One-Dimensional Polyaniline Nanostructures with Controllable Surfaces and Diameters Using Vanadic Acid as the Oxidant

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Received March 18, 2007; Revised Manuscript Received July 16, 2007

ABSTRACT: One-dimensional polyaniline nanostructures with controllable surfaces and diameters have been synthesized using vanadic acid as the oxidant in the absence of porous templates and structural directing molecules. The synthetic parameters, such as the concentrations of HCl, and types of oxdiants on the morphologies, diameters, and molecular structures of one-dimensional polyaniline nanostructures have been investigated. As the concentration of HCl is low, polyaniline nanorods with diameters of 10−20 nm and length up to 50−60 nm can be aligned radially along the length axis on the surfaces of polyaniline nanofibers. With the concentration of HCl increased, the diameters of one-dimensional polyaniline nanostructures decrease from 150−300 to 40−100 nm, and the surfaces of one-dimensional polyaniline nanostructures become smooth. The possible formation mechanism of one-dimensional polyaniline nanostructures using vanadic acid as the oxidant has been discussed.

Introduction

Polyaniline, one of the conducting polymers, is of interest due to its simple and reversible acid doping/base dedoping properties and optical and electronic applications.[1,2] It can be synthesized easily through either chemical polymerization or electrochemical polymerization. One-dimensional (1D) polyaniline nanostructures, such as nanorods, nanofibers, nanotubes, and nanobelts, have attracted intensive interest because they possess the advantages of both low-dimensional system and organic conductors and have potential applications including polymeric conducting molecular wires,[3] chemical sensors,[4−9] biosensors,[10] and light-emitting and electronic devices.[11] In recent years, considerable efforts have been made on the synthesis of 1D polyaniline nanostructures by the chemical oxidation polymerization of aniline in aqueous medium. The synthetic approaches to 1D polyaniline nanostructures include interfacial polymerization,[5,12] seeding polymerization,[13,14] oligomer-assisted polymerization,[15] rapidly mixed reaction,[16] dilute polymerization,[17,18] use of porous templates,[3,19,20] and structural directing molecules such as surfactants,[21−23] specific dopants,[24−29] and DNA.[30] In the chemical synthesis, different oxidants such as ammonium peroxydisulfate,[2,12−29] chloroaurate acid,[31] ferric chloride,[32] and horseradish peroxidase[30] have been used to adjust the molecular structures and physical properties of 1D polyaniline nanostructures. Recently, our group[33] has synthesized polyaniline−vanadium oxide nanocomposite nanosheets by in-situ intercalation polymerization of aniline with layered V_2O_5 powder under hydrothermal conditions. Herein, we report a new and facile approach for the synthesis of 1D polyaniline nanostructures with controllable surfaces and diameters using vanadic acid as the oxidant without the aid of any porous templates and structural directing molecules.

Experimental Section

Synthesis of 1D Polyaniline Nanostructures. In a typical synthesis, 0.15 g of V_2O_5 powder was dissolved in 20 mL of 0.75 mol/L hydrogen chloride (HCl) solution with magnetic stirring to form a light yellow vanadic acid aqueous solution. The solution was poured into an aqueous solution of aniline (0.1 g) in 0.75 mol/L HCl (20 mL). The mixture was stirred to ensure sufficient mixing before polymerization begins. The polymerization reaction was carried out under static conditions at 0−5 °C for 24 h. The resulting dark green precipitate was filtered, washed with deionized water and ethanol several times, and dried at room temperature for 24 h. The as-synthesized 1D polyaniline nanostructures can be dispersed in water to form a homogeneous suspension under ultrasonic vibration for 5 min.

Characterization. The morphologies and sizes of the resulting products were determined by field-emission scanning electron microscopy (FE-SEM, JSM 6700F). The elemental analysis of 1D polyaniline nanostructures synthesized using vanadic acid as the oxidant with 0.75 mol/L HCl at 0−5 °C for 24 h was performed on energy dispersive X-ray microanalysis system (EDS, Oxford Instrument, UK). The molecular structures of the resulting products were measured by Fourier transform infrared (FTIR, Nicolet Magna IR-750 spectrophotometer) spectroscopy and UV−vis spectroscopy (Cary 500 UV−vis−NIR spectrophotometer). The cyclic voltammograms of the as-synthesized 1D polyaniline nanostructures were determined in 0.1 M HCl aqueous solution with a scan rate of 0.1 V/s by a CHI660C electrochemical workstation.

Results and Discussion

Figure 1 shows SEM images of 1D polyaniline nanostructures synthesized using vanadic acid as the oxidant with 0.75 mol/L HCl at 0−5 °C for 24 h. Low-magnification SEM image (Figure 1A) reveals that the dark green precipitate is composed of a large quantity of 1D polyaniline nanostructures with diameters of 150−300 nm and length up to several micrometers. In a high-magnification SEM image (Figure 1B), it is interesting that these 1D polyaniline nanostructures comprise of nanorods with diameters of 10−20 nm and length up to 50−60 nm. The nanorods are aligned radially on the surfaces of polyaniline nanofibers along the length axis to form 1D polyaniline superstructures. The elemental composition of 1D polyaniline nanostructures is shown in Table S1 (see Supporting Information). It is found that only a small amount of residual V exists in the product, which might have resulted from the adsorption or doping of vanadic acid. SEM image of polyaniline synthesized using ammonium peroxydisulfate as the oxidant in 0.75

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10.1021/ma070650o CCC: $37.00

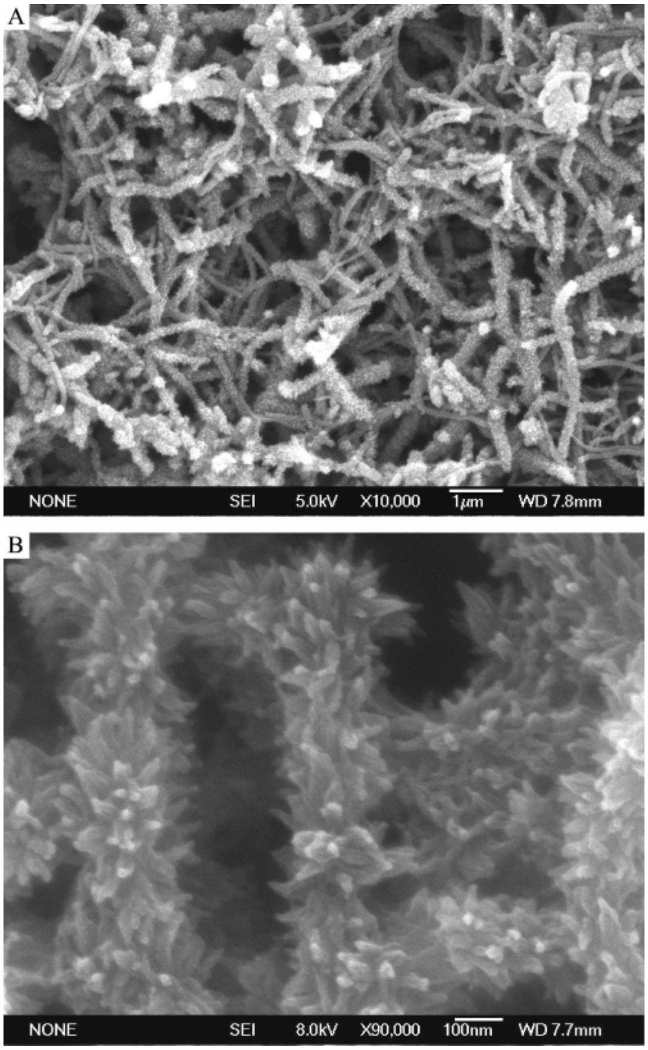

Figure 1. SEM images of 1D polyaniline nanostructures synthesized using vanadic acid as the oxidant with 0.75 mol/L HCl at 0−5 °C for 24 h: (A) at low magnification and (B) at high magnification.

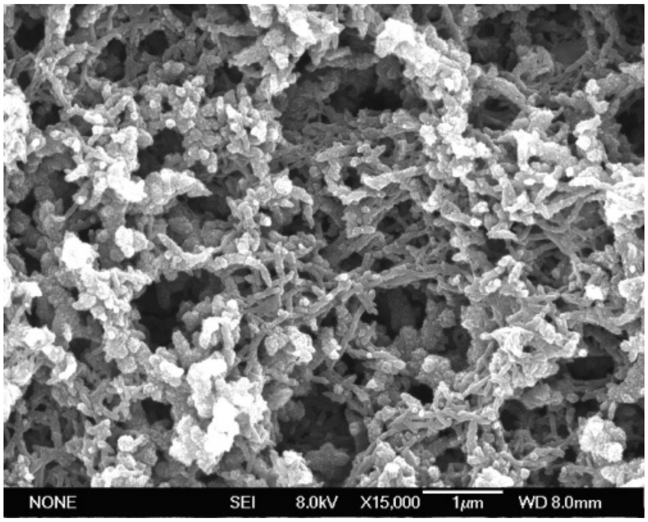

Figure 2. SEM image of polyaniline synthesized using ammonium peroxydisulfate as the oxidant in 0.75 mol/L HCl solution.

mol/L HCl solution (Figure 2) shows that there is a small portion of nanofibers in addition to granular particle agglomerations, so vanadic acid used as the oxidant in the reaction plays an important role in the formation of polyaniline nanofibers.

The influences of the synthetic parameters, such as the molar concentrations of HCl, and different types of oxdiants on the morphologies of 1D polyaniline nanostructures have been investigated. SEM images of polyaniline nanostructures synthesized using vanadic acid as the oxidant with different concentrations of HCl at 0−5 °C for 24 h are presented in Figure 3. Low-magnification SEM images reveal that all 1D polyaniline nanostructures were obtained with different concentrations of HCl. The typical length of all the 1D polyaniline nanostructures is about several micrometers. As shown in Figure 3A, when the concentration of HCl is 1.00 mol/L, 1D polyaniline nanostructures with diameters of 150−250 nm are formed. In a high-magnification SEM image in the inset in Figure 3A, it is found that nanoparticles coexist with nanorods on the surfaces of 1D polyaniline nanostructures. Figure 3B shows SEM images of 1D polyaniline nanostructures synthesized with 1.25 mol/L HCl. The diameters of 1D polyaniline nanostructures are in the range of 70−130 nm, as shown in the inset in Figure 3B. When the concentration of HCl increases to 1.50 mol/L, the diameters of polyaniline nanofibers in Figure 3C and the inset are about 40−100 nm. Compared with Figure 1 and Figure 3A, the surfaces of 1D polyaniline nanostructures become smooth with the concentration of HCl increased.

When the mixture of vanadic acid and ammonium peroxydisulfate was used as the oxidants (the molar ratio of vanadic acid and ammonium peroxydisulfate is 1:2), as shown in Figure 4A, a large quantity of polyaniline nanofibers is obtained. In a high-magnification SEM image (Figure 4B), it is clear that the polyaniline nanofibers are interconnected to form netlike nanostructures. The diameters of polyaniline nanofibers are in the range of 30−60 nm. In comparison with Figure 2, the amount of polyaniline nanofibers increases clearly, indicating that the oxidant of vanadic acid is important for the formation of polyaniline nanofibers.

Figure 5A shows a typical FTIR spectrum of 1D polyaniline nanostructures synthesized with vanadic acid as the oxidant at 0−5 °C for 24 h. The characteristic peaks at 3455 cm^{-1} are due to the O−H stretching vibrations of vanadic acid. The characteristic peaks at 1633 and 1465 cm^{-1} are assigned to the C=C stretching of quinoid rings and benzenoid rings, respectively.[22,24] It can be found that the relative intensity of quinoid rings is larger than that of benzenoid rings, indicating that the fully pernigraniline phase is predominant in the polyaniline chain. The FTIR spectrum of 1D polyaniline nanostructures synthesized with the mixture of vanadic acid and ammonium peroxydisulfate as the oxidants is presented in Figure 5B. It is clear that the characteristic peaks corresponding to C=C stretching of quinoid rings appear at 1633 and 1579 cm^{-1}, which are related to vanadic acid and ammonium peroxydisulfate, respectively. The characteristic peak at 1486 cm^{-1} is assigned to the C=C stretching of benzenoid rings. It is indicated that the molecular structures of polyaniline can be affected by the types of the oxidants, especially the oxidation/reduction potential of $E_{ox} = 1.00$ V (vanadic acid) and $E_{ox} = 2.01$ V (ammonium peroxydisulfate). The typical UV−vis spectra of 1D polyaniline nanostructures synthesized with vanadic acid as the oxidant at 0−5 °C for 24 h are shown in Figure 6. 1D polyaniline nanostructures can be dispersed in water to form a homogeneous green suspension, corresponding to doped polyaniline (Figure 5A). Dedoped polyaniline is obtained by treatment with aqueous ammonium hydroxide solution (Figure 5B). As shown in Figure 6A, the peaks at about 360, 430, and 850 nm are attributed to the $\pi \rightarrow \pi^*$ transition,

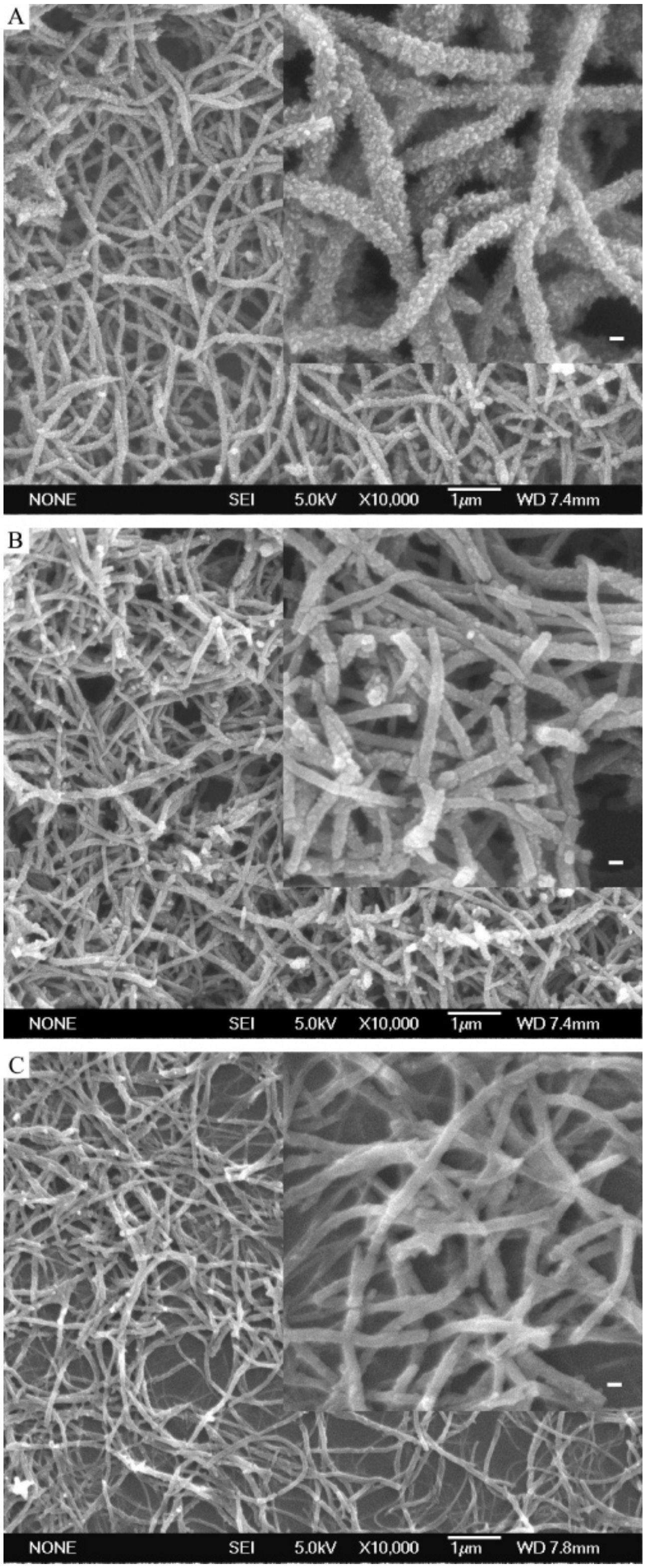

Figure 3. SEM images of 1D polyaniline nanostructures synthesized using vanadic acid as the oxidant with different concentrations of HCl at 0−5 °C for 24 h: (A) 1.00, (B) 1.25, and (C) 1.50 mol/L. The insets show high-magnification SEM images of polyaniline nanostructures. The scale bar in the inset is 100 nm.

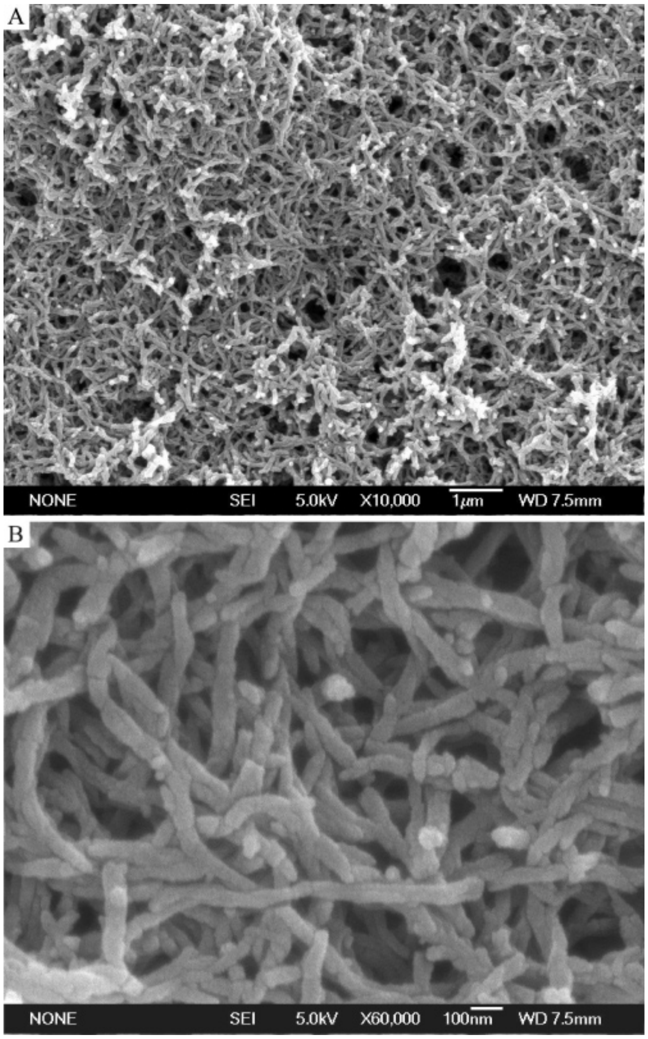

Figure 4. SEM images of 1D polyaniline nanostructures synthesized with the mixture of vanadic acid and ammonium peroxydisulfate as the oxidants in 0.75 mol/L HCl solution at 0−5 °C for 24 h: (A) at low magnification and (B) at high magnification.

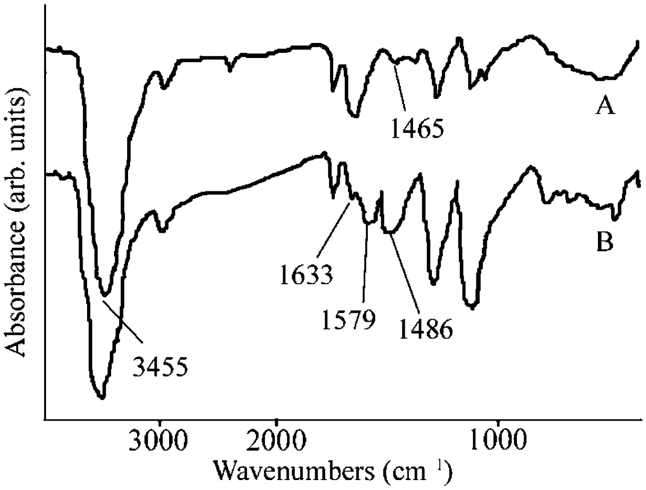

Figure 5. FTIR spectra of 1D polyaniline nanostructures synthesized with different oxidants in 0.75 mol/L HCl solution at 0−5 °C for 24 h: (A) vanadic acid; (B) mixture of vanadic acid and ammonium peroxydisulfate.

the polaron band $\rightarrow \pi^*$ transition, and the π to the localized polaron band of doped polyaniline, respectively.[5,13] The as-synthesized polyaniline is doped in the presence of hydrochloride acid, which is consistent with that in Figure 5. The peaks at about 340 and 650 nm are related to the $\pi \rightarrow \pi^*$ transition of benzenoid ring and quinoid ring, respectively, which are identical to that of dedoped polyaniline (Figure 6B).

The cyclic voltammograms of the as-synthesized 1D polyaniline nanostructures performed in 0.1 M HCl aqueous solution

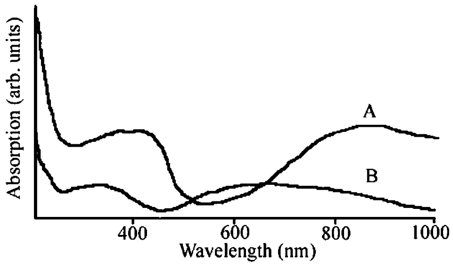

Figure 6. UV−vis spectra of 1D polyaniline nanostructures synthesized with vanadic acid as the oxidant in 0.75 mol/L HCl solution at 0−5 °C for 24 h: (A) polyaniline doped with hydrochloride acid; (B) polyaniline dedoped with ammonium hydroxide.

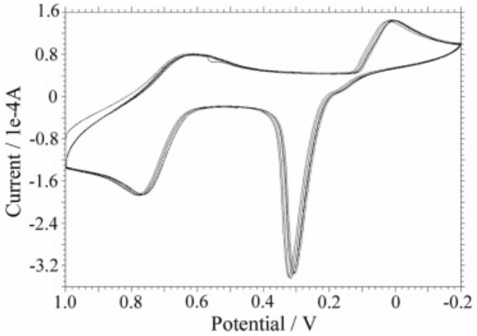

Figure 7. Cyclic voltammograms of the as-synthesized 1D polyaniline nanostructures performed in 0.1 M HCl aqueous solution with a scan rate of 0.1 V/s.

with a scan rate of 0.1 V/s are shown in Figure 7. Two typical redox peaks can be seen clearly. Two anodic peaks at 0.31 and 0.76 V can be assigned to oxidation of polyaniline from leucoemeraldine to emeraldine and to further oxidation from emeraldine to pernigraniline, indicating that the aqueous electrochemistry of polyaniline are not significantly affected by the morphology.[34]

This synthetic process is very simple and free of any templates and surfactants. In our precious work,[33] the bulk layered V_2O_5 was exfoliated to form tremella-like nanosheets of polyaniline−vanadium oxide hybrid nanocomposites at low concentration of HCl due to the in-situ intercalation polymerization. In the reaction system, V_2O_5 was dissolved in the aqueous HCl solution to form vanadic acid (VO_2^+), which was used as the oxidant. The polymerization rate of aniline is lower than that using ammonium peroxydisulfate as oxidant because of the different oxidation/reduction potential of vanadic acid ($E_{ox} = 1.00$ V) and ammonium peroxydisulfate ($E_{ox} = 2.01$ V). No V_2O_5 nanofibers are found in the solution, so the synthetic approach is different from that using V_2O_5 nanofibers as seed templates.[13] In this present work, the formation of 1D polyaniline nanostructures is probably related to the chemical oxidation polymerization process itself and the linear nature of polyaniline molecular chains,[12,16,35] so the traditional polymerization of aniline can lead to the formation of a small amount of polyaniline nanofibers. As the polymerization begins, the oxidant can induce the polymerization of aniline monomers to form polyaniline oligomers according to the formula $VO_2^+ + 2H^+ + 2e = VO^{2+} + H_2O$. VO_2^+ can be reduced by VO^{2+} by aniline during the process of polymerization. The appropriate oxidation/reduction potential of oxidants and static condition are in favor of the formation of polyaniline nanofibers due to homogeneous nucleation.[36,37] The formed polyaniline nanofibers can induce heterogeneous nucleation to form nanoparticles (Figure S1, Supporting Information) and then nanorods (Figure 1) on their surfaces as the reaction time increases.

Conclusions

In summary, 1D polyaniline nanostructures with controllable surfaces and diameters have been synthesized using vanadic acid as the oxidant in the absence of porous templates and structural directing molecules. 1D polyaniline nanostructures with polyaniline nanorods aligned radially along the length axis can be obtained with low concentration of HCl. The diameters of 1D polyaniline nanostructures decrease from 150−300 to 40−100 nm, and the surfaces of 1D polyaniline nanostructures become smooth as the concentration of HCl increases. Vanadic acid, used as the oxidant, plays an important role in the formation of one-dimensional polyaniline nanostructures.

Acknowledgment. This work was supported by the Nature Science Foundation of Qingdao Bureau of Science and Technology (Grant No. 05-1-jc-90) and the Research Fund for the Doctoral Program of Qingdao University of Science and Technology.

Supporting Information Available: Elemental composition of 1D polyaniline nanostructures and SEM image of 1D polyaniline nanostructures synthesized using with 0.75 mol/L HCl at 0−5 °C for 3 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA070650O