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Short communication

## Synthesis of self-assembled rectangular-shaped polyaniline nanotubes and their physical characteristics

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### ABSTRACT

We reports synthesis of polyaniline (PANI) nanotubes with a rectangular cross-sectional shape by simply changing both molar ratio of organic dopant acid to monomer and reaction time. The PANI nanotubes were fabricated with a controlled rectangular pore structure by an in-situ chemical oxidation polymerization process in the absence of surfactant and template. Morphology of citric acid (CA)-doped PANI was observed via scanning electron microscopy and transmission electron microscopy. Fourier transform infrared spectroscopy and X-ray diffraction confirmed chemical structure and hydrogen bonding between amine group of PANI and hydroxyl and carboxyl group of CA, is the driving force for this self-assembly.

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### Introduction

Because of the disadvantages of conducting polyacetylene doped with iodine, such as its difficult processability and instability in air, the first discovered electrically conducting polyacetylene was replaced with more stable and highly electrically conducting polymers, such as polypyrrole, poly(3,4-ethylenedioxythiophene) and polyaniline (PANI) [1]. These conducting polymers have attracted attention for a range of engineering applications [2], including transparent electrodes [3], waste-water treatment [4], electromagnetic shielding [5], electrorheological (ER) materials [6] etc. In recent years, conducting polymers have been also employed actively as biocompatible materials [7].

Among the various conducting polymers, PANI has attracted considerable interest owing to its facile synthesis [8], excellent chemical and thermal stability, good environmental stability, cost effectiveness [9], and controllable conductivity with reversible acid/base doping/dedoping process [10]. The crucial properties of PANI are determined by its morphology and size, such as micro/nanotubes [11,12], micro/nanowire [13], micro/nanofibers [14], micro/nanospheres [15], and micro/nano-rods [16] owing to its dimensions. To fabricate the special morphology of PANI for its suitable application, recently studies of diverse structure-directing soft templates have attracted attention. In fact, using different

organic dopant acids, doped PANI with a range of morphologies through a self-assembly process can be fabricated.

As an important conducting nanomaterial, the PANI nanostructure is expected because of its nano-effect fitting innovative applications [17] and has been fabricated through either a hard or soft template in the polymerization of aniline. On the other hand, the use of hard templates requires a complex preparation process and post-treatment of obtained samples, which makes it slightly difficult to remove the templates. Zhang et al. [18] reported that aniline monomer and organic acids form micelles in the reaction medium and act as a template for the successive growth of PANI nanotubes in absence of any external template through a self-assembly process.

The one-dimensional materials such as nanowires, nanotubes, nanofibers etc, have received a great attention because of their extremely high surface area regardless of increasing the device dimension. Therefore, they have been evaluated as an effective electroactive material for supercapacitor applications such as gas sensors [19–21] because they furnish a comparatively shorter ion diffusion path and enhance the performance in energy storage [22]. Especially, PANI nanotubes with long aspect ratio have larger surface areas per unit mass and allow easier addition of surface functionalities when compared with agglomerated PANI [21].

Also, owing to their tubular morphology, the PANI tubes can produce uncommon magnetic loss at the microwave frequency due to the order arrangement of the ion-polaron as a charge carrier [23]. Because of their electrical and optical properties, PANI nanotubes have the potential applications such as bio-sensor, field

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effect transistors, electrochromic displays, nano-diodes, super-capacitors, drug delivery, energy storage, neural interfaces and so on [24–27]. Furthermore, PANI nanotubes either covered with nanorods or fabricated with a different dopant of oxalic acid have been adopted as ER materials [28,29], whose rheological characteristics can be reversibly and precisely controlled by applied electric field strength [30,31].

This paper reports the self-assembled PANI nanotubes shaped with rectangular cross sections, which were synthesized by a chemical soft template method in the presence of citric acid as the dopant. This technique is environmentally friendly because it does not require any surfactant and template. In particular, the morphology of citric acid (CA)-doped PANI tubes observed by just changing the molar ratio of CA to aniline shows that CA acts not only as a dopant acid, but also as a template. In addition, by increasing the reaction time from 10 to 20 h, the optimal condition of the synthesis of rectangular PANI nanotubes was found. When the nano-tubular structure is formed, CA molecules and aniline self-assemble together through hydrogen bonding, which can be used as a facile, low-cost and available method for the one-step fabrication of PANI nanotubes.

## Experimental

### Materials and synthesis

Aniline (AN, Sigma Aldrich, 99%), ammonium persulfate (APS, Mw = 228.18 g/mol, density: 1.98 g/ml, Dae-Jung), citric acid anhydrous (CA, 99.5%, Mw: 192.43 g/mol, Fluka Guarantee), and deionized water were used in all the experiments.

For the preparation of PANI tubes, a solution composed of 0.5 ml of aniline and a specific molar quantity of CA as a template was dispersed in 80 ml of deionized water at room temperature and stirred for 30 min. In another beaker, 20 ml of an aqueous solution containing 1.141 g of APS was prepared. When the aniline solution was cooled to 4 °C, the APS solution was added drop-wise. The resulting solution was carried out for 12 h in an ice bath. The resulting PANI-nanotubular particles were washed several times with ethanol and deionized water to remove the residual initiator and monomer. Finally, rectangular PANI nanotubes were dried at 60 °C in a vacuum oven for 24 h. To identify the influence of the [CA]/[An] molar ratio and reaction time, different molar ratios ([CA]:[An] = 1:4, 1:5 and 1:6) and different reaction times (7 h, 10 h, 12 h, 14 h, 16 h, and 20 h) were investigated. In all experiments, the aniline to APS ratio was fixed through this study.

### Characterization

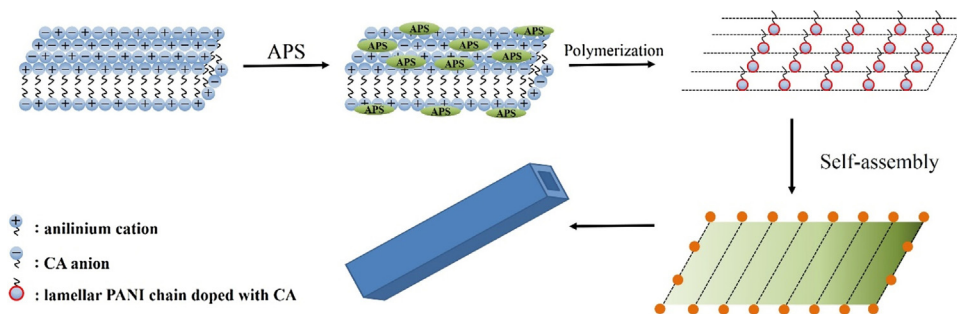
The morphology of the PANI nanostructures was observed by both high resolution scanning electron microscopy (HR-SEM, SU8010) and transmission electron microscopy (TEM, Philips CM200). The particle density of the synthesized PANI nanotubes

was measured using a pycnometer (Accupyc 1330, Gas pycnometer, USA), while their electrical conductivity was examined using a standard four-point probe technique using a resistivity meter (Mitsubishi Loresta-GP and Hiresta-UP). Note that for the conductivity measurements, the dried PANI nanotubes were pelletized at 1500 psi for 5 min. The chemical structures of the PANI nanotubes were characterized by Fourier transform infrared (FT-IR, PerkinElmer System 2000) spectroscopy in the range of 4000–400 cm<sup>-1</sup>. X-ray diffraction was conducted using a DMAX-2500 (Rigaku). A full automatic physisorption analyzer (BET, ASAP ZOSO) was also applied to confirm the pore properties of the PANI tubes through nitrogen adsorption/desorption isotherms at 77 K.

## Results and discussion

Scheme 1 presents the possible profile of the formation mechanism of the rectangular PANI nanotubes. When aniline and CA are added to an aqueous solution, CA anions and anilinium cations will form bilayer micelles with a lamellar shape, acting as templates [32]. When an APS solution is added, polymerization of the aniline takes place at the interface because of the hydrophilicity of the APS. Also, due to the hydrophobic internal cavity, the monomer, aniline, doped with CA would incline to fill the internal surface of APS. Thus, at the first step, the bilayer-lamellar-micelles, which be made by the host-guest inclusion complex at the early stage, would lead the growth of oligomers to act as seeds to form flakes because of the interaction between APS and PANI oligomers. In other words, the hydrogen-bonding and  $\pi$ - $\pi$  electron interactions come into the driving force for the self-assembly of PANI chains [32]. Finally, the flakes are united to form a tube-shape structure due to the reaction of the active center on the edges, in which the reactive center on the edges of the flakes-sheets produces quite possible sites for coupling reactions, forming the rectangular nanotubes [17]. Therefore it could be considered that the bilayer lamellar-micelles act as template-seeds for the formation of the polymer flakes, resulting in the formation of the rectangular PANI nanotubes by the combined reaction [39]. Therefore, when the tubular structured PANI with a rectangular cross section was synthesized following this mechanism, the CA concentration is regarded to be an important factor because the increased concentration of CA enlarges the distance between the interactive groups.

As it is well known on the polymerization mechanism, the aniline oligomers could continue the reaction with the other oligomers or monomer at the chain-end. As is generally known, in the self-assembly process of PANI structures, hydrogen bonding plays a significant role [21,33,34]. One possible formation mechanism is that three hydrophilic carboxyl groups in the CA and the hydrophobic amine group of aniline form micelles. The addition of hydrophilic APS as an oxidant begins the polymerization process of aniline at the water-micelle interface. As polymerization proceeds, the CA-PANI tubes are growing via the



Scheme 1. Formation mechanism for synthesizing the PANI-CA nanotubes.

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