

Fabrication of DBSA-Doped Polyaniline Nanorods by Interfacial Polymerization

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Received 26 January 2007; accepted 16 January 2008

DOI 10.1002/app.28355

Published online 20 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An interfacial polymerization was used to fabricate dodecylbenzenesulfonic acid (DBSA)-doped polyaniline (DBSA-PANI) nanorods with diameter range from 40 nm to 1 μm . The molar ratio of aniline to ammonium peroxydisulfate (APS), the concentrations of DBSA and reaction temperature had an effect on the morphology and size of products. It was found that lower concentration of DBSA and lower temperature will be helpful to the forma-

tion of rod-like PANI nanostructures with a relative small diameter. UV-vis and FTIR measurements were used to characterize the chemical structure of the obtained samples. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2842–2847, 2008

Key words: interfacial polymerization; nanorods; polyaniline; dodecylbenzenesulfonic acid

INTRODUCTION

Recently, One-dimensional (1D) structured nanomaterials have attracted considerable attention due to their unique optical, electrical, and magnetic properties, and their potential applications in nanodevices.^{1,2} Nanorod material can usually offer larger surface areas than that corresponding solid film or bulk material, and become a prime candidate to replace conventional bulk materials in micro- and nanoelectronic devices,^{3,4} and in chemical^{5,6} and biological^{7,8} sensors. Polyaniline is emerging as an important material due to its versatile properties, and it has been exploited into various applications.^{9,10} Compared with other conducting polymers, PANI has significant importance because it exhibits good environmental stability, ease of processability and high conductivity,^{11–13} and especially a simple and reversible acid/base doping/de-doping property.¹⁴ Recently, it becomes a very interesting focus to synthesize 1D nanostructured conducting polymers, since it is a kind of desirable molecular wire material due to its unique metal-like and tunable conductivity.

By now, various methods, for example, hard template synthesis,^{15–21} self-assembly^{12,22,23} electrochemi-

cal polymerization,^{24,25} interfacial polymerization,^{26–28} and electrospinning technique,^{29–31} etc, have been used to synthesize 1D nanostructures of polyaniline. Among a variety of methods, interfacial polymerization developed by Kaner and coworkers²⁴ is the latest and effective method to synthesize polyaniline nanofibers.³² In this method, polymerization was performed at the interface of immiscible aqueous/organic biphasic system and can produce PANI nanofibers with diameters from 30 to 120 nm based on the different kinds of dopant acids. The concentration of the dopant acid also plays an important role on the formation of PANI nanofibers. Larger yields of high-quality nanofibers could be obtained at a relatively high concentration of acid (0.5–2M), while the lower the concentration of acid was used, the lower fraction of nanofibers could be observed in the product. When the concentration (HCl in that case) is lowered, the quantity of granular particles starts to increase and finally prevails over the nanofibers. Similar results have been also obtained in the case of camphorsulfonic acid.²⁵

Here, a similar interfacial polymerization method is performed to prepare polyaniline nanorod (40 nm to 1 μm in diameters) in which a relative low concentration (0.2–0.5M) of DBSA is used and the whole reaction is schemed in Figure 1. Our results indicate that not only the concentration of DBSA aqueous solution, but also the factors of the molar ratio of aniline to APS and reaction temperature have serious influences on the morphology of the resulting product, which is different from the recent report of Kaner.²⁷ Furthermore, the formation mechanism was also proposed.

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Contract grant sponsor: National Major Project for Fundamental Research of China; contract grant number: G2003CB615604.

Contract grant sponsor: National Nature Science Foundation of China; contract grant numbers: 50473007, 20674027.

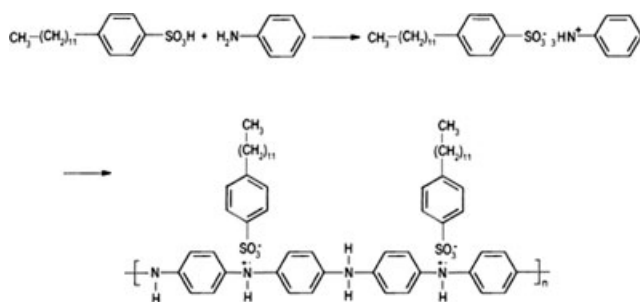


Figure 1 Scheme of the preparation of the DBSA-doped PANI.

EXPERIMENTAL

Materials

Aniline monomer was distilled under reduced pressure. Ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, APS), DBSA, xylene, methanol, acetone and other reagents were used as received.

Preparation of DBSA-PANI nanorods

The typical synthetic process of DBSA-PANI nanorods was performed as following: 1 mmol aniline was dissolved in 20 mL xylene and stirred for a while to obtain a homogeneous solution (A); a certain proportional amount of APS was dissolved in 20 mL DBSA aqueous solution and after several minutes stirring, a homogeneous solution (B) was obtained. Then solution (A) was carefully transferred into solution (B), generating an interfacial reaction between these two phases. The aniline/xylene solution forms the upper organic layer, and the APS/DBSA solution forms the lower aqueous layer. The resulted two-phase system was placed for 24 h. Then, the prepared PANI was collected by filtration and washed several times with methanol, acetone, and distilled water. Finally it was dried under vacuum at 60°C for 24 h.

Measurement

The morphology of these resulted products was measured by a scanning electron microscope (SEM,

HITACHI-S-570, on Au substrate) and a transmission electron microscope (TEM, HITACHI-600). The UV-vis spectroscopy and FTIR spectroscopy were also used to characterize the molecular structure of these resulted PANI materials. UV-vis spectra (Cary 500 Scan UV/Vis-NIR Spectrophotometer, Varian, USA) of these samples dissolved in *N,N*-dimethylformamide (DMF) medium were obtained (DMF as reference). FTIR measurements were performed using BRUKER VECTOR22 Spectrometer (in a KBr pellet).

RESULTS AND DISCUSSION

As seen in Table I, the synthetic conditions show various influences on the morphology of these resulted nano-structured DBSA-PANIs (PANI 1-6). Figure 2 shows the morphologies of the obtained DBSA-PANI products. It is found that the resulting DBSA-PANI synthesized under the condition of $[\text{An}]/[\text{APS}]$ (the molar ratio of An and APS) = 1 : 1 at room temperature is mostly rod-like shapes, and these rods are straight with almost uniform diameters in the range of 100–300 nm, and the lengths are more than 2 μm . It is found that $[\text{An}]/[\text{APS}]$ ratio has a remarkable influence on the morphology of the obtained DBSA-PANI products. When increasing the $[\text{An}]/[\text{APS}]$ ratio into 2 : 1, 4 : 1, and 10 : 1, the TEM images of corresponding samples are shown in Figure 3. It can be found in Figure 3(a) that the DBSA-PANI ($[\text{An}]/[\text{APS}] = 2 : 1$) is composed of many rods with various diameters of 100 nm to 1 μm and similar average lengths of more than 2 μm . When the $[\text{An}]/[\text{APS}]$ ratio is changed to 4 : 1, although the shape of the product is still rod-like, TEM image reveals that these rods have the nonuniform diameter ranging from 250 nm to 1 μm [as shown in Fig. 3(b)]. As the $[\text{An}]/[\text{APS}]$ ratio further increases to 10 : 1, nanoparticles with the diameter of 60–80 nm could be obtained instead of those rods [Fig. 3(c)]. The different morphology was assigned to the different reaction rate by adding different amount of APS.

The UV-vis spectra of PANI1 (curve a), PANI2 (curve b) and PANI3 (curve c) dissolved in DMF were presented in Figure 4. In those three spectra, each of them exhibits two individual bands at 331

TABLE I
Influence of Synthetic Conditions on the Morphology of those Nanostructured DBSA-PANI

Sample	[An]/[APS]	Temperature	DBSA solution	System color		Morphology	
				Organic layer	Aqueous layer	Shape	Rods diameter
PANI 1	1 : 1	Room temperature	0.2 M	Red-orange	Dark green	Rods-most, Fibers-few	100–300 nm
PANI 2	2 : 1	Room temperature	0.2 M	Red-orange	Dark green	Rods-most, Fibers-few	100 nm to 1 μm
PANI 3	4 : 1	Room temperature	0.2 M	Red-orange	Dark green	Rods-most, Fibers-few	250 nm to 1 μm
PANI 4	10 : 1	Room temperature	0.2 M	Red-orange	Dark green	Particles	–
PANI 5	1 : 1	4°C	0.2 M	Red-orange	Dark green	Rods-most, Fibers-few	40–80 nm
PANI 6	1 : 1	Room temperature	0.5 M	Dark green	Colorless transparent	Rods-few, Fibers-most	100–200 nm

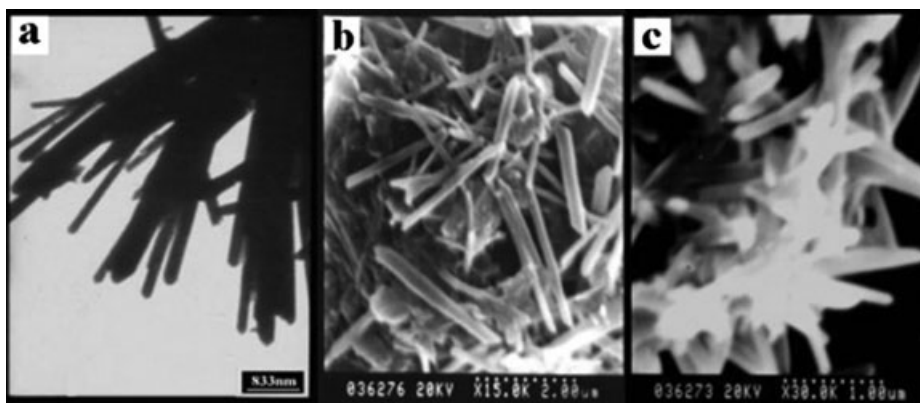


Figure 2 TEM and SEM images of PANI1: (a) TEM, (b, c) SEM.

and 630 nm (in curve a), 331 and 626 nm (in curve b), 341 and 627 nm (in curve c) respectively. It can also be observed that these UV-vis spectra of these three DBSA-PANI samples were quite similar to bulk material of PANI, suggesting that the backbone of these obtained PANI samples are almost identical.

In addition, FTIR spectra of PANI1 (curve a), PANI2 (curve b), and PANI3 (curve c) have been also obtained as shown in Figure 5. It can be found that all these IR peaks of PANI1 ([An]/[APS] = 1 : 1) can be well assigned to the vibration modes of a known PANI material, as reported early.^{25,33,34} The characteristic peaks at 1561 and 1454 cm^{-1} can be assigned to the C=C stretching vibration of quinoid ring and benzenoid ring, respectively. The peak at 3433 cm^{-1} can be assigned to the N-H stretching mode, and 1290 cm^{-1} to C-N stretching mode of N-Ph-N units. The peak at 1118 and 809 cm^{-1} are attributed to the in-plane and out-of-plane bending vibration of C-H on the 1,4-disubstituted ring, respectively. In addition, the vibration of S=O (1027 cm^{-1}), C-H in $-\text{CH}_2$ (2924 cm^{-1}) and $>\text{CH}$ in benzenoid rings of DBSA (1002 cm^{-1}) also appeared in the sample, which are in great agreement with the characteristic absorption of DBSA. Similar result can also be observed in the spectra of PANI2 and

PANI3. However, the yield of PANI ([An]/[APS] = 1 : 1) is much higher than that of other samples, so the optimum [An]/[APS] = 1 : 1 in this synthesis should be proposed.

To further explore the influence of other factors, especially reaction temperature, on the morphology of this nano-structured PANI material, the interfacial polymerization was also carried out at a lower temperature, 4°C ([DBSA] = 0.2M, [An]/[APS] = 1 : 1). In comparison with the result at room temperature, the synthesis at lower temperature shows a relatively small diameters ranging from 40 to 80 nm with the lengths of about 2 μm (Fig. 6). It can be concluded that using the lower temperature is more advantageous to decrease the diameter of DBSA-PANI nanorods in this interfacial polymerization, which was the same results as that of Kaner and coworkers.²⁶

The snapshots of these various reaction systems are shown in Figure 7, which provide a direct view to demonstrate the difference of the interfacial polymerization while the concentration of DBSA in aqueous solution is changed from 0.2 to 0.5M. It can be resulted that once the concentration of DBSA higher than 0.2M was used in the preparation, the color of the organic/aqueous phases, especially the color of the aqueous phase, would change remarkably. It can

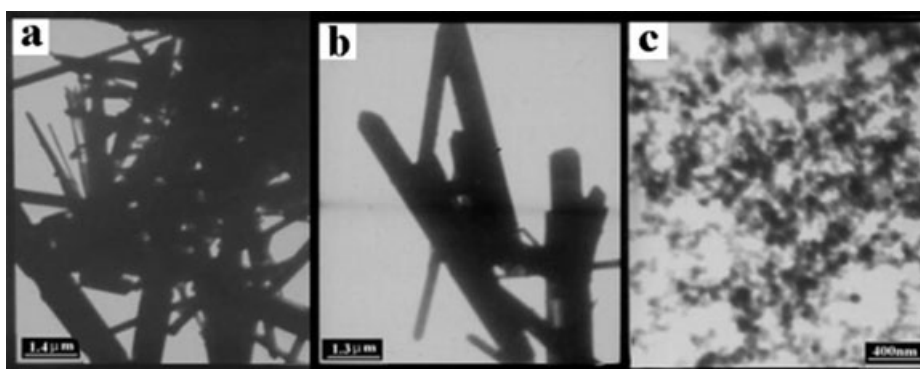


Figure 3 TEM images of (a) PANI2, (b) PANI3, and (c) PANI4 as marked in Table I.

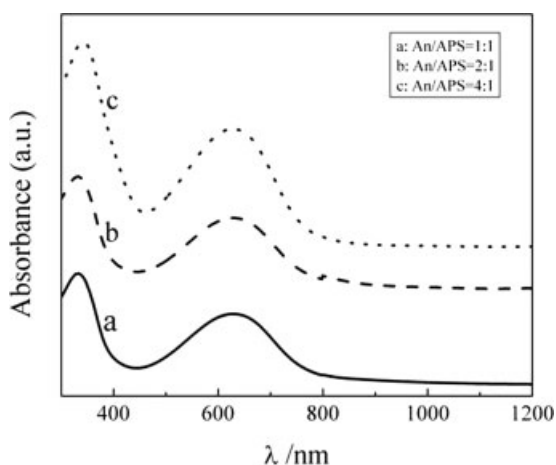


Figure 4 UV-vis spectra of (a) PANI1, (b) PANI2, and (c) PANI3 as marked in Table I.

be seen clearly that the color of the underlayer is changing from dark green [Fig. 7(a)] to transparency [Fig. 7(c-e)]. In Figure 7(b), the synthesized PANI has partially diffused into the aqueous solution.

This change in color as shown in Figure 7 can be considered as following: when the concentration of DBSA is lower than 0.2M, aniline can diffuse more easily into the aqueous solution to be reacting with APS, then the lower solution presents dark green; as [DBSA] was increasing (>0.2M), the viscosity of the solution increased gradually, which made it much difficult to diffuse into this aqueous phase, so the aqueous phase shows partly transparent [Fig. 7(b)], even completely transparent [Fig. 7(c-e)]. When the concentration of DBSA is 0.5M, the diffusion process was restricted completely. And it was found that very few nanorods [shown in Fig. 8(a) and (b)] was obtained in this case, only nanofibers with the diameters of 20–50 nm [shown in Fig. 8(c)] was predominant.

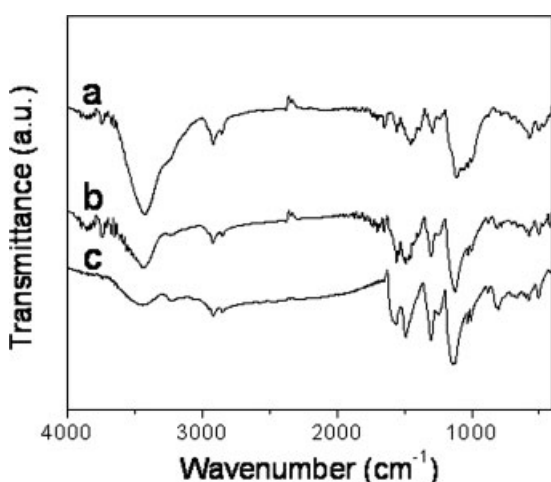


Figure 5 FTIR spectra of (a) PANI1, (b) PANI2, and (c) PANI3 as marked in Table I.

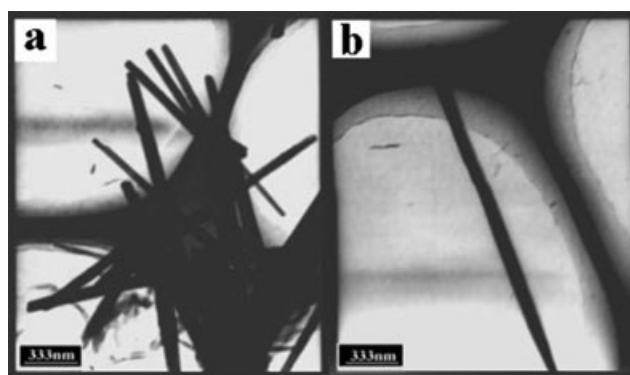


Figure 6 TEM images of PANI5 as marked in Table I: (a) high density nanorods and (b) single nanorod.

As well known, DBSA is a surfactant which consists of hydrophilic $-\text{SO}_3\text{H}$ group and a long and hydrophobic alkyl tail. When a DBSA aqueous solution with a proper concentration is exposed to the air [as shown in Fig. 9(a)], such surfactant chains at the interface outspreaded their hydrophobic alkyl tails towards the air at random. The orientation of the added aniline in the organic phase is regulated into an ordered arrangement by the hydrophobic tail group of DBSA [as shown in Fig. 9(b)] due to a strong polarization at the interface as well as the rigidity of DBSA alkyl chains. Then those aniline monomers in the upper organic solution can diffuse into the interface layer which is easily to form a white aniline-DBSA composite at the interface [as shown in Fig. 9(c)]. Finally, the aniline-DBSA composites are subsequently oxidized into the ordered and rod-like DBSA-PANI composite by APS in the lower DBSA solution (as shown in Fig. 9 days).

CONCLUSIONS

Nanorods of DBSA-PANI were synthesized through an interfacial polymerization method. Controllable diameters of DBSA-PANI nanorods from 40 nm to 1 μm could be obtained by tuning the molar ratio of aniline to APS. It was also found that the morphology, size of the nanostructures also depended on the concentration of DBSA aqueous solution as well as the reaction temperature. Lower concentration of DBSA and lower temperature will be helpful to the formation of rod-like nanostructures with a relative small diameter. UV-vis and FTIR measurements confirmed that the main chain structure of these PANI products were identical to the emeraldine salt form of PANI. And a possible mechanism of the formation of the rod-like DBSA-PANI was proposed. In summary, DBSA-PANI nanorod materials could be synthesized well by a controllable interfacial polymerization with the proper conditions.

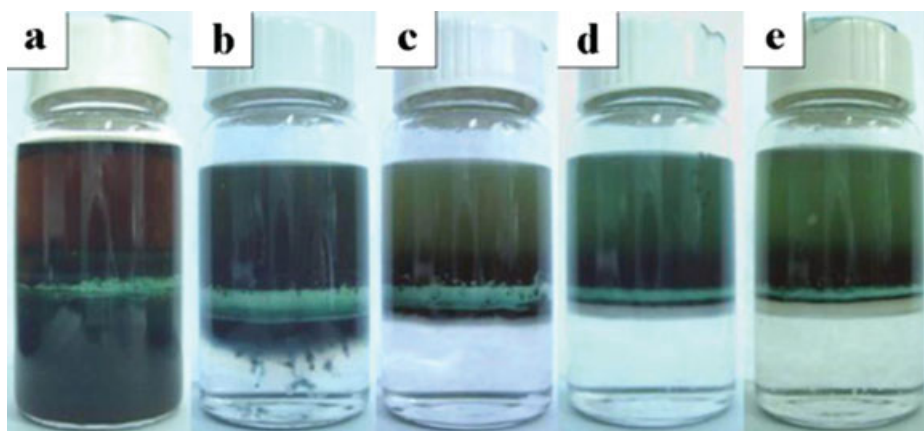


Figure 7 Snapshots of the preparations at different concentrations of DBSA: (a) [DBSA] = 0.2M, (b) [DBSA] = 0.25M, (c) [DBSA] = 0.3M, (d) [DBSA] = 0.6M, (e) [DBSA] = 0.5M. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

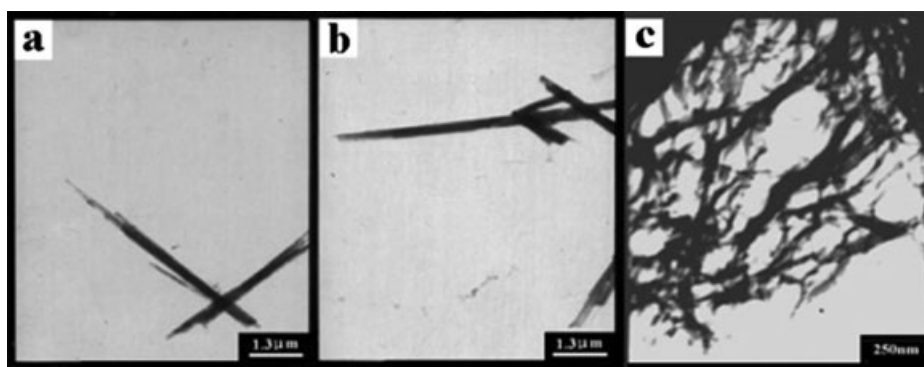


Figure 8 TEM images of PANI6 as marked in Table I: (a), (b) nanorods, and (c) nanofibers.

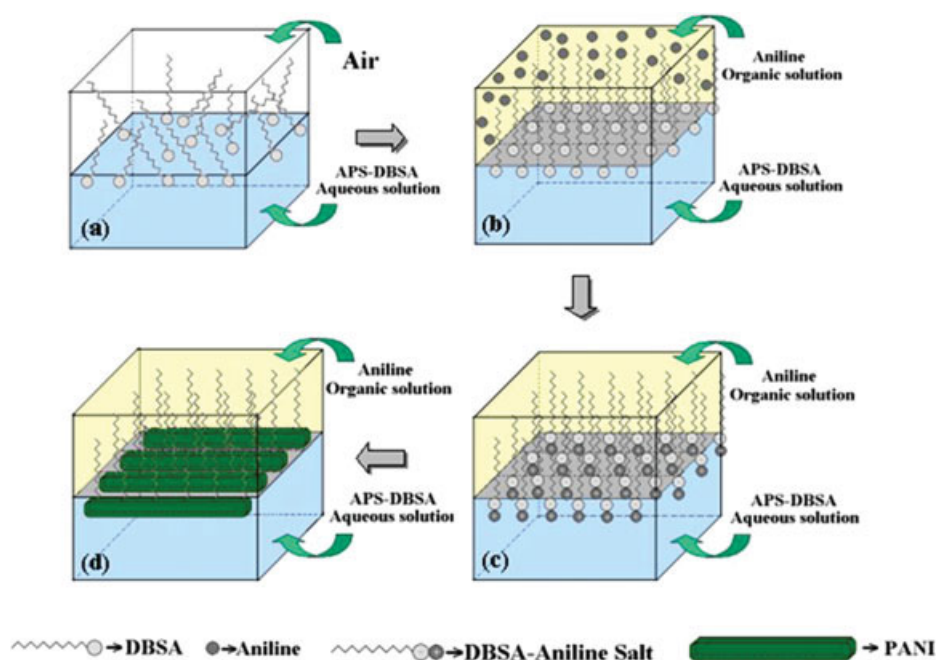


Figure 9 Scheme of the polymerization at the interface of aqueous-organic solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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