Formation mechanism of a nanotubular polyanilines prepared by an emulsion polymerization without organic solvent

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A B S T R A C T

A nanotubular polyaniline (PANINT) was prepared from a simple emulsified polymerization method without oil solvent present. A mechanism of the formation of the nano-fibers/tubes was proposed to show that it started with the connecting arrangement of the neighboring anilinium micelles before and during polymerization, which resulted in the formation of the intermediate morphology of centipedes converting into rod-like nanofibers later. The obtained PANINTs displayed not only nanofibrous structure but owned an unusual dispersing behavior in toluene. SEM and TEM showed the dendrite-like networks of nanofibers connected and glued together by the free (not complexed to polyaniline backbone) n-dodecylbenzene sulfonic acid (DBSA) molecules. After removing the free DBSA by acetone, the clear/well-defined empty nanotubes can be seen from TEM in the magnified micrograph. The Atomic force microscopic (AFM) microgaphs demonstrated the cottage like surface morphology of the un-perturbed PANINTs and the morphology was converted to an anisotropic/oriented rods after rubbing on the wet/cast PANINTs' dispersion of toluene before entire evaporation.

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1. Introduction

Polyaniline (PANI) is a typical conducting polymer that has been found lots of applications in the field of biosensors [1], electrochemical displays [2], corrosion protection [3,5], rechargeable batteries [4,6], etc. Traditional way of synthesizing PANI via chemical oxidize [7–10] or electrochemical route [9] came out with particle-accumulated cluster morphology. In order to obtain a PANI with higher reactive surface area, higher ordered structure, and higher conductivity, a nanofibrous or nanotube-like structure is necessary. Traditional chemical oxidative polymerization approaches for nano-structured polymers include the use of insoluble solid templates such as zeolites [11], opals [12], controlled pore-size membranes [13], and anodic aluminum oxide (AAO) [14] or soluble templates such as polymers [15] and surfactants [16]. Some physical methods, such as electrospinning [17] and mechanical stretching [18] can also produce conducting polymer nanofibers without templates. When organic dopants with surfactant functionalities are used, emulsions or micelles can be formed leading to

microtubes, -fibers, or -rodlike structures [19–23]. Kaner and co-workers prepared nanofibrous PANI by interfacial polymerization with aniline monomers soluble in an organic solvent [23,24]. Haba et al. reported a nanofibrous morphology of DBSA doped polyaniline originated from the filling of the nanopores of the polyaniline spherical particles into nanorods without the presence of any organic solvent with low conductivity due to the absence of the strong acid to gain high degree of doping [25]. Additionally, other novel methods like sonochemical [26] and gamma irradiation [27] methods were also used for the preparation of the nano-structure of polyanilines.

The presence of the large amount of long alkyl protonic acid dopant to maintain the lower pH value for polymerization did give us a nanofibrous conformation of polyaniline via emulsion polymerization. However, the nanofibers can only be seen after washing with lots of organic solvents and the conductivity is so good due to the lower degree of doping of mild acid nature of DBSA. Stejskal et al. proposed the presence of the phenazines in the early stage of polymerization when the pH value is not too small. The phenazines behaved as the tubular nuclei for the formation of helical polyanilines into nanofibers in the later stage with lower pH values [28–30]. We are going to present an easy method of emulsion-polymerizing (the aqueous initiators are actually starting the

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polymerization at the hydrophilic outer part of the micelles) ani-linium monomer micelles into polyaniline nanotubes (PANINTs) without using any organic solvent in the presence of two different dopants, HCl and DBSA to obtain a nanofibrous polyaniline with high conductivity. In our studies, the pH values were already low in the beginning of polymerization due to the presence of large amount of hydrochloric acid in the reaction mixtures. Therefore, the nucleation of a nanotubular polyaniline was not resulted from the formation a phenazine as nucleus. A supramolecular structure of the formed anilinium micelles will be proposed, which can ex-plain the formation of the centipede-like and helical nanofiber/tubes of the resultant polymers. All kinds of electronic microscopies such as SEM, TEM, and AFM were used to characterize various nano-polyaniline molecules.

2. Experimental part

2.1. Preparation of PANINTs

To dissolve 3 g (0.091 mol) n-dodecylbenzenesulfonic acid (DBSA: Tokyo Kasei Kogyo Co.) in 50 ml de-ionized water, the mixture was slowly stirred until a homogeneous solution was formed, then 9 g (0.0968 mol) aniline monomer (Tokyo Kasei Kogyo Co.) was added and kept stirring to become emulsified then 9 ml, 1 M HCl (Riedel-de Haën) was mixed with mixture, linking the micelles together and enhancing the emulsification. The mixture became less transparent with the addition of HCl. An ammonium persulfate (APS: Showa Chemicals Instrument Co.) aqueous solu-tion prepared in another beaker by dissolving 7.33 g (0.0323 mol) APS in 30 ml de-ionized water was kept in low temperature in a freezer several hours before using and was poured directly into the reaction mixture followed by a vigorous stirring with a mag-netic stirrer. With the proceeding of the polymerization, the tem-perature rose up quickly after 10–15 min, followed by the darkening of the reaction mixture and the polymerization was proceeded for 3 hrs before polyaniline was isolated by filtration, followed by washing with some isopropanol and the obtained filter cakes were dried in an oven at 60 °C for 12 h.

2.2. Preparation of PANINT dispersion of toluene

A 0.5 g PANINT powder was mixed with 10 ml toluene and zir-conium oxide mini-balls in a cell for vibrating ball-milling. The cell was vibrated in a ball-miller (Retsch MM301) three times with 10 min for each interval to become a well-dispersed state of dispersion.

2.3. Polarized optical microscopy (POM)

Emulsified monomers solution was cast on a microscope glass plate (7.6 × 2.54 × 0.1 cm) and covered with cover glass to prevent the evaporation of water and taken polarized optical microgaph by Olympus BH-2 optical microscope.

2.4. Scanning electron microscopy (SEM)

Samples of PANINTs and EB type were taken microgaph in a Field emission SEM, HR-SEM (Hitachi S-4200: accelerating volt-age of 15 kV) prepared from strewn on carbonic tape and followed by posting on ferric stage.

2.5. Transmission electron microscopy (TEM)

Samples for Field emission transmission electron microscopy, HR-AEM (Hitachi FE-2000) were prepared from acetone dispersion and dropped on carbonic-coated copper grids.

2.6. Atomic force microscopy (AFM)

Samples for Atomic force microscopy, AFM (CSPM 4000) were PANINTs dispersion cast directly onto a glass plate.

2.7. Conductivity

A 4-probes Milliohm meter (LUTRO MO-2001) was used to measure the conductivity of PANINT powders which were pressed into tablets.

3. Results and discussion

3.1. Mechanism

The anilinium monomer micelles were derived from the com-plexation of aniline with first DBSA then HCl in the aqueous mixture and no anilinium ions were present in the inner cores of micelles composed of hydrophobic long alkyl tails as depicted in Scheme 1. The anilinium ions countered with the aqueous ends of DBSA stayed and well distributed in the outer part of micelles. When HCl was introduced, the micelles were further expanded by the insertion of the HCl complexed anilinium ions that pointed outward due to their hydrophilic nature of the chloric counter ions. Before HCl was in-troduced, the DBSA-complexed anilinium emulsion solution was cloudy white (Fig. 1(a)) with a smaller, averaged micelle size of around 246 nm (Fig. 2). The introduction of the hydrochloric acid enlarged the size 1000 times to 392.8 μm from 246 nm (Fig. 2(b)) with neighboring micelles connected together and the emulsifica-tion was then enhanced through chloric ions' bridges as described in Scheme 1. Then sudden increase of size attributed from the
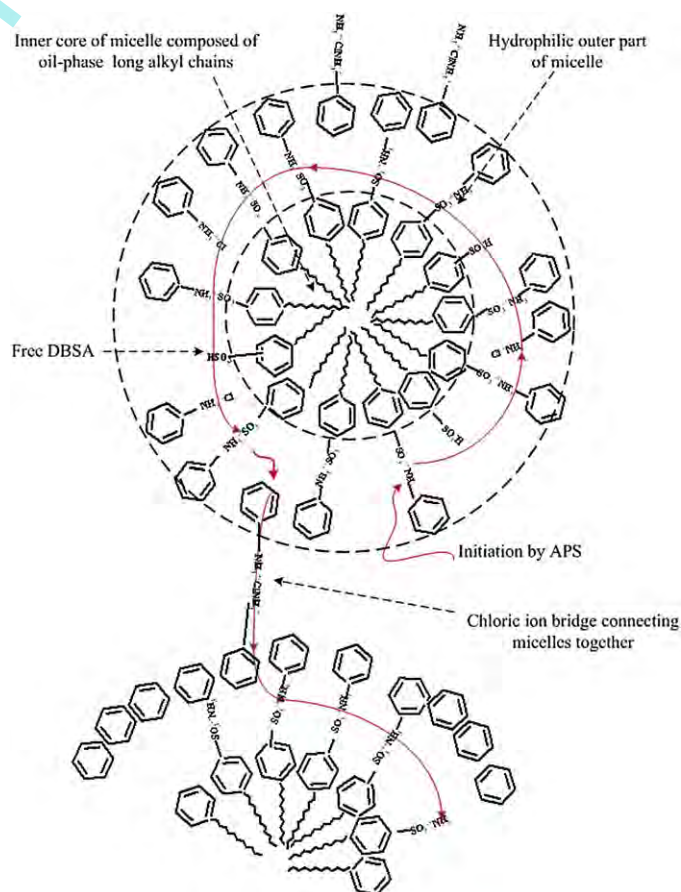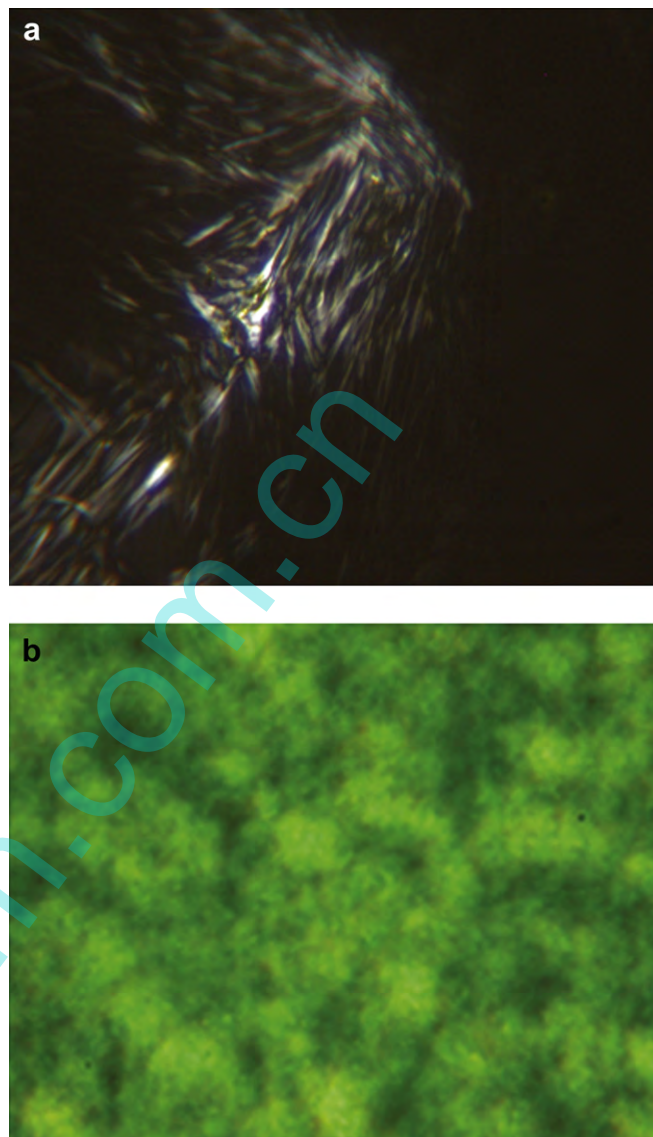

Scheme 1. Schematic diagram of micelles.
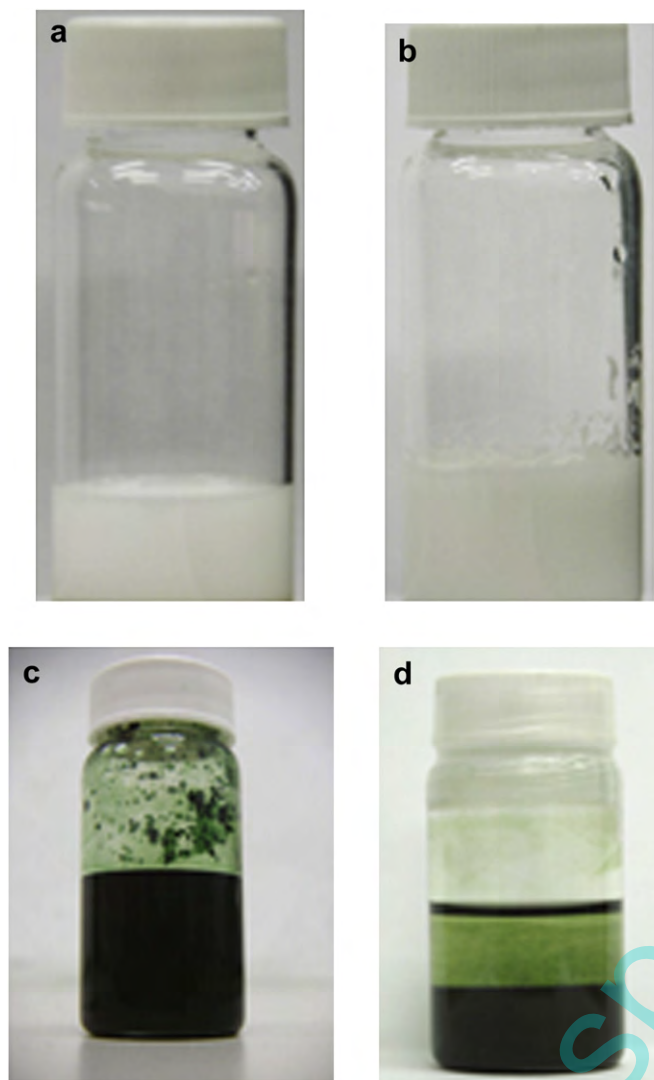
Fig. 1. Microgaphs of (a) slightly emulsified solution of anilinium monomers of DBSA; (b) highly emulsified solution of anilinium monomers of DBSA and HCl; (c) 5 wt% of PANINTs in toluene; (d) 1 wt% of PANINTs in toluene.


Fig. 3. (a) Polarized optical microscopic picture of anilinium salt aqueous solution; (b) Non-polarized optical picture of toluene cast PANINTs with 400× magnification.

formation of association of the micelles which became a rather dense/darker milky emulsified solution as seen in Fig. 1(b). Surprisingly, an ordered morphology was found for the micelle solution after treating with HCl under the polarized optical microscope as

shown in Fig. 3(a). The ordered, supramolecular structures were believed from the ordered alignment of the micelles with the connection of ionic bridges composed of chloric ions as described in
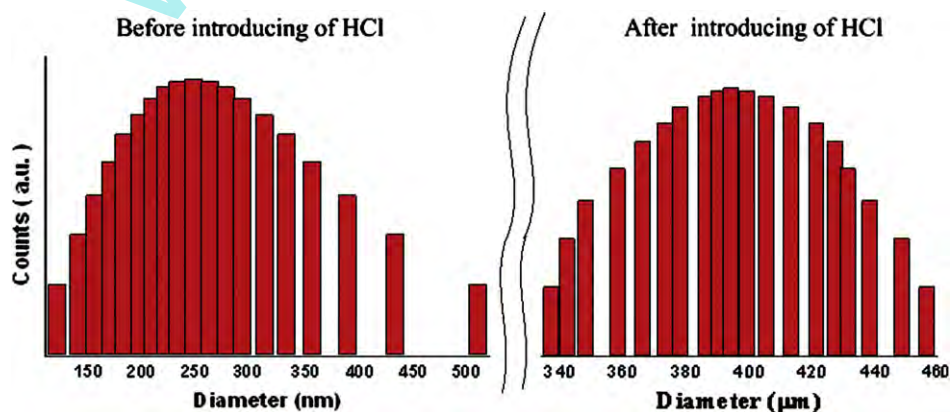
Fig. 2. Size and size distribution of anilinium emulsion solution before and after introduction of HCl.
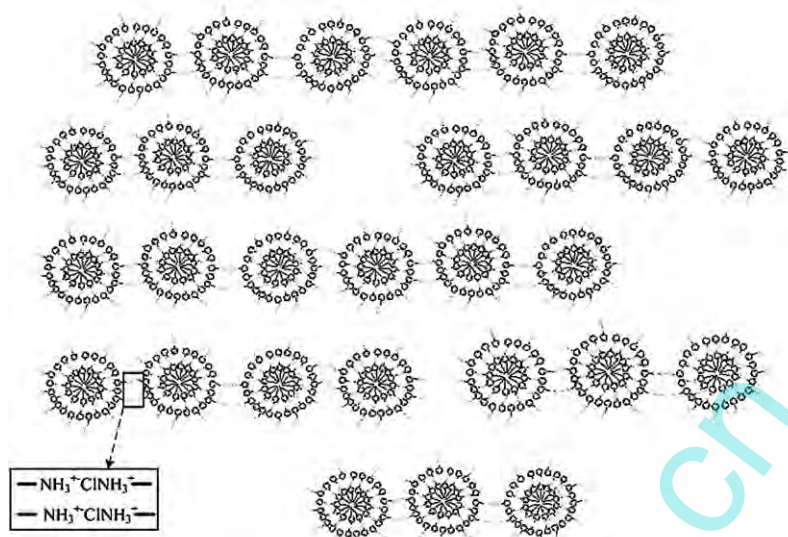
**Scheme 2.** LC-like supramolecular structures of associated micelles.

Scheme 2. With the ignition of the polymerization by hydrophilic APS initiators which are more likely to stay in the hydrophilic outer part of the micelle, the propagation of the polymerization remained in the outer part of the micelles, resulting in the circular conformation of the resultant helical molecules with both complexed and free DBSAs captured inside and the proceeding of the polymerization can extend to neighboring micelles through the chloric ion bridge to create a centipede structure composed of helical molecules which later becomes a nanofibrous or nanotubular structure as described in Scheme 2. The description about the formation of nanotubular polyanilines from the mentioned mechanism could be confirmed by the presence of a centipede-like SEM and TEM microgaphs of PANINTs discussed later Scheme 3.

3.2. Solubility in toluene

The obtained polyaniline was ball-milled in the presence of toluene into a 5% dispersion of PANINTs [31] (Fig. 1(c)) which was then cast on a glass plate. After the toluene solvent was removed by vacuum, a light green color can be seen clearly in the non-polarized optical microscope as shown in Fig. 3(b). The optical picture taken with $400\times$ magnification demonstrated a shining green color, indicating its high dispersibility in 5% dispersion of toluene and the conductivity was measured to be about 3.8 S/cm, higher than the averaged conductivity of common polyanilines, which are mostly below 1 S/cm or even 0.1 S/cm. Additionally, the conductivity is also higher than the nanofibrous polyaniline prepared in the presence of weak acids [30] like acetic acid, oxalic acid, DBSA, etc. Surprisingly, the inner surface of the vial containing 5% PANINT dispersion illustrated in Fig. 1(c) was permanently blurred with green spots which cannot be easily removed by brushing in water, indicating some of the nanotubes were deeply implanted in the tiny pores of the glass-plate surface.

A good toluene dispersible nanotubular or nanofibrous polyaniline (PANINT) was obtained and its dispersibility in toluene originated from the complexed DBSA that can provide both enough
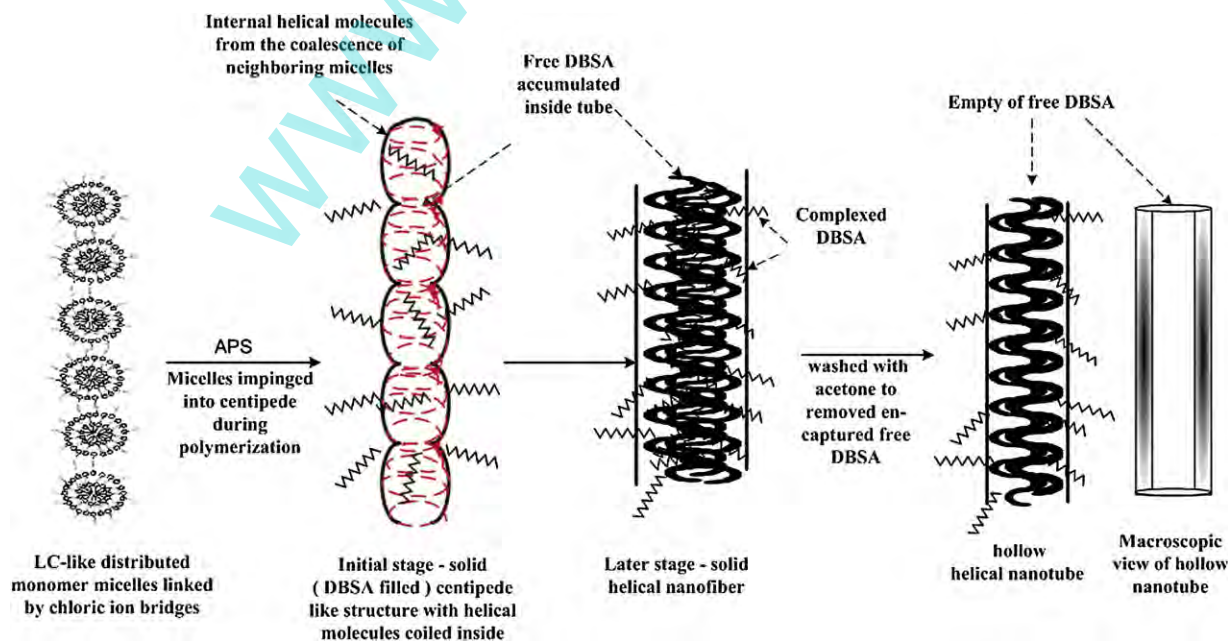
Scheme 3. Schematic diagram of the formation of PANINTs.

space for the solvent molecules and improve its solubility in toluene since DBSA itself is highly soluble in toluene. The presence of the free/excess DBSA (not complexed to polyaniline backbone) within or between the PANINTs can improve the toluene solubility of PANINTs. Amazingly, if the concentration of the PANINTs is reduced to 1% as seen in Fig. 1(d), which means more toluene (99%) is available to dissolve/abstract the less free DBSA (the percentage of DBSA in PANINTs is constant and 1% dispersion of toluene has less DBSA than 5%) out of the PANINTs, its solubility in toluene is significantly decreased, leading to the sedimentation of the PANINTs from toluene. Similar phenomenon was found when the free DBSA of PANINTs was fully removed by acetone which is a better solvent for DBSA compared to isopropanol or toluene, it became entirely non-dispersible in toluene any more no matter it is prepared as a 1% or 5% dispersion of toluene. Commonly accepted concept that low-concentration solution has a better solubility is not true here for PANINTs in toluene. Therefore, to achieve a good dispersibility of the PANINTs in toluene, polyaniline itself should have some free DBSA molecules inside/around the nanotubes and a concentration higher than 3% PANINTs is necessary to provide enough free DBSA to maintain its dispersibility in toluene.

3.3. Electronic microscopic micrograghs of PANINTs

3.3.1. SEM micrograghs

The SEM micrograghs of various PANINTs shown in Fig. 4(b) and (d) were taken and compared with common non-nanotubular polyaniline in (a) which illustrated a particle-assembled morphologies of common polyaniline prepared on a non-emulsified condition [32–38]. The outer anilinium ions were favorable to coil up into a helical conformation to become a nanotube. In the early stage

of polymerization when the color of the reaction mixtures just turned green, the reaction was terminated by pouring the mixtures into isopropanol (IPA) and the precipitated polyaniline showed a centipede-like morphology seen in Fig. 4(b). It tells that the possible mechanism of the formation of the centipede morphology originated from the coalescence of the neighboring propagating micelles. The centipede-like morphology was not found if DBSA was the dopant for emulsion polymerization. At the later stage, a well-defined nanofibers of polyaniline (PANINTs) can be found. PANINTs with averaged 100 nm diameter are shown in Fig. 4(b) and (c) compared to the common polyaniline's particle-accumulated morphology in (a). Even after dedoping with ammonium water into EB type of PANINT, the nanofibrous morphologies are still maintained. The dedoping by ammonium water was found to be very difficult and it took twice as much time as dedoping a non-tubular polyaniline (48 h compared to 24 h). With its denser structure, ammonium ions were not easily able to penetrate into the PANINTs to carry out the dedoping. The redoping on the EB type PANINTs either by ultrasonication or by ball-milling in the presence of concentrated HCl, H_2SO_4, DBSA turned out impossible and what we obtained was still a blue EB dispersed in the acids. It is believed that due to the strong H-bonding interaction between the individual helical EB molecules nanofibrous EBs are impenetrable by any acid. And these densely arranged H-bondings also induced the shrinkage of hollow nanotubes into smaller solid nanofibers when we compared Fig. 4(d) with (c).

3.3.2. TEM micrograghs

The TEM micrograph in Fig. 5(a) also illustrates a dendrite-like structure with interconnected nanofibers of polyaniline, the interconnection and overlapping are believed from the presence of
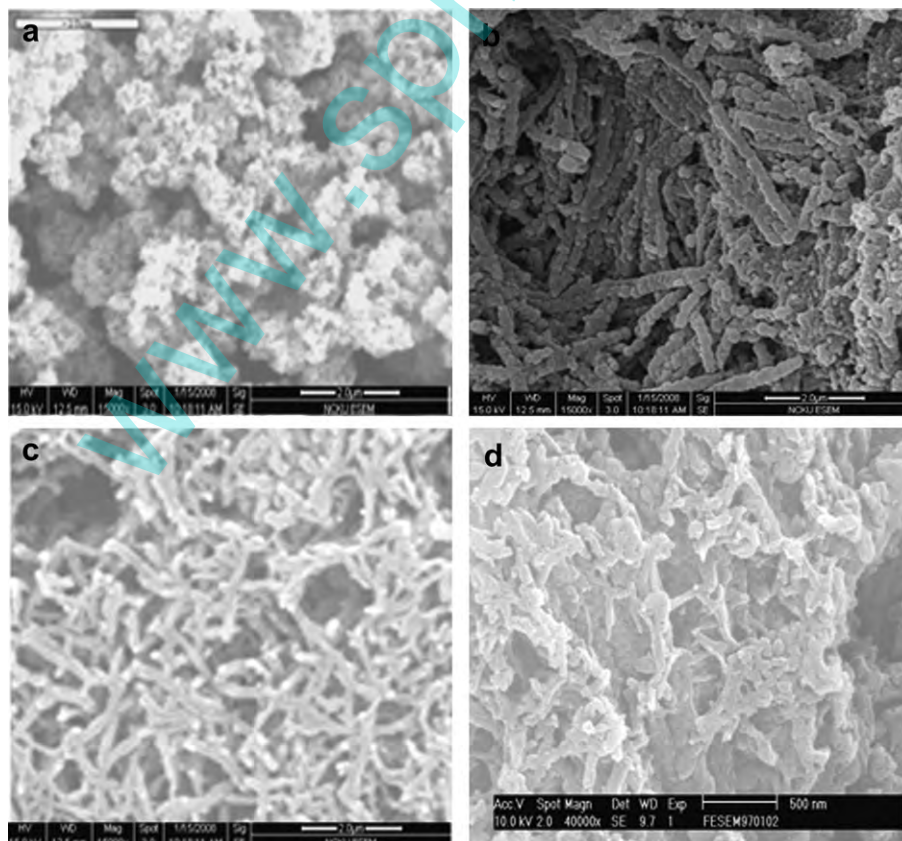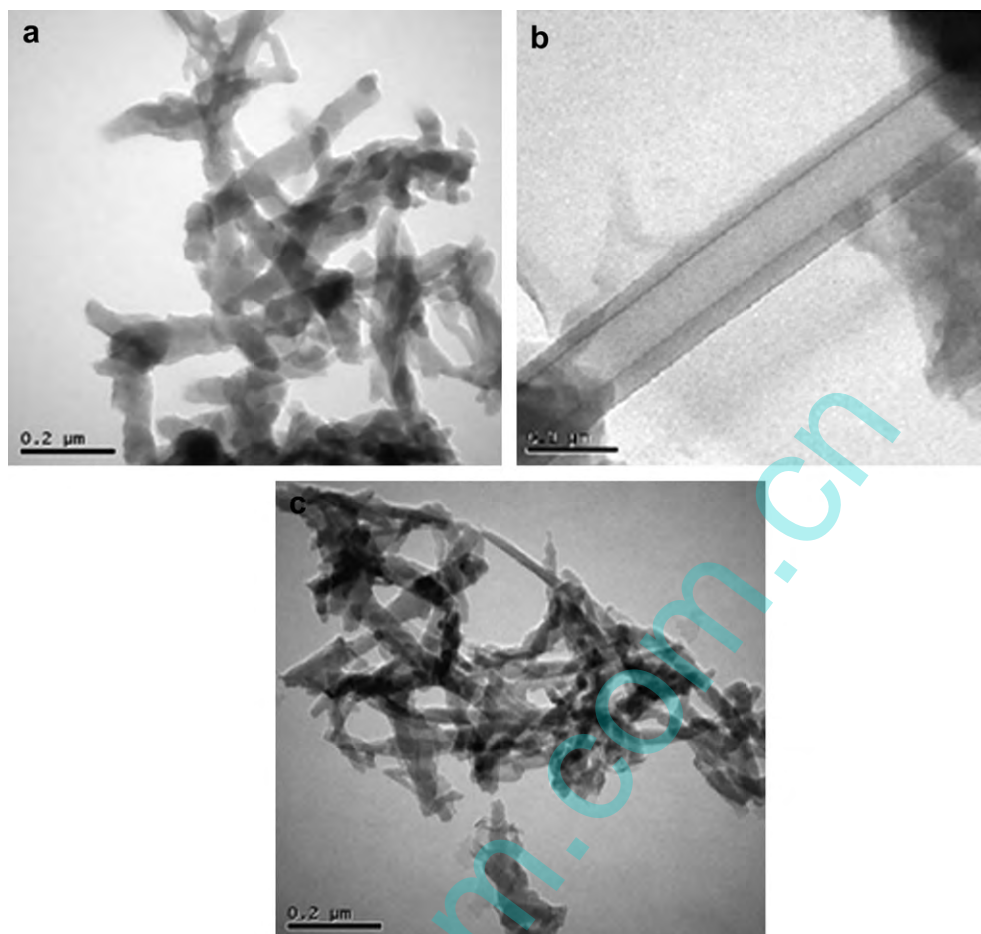

Fig. 4. SEM micrograghs of (a) PANI prepared in a non-emulsified way; (b) early stage form of acetone washed PANINTs; (c) as-polymerized PANINTs; (d) emeraldine base of PANINTs.

Fig. 5. TEM microgaphs of (a) fully polymerized PANINTs; (b) single/hollow PANINT obtained from washing with acetone; (c) emeraldine base prepared from the dedoping of PANINTs.

the excess/free DBSA dopants, behaving as glues. After washing with acetone to remove free DBSA, these interconnected nano-networks dissociate into individual hollow/single nanotubes as shown in Fig. 5(b), revealing that DBSA is present not only between the neighboring nanotubes but some of them were captured inside the tubes, which can only be removed by a better solvent like acetone. In other words, the obtained PANINTs was actually hollow but was looked like solid because DBSAs were captured and filled inside the nanotubes during polymerization. Likewise, the TEM microgaph of the dedoped PANINTs (EB type) still retains the nano-fibrous/dendrite-like morphology with the diameter reduced to about 50 nm as seen in Fig. 5(c). However, the hollow tubular structure cannot be found for EB type PANINTs since the tubes shrink into solid nanofiber from strong intermolecular H-bonding after complexed DBSA was entirely removed by ammonium water (neutralization).

3.4. Atomic force microscopic micrograph of PANINTs

The excellent solubility of the PANINTs in toluene allowed us to prepare a solvent cast sample for AFM studies. The AFM micrograph of a toluene cast PANINTs is demonstrated in Fig. 6(a), which illustrates a cottage-like surface morphology. The cottage structure was built with nanorods piled up with each other like the schematic diagram illustrated in Fig. 6(a)′. The surface of the sample was rubbed and orientated by glass bar before the evaporation of the toluene solvent, resulting in a flattened, aligned rods oriented in one direction as shown in Fig. 6(b). Its schematic diagram is also

shown in Fig. 6(b)′ with all nanorods pointing to one direction. An AFM microgaph of a common polyaniline is also shown in Fig. 6(c) in comparison with the PANINTs and a drastically different morphology can be seen. These are the first AFM microgaphs of nano-tubular polyaniline, which were seldom seen in the literatures.

4. Conclusion

A simple emulsion polymerization method can be used to prepare a highly conducting nanotubular polyaniline with two kinds of protonic dopants of DBSA and hydrochloric acid present without the addition of any organic solvent. The obtained polyaniline nanotubes (PANINTs) were found non-dispersible in toluene until their concentration is higher than 3 wt%. The polarized optical picture illustrated an ordered structure due to the presence of the chloric ion that connecting the neighboring micelles.

The early stage of polymerization of polyaniline demonstrated a centipede-like morphology through the formation of chloric ion bridges. Both SEM and TEM microgaphs illustrated the networks of PANINTs before free DBSA molecules was removed and the separated hollow nanotubes can be seen after removing the en-captured free DBSA by acetone. A mechanism illustrating the formation of the hollow polyaniline nanotubes was then postulated.

AFM microgaphs demonstrated that PANINTs were able to orientate to uni-direction by rubbing before the entire evaporation of toluene.

The future work would include finding out the relationships between the formation of a nanotubular polyaniline molecules
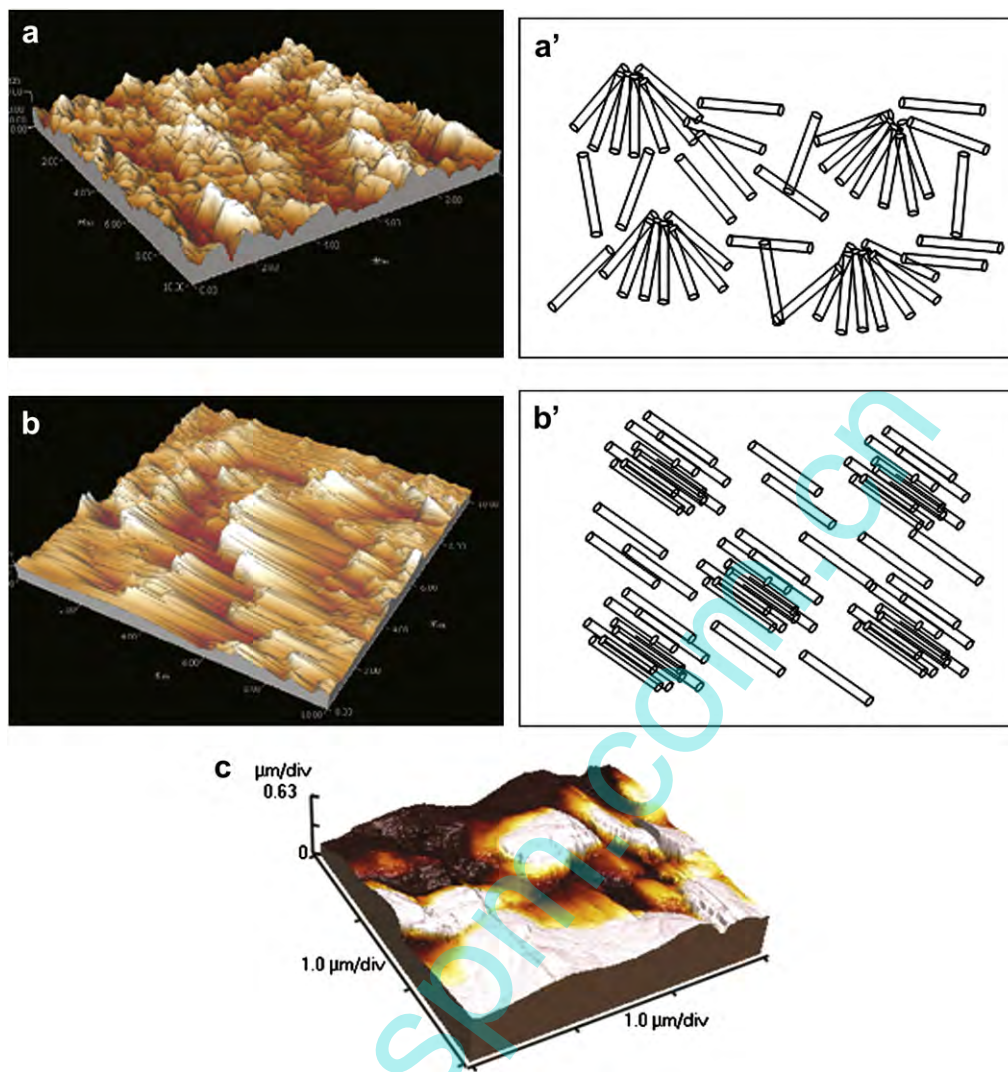
Fig. 6. AFM micrographs of (a) cast PANINTs from toluene (roughness: 53.1 nm); (a)′ schematic diagram of PANINTs; (b) flattened PANINTs by rubbing before evaporation of toluene; (b)′ schematic diagram of flattened PANINTs; (c) PANIDBSA.

and types of dopants, ratio of two dopants, concentration of dopants, etc.

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