Synthesis of Polyaniline Hierarchical Structures in a Dilute SDS/HCl Solution: Nanostructure-Covered Rectangular Tubes

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ABSTRACT: We reported the synthesis of nanostructure-covered rectangular submicrotubes of polyaniline in the doping state via the oxidation polymerization of aniline in the acidic solution of anionic surfactant. Both the concentrations of surfactant and inorganic acid employed in this preparing system are relatively low, which were essential to the successful fabrication of polyaniline hierarchical structures. We discussed the temperature dependence of polyaniline morphology and found that this synthesis admitted a wide range from 20 to 40 °C. After observing their growth processes, a tentative interpretation has been proposed to elucidate the formation of the tubular hierarchical structures in such a system. It was also found in this report that both SDS and HCl had profound impacts on the morphology of resulting product.

Introduction

Polyaniline (PANI) is one of the mostly studied intrinsically conducting polymers owing to its better environmental stability, tunable conductivity switching between insulating and semiconducting materials, and reversible redox behavior.[1] Conventional PANI has been shown to have a lot of promising potential applications in the fields of batteries, corrosion protection, microwave absorptions, and so on.[2] When it is nanostructured, PANI can yield better performances in these already established areas and even create new properties.[3] Recently, the interest in nanostructured PANI, especially, one-dimensional (1D) nanostructures including nanofibers, nanorods, or nanotubes, increased extensively. A variety of chemical methods that have been reported to produce high-quality 1D PANI nanomaterials are reported, such as template method,[4] seeding polymerization,[5] interfacial polymerization,[6] and dilute polymerization.[7] On the other hand, as is well known, integrating these 1D nanomaterials into devices has been the next important step in the development of nanotechnology.[8] As an extension of this trend, many applications of PANI, such as microelectronic devices and light-emitting, require the controlled alignment and the hierarchical assembling of the nanostructures.[9] In this regard, the parallel array of PANI,[9] the radially aligned dendrites,[10] micromats of PANI nanofibers,[11] and flowerlike architectures[12] have been obtained by the self-assembly processes with or without additive. However, there are spare researches which reported the fabrication of nanostructures on hollow PANI tubes, especially for rectangular tubes which have better potential applications in the fields of electronics, optics, catalysis, and energy storage.[13]

Basically, the polymerization reaction in concentrated solution of sodium dodecyl sulfate (SDS) could produce granular PANI,[14,15] while the PANI nanofibers were obtained in high HCl reaction system.[6,16] In our previous works, PANI rectangular submicrotubes[17] and rectangular-tube-based fanlike PANI[18] have been synthesized by the oxidation of aniline in the dilute SDS and HCl solution, respectively. Herein, we find that the preparing system synchronously containing low-concentration SDS and HCl creates nanostructure-covered rectangular submicrotubes of PANI. Since the synthesis can be carried facilely out at room temperature (25 °C) in dilute SDS/HCl aqueous solution, this reaction route is believed to be very convenient and low-cost from the chemical point of view. What is more, the tubular hierarchical PANI as a novel nanoarchitecture is produced for the first time by this synthesis.

Experimental Section

Materials. Aniline monomer (Shanghai Chemical Co.) was distilled under reduced pressure. Sodium dodecyl sulfate (SDS, Aldrich, 99%), APS ($(NH_4)_2S_2O_8$, Shanghai Chemical Co.), and other reagents were used as received.

Synthesis of PANI. Typical synthetic processes of PANI were as follows: 0.045 g of aniline (distilled), 0.300 mL of HCl aqueous

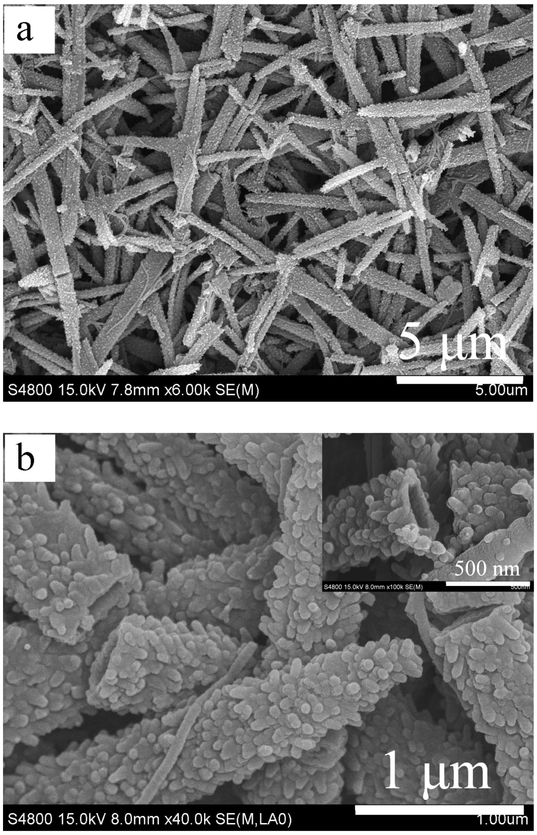

Figure 1. FESEM images of PANI synthesized in dilute SDS/HCl solution. Synthetic conditions: [SDS] = 0.53 mM; [HCl] = 0.38 mM; [aniline] = 24 mM; [APS]/[aniline] = 1.0:1; 25 °C; 24 h.

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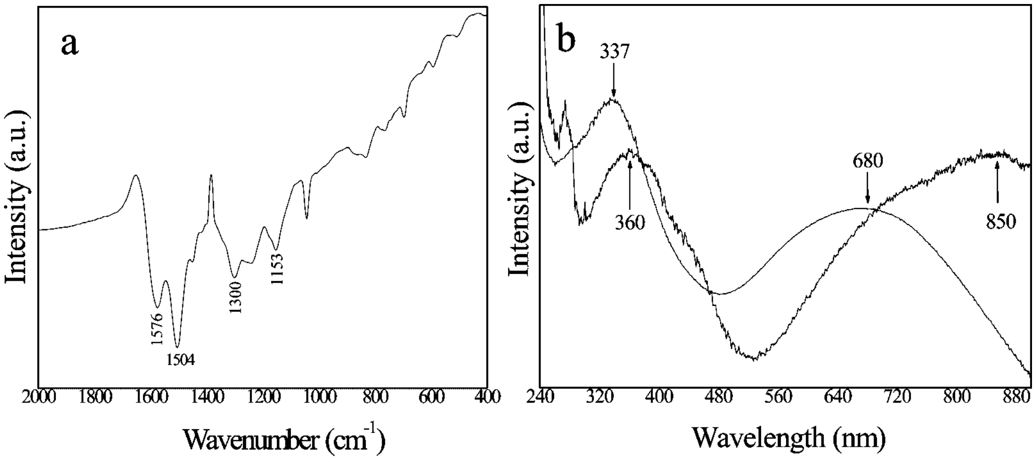

Figure 2. (a) FTIR and (b) UV−vis spectra of PANI synthesized in SDS/HCl dilute solution. Synthetic conditions: [SDS] = 0.53 mM; [HCl] = 0.38 mM; [aniline] = 24 mM; [APS]/[aniline] = 1.0:1; 25 °C; 24 h.

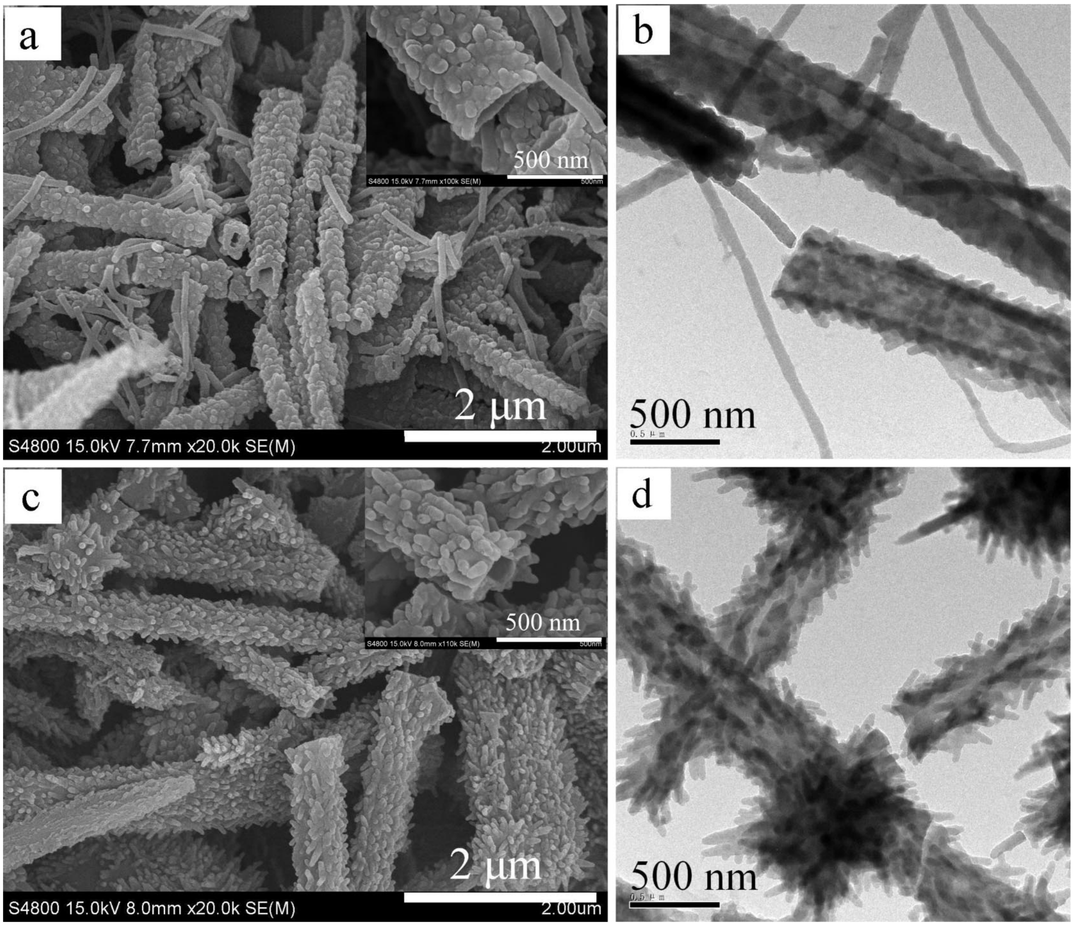

Figure 3. (a, c) FESEM and (b, d) TEM images of PANI synthesized in SDS/HCl dilute solution under different temperatures (°C): (a, b) 20; (c, d) 40. Other synthetic conditions: [SDS] = 0.53 mM; [HCl] = 0.38 mM; [aniline] = 24 mM; [APS]/[aniline] = 1.0:1; 24 h. Insets in (a, c) show the rectangular cross sections and nanostructure-covered surfaces of tubes.

solution (0.25 M), and 0.005 g of SDS (from Aldrich) were dispersed in 18 mL of deionized water with magnetic stirring at room temperature for 20 min to obtain a uniform solution. After that, 2 mL of ammonium persulfate (APS, A.R.) aqueous solution (0.24 M) was added to the above mixture in one portion. The resulting solution was stirred violently for another 0.5 min to ensure complete mixing, and then the reaction was allowed to proceed without agitation for 24 h at 25 °C. Finally, the products were washed with deionized water until the filtrate became colorless and then dried in a vacuum at 60 °C for 24 h.

Characterization. The morphologies of products were examined by a field-emission scanning electron microscope (FESEM, S-4800, Hitachi Co., Japan) and a transmission electron microscope (TEM, Tecnai-12 Philip Apparatus Co.). The FTIR spectrum (Nicolet-740) was recorded in the range of 400−4000 cm^{-1}. The UV−vis spectra (UV-250, Shimadzu Corp., Japan) of samples dissolved in aqueous solution were measured in the range between 240 and 900 nm. The conductivity of product was measured by a four-point technique on pellets from polymer powders at room temperature.

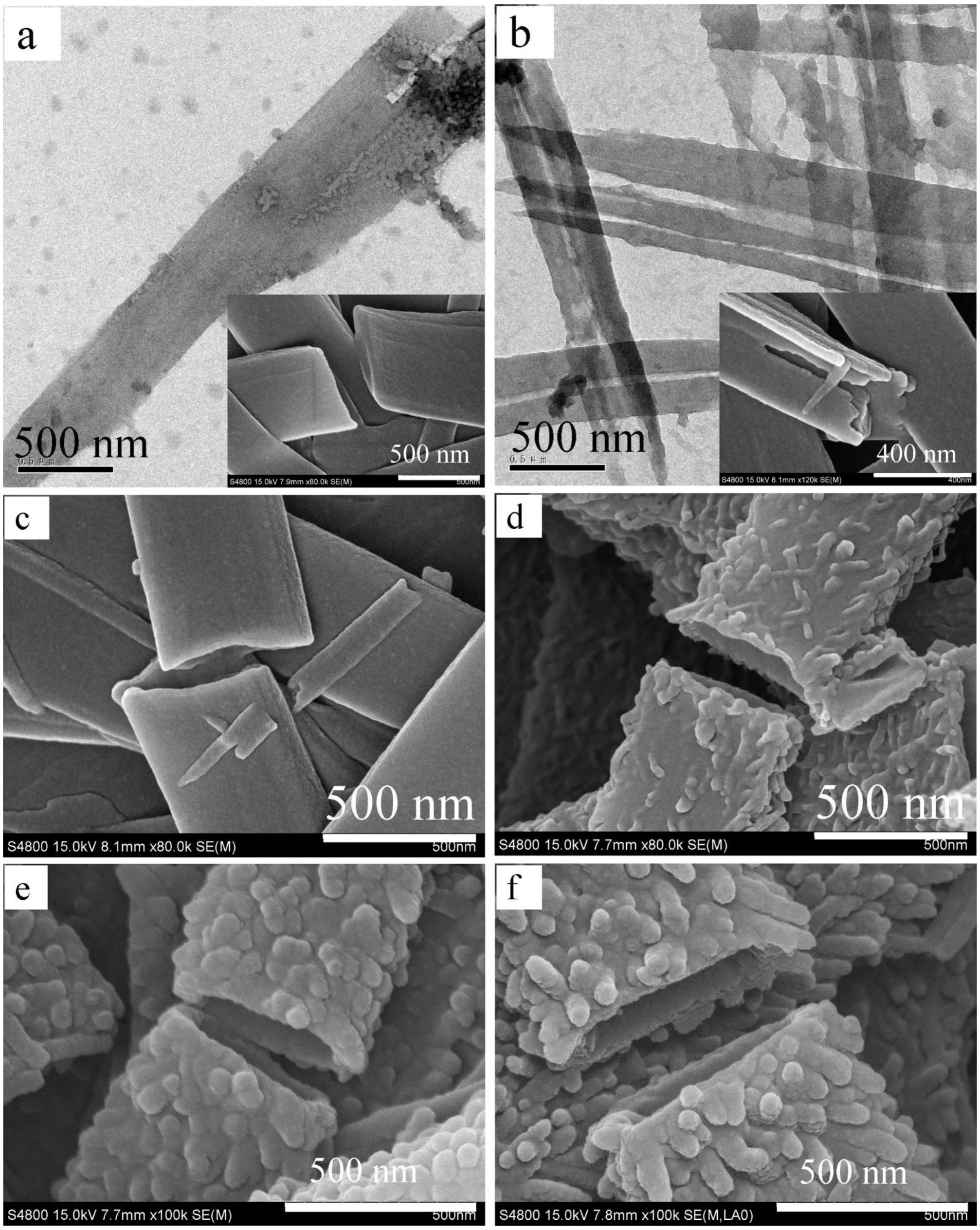

Figure 4. (a, b) TEM and (c−f) FESEM images of products obtained with different reaction times: (a) 15 min; (b) 30 min; (c) 1 h; (d) 2 h; (e) 3 h; (f) 4 h. Synthetic conditions: [SDS] = 0.53 mM; [HCl] = 0.38 mM; [aniline] = 24 mM; [APS]/[aniline] = 1.0:1; 25 °C. The insets in (a, b) illustrate the crossed sections of beltlike structures and half-tube.

Results and Discussion

Morphology and Chemical Structures. Figure 1 displays the morphology of product synthesized in dilute SDS (0.53 mM) and HCl (0.38 mM) solution. The low-magnification FESEM image (Figure 1a) discloses that the as-obtained dark-green precipitate is composed of a large quantity of 1D structures with the diameters of 400−600 nm and the length up to several micrometers. In a high-magnification FESEM image (Figure 1b), it is interestingly found that these 1D PANI structures are covered with nanorods 50−70 nm in diameter and 100−150 nm in length. These nanorods are orderly aligned on the surface of these 1D structures along the axis to form hierarchical structures. A closer look at the end of the 1D structures shows that most of them have rectangular cross sections and hollow centers (inset of Figure 1b), which indicates that they are rectangular tubes, and the interior dimensions of rectangular tubes are 300−500 nm. Suspicion of rectangular-shaped PANI as a result of some compression in the sample preparation can be ruled out as supported by the fact that products sampled directly from reaction vessel without washing and filtration procedures or from a very dilute solution also show rectangular shape (Figure S1, Supporting Information).

In the FTIR spectrum (Figure 2a), the characteristic absorption peaks of PANI such as 1576 and 1504 cm^{-1}, corresponding to the C═C stretching vibration of quinoid and benzenoid rings, respectively, can be observed first. The peak seen at 1300 cm^{-1} is correlated with the C−N stretching vibration with aromatic conjugation, and the peak situated at 1153 cm^{-1} is assigned to the electronic-like absorption of N═Q═N (Q representing quinoid ring).[19] The UV−vis spectrum of product dispersed in water (Figure 2b) exhibits two obvious adsorptions at about 360 and 850 nm, which are attributed to the $\pi-\pi^*$ transition in the benzenoid rings and the π−polaron transition, respectively.[20] Meanwhile, almost no absorption peak is observed at the region from 450 to 600 nm, possibly owing to the doping of SDS in product.[20] After dedoping with 0.1 M NH_4OH, the product

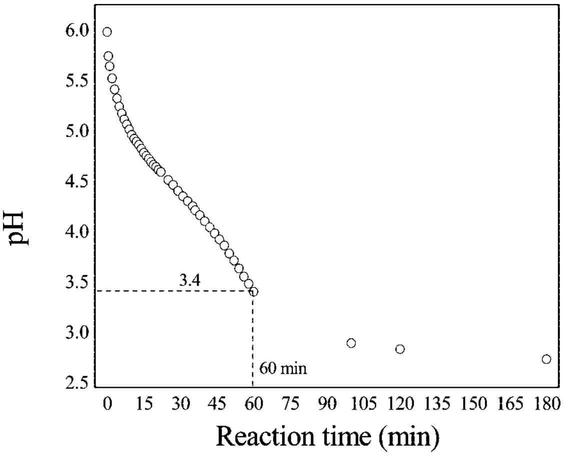

Figure 5. Value of solution decreasing as aniline polymerizes due to released protons. Synthetic conditions: [SDS] = 0.53 mM; [HCl] = 0.38 mM; [aniline] = 24 mM; [APS]/[aniline] = 1.0:1; 25 °C.

converts to the emeraldine base form, proved by the two absorptions, 337 and 680 nm, due to the $\pi-\pi^*$ transition of benzenoid ring and quinoid ring, respectively. These absorption features mean that product synthesized in dilute HCl/SDS solution is PANI in doping state and can be reversibly dedoped with basic media. We determine that the pressed pellet room temperature conductivity of as-synthesized product is ~2.1 × 10^{-4} S cm^{-1}after redoping by 1 M HCl(aq), and the yield of the reaction is about 54.2%.

In our experiments, the temperature of oxidation reaction is altered in the range of −10 to 50 °C in order to investigate its influence on the morphology of product. First of all, it is found that if the reaction temperature is lower than 0 °C, only beltlike structures and individual nanowires are observed in sample, and there are a few nanorod-covered rectangular tubes besides these individual nanowires seen in the product obtained at 5 °C, whereas the product synthesized at 50 °C mainly consists of beltlike or flakelike structures decorated by nanospheres (Figure S2, Supporting Information). At 20 °C (Figure 3a,b), a large amount of rectangular tubes is synthesized by the oxidization polymerization, whose surfaces are covered with the scale-shape nanosheets with the thickness of ca. 20 nm. Under the higher temperature of 40 °C (Figure 3c,d), the average diameter and length of the nanorods on the as-prepared rectangular tubes are estimated to be 50 and 400 nm, respectively. From these observations, one can know that temperature is an important influencing factor on the morphology of product.

Growth Processes and Formation Mechanism. To gain insight into the formation mechanism of such PANI architectures, the morphologies of products extracted with different polymerization stages are observed by FESEM (Figure 4). Clearly, the polymerization reaction with 15 min primarily generates beltlike structures with ca. 50 nm in thickness (Figure 4a). Nevertheless, the half-tubes are produced with the reaction time of 30 min (Figure 4b) which may originate from the rolling up of the beltlike structures along the direction of its long axis. With the reaction time of 1 h, the oxidation polymerization produces surface-smooth rectangular tubes (Figure 4c); when it is further extended to 2 h, the surfaces of rectangular tubes outgrow nanoparticles or nanorods (Figure 4d). In the samples extracted at 3 and 4 h, these nanostructures gradually grow from nanoparticles to nanorods on the tubes (Figure 4e,f).

The time-dependent experiment of product morphology points to the growth processes of tubular hierarchical structures in dilute SDS/HCl solution. It has been well-known that anionic surfactant SDS can dope into offspring via the electrostatic interaction with the anilinium cation[14,15] and then form a supramolecular structure with aniline oligomer through chaining

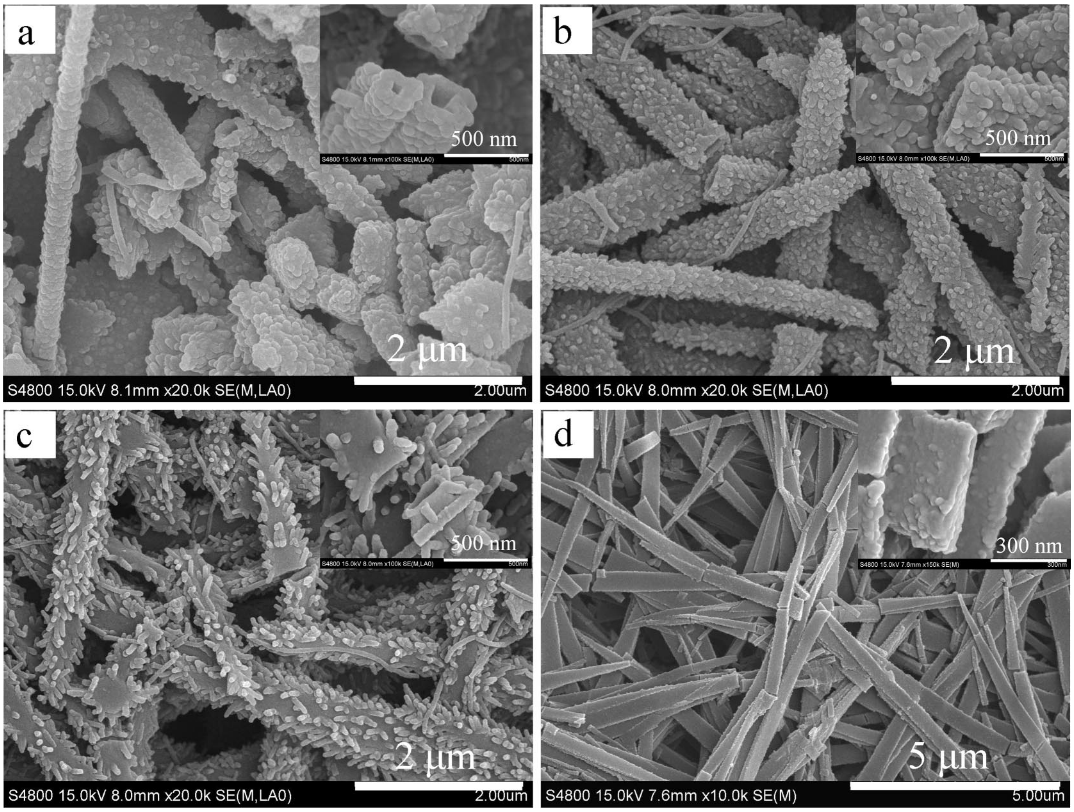

Figure 6. FESEM images of PANI synthesized with different SDS concentrations (mM): (a) 0.20; (b) 0.53; (c) 0.88; (d) 1.27. Other synthetic conditions: [HCl] = 0.38 mM; [aniline] = 24 mM; [APS]/[aniline] = 1.0:1; 25 °C; 24 h. Insets exhibit the cross sections and surfaces of tubes or belts.

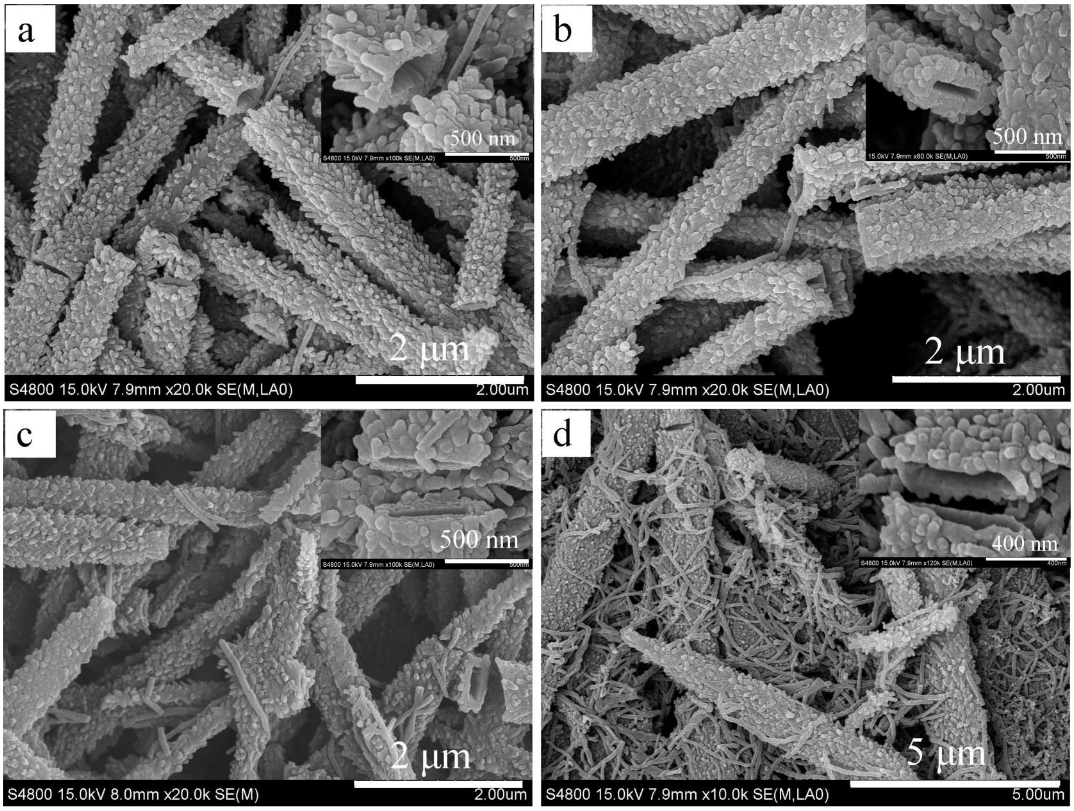

Figure 7. FESEM images of PANI synthesized with different HCl concentrations (mM): (a) 0.075; (b) 1.15; (c) 2.5; (d) 5.25. Other synthetic conditions: [SDS] = 0.53 mM; [aniline] = 24 mM; [APS]/[aniline] = 1.0:1; 25 °C; 24 h. Insets show the rectangular cross sections and nanostructure-covered surfaces of tubes.

cationic monomers into polymer, which are prone to the generation of beltlike structures in the beginning of polymerization.[21,22] The SDS counterion should have little interaction on the final product since both PANIs and the Na^+ ions are positive charged. With the reaction ongoing, the increasing SDS doped degree and the ascending oxidative level of product might cause the conformational variation and the torsional movement of PANI chains, further promoting the rolling up of these beltlike structures along the long axis.[23] And then the polymer chain might assume the new molecular conformation with a dihedral angle close to 90°, which should be responsible for the construction of right angles of rectangular tube.[23a] In this synthesis, the addition of low-concentration HCl admits the polymerization of aniline starting in the weak acidic medium ($pH = 5.8$, Figure 5), which slows the reaction processes.[24] After the construction of rectangular tubes, the polymer chains yielded subsequently in acidic solution,[22] would deposit on the solid surface available (tubes) to reduce surface energy,[25] forming the nanostructures. Owing to the release of protons during the polymerization, the latter reaction proceeds in the stronger acidic medium ($pH = 3.4$, marked in Figure 5) after 1 h, which is beneficial for the fabrication of 1D nanostructures (such as nanorods) as an intrinsic morphology on tubes surfaces.[6] In the dilute solution, the electrostatic repulsion between protonated polymer chains would orchestrate the ordered arrangement of nanostructures on the rectangular tubes.[26]

For a full understanding the formation of such hierarchical structures, we study the effect of the SDS concentration on PANI morphology. When the SDS amount is very little (e.g., <0.20 mM), there are irregular particles and few platelike structures just seen in the sample. As its concentration gradually rises, the rectangular tubes appear at 0.20 mM (Figure 6a) and become a primary morphology in sample at 0.53 mM (Figure 6b). Compared with the insets of Figure 6a,b, one can also find that the knaggy surface of rectangular tubes evolves to the arrangement of nanoparticles with the increasing SDS concentration. If the SDS concentration is increased to 0.88 mM (Figure 6c and inset), the nanostructure on the tubes become nanorods with the length of about 100 nm and the diameter of 50 nm, and their density is reduced. Further augmenting the surfactant concentration to 1.27 mM (Figure 6d and inset), only large beltlike structures with about 100 nm in thickness and 500 nm in mean width are synthesized by the polymerization reaction of aniline. In light of the proposed mechanism, the doping of SDS into product determines the generation and rolling up of beltlike structures. At very low concentration of SDS (<0.53 mM), less beltlike structures could be yielded at the early stage of polymerization due to the limited doped degree of SDS, reducing the possibility for belts rolling into tubes. Whereas at higher SDS concentration (≥1.27 mM), these belts formed become larger and thicker in the dimensions with sufficient SDS and need stronger driving force for rolling up than that available, hence suppressing themselves curving into tubes.

In the absence of inorganic acid, the oxidation polymerization of aniline in dilute SDS solution only creates these rectangular tubes decorated by unordered and irregular nanoparticles.[17] However, the introduction of low-concentration HCl leads to the growth of ordered and well-defined nanostructures on the rectangular tubes, so it is necessary to probe the effect of HCl concentration on the product morphology. As shown by Figure 7a and inset, the rectangular submicrotubes covered with ordered nanorods (100 nm in average diameter and ca. 250 nm in length) are obtained in the very dilute HCl solution (0.075 mM). With the inorganic acid concentration increasing, the nanostructures on the tubes change to the shorter nanorods with the length of 150 nm at 1.15 mM (Figure 7b and inset) or the nanoparticles with the size of 100 nm at 2.5 mM (Figure 7c and inset). At the higher HCl concentration of 5.25 mM (Figure 7d), the individual nanowires with mean diameter of 80 nm are dominating in sample, while the proportion of rectangular tubes covered by uniform nanoparticles decreases. The nanostructures on the tubes change from nanorods to nanoparticles with the increasing concentration of inorganic acid, which is identical to that PANI 1D nanostructures could be obtained in weaker acidity condition, while the stronger acidic system leads to granular PANI.[27]

Conclusion

Nanostructure-covered rectangular submicrotubes of PANI as a novel hierarchical architecture have been successfully fabricated by the oxidation polymerization of aniline in dilute SDS/HCl aqueous solution for the first time. The chemical structures, conductivity, and yield were measured in order to know the properties and potential application of PANI synthesized in this system. It was found that the reaction temperature, the concentrations of surfactant, and inorganic acid had profound impacts on the morphology and size of PANI nanomaterials. On the basis of the observation to the growth processes, we have shown a tentative interpretation to the formation through discussing the polymerization courses and the roles of SDS and HCl. This method is expected to offer a simple approach to tailor the assembly of conjugated polymers nanostructures as an important step toward the integration of the nanomaterials into devices.

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Supporting Information Available: FESEM images of PANI. This material is available free of charge via the Internet at http://pubs.acs.org.

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