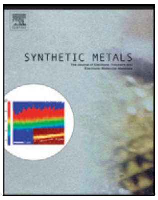
Synthetic Metals 159 (2009) 757–760

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Letter

Tuning of different polyaniline nanostructures from a coacervate gel/sol template

ARTICLE INFO

Keywords:
Polyaniline
Nanofiber
Nanotube
Interconnected network

ABSTRACT

The morphology of polyaniline nanostructure is tuned from nanotube to nanofiber to three-dimensional network by polymerizing aniline in a cetyl trimethyl ammonium bromide (CTAB)–lauric acid (LA) complex coacervate gel template by changing the physical state of initiator and also that of the gel. This synthesis is easily reproducible even in large scale, very cheap, and one-step method. The HCl doped samples have average conductivities in the ranges 10^{-2}–10^{-3} S/cm that may be considered high enough in view of potential applications in several fields.

Polyaniline (PANI) is an important conducting polymer due to its easy polymerization procedure, good chemical stability, convenient acid doping process and high conductivity [1]. Depending on the morphology and electronic state of PANI it is used in chemical and biological sensors [2a,b], gas separation membranes [2c,d], electronic devices [2e,f], light weight battery electrodes [2g], anticorrosion coatings [2h], etc. Synthesis of nanostructured polyaniline is of great interest because it can be used to enhance sensor properties for its large surface area and low dimensional conductivity [3–7]. Nanostructured PANI (nanofiber/nanotube) can be prepared both chemically and electrochemically by polymerizing the monomer using soft [4] and hard templates [5]. Besides, surfactant-assisted polymerization [6a], dilute solution polymerization [6b], template free polymerization [6c] and interfacial polymerization [6d] are presently used to prepare different PANI nanostructures. By simply changing molar ratio of dopant and monomer Wan and coworkers tailored the synthesis of PANI from nanotubes to hollow microspheres [7]. Recently PANI nanostick and dendritic nanofibers are produced from gel template [2c,3f] but to our knowledge, yet there is no report of tuning different PANI morphology using the same gel template. Here, we report the preparation of PANI nanofiber, nanotube and interconnected network structures by changing the polymerization condition in a soft template. We have developed a new technique to tune PANI morphology from nanofiber to nanotube to interconnected network structure by changing polymerization conditions in a complex coacervate gel template.

In this work, cetyl trimethyl ammonium bromide (CTAB) and lauric acid (LA) are used for formation of hydrogel (Suppl. Fig. 1) which is used as template for polymerization. Two different procedures are adopted: (i) aniline (5×10^{-4} mol), LA (1.2×10^{-3} mol) and aqueous CTAB solution (5 ml 3×10^{-2} M) are mixed together by sonication and left at 30 °C for 10 min when the system gels. Then 2 ml 0.25 M ammonium persulphate (APS) solution are added at the top of the gel and kept undisturbed for 24 h. The APS solution gradually diffuses into the gel from the top and polymerization proceeds producing first oligomer (brown color) then polymer (green color) [8] (Suppl. Fig. 2). (ii) In the second procedure 114 mg (0.5 mmol) powder APS was spread over the above gel surface and left undisturbed for 24 h at 30 °C. Here also the gel first transforms into brown and then become completely green after polymerization. The rate of polymerization is faster in APS solution than that of solid APS as evident from change in color of the gel (Suppl. Fig. 2) indicating persulphate ions in solution easily diffuse into the gel than that in solid state. After polymerization syneresis of gel takes place probably due to the rejection of polar water molecules by PANI from the coacervate interstices. The same techniques were repeated for the polymerization at 42 °C when the soft template is melted to the sol state. All the resulting polymers were repeatedly washed with water and then with methanol to leach out the surfactant and they were dried in vacuum. In Fig. 1 the SEM morphology of differently polymerized systems are compared. In micrograph A the morphology of gel templated polymers produced by APS solution is long tubes while in micrograph B (polymerized using solid APS), PANI fibers are produced. The same polymerizations performed in sol state (42 °C) using APS solution produce interconnected tubular network (micrograph C) but use of solid APS yields only tubular morphology (micrograph D). However, the tubes in micrograph C are much shorter than that in micrograph (A). In Fig. 2 the TEM micrographs of tubes and fibrils obtained from gel are presented and the average diameter of the fibers is 31 ± 4 nm and the average outer diameter of tubes is 166 ± 8 nm (i.d. 33 ± 9 nm). The TEM micrographs of network structure and short tubes obtained from the sol state are also presented in micrographs C and D, respectively. An elemental (C, N, H) analysis of the tube and the fiber produced from the gel state are 65, 11.9, 4.3 and 66.9, 11.7, 4.4% (w/w), respectively. The atomic ratios of C:N is 6.4:1 and 6.7:1 and the atomic ratio H:C = 0.79 and 0.78 for tube and fiber, respectively. The C:N ratio values are higher than the usual value of 6:1 for all forms of standard PANI and may be indicative of the formation of phenazine units acting as initiation center for the growth of PANI [9]. The two peaks at 1502 and 1587 cm^{-1} in the FTIR spectra (Fig. 3) indicate the presence of benzenoid and quinonoid moiety of PANI, respectively [10]. The quinonoid deformation vibration requires higher energy in the tubes than that in fibers (1569 cm^{-1}), indicating π electrons of quinonoid rings in fibers are better delocalized due to

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doi:10.1016/j.synthmet.2008.12.004

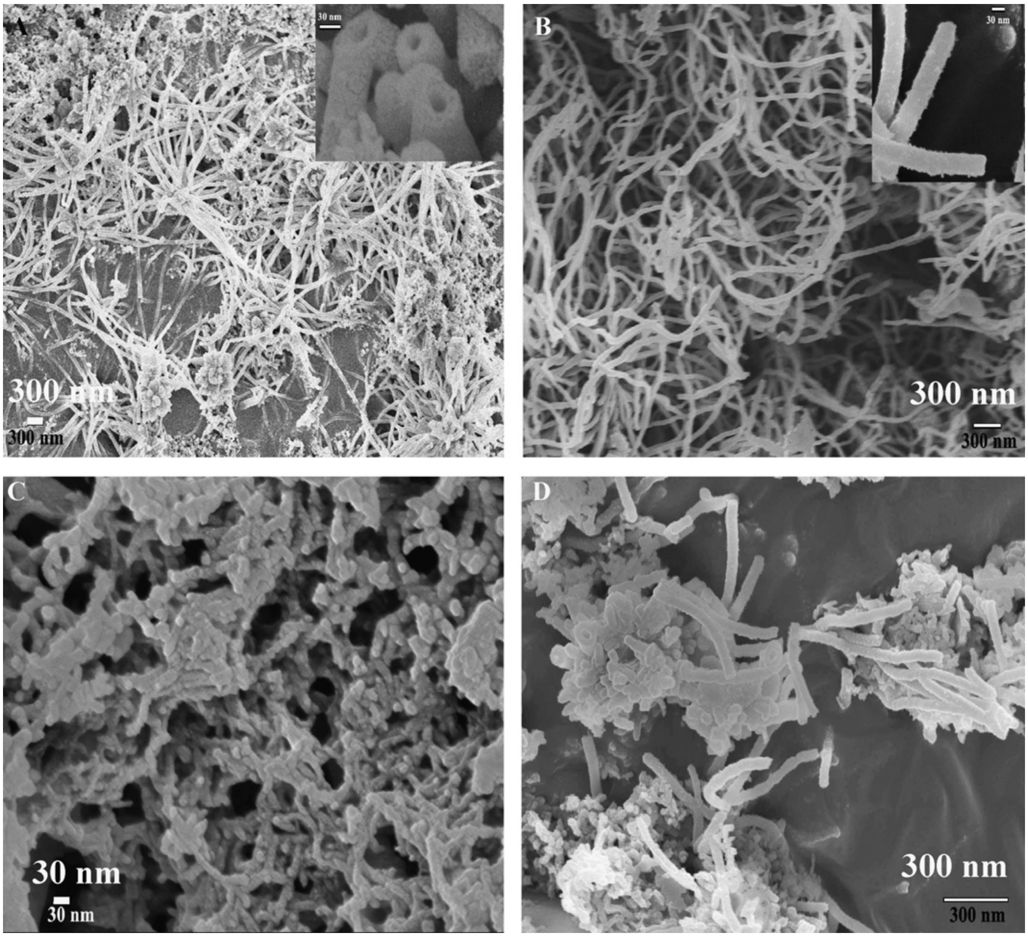

Fig. 1. SEM micrograph of different morphology of polyaniline (A) nanotube (higher length) (B) nanofiber (C) interconnected network structure (D) nanotube (lower length).

more ordered packing of PANI chains in the fibers. Also PANI tubes has peaks at ~1414 cm^{-1} indicating the presence of phenazine ring in the PANI nanotubes [9].

The mechanism of different morphology formation is yet to be completely understood and a probable mechanism from the complex coacervate gel formation of CTAB and LA mixture is proposed [11]. The detailed structure of the complex coacervate is unknown, but it is widely accepted that the structure is stabilized by ionic interaction between the mixed surfactant strands [11]. Aniline is trapped in the interstices of the surfactant strands as anilinium ion along with water. A schematic two-dimensional presentation of the complex coacervate is presented in (Suppl. Fig. 3). A numerical calculation considering the 1:1 structure of the coacervate indicate the presence of an excess of LA molecules (10.5×10^{-4} mol in 5 ml of mixture). This excess of LA is partially used up in forming anilinium ions, making aniline to be water soluble and keeping 5.5×10^{-4} mol of excess LA in 5 ml of the mixture. This provides a LA concentration of 0.11 M in the polymerization medium. As the CMC of LA in water at 25 °C is 2.55×10^{-2} M [12] so there exists some LA micelles which may act as linker between the coacervates assisting gel formation. This is because below 7×10^{-2} M LA concentration the 3×10^{-2} M CTAB solution do not produce gel. All the anilinium ions exist in the interstices of CTAB–LA complex coacervate and the polymerization is mainly taking place on the coacervate surface as anilinium ion cannot enter into the interior of micelles due to its ionic nature. A probable support of the existence of coacervate and micelles can be obtained from the SAXS peaks of CTAB–LA gels showing d spacings at 2.71 and 3.95 nm, respectively (Suppl. Fig. 4). The former arise due to the lamellar structure of coacervate strands while the later is for lauric acid micelles [13].

The PANI morphology is controlled by polymerization process arising from the different diffusion processes of the initiator within the complex coacervate. In the APS solution initiated polymerization the initiator molecules diffuse surrounding the coacervate easily but cannot enter into the core due to electrostatic repulsion by LA anions attached to aniline molecules. Due to random distribution of initiators at the coacervate surface, attack on both ortho (o)- and para (p)-position of aniline occurs producing phenazine unit as the initiating species. It has planner sheet like structure and with time as the chain grows it bends surrounding the coacervate and nucleates the tube [9]. After complete polymerization and after the removal of surfactant strands by leaching with water and methanol the nanotube morphology comes out. The 30 nm i.d. of the tube suggests that about 100 columnar strands (diameter = 3 nm) are present in the coacervate column. The o.d. of PANI tubes is dictated from availability of aniline molecules and strain of the PANI chains grown on coacervate surface. On the other hand, when solid APS is used as initiator, the polymerization starts at the solid initiator surface at the top and it propagates quasi one-dimensionally (1D) downwards by absorbing anilinium ion. Such 1D polymer chains crystallize together to produce nanofibril. The diameter of fibrils is ~30 nm indicating the nanofibrils generated at the different interstices of coacervate interacts by cohesive force of interaction producing the fibril. The same values of i.d. of tubes and the diameter of fibers support that coacervate columns take the key role in tuning the morphology. In the sol state [at 42 °C, near