Introduction of methanol in the formation of polyaniline nanotubes in an acid-free aqueous solution through a self-curling process

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ABSTRACT

This study reports the synthesis of polyaniline (PANI) nanotubes with the introduction of methanol in aqueous solutions. SEM images indicate that well-dispersed PANI nanotubes are produced when the concentration of methanol increases up to 1 M. On the other hand, polymers primarily form irregular agglomerates when only monomers and oxidant are used in the absence of methanol. Transmission electron microscopy (TEM) reveals that the resulting nanotubes have an outer diameter of about 200 nm and an inner diameter of 0–50 nm. Fourier transform infrared (FT-IR) spectra indicate that the intermediate samples obtained at a reaction time of around 60 min have a structure consisting of a head of phenazine-like units and a tail of *para*-linked aniline units. Ultraviolet–visible (UV–vis) spectra indicate that emeraldine salt polyaniline (ES-PANI) appears in sequence as the reaction time reaches 75 min. At the time interval of 60–75 min, the self-curling behavior of the PANI intermediates first appears at 60 min, and PANI nanotubes can be observed starting at 75 min. This is the first study to observe this self-curling process and propose that it explains the formation of PANI nanotubes. Noteworthily, the nanotubes transform into irregular agglomerates after a de-doping process.

1. Introduction

Polyaniline (PANI) is one of the most useful conducting polymers due to its easy synthesis and environmental stability. It also has a wide range of electrical properties which can be easily controlled by changing its oxidation and protonation states [1,2]. Researchers have recently shown interest in PANI nanotubes due to their one-dimensional structure and high specific surface. The nanotubes can be produced with or without templates. PANI templates can be categorized as "hard templates" and "soft templates." In the hard template approach, various authors have reported several kinds of template, including anodized alumina membranes, porous polymer membranes, and zeolite channels [3–5]. Although the dimensions and morphology of polymer structures can be easily defined by the types of porous support, the post-etching process used for the removal of templates may damage the soft polymeric structures [6]. Therefore, some researchers have proposed a simpler and less expensive method that eliminates the use of a solid template. This method produces PANI nanotubes with

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the aid of structure-directing molecules, and is called the soft template method [7–10].

Recently, Wan et al. [11,12] reported a template-free method for synthesizing PANI nanotubes. They reported that micelles formed by anilinium cations in the absence of a surfactant functioned as templates for producing PANI nanotubes. The doping acid and its anilinium salt in this approach presumably form special micelle particles in the emulsion, and free aniline monomers in the reaction solution diffuse into the micelles to form free aniline-filled micelles. According to this theory, polyaniline nanotube synthesis usually requires low concentrations of organic acids with respect to aniline [13,14]. To date, the concept of micelle templates is the most popular theory to explain the formation of nanotubes.

Although researchers often use the concept of micellar templates to explain the formation of PANI nanotubes, Konyushenko et al. [15] criticize the micellar templates theory by raising important issues: (1) the presence of cylindrical template micelles has never been proved, and (2) the inner diameter of nanotubes is much larger than that of the potential micelles produced by aniline salt. Stejskal et al. [15–17] proposed that the self-assembly of hydrophobic aniline oligomers (phenazine-like units), and not that of aniline monomers, predetermines the supramolecular structure of the PANI nanotubes. They believed that the oligomers (phenazine derivatives) produce columnar aggregates and thus serve as templates for the nucleation of PANI nanotubes. However, when

the solution acidity is low enough (solution pH value <2), the resulting phenazinium units are hydrophilic, and the self-ordering ability of phenazinium units is then lost. According to this theory, irregular PANI particles would then appear.

Several studies show that the PANI nanotubes can also be produced without the addition of acid [15,17–19]. Epstein et al. [18] reported that excess oxidants can work as dopants that form anilinium cations and produce PANI nanotubes. However, Stejskal et al. [15,17] reported that nanotubes obtained in the absence of acid are inferior to those prepared in acid solutions. Moreover, Wan et al. [19] reported that PANI changes its morphology from nanotubes to rose-like agglomerates when the aniline concentration increases from 0.06 M to 0.2 M.

Recently, several researchers [20,21] reported that the intermolecular H-bonding between PANI chains and alcohols has significant effects on PANI morphology. Zhou et al. [22] discovered that an appropriate proportion of methanol in the HCl acid solution produces well-extended PANI nanofibers. The present study synthesizes PANI nanotubes in an acid-free methanol solution, and further prepares PANI nanotubes at a relatively higher aniline concentration solution (0.2 M). This study also characterizes products obtained at different reaction stages using Fourier transform infrared (FT-IR) spectra, ultraviolet–visible (UV–vis) spectra, and transmission electron microscopy (TEM) to investigate the formation mechanism of PANI nanotubes. Specifically, this study demonstrates the formation of PANI nanotubes through the self-curling process. To the author's best knowledge, this is the first attempt at introducing methanol in the absence of any acid in the preparation of PANI nanotubes. This study first defines self-curling behavior and uses it to explain the formation of PANI nanotubes.

2. Experimental

2.1. Materials

Aniline monomers (≧99.5%) were purchased from Fluka. Ammonium persulfate [$(NH_4)_2S_2O_8$, APS] was obtained from Riedel-de Haën. All reagents were used as received without further purification.

2.2. Polymerization

Reactions were conducted in a 20 mL vial. Aniline (0.2 mmol) was oxidized with ammonium peroxydisulfate (APS, 0.25 mmol) in methanol solutions. Solutions of aniline monomer and oxidant were poured rapidly into glass vials at room temperature to start the oxidation. The solutions were shaken vigorously for 30 s, and then put in an ultrasonic water bath (Branson 5210, USA) at 0 °C for 2 h. The resulting PANI samples were isolated by gravity filtration and washed with de-ionized water. Finally, the products were dried in an oven for 1 day.

2.3. Characterization

PANI morphologies were examined by transmission electron microscopy (TEM, JEOL JEM-2010) and field emission scanning electron microscopy (FESEM, JEOL JSM-7401F). For the TEM morphological evolution experiments, PANI samples were extracted from the reaction solutions at different reaction stages and immediately diluted in distilled water. An appropriate amount of this suspension was then poured onto formvar-coated copper TEM grids. Specifically, the grids were placed on a filter paper to absorb excess suspension and facilitate rapid drying, thus suppressing the extension of the polymerization process described elsewhere [23].

Ultraviolet–visible (UV–vis) spectra were recorded from a dilute dispersion of PANI in de-ionized water with a UV–vis spectrophotometer (Perkin Elmer, Lambda 850). Infrared spectra were obtained with a Fourier transform infrared spectrophotometer (FT-IR, Perkin Elmer, Spectrum One) and recorded by averaging 32 scans at a resolution of 4 cm^{-1}.

3. Results and discussion

Fig. 1 shows the SEM images of the PANI samples synthesized in methanol solution with different concentrations at an [ANI]/[APS] molar ratio of 0.8:1 for 2 h. As Fig. 1(a) shows, the presence of PANI sheets accompanied with irregular aggregates was primarily observed when no methanol was introduced into the solution. Similar sheets or flakes are also observed in other literatures when only aniline and ammonium persulfate are used [15]. On the other hand, with the addition of methanol, Fig. 1(b)–(d) shows an increased amount of one-dimensional polyaniline nanotubes. Further, note that the polyaniline nanotubes obtained in the 1 M methanol solution have a relatively uniform morphology compared with samples obtained in lower methanol concentration solutions. Therefore, the following sections use 1 M methanol aqueous solution for the preparation of PANI samples. Figs. 1(d) and 2 show the SEM and TEM images of typical PANI nanotubes produced in these experiments, with an outer diameter of about 200 nm and an inner diameter of 0–50 nm.

These results show that methanol plays an important role in the formation of PANI nanotubes. Recently, Al-Ghamdi and Al-Saigh [24] reported that strong intermolecular H-bonding occurs between PANI molecules and methanol. Zhou et al. [22] indicated that the intermolecular H-bonding interaction perpendicular to PANI chains between methanol molecules pushed the polymer chains apart, promoting the one-dimensional growth of PANI nanofibers. Similar results were also found when ethanol was used to prepare PANI nanofibers. Kan et al. [21] reported that the interaction between ethanol and PANI wrapped the PANI chains with ethanol molecules, preventing the aggregation of PANI particles during the polymerization process. It is therefore reasonable to deduce that intermolecular H-bonding interaction plays an important role in the formation of well-dispersed one-dimensional PANI nanotubes.

3.1. FT-IR spectra

Based on the successful preparation of PANI nanotubes with the addition of methanol, this study explores the growth of PANI nanotubes. Intermediate samples at different reaction stages were prepared and analyzed by FT-IR spectra, UV–vis spectra, and TEM images to reveal the formation mechanism of PANI nanotubes.

Fig. 3 shows the FT-IR spectra of PANI products obtained at different reaction stages. The characteristic peaks of phenazine-like units appear in the early stages of polymerization (reaction time shorter than 45 min). The presence of significant amount of 1,2,4-trisubstituted rings, indicative of the formation of branched and/or substituted phenazine-like segments, appears in bands at 862 and 846 cm^{-1} [25]. The peak observed at 1414 cm^{-1} represents the totally symmetric stretching of the phenazine heterocyclic ring [26,27]. The band at 1622 cm^{-1} corresponds to the absorption of the C=C ring stretching vibration in newly formed substituted phenazine-like segments [15–17,28].

Note that the absorption bands change after a reaction time of 45 min. The band at 1622 cm^{-1} shows that the absorption of the C=C ring stretching vibration in substituted phenazine-like segments decreases significantly after a reaction time of 45 min. The band almost disappears as the reaction time reaches 60 min. In
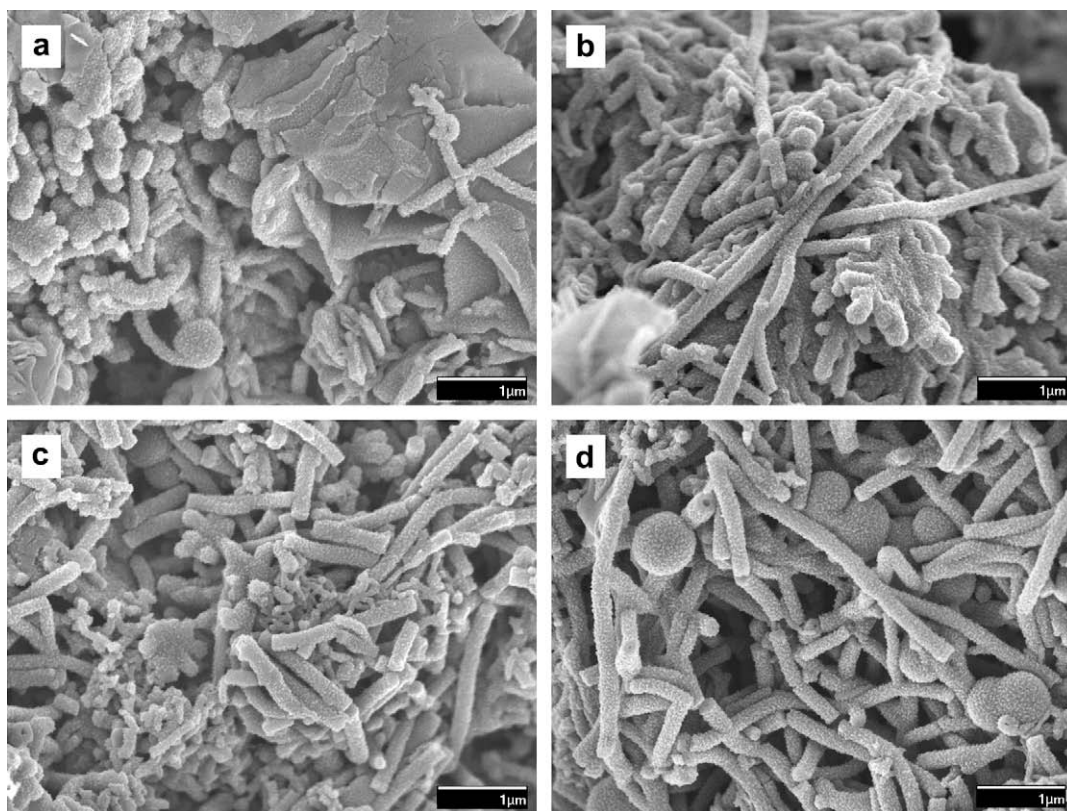
Fig. 1. SEM images of PANI obtained in aqueous solutions with different methanol concentrations (a) 0 M, (b) 0.25 M, (c) 0.5 M, (d) 1 M.

contrast, the C–H out-of-plane bending vibrations assigned to a *para*-substitution pattern can be observed at 821 cm^{-1} when the reaction time exceeds 60 min. This newly formed characteristic band indicates the head-to-tail coupling of aniline in this stage. The characteristic peaks located at 1579 and 1496 cm^{-1} represent the C=C stretching vibrations of the quinoid and benzenoid rings,

respectively. The N=Q=N absorption peak (with Q representing the quinoid ring) at 1141 cm^{-1} is also apparent. The PANI sample structures obtained after a reaction time of 45 min are consistent with the traditional PANI structures reported in previous studies [12,29]. According to the FT-IR spectra, the formation of PANI structures in the polymerization process can be divided into two stages. The first stage includes reaction times shorter than 45 min, where the aniline molecules form phenazine-like segments. The second stage includes the head-to-tail coupling of aniline molecules during extended reactions.
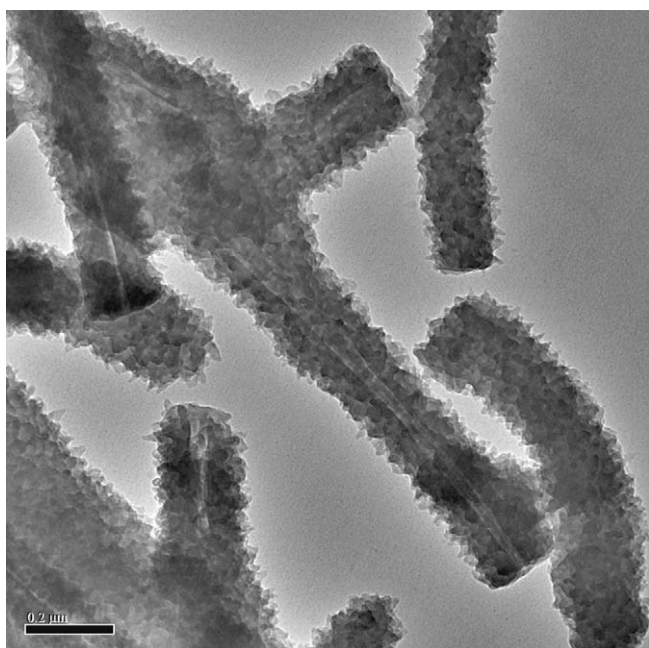

Fig. 2. TEM image of PANI nanotubes obtained in 1 M methanol aqueous solution.
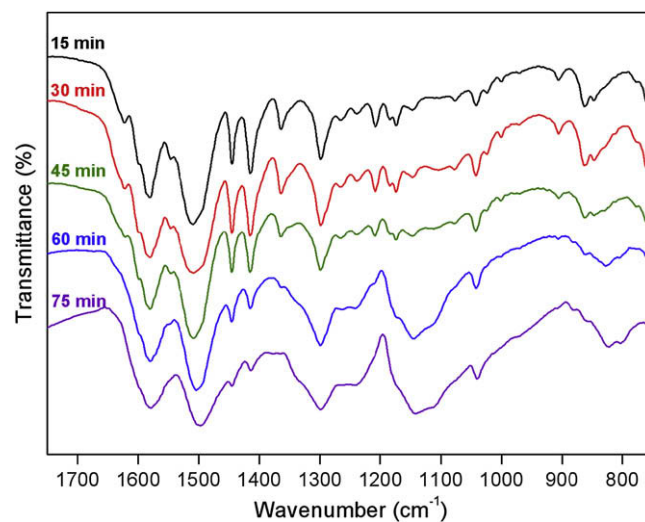

Fig. 3. FT-IR spectra of PANI intermediates obtained at different reaction stages during the polymerization process in 1 M methanol aqueous solution.

This change in PANI structure may be caused by an increase of solution acidity during the polymerization process. Previous studies report the oxidation of PANI in aqueous solution with two subsequent phases [15–17]: (1) the oxidation of the neutral aniline molecules at low acidity, and (2) the oxidation of the anilinium cation after the solution acidity increases. Fig. 4 shows the change of solution pH value as a function of reaction time. The pH value decreases as the reaction time increases, and finally level off at 1.2. This trend agrees well with previous studies [15–17,19]. Hydrogen atoms abstracted during the oxidation of amino groups and benzene rings as protons are responsible for this decrease in pH value.

3.2. UV–visible spectra

To further examine the characterization of intermediate samples obtained at different reaction stages, this study presents and analyzes the UV–vis spectra of PANI intermediates in Fig. 5. The oxidized products obtained in early polymerization stages exhibit an absorption band at about 430 nm, which may represent the formation of *p*-aminodiphenylamine structures [30,31] or *o*-aminodiphenylamine structures [32,33]. However, as the FT-IR spectra have confirmed the formation of *ortho*-coupling phenazine units in the initial polymerization stages in previous section, it is thus reasonable to conclude that aniline monomers formed the *o*-aminodiphenylamine structures in the early polymerization stages. Moreover, as the reaction proceeds, characteristic absorption bands at wavelengths of 320–360, 400–420 and 600–700 nm appear after a reaction time of 75 min. These bands indicate the formation of emeraldine salt polyaniline (ES-PANI) at this stage. The first absorption band arises from π–π^* electron transition within the benzenoid segments. The second and third absorption bands are related to the acid-doped state and polaron formation, respectively [34,35].

Note that in Fig. 5, the absorbance of the band located at 400–420 nm increases as the reaction time increases from 75 to 90 min, indicating a higher doping level of PANI samples. In addition, previous research [16] reports that the hydrogen sulfate produced by the combination of hydrogen atoms abstracted during the oxidation and the sulfuric groups from the oxidant (APS) is a dopant.

According to the FT-IR and UV–vis spectra, PANI structure changes during the polymerization process can be summarized as follows. (1) In the earlier stages of polymerization, aniline
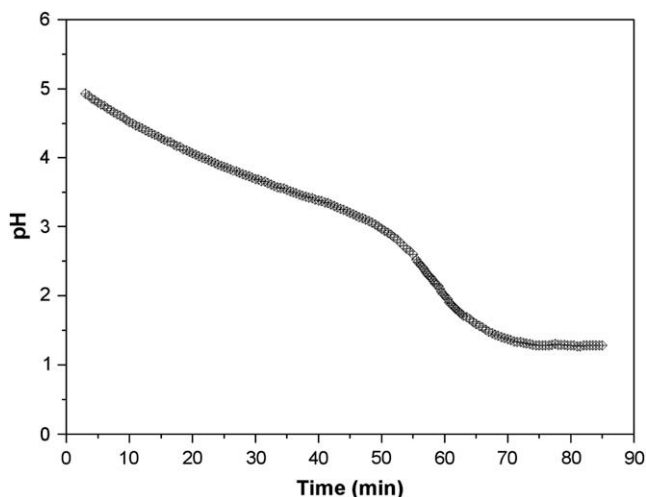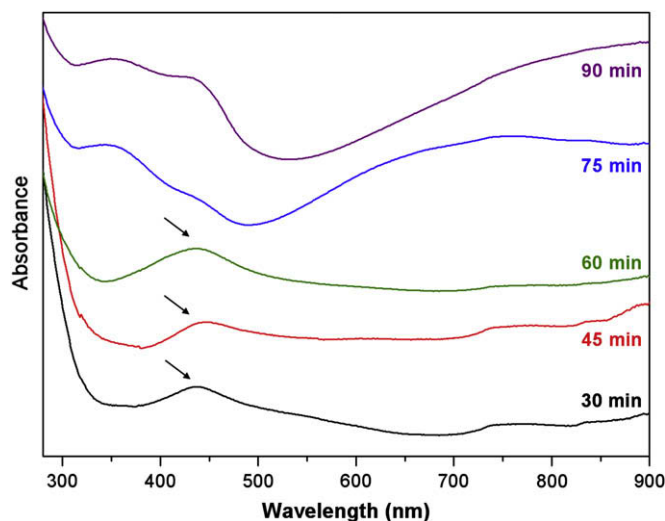

Fig. 5. UV–vis spectra of PANI intermediates obtained at different reaction stages during the polymerization process with an [ANI]/[APS] ratio of 0.8/1 in 1 M methanol aqueous solution.

monomers form phenazine-like units that may act as the initiating centers for the growth of traditional PANI. (2) As the solution acidity increases, the aniline monomers link to the initiating centers and polymerize through head-to-tail coupling. The resulting PANI is therefore expected to have a head of phenazine-like units and a tail of *para*-linked aniline units (reaction time ≧60 min). On the other hand, UV–vis spectra indicate that acid-doped *para*-coupling polyaniline appears after the formation of head-to-tail coupling structures (reaction time ≧75 min). Along with the change of molecular structure and the protonation of *para*-linked aniline units, the morphology changes of as-synthesized PANI at different reaction stages are worthy of further study to reveal the formation mechanisms of PANI nanotubes.

3.3. Evolution of morphology by TEM images

Fig. 6 shows the TEM images of PANI intermediates obtained at different reaction stages. At the beginning of the reaction (7 min, Fig. 6(a)), aniline monomers form shapes like tree trunks with several branches. As the reaction proceeds to 35 min, the free aniline monomers continuously polymerize on the surface of pre-formed intermediates, forming elongated and thickened objects, as Fig. 6(b) shows. As the reaction proceeds to 60 min, Fig. 6(c) shows that the self-curling phenomenon can be observed in each trunk and branch of these tree-like intermediates. Therefore, PANI nanotubes can be obtained after this curling process at a reaction time of 75 min. Moreover, these semi-curling PANI nanotubes were also identified in the TEM images shown in Fig. 7. These results strongly suggest that PANI nanotubes form through a self-curling behavior. Recently, Wu et al. [36] reported a similar mechanism for the formation of PANI-intercalated $WO_3 \cdot H_2O$ nanotubes. They suggested that $WO_3 \cdot H_2O$ nanotubes may be produced through a rolling mechanism from $WO_3 \cdot H_2O$ nanosheets with the aid of intercalated PANI, which provides the major driving force of the rolling mechanism due to its preference for helical conformation. The current study provides first-hand evidence that coordinates with their observations.

It is very interesting to see that the PANI intermediates change their morphology from objects as tree branches stemming from trunks to nanotubes accompanied with the formation of ES-PANI during the polymerization process. FT-IR and UV–visible spectra
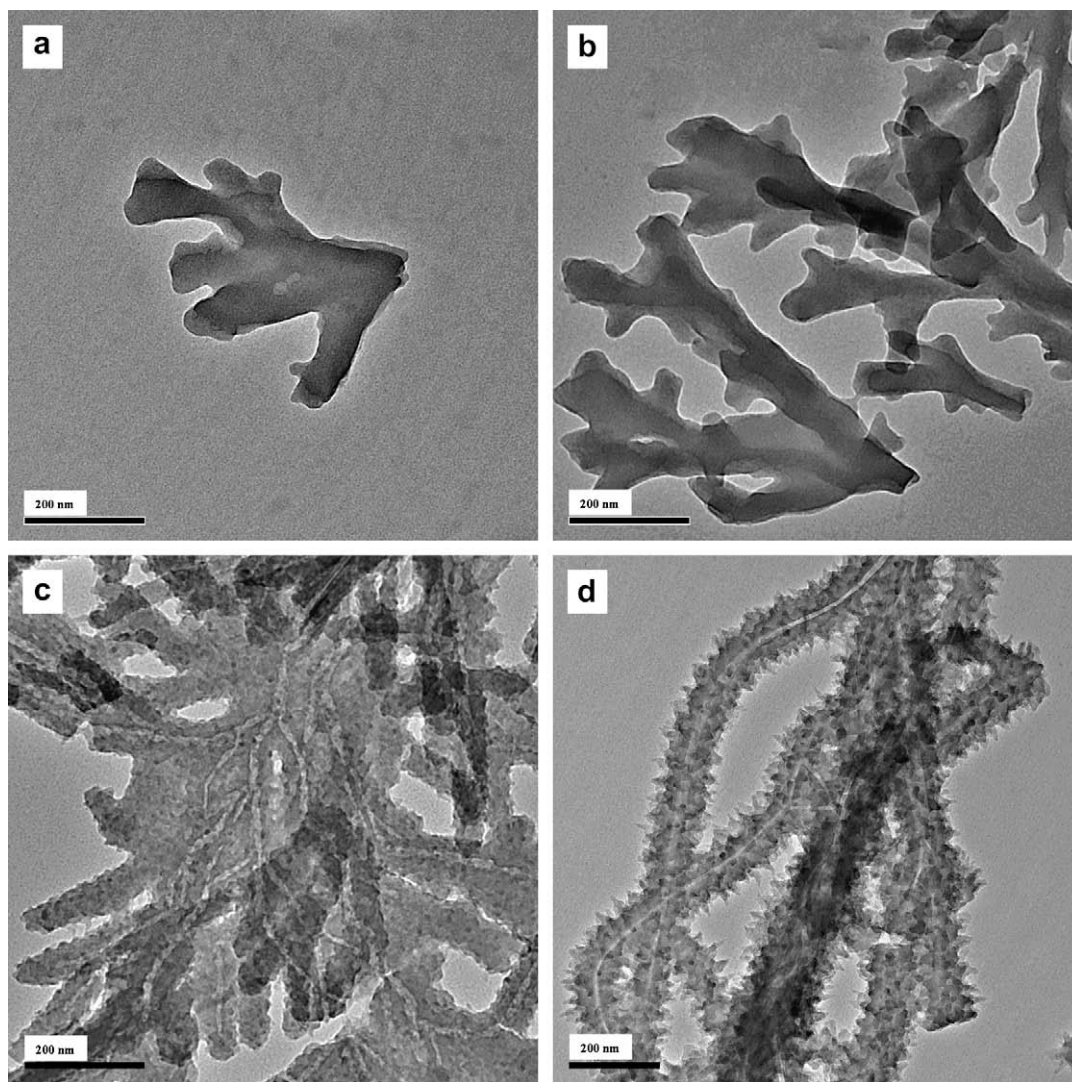

Fig. 4. The change of solution acidity during the oxidation of aniline with an [ANI]/[APS] ratio of 0.8/1 in 1 M methanol aqueous solution.

Fig. 6. TEM images of PANI intermediates obtained at different reaction times during the polymerization process with an [ANI]/[APS] ratio of 0.8/1 in 1 M methanol aqueous solution (a) 7 min, (b) 35 min, (c) 60 min, and (d) 75 min.

confirm the formation of *para*-coupling PANI and the protonation of these segments at reaction times of 60 and 75 min, respectively. TEM images also confirm the self-curling phenomenon of PANI intermediates (60 min) in this 60–75 min time interval, and PANI nanotubes were consequently obtained at a reaction time of 75 min. These findings support the conclusion that the protonation of the traditional head-to-tail coupling PANI enables the PANI intermediates to curl into nanotubes.

Epstein et al. [37,38] reported that a gradual change from expanded-coil to compact-coil PANI conformation can be observed due to a decrease in electrostatic repulsion between similarly charged units when additional counter anions are added. Li et al. [39] also reported the combination of the negative ions to the imine nitrogen atoms of the PANI chains can release the repulsion, resulting in a compact-coil conformation of the PANI chains with the doping process. Accordingly, we consider that the conformation change of PANI during the doping process may provide the primary driving force for PANI to curl into nanotubes.

To further demonstrate that the protonation process of *para*-coupling PANI plays an important role in the formation of PANI nanotubes, the morphology changes of PANI nanotubes after the de-doping process were observed by SEM images. Fig. 8 shows that

the PANI morphology changes from nanotubes to irregular agglomerates after they are de-doped in 1 M NH₄OH solution for 1 day. Previous studies [37,38] reported that the emeraldine base polyaniline (EB-PANI) intends to form an expanded coil conformation contrast to a compact-coil conformation of ES-PANI. Accordingly, this study assumes that morphology changes may be due to the removal of the dopant. This result enhances the earlier inference that the protonation of *para*-coupling PANI may be the primary reason for the formation of PANI nanotubes.

3.4. Effect of polymerization rates

The experiments in this study controlled the polymerization rates in terms of aniline and oxidant concentrations to determine their effects on the formation of PANI nanotubes. The polymerization rate is related to the change rate of solution acidity because the hydrogen atoms abstracted during the oxidation of amino groups and benzene rings are released as protons. Recently, Wan et al. [19] reported that a high polymerization rate from a high aniline concentration creates a sharp decrease in the solution pH value. This rapid decrease quickly causes the aniline micelles to aggregate into a rose-like morphology.
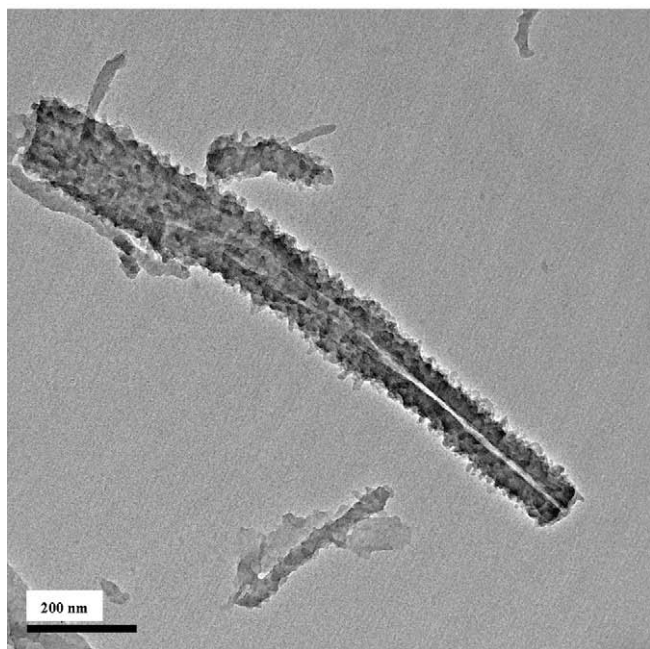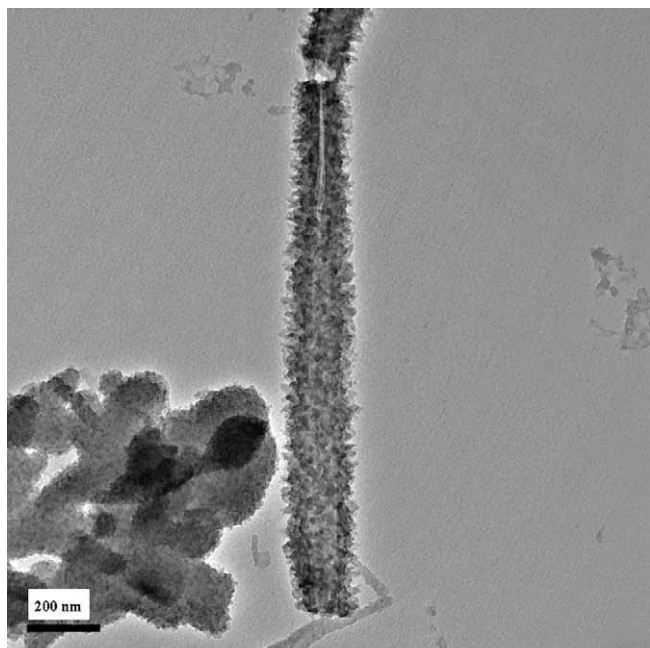
Fig. 8. SEM image of PANI after the de-doping process.

Fig. 7. TEM images of semi-curling PANI nanotubes obtained at the reaction time of 60 min.

Fig. 9 shows the FT-IR spectra of the PANI intermediate samples obtained at different reaction stages with a 0.1 M aniline concentration. The FT-IR spectra indicate that the time required for the formation of *para*-coupling PANI decreases from 3 h to 75 min when the [ANI]/[APS] ratio decreases from 0.8/1 to 0.4/1. Table 1 summarizes the reaction times required to detect or observe the formation of *para*-coupling PANI, ES-PANI, and PANI nanotubes. The time required for the formation of *para*-coupling PANI decreases to 60 min when a higher aniline concentration of 0.2 M and a higher [ANI]/[APS] ratio of 0.8/1 are used. The higher polymerization rate due to higher oxidant and aniline concentrations caused a higher proton extraction rate, and thus resulted in a faster rise of solution acidity. Accordingly, the solution acidity level at which aniline monomers form *para*-coupling units can be
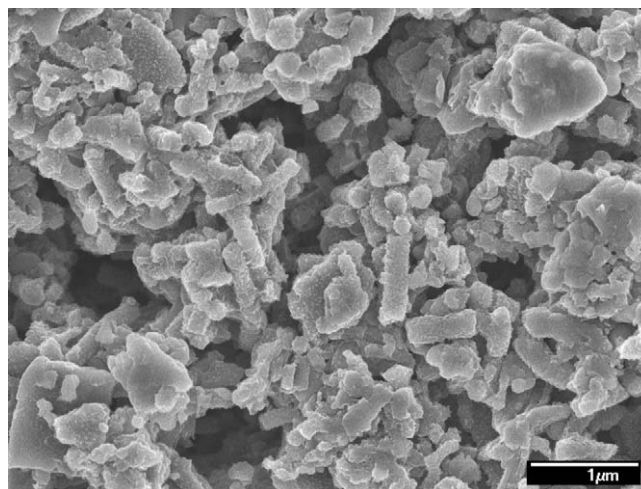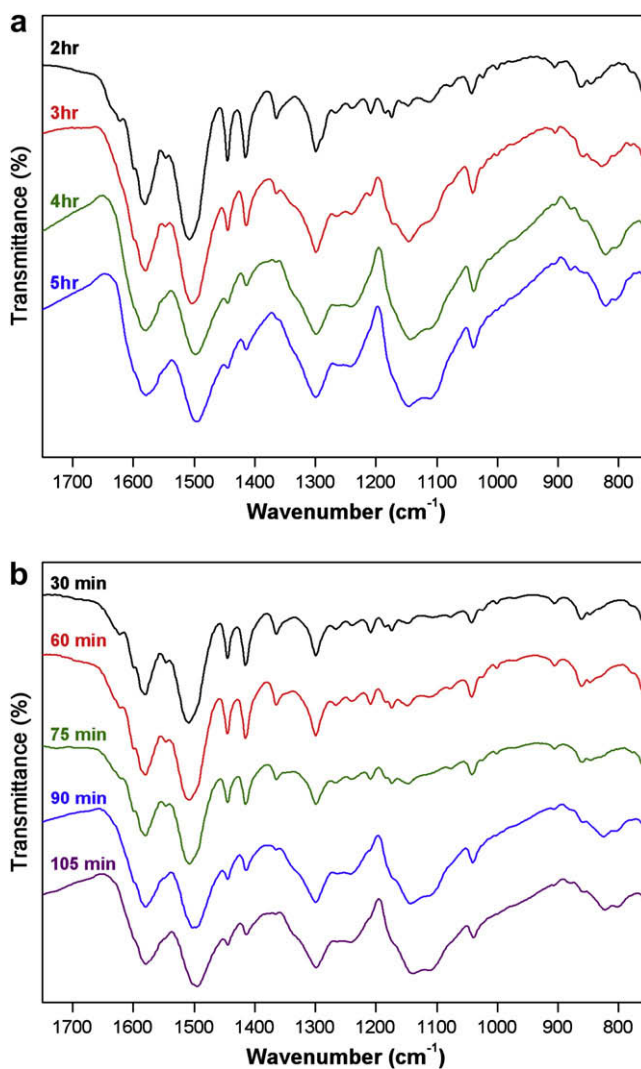

Fig. 9. FT-IR spectra of PANI intermediates obtained at different reaction stages during the polymerization process in 0.1 M aniline solutions with different [ANI]/[APS] ratios (a) 0.8/1; (b) 0.4/1.

Table 1
Effects of the aniline concentration and the [ANI]/[APS] molar ratio on the reaction times required to observe the formation of *para*-coupling PANI, ES-PANI and PANI nanotubes.

[ANI] (M)	[APS]/[ANI] ratio	The reaction time to observe the formation of *para*-coupling PANI	The reaction time to observe the formation of ES-PANI	The reaction time to observe the formation of PANI nanotubes
0.2	0.8/1	45–60 min	60–75 min	75 min
0.1	0.8/1	2–3 h	3–4 h	4 h
0.1	0.4/1	75–90 min	90–105 min	105 min

obtained earlier in higher oxidant and/or aniline concentration conditions.

Once the *para*-coupling PANI formed, the ES-PANI was subsequently obtained and then identified by UV–vis spectra as shown in Fig. 10. Moreover, Table 1 shows that PANI formed nanotubes accompanied the formation of ES-PANI under all polymerization conditions. For example, when an aniline concentration of 0.1 M and an [ANI]/[APS] ratio of 0.8/1 were used, the formation of ES-PANI and PANI nanotubes both appears at a reaction time of 4 h. The TEM image in Fig. 11(a) shows the PANI nanotubes obtained at a reaction time of 4 h using a 0.1 M aniline solution and an [ANI]/[APS] ratio of 0.8/1, while Fig. 11(b) shows the PANI nanotubes obtained at a reaction time of 105 min using a 0.1 M aniline solution and an [ANI]/[APS] ratio of 0.4/1. Obviously, PANI obtained in the ES-PANI formation stage has a similar nanotube morphology regardless of the [ANI]/[APS] ratio, which is related to the polymerization rate. These results imply that the formation of PANI nanotubes depends greatly on the formation of ES-PANI. This relationship also implies that the formation of ES-PANI provides the driving force that causes PANI to curl into nanotubes as discussed earlier.

3.5. Proposed formation mechanism

Based on the above findings and results, Fig. 12 illustrates the formation mechanism of PANI nanotubes through several steps in the polymerization. First, the aniline monomers form phenazine-like units with a morphology much like tree branches stemming from trunks in the early stages. This is followed by a stage where
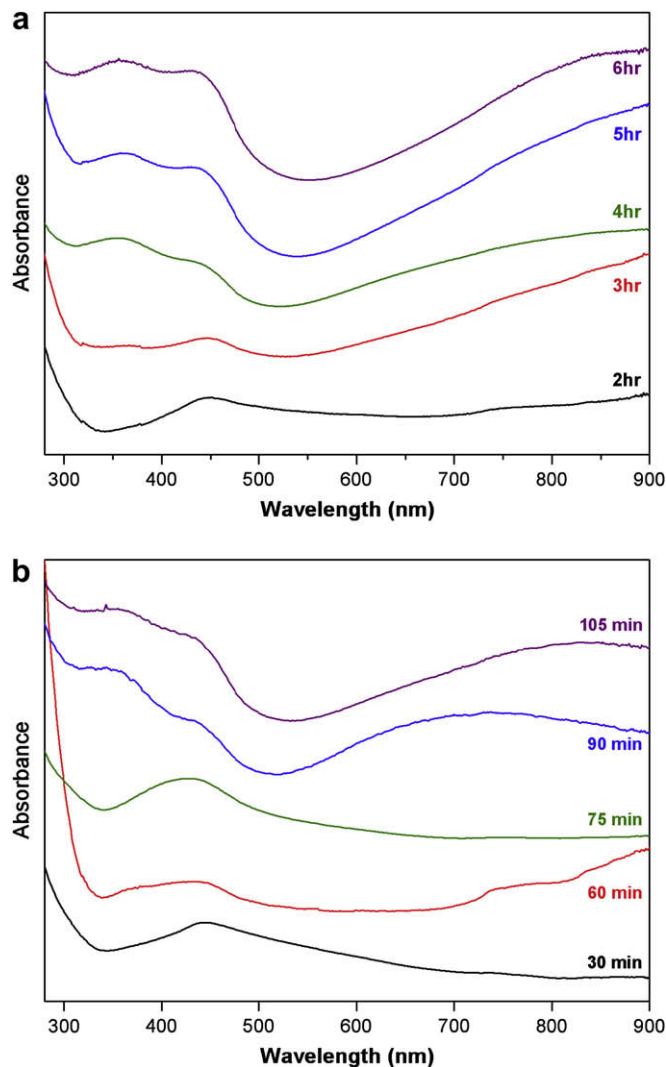

Fig. 10. UV–vis spectra of PANI intermediates obtained at different reaction stages during the polymerization process in 0.1 M aniline solutions with different [ANI]/[APS] ratios (a) 0.8/1; (b) 0.4/1.
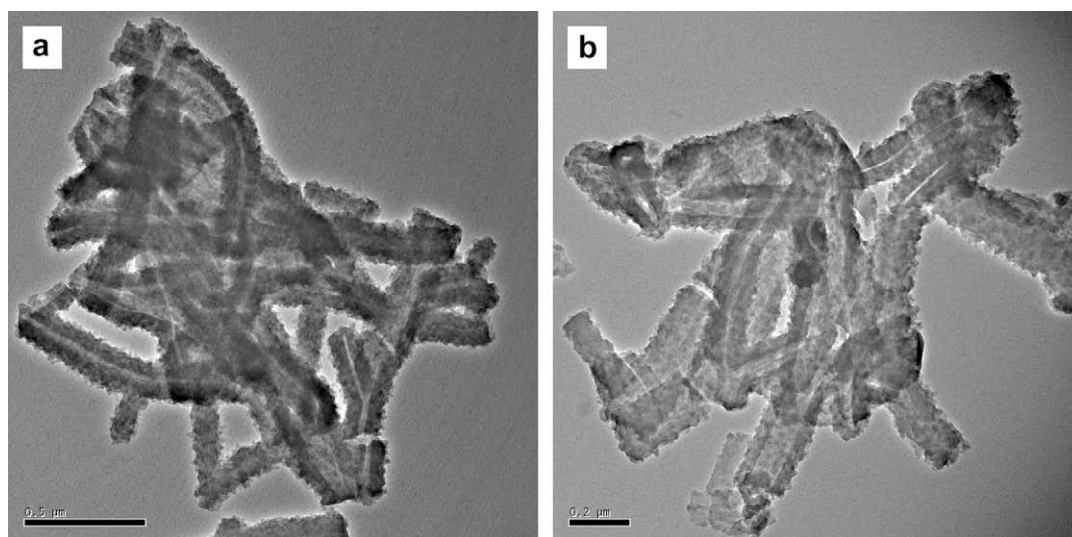

Fig. 11. TEM images of PANI nanotubes obtained at different reaction rates in 0.1 M aniline solutions (a) [ANI]/[APS] of 0.8/1 and reaction time is 4 h; (b) [ANI]/[APS] of 0.4/1 and reaction time is 105 min.
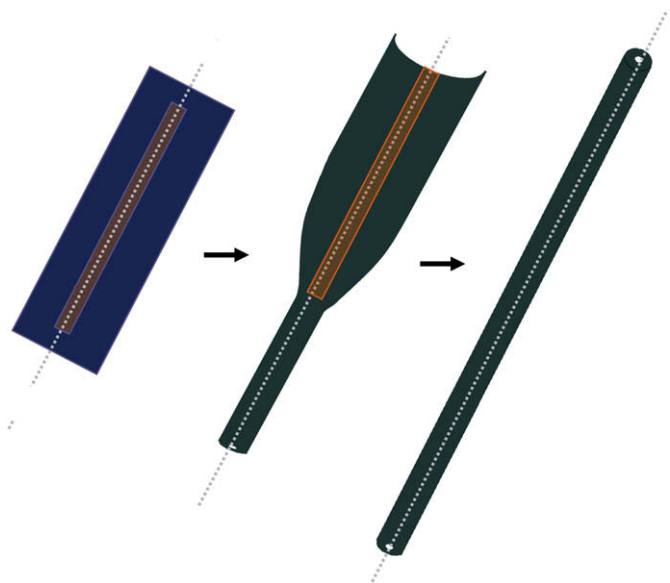
Fig. 12. Scheme of the self-curling process of PANI nanotubes.

free aniline monomers diffuse onto the preformed PANI oligomers. The oligomers continue to grow, and form elongated and thickened objects which have a head of phenazine-like units and a tail of para-linked aniline units. The protonation of *para*-coupling PANI occurs subsequently, and may provide the primary driving force to cause the trunk and branch of PANI intermediates to curl into nanotubes. The phenazine units, which have non-linear structures, can serve as the axis for PANI nanotube curling. The final resulting product comprises PANI nanotubes.

Recently, Stejskal et al. [15–17] presented a model in which the self-assembly of hydrophobic phenazine-like units predetermines the supramolecular structure of nanotubes. However, when the polymer became hydrophilic, the self-ordering ability of polymer chains is lost and irregular PANI particles are consequently formed. In contrast to that model, this study reports that PANI nanotubes are produced when PANI remains in an acid-doped state, in which PANI exhibits a hydrophilic character. Unlike the template method, this study proposes that the self-curing is the primary process by which PANI nanotubes can be formed.

4. Conclusion

This study reports the synthesis of well-dispersed one-dimensional polyaniline nanotubes in acid-free methanol aqueous solutions. The introduction of methanol was found to have the ability to suppress the formation of PANI agglomerates. Specifically, this study identifies the different molecular structures and morphologies of PANI obtained at different reaction stages. In the early stages of polymerization, FT-IR spectra indicate that the oxidation of aniline monomers forms phenazine-like units. As the solution acidity increases, the aniline monomers link to phenazine-like units and polymerize through head-to-tail coupling. The resulting PANI structure has a head of phenazine-like units and a tail of *para*-linked aniline units. UV–vis spectra indicate that the protonation of *para*-coupling polyaniline follows the formation of *para*-coupling

PANI. Specifically, in the time interval of the protonation and the *para*-coupling of polyaniline, TEM images show that the PANI intermediates transform into nanotubes through a self-curling process. On the other hand, PANI forms agglomerates instead of nanotubes when thoroughly de-doped. An intensive examination indicates that PANI formed nanotubes accompanied the formation of ES-PANI under all polymerization rates. Therefore, we believe that the protonation of *para*-coupling PANI provides the primary driving force that causes PANI intermediates to transform into PANI nanotubes through a self-curling process.

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