



Controlling the morphology and chiroptical properties of polyaniline nanofibers by unusual interfacial synthesis



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ABSTRACT

Several polyaniline, PANI, nanofibers, with controlled morphology and chiroptical properties were fabricated by using two developed unusual interfacial syntheses, UIS. Taking the L- and D-camphorsulfonic acid, CSA, as guiders, the first developed UIS is to prepare the bi-phase volumes in asymmetrical by setting the top phase volume/bottom phase volume, TPV/BPV, at 1/2 and 2/1 (vol%), respectively. The second developed UIS is to vary the diameter, Φ , of interfacial area at bigger, e.g. 71 mm, or smaller e.g. 52 mm, respectively. FESEM images showed that the reduction of the TPV and the increase of the interfacial area both would reduce the diameter of L/D-CSA doped PANI nanofibers. CD spectra showed that the reduction of the TPV and the increase of the interfacial area both would enhance the chiroptical properties of PANI nanofibers.

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1. Introduction

Chiroptical property is one of the particular and significant properties of natural materials and has been introduced to conducting polymers. In terms of literature, the induction of chiroptical property into polymers can be performed by using the chiral catalysis [1], asymmetric synthesis [2,3], chiral sensors [4–6], separation of enantiomers [7], molecular imprinting [8–10]. As an example, the chiral conducting polyanilines, PANI, can be prepared by doping the chiral camphorsulfonic acid, CSA [11,12]. The use of CSA to dope PANI was pioneered by Majidi et al. [11] and Havinga et al. [12]. Following the use of both L- and D-CSA, the induction of amino acids, chondroitin sulfate and cyclodextrin sulfate into PANI have been subsequently applied and reported elsewhere [13–16].

Among various CSA-doped PANI cases, Huang et al. [17] have applied the interfacial synthesis method by preparation of bi-phases, e.g. the top aqueous phase, AP, and the bottom oil phase, OP. Following this normal interfacial synthesis method [17], it was furthermore noted that some unusual interfacial syntheses were developed and reported elsewhere [18–22]. For example, Chen et al. [18] and our group [19] have respectively alternated the bi-phase places by taking the AP as the bottom phase and the OP as

the top phase to form PANI nanofibers. Our results consistently indicated that this change benefit the formation of PANI nanostructure because the OP placed at the top to be a gravity to enhance the diffusion rate for formed PANI at interface to go to the bottom AP. In other words, this change enhanced the stability of PANI nanostructure in AP. Zhang et al. [20] have varied the interface area at larger, middle and smaller, and found that the decrease of the interfacial area would limit the PANI fibre growth. Dutta et al. [21] and Lei et al. [22] have respectively developed a tri-phases interfacial synthesis method to prepare PANI by placing the AP as a sandwich between two OPs. According to Dutta et al. [21], this tri-phases interfacial synthesis can increase the sample amount because the PANI can be formed at two interfaces then stabilized in both the upper and bottom phases.

Taking all above mentioned usual [17] and unusual interfacial syntheses, UIS [18–22], into account, the aim of this work is to furthermore develop UIS then apply to prepare PANI nanofibers with controlled structure and properties. Experimentally, we employed both the L/D-CSA as two guiders, and developed two UISs. The one UIS is to vary the volume ratio of AP/OP phases asymmetrically at 2/1 and 1/2 (vol%) as Fig. 1 upper described, and another UIS is to vary the interface area at bigger and smaller as Fig. 1 bottom described, respectively. Here, the difference between the latter and the case of Zhang et al. [20] is in the use of CSA in this case.

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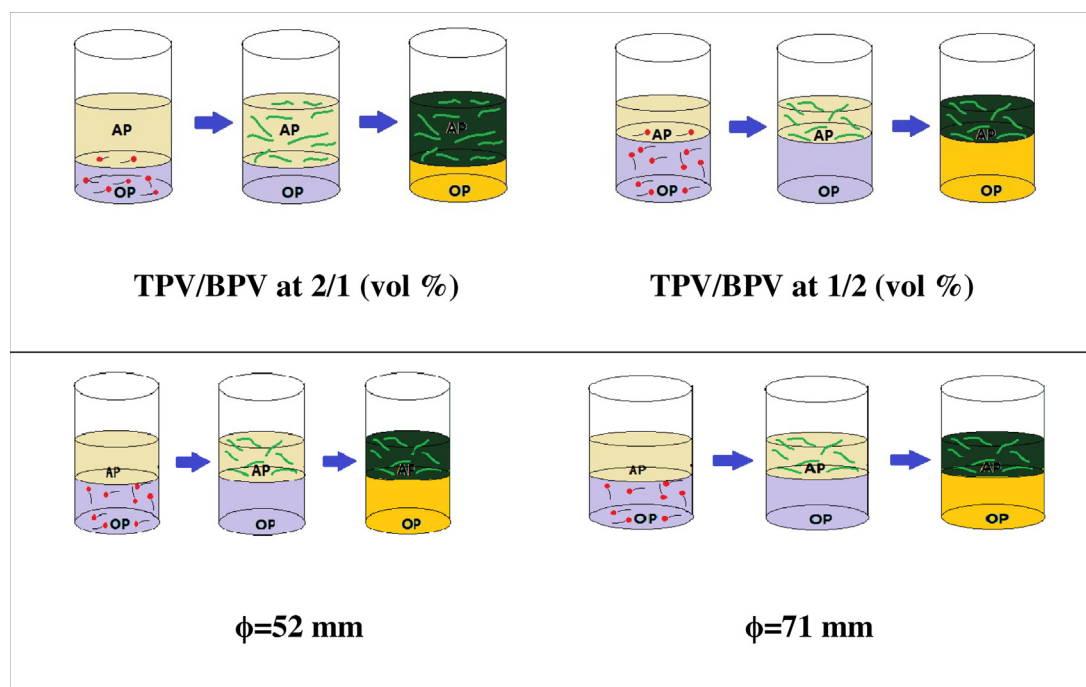


Fig. 1. Scheme on the interfacial synthesis of CSA-doped PANI with asymmetric bi-phase volumes, e.g. the top phase volume (TPV)/bottom phase volume (BPV) at 2/1 or 1/2 (vol%) (upper), and varied interfacial areas by setting the area diameter, ϕ , at 52 or 71 mm (bottom). The aqueous phase, AP, was formed by dissolving the APS and CSA in water, and the oil phase, OP, was formed by dissolving the ANI in organic solvent.

2. Materials and methods

2.1. Materials

As previous used, the aniline (99%), ammonium peroxodisulfate, APS (99%) were obtained from the Sinopharm Chemical Reagent Co., Ltd. at Shanghai, China, and used as received without further treatment [19].

The *L*- and *D*-CSA as well as the chloroform all were purchased from above mentioned store and used as received.

The laboratory made distilled water was used though the whole work.

2.2. Unusual interfacial synthesis of *L*- and *D*-CSA doped PANI with asymmetric bi-phase volumes

In this UIS case, the top phase volume, TPV, and bottom phase volume, BPV, were specially prepared by setting the TPV/BPV ratio at 1/2 and 2/1 (vol%), respectively, as Fig. 1 (upper) described using a glass beaker with a volume of 250 ml. In this case, the AP was always placed at the top and the OP was always placed at the bottom.

During the synthesis of TPV/BPV at 2/1 (vol%), the AP was prepared by dissolution of 1.09 g APS and 0.55 g CSA in 100 ml water, and the OP was prepared by dissolution of 0.45 ml ANI in 50 ml CHCl_3 .

During the synthesis of TPV/BPV at 1/2 (vol%), the AP was prepared by dissolution of 1.09 g APS and 0.55 g CSA in 50 ml water, and the OP was prepared by dissolution of 0.45 ml ANI in 100 ml CHCl_3 .

In this case, the ratio of ANI/CSA was always fixed at 1/10 for each run, and the whole synthesis was performed about 48 h at 0°C . After polymerization, the obtained PANI powder was washed by deionized water and ethanol respectively for several times until

the filtrate presented colourless then be vacuum oven dried at 60°C for 24 h.

2.3. Unusual interfacial synthesis of *L*- and *D*-CSA doped PANI with varied interface areas

This UIS was performed as Fig. 1 (bottom) described by varying the glass beaker diameter ϕ at 52 (100 ml) and 71 mm (250 ml), respectively. During this case, the top AP was prepared by dissolution of 0.456 g APS and 4.64 g CSA in 20 ml water, and the bottom OP was prepared by dissolution of 0.18 ml ANI in 20 ml CHCl_3 . The ratio of ANI/CSA was the same as above fixed at 1/10 for each run, and the whole synthesis was also the same as above for 48 h at 0°C . After polymerization, the obtained PANI powder was treated as the same as above.

2.4. Characterization

The field emission scanning electron microscopy (FESEM) images were performed by a JEOL JSM-6700-F field emission SEM microscope.

Circular dichroism (CD) spectra were recorded using a Jasco J-815 CD Spectropolarimeter and a Fast Fourier Transform to filter out high frequency noise.

3. Results and discussion

3.1. Morphology and chiroptical properties of *L/D*-CSA-doped PANI nanofibers prepared by unusual interfacial synthesis with asymmetric bi-phase volumes

The morphologies of *L/D*-CSA-doped PANI samples corresponding to the bi-phase volume asymmetrically as the TPV/BPV at 1/2 and 2/1 (vol%) were presented in Fig. 2, where the statistic charts

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