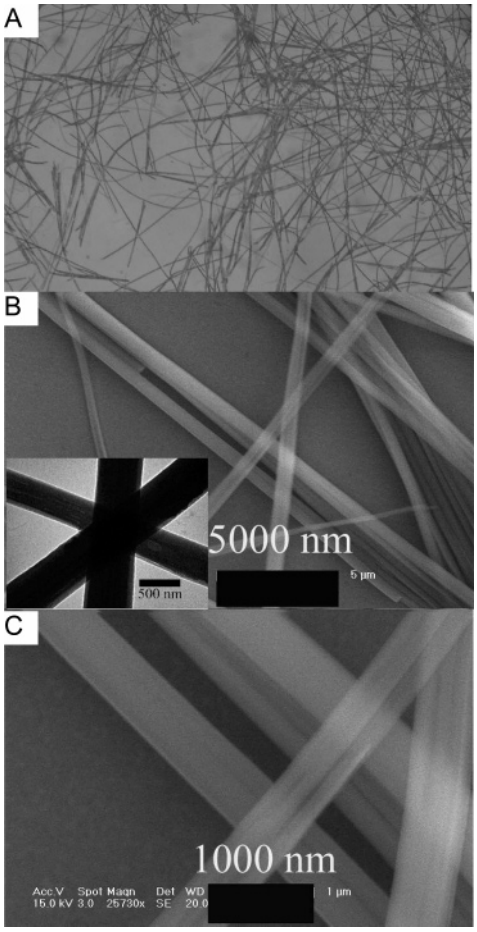

Figure 1. Optical microscope (A) and SEM (B, C) images of the PPD nanobelts prepared. The inset of B shows corresponding TEM image of the PPD nanobelts. The concentration of OPD is 0.1 M.

Therefore, it is necessary to introduce an easy, rapid, inexpensive, environmentally friendly, and gram-scale one-step method to produce highly pure, uniform nanobelts with controllable average widths in bulk quantities to meet the requirements for potential uses in nanodevices and nanosensor, etc. In this communication, we develop a rapid approach for the synthesis of width-controlled, high-quality ultralong PPD nanobelts via simply mixing o-phenylenediamine (OPD) and $FeCl_3$ aqueous solution. The advantage of the process includes simplicity, high speed, high quality, ease of scale-up, good reproducibility, and low cost. Gram-scale products can be synthesized that contain almost exclusively polymer nanobelts.

The PPD nanobelts with controllable width were successfully prepared by chemically oxidative polymerization. $FeCl_3$ and OPD were purchased from Beijing Chemical Factory. In a typical synthesis, 1 mL of 0.5 M $FeCl_3$ aqueous solution was rapidly added into 5 mL of 0.1 M OPD solution under vigorous stirring. A quick color change was observed upon the addition of $FeCl_3$. After stirring for 15 min, the solution was centrifuged two times and stored at ambient condition for characterization.

The morphology of the resulting precipitates was characterized with optical microscope and a XL30 ESEM FEG scanning electron microscopy (SEM) at an accelerating voltage of 15 kV. Figure 1A shows the optical microscope image of the product, which exhibits a yellow color. Images

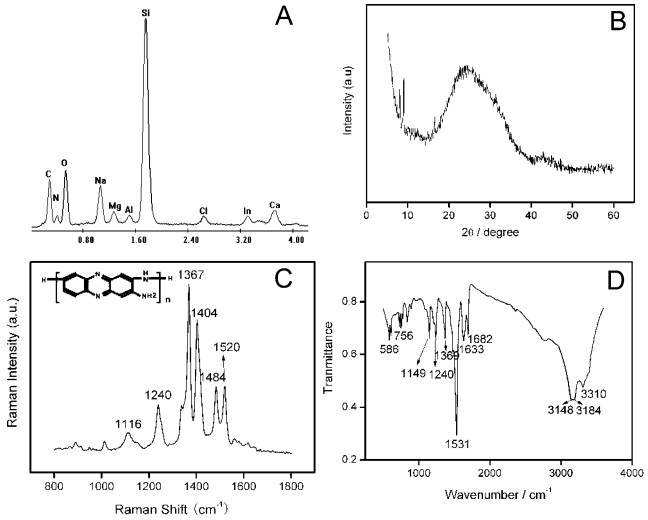

Figure 2. EDX image (A), XRD pattern (B), FT-Raman (C), and FTIR (D) of the nanobelts obtained. The inset of Figure 2C shows the phenazine-like structure. The concentration of OPD is 0.1 M.

B and C in Figure 1 show typical SEM images of the resulting precipitates. A low-magnification image (Figure 1B) reveals that the precipitates consist of a large quantity of uniform one-dimensional structures. The higher-magnification image (Figure 1C) demonstrates that these nanostructures in the radial direction are plat (transparent nanobelts) several tens of nanometers in height. Transmission electron microscopy (the inset of Figure 1B) indicates that these nanobelts are uniform with 500 nm in width. It is important to note that all these nanobelts are separated from each other with high quality.

The chemical composition of these nanobelts obtained was further determined by energy-dispersive X-ray spectroscopy (EDX) analysis of the resulting precipitate coated on indium tin oxide (ITO) glass slide. The peaks of C and N are noticed (other peaks originated from ITO glass substrate), as shown in Figure 2A. It can be concluded that these nanobelts are OPD polymer. The X-ray diffraction (XRD) analysis of the resulting precipitates was carried out on a D/MAX 2500 V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation. Figure 2B shows the XRD pattern obtained. The broad peak centered at ~25° can be ascribed to the formation of amorphous OPD polymer, and the occurrence of a strong diffraction peak at a low Bragg angle can be attributed to the larger crystalline size.[18,19]

Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy were used to characterize the structure of PPD nanobelts. It is found that the Raman spectrum of PPD nanobelts (Figure 2C) is similar to those found in the literature.[20,21] The peaks at 1404, 1484, and 1367 cm^{-1} correspond to the phenazine-like structure, the stretching vibrations of C═N and C−N groups, respectively. Figure 2D is the FTIR spectrum of PPD nanobelts. The peak at 3310 cm^{-1} corresponds to the N−H stretching vibrations of the NH group, and the two peaks centered at 3148 and 3184

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cm^{-1} are assigned to the N−H stretching vibrations of the NH_2 group. Two sharp peaks at 1633 and 1531 cm^{-1} are associated with the C═N and C═C stretching vibrations in the phenazine ring, respectively.[21] The peaks at 1240 and 1369 cm^{-1} are ascribed to the C−N stretching in the benzenoid and quinoid imine units, respectively.[21] Both of the above Raman and FTIR data reveal that PPD nanobelt has the structure shown in the inset of Figure 2C. On the basis of the Raman and FTIR data and reference,[20−24] the formation mechanism of these nanobelts was proposed initially. Dong's group[20] reported a large-scale facile reprecipitation route to fabricate uniform PPD 1D nanomaterial on the macroscopic length scale. It was found that $\pi-\pi$ interactions between OPD oligomers that facilitated the formation of 1D structures became predominant when they were transferred from *N*-methyl pyrrolidone (NMP) to deionized water. In this process, sudden changes in the environment (reduced solubility) induce the self-assembly of the molecule. Many literatures have been reported to the synthesis of 1D conjugated organic nanomaterial using the above method.[22−24] In fact, in our synthesis system, a phenazine-like structure (OPD oligomer) was formed quickly through the redox reaction between $FeCl_3$ and OPD. Because there are a great number of π electrons in the phenazine-like structure, which was proved by the Raman and FTIR data, $\pi-\pi$ interactions between OPD oligomers formed are quite large. Because of their strong $\pi-\pi$ interactions between the phenazine-like structures and limited solubility in water, these OPD oligomers will self-assemble into a 1D superstructure, resulting in these novel nanobelts. However, the detailed mechanism of the formation of the nanobelts in this synthesis is not very clear at present time and needs further investigation.

We also examined the influence of the concentration of reactants on the morphologies of the structures thus formed. We prepared two samples, under identical conditions used for preparing sample 1 (see the above part), by decreasing the concentration of reactants to 1/5 and 1/20, respectively. To our surprise, the width of nanobelts can be controlled by changing the concentration of reactants. When the concentration of reactants was decreased to 1/5, the width of nanobelts was about 300 nm (Figure 3A). Figure 3A shows typical SEM images of the obtained precipitate. Higher magnification reveals that most of the nanobelts own the width of about 300 nm. By continuously decreasing the concentration of reactants, the width of nanobelts is further decreased. Figure 3B shows the SEM image of the obtained product. Uniform PPD nanobelts can be observed. The corresponding TEM image (the inset of Figure 3B) indicates that the width of the nanobelts is close to 200 nm. It is noted that some positions of nanobelts were broken, which indicates these nanobelts are thin. Thus, the width of nanobelts can be controlled by simply changing the concentration of reactants.

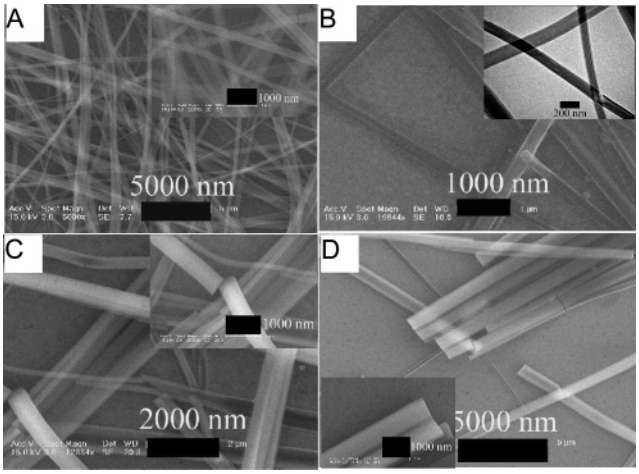

Figure 3. SEM images of the precipitate obtained with concentrations of 1/5 (A) and 1/20 (B) under identical conditions used for preparing sample 1; with 4:1 (C) and 8:1 (D) $FeCl_3$:OPD molar ratios, the concentration of OPD is 20 mM.

In addition, when the concentration of OPD was unchanged (20 mM), the influence of the molar ratio of reactants on the morphologies of the resulting product was investigated. When the molar ratio of $FeCl_3$ to OPD was 4, the mixture of nanobelts and nanobeams was obtained, as shown in Figure 3C. Specifically, uniform PPD nanobeams dominated in the product after changing the molar ratio to 8 (Figure 3D). Therefore, the morphologies of PPD nanostructures can be controlled from the width-controlled nanobelts to nanobeams, which will find potential applications in nanodevices and nanosensors, etc.

In conclusion, we have demonstrated a facile, rapid, and simple approach for fabricating uniform PPD nanobelts on a large scale. It is found that the width of nanobelts can be easily controlled by changing the concentration of reactants. In addition, when changing the molar ratio of reactants, uniform 1D PPD nanobeams can be easily produced. Raman and FTIR spectra indicate that $\pi-\pi$ interactions between OPD oligomers might facilitate the formation of the 1D nanostructure. Large amounts of PPD 1D nanobelts and nanobeams can be fabricated in a simple, rapid, and low-cost process, which will make industrialization of these novel 1D nanostructures easy.

Acknowledgment. This work was supported by the National Science Foundation of China. (20575064, 20427003)

Supporting Information Available: Description of the apparatus (Word). This material is available by free of charge via the Internet at http:// pubs.acs.org.

CM071331E

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