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Self-assembly growth of oriented polyaniline arrays: A morphology and structure study

Jihuai Wu*, Qunwei Tang, Qinghua Li, Jianming Lin

The Key Laboratory for Functional Materials of Fujian Higher Education, Institute of Material Physical Chemistry, Huaqiao University, Quanzhou 362021, China

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ABSTRACT

Highly ordered polyaniline (PANI) array was prepared by self-assembly method and using inorganic acids as dopants. The PANI array was characterized by scanning electron microscopy, Fourier transform infrared spectra, and X-ray diffraction, and the influence of preparation conditions on the morphology and structure of the PANI arrays is discussed. It is found that the morphology and structure of the PANI arrays strongly depend on the kinds of dopant. The resulted PANI has a emeraldine molecular structure and highly oriented arrangement.

1. Introduction

Polyaniline (PANI) is one of the most promising electrical conductive polymers due to its ease of synthesis, low cost, versatile processibility, relatively stable electrical conductivity, and can be exploited in various applications including batteries, capacitors, electrochromic windows and displays, actuators, photovoltaic cells, and light-emitting electrochemical cells [1–3]. Recently, ordered PANI has aroused widely attention since ordered PANI possesses better properties and more application than PANI does [4–10].

Template synthesis is a common and effective method for synthesizing the ordered micro-/nano-conducting polymers. However, to get pure conducting polymers, the template has to be removed after the polymerization. This is difficult in most cases, and the ordered structure of resulting materials is altered or even destroyed during recovery from the templates [11–14]. Wan et al. [15–18] developed a self-assembly technique for PANIs in the presence of organic acids with long molecular chains such as β-naphthalene sulfonic acid and azobenzenesulfonic acid as dopants. Different from the template synthesis method, the long chain acids do not need to be removed after polymerization because they are used as dopants of PANI at the same time. Compared with template synthesis, the self-assembly method is simple and inexpensive. However, the structures and shapes of PANI synthesized by self-assembly method are always random and misaligned, which limit the application for PANI [19].

In this paper, an ordered PANI array was prepared by self-assembly method using inorganic acids as dopants. The PANI arrays were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectra, and X-ray diffraction (XRD). It was found that the morphology and structure of PANI arrays depend on the aniline concentration, inorganic acids concentration and kinds.

2. Experimental

2.1. Materials

Aniline (ANI) monomer was distilled under pressure prior to use. Potassium peroxydisulfate ($K_2S_2O_8$, KPS) as a radical oxidant for PANI, was purified by recrystallization from 66 wt.% ethanol/water solution. Inorganic acids such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3) and phosphoric acid (H_3PO_4) were used as the dopants for PANI. All aqueous solutions were prepared in 18 MΩ water obtained by purification of deionized water with a Millipore Milli-Q system. All the reagents were purchased from Shanghai Chemical Reagents Co., China.

2.2. Synthesis of PANI arrays

The oriented PANI fiber was synthesized by an aqueous solution polymerization method. 1 ml ANI monomer was mixed with 125–400 ml deionized water and 16.5–200 ml HCl (or H_2SO_4, HNO_3, H_3PO_4) (1 M) aqueous solution. Under a surrounding atmosphere and stirring, the ANI solution was heated to 80 °C in a water bath, and then 2.97 g KPS was quickly added to the ANI solution. After the system was kept at 80 °C for 10 min and all the KPS was dissolved,

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* Corresponding author. Tel.: +86 595 22693899; fax: +86 595 22693999.
E-mail address: jhwu@hqu.edu.cn (J. Wu).

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the system was kept at 0 ± 3 °C for 10 h without stirring (Caution: any stir or shake is absolutely unallowed), and a green PANI was formed gradually. The product was filtrated and washed with deionized water for five times, and finally vacuum dried for 24 h to obtain dark-blue PANI arrays.

2.3. Characterizations

The PANI arrays were mounted on a metal table; their morphologies were observed and photographed by a SEM. PANI was identified by infrared spectroscopy on a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets. The X-ray powder diffraction pattern of the PANI arrays were characterized using D8 ADVANCE X-ray diffractometer of Germany BRUKER Co., Cu Kα with wavelength 0.154 nm, running at 40 kV and 40 mA, scanning from 2° to 40° at a speed of $1^\circ\ \mathrm{min}^{-1}$.

The electrical conductivity of ordered PANI array was measured on a four-probe conductivity test meter (RTS-9, China, Guangzhou). Cyclic voltammetry (CV) of PANI fiber was measured with a three-electrode electrochemical cell using a CHI660C potentiostat. Acetonitrile solution containing 0.1 M $LiClO_4$, 10 mM LiI and 1 mM I_2 was used as the supporting electrolyte. This system consisted of film samples as the working electrode with the same dimension of $1 \times 1\ \mathrm{cm}^2$, a 1.5 mm-diameter platinum foil as the counter electrode, and an Ag/AgCl as the reference electrode.

3. Results and discussions

3.1. Polymerization of ANI in acidic media

The oxidation of ANI in strong acid (HCl) solution has become a standard procedure for preparing conductive PANI [20]. The whole oxidation is an intricate interaction of oxidation and protonation processes (Figs. 1 and 2), depending on the concentration of acid and strength of oxidant, and resulting in different morphology and structure. To obtain a PANI with ordered molecular structure and high conductivity, emeraldine state is required.

When the oxidation of ANI starts in acidic conditions, the ANI molecules react with H^+ to form anilinium cations (Fig. 2) because of the weak base of ANI molecule ($pK_a = 4.6$ at 25 °C) [21]. Whereas two oxidation processes initially from ANI molecules and anilinium cations coexist. The ANI molecules and anilinium cations have different electron density distributions and, consequently, different oxidation reactivities and reaction rates. Neutral ANI molecules are easily oxidized to produce a dimer, and to further add ANI molecules to produce higher oligomers. In this case, both the ortho- and the para-coupling of ANI are possible [22], thus, the resultant PANI is not a conjugated system and nonconducting. Anilinium cations cannot be oxidized directly in the presence of KPS, because the electron pair on nitrogen, which is delocalized in neutral ANI molecules, becomes localized on the anilinium cations [21], the polymerization reaction starts from residual ANI molecules. With the proceeding of oxidation, the released protons increase the acidity. The equilibrium between the neutral ANI molecules and anilinium cations shifts in favor of the latter species (Fig. 2). Although anilinium cations are difficult to be oxidized, they are easily added to propagate the pernigraniline form PANI chains [23]. After the reduction by the residual ANI, the desired product, a green emeraldine form of PANI is thus obtained.

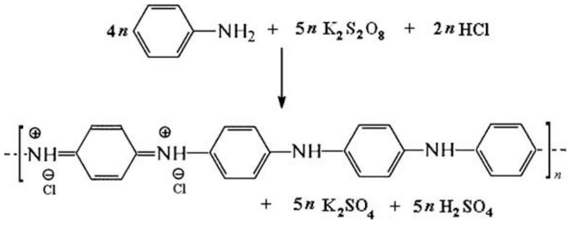

Fig. 1. Synthesis of emeraldine PANI in the presence of KPS and HCl.

On the other hand, the oxidation polymerization reaction is an exothermic reaction and the nonconducting PANI states come from neutral ANI molecules; we controlled the oxidation polymerization at 80 °C for 10 min, then at about 0 °C for 1 h; longer reaction time at lower temperature is available to decrease the reaction rate and increase the content of conducting emeraldine state.

3.2. Effect of [ANI] on morphology of PANI arrays

SEM images show the morphology of the PANI arrays prepared with different ANI concentrations ([ANI]). When the [ANI] is at a low value of 2.64×10^{-2} M (Fig. 3a,b), the resulted PANI is typically oriented rods with an average diameter of 1.5 μm and length of 12–30 μm. When the [ANI] increases to 3.48×10^{-2} M (Fig. 3c,d), PANI shows a rod with 1 μm diameter and 12 μm length, and disc-like flakes with an average diameter of 6 μm. When the [ANI] further increases to 4.13×10^{-2} M (Fig. 3e,f), the more disc-like PANI are formed, the size of PANI has approximately 500 nm thickness and 40–70 μm diameter. When the [ANI] is a high value of 7.78×10^{-2} M (Fig. 3g,h), the resulted PANI flakes are highly oriented with an individual thickness of 0.5–3 μm, width of 6–15 μm, and length of 250 μm. This result indicates that changing the [ANI] might be one way to improve the morphology of oriented PANI arrays synthesized by self-assembled method. Different PANI morphologies in different [ANI] can be attributed to different microenvironments in self-assembly process. The morphology control of PANI by [ANI] also was found by Jing et al. [24] and Xia et al. [25] in solution precipitation, rapid mixing polymerization, and interfacial polymerization.

3.3. Effect of [HCl]/[ANI] molar ratio on morphology of PANI arrays

Fig. 4 shows the SEM pictures of the PANI arrays prepared with different [HCl]/[ANI]. When [HCl]/[ANI] is 1.14 (Fig. 4a,b), the resulted product is composed of bulks, spheres (600 nm in diameter), and rods (50 nm in diameter) with an average length of 1.2 μm. When [HCl]/[ANI] is 1.50 (Fig. 4c,d) oriented PANI flake arrays start to appear, which are made up of oriented single flakes with thickness of 0.5–3 μm, width of 6–15 μm, and length of 250 μm. Once the [HCl]/[ANI] is increased to 9.09, interestingly, large number of PANI arrays with average diameter of 1.2 μm and highly ordered structure are produced (Fig. 4e,f). From above, the dosage of HCl is important factor for controlling the morphology of ordered PANI.

3.4. Effect of acids on morphology of PANI arrays

Fig. 5 shows the typical morphologies of PANI synthesized with different inorganic acids as dopants. It is found that the size and morphology of PANI strongly depend on the kind of dopant. For instance, the diameter of oriented PANI rods is approximately 1 μm and the length is 12 μm when HNO_3 is used as dopant (Fig. 5a). In the case of H_2SO_4 doped PANI (Fig. 5b), the PANI product is random with large size (>30 μm). Whereas H_3PO_4 is introduced, PANI is netlike with an interpenetrating structure (Fig. 5c). The similar conclusions were also found by Wan et al. in synthesizing PANI nanostructures with inorganic acids [18].

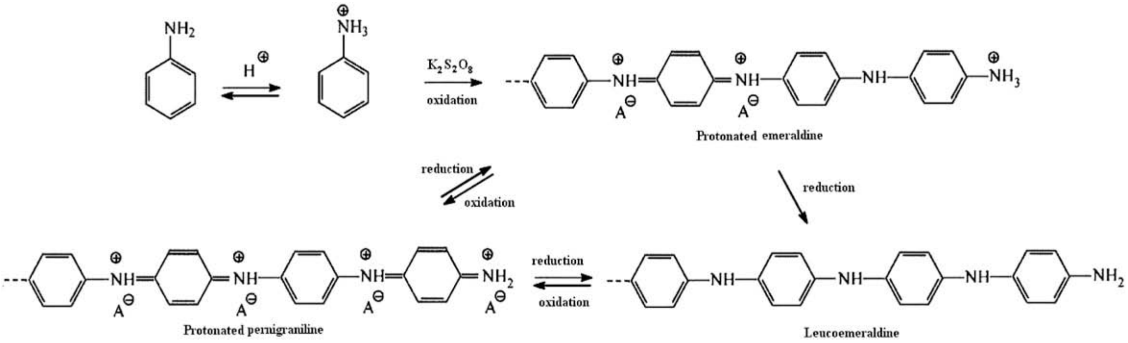

Fig. 2. Polymerization process of emeraldine and interconversions among the various intrinsic oxidation states in PANI.

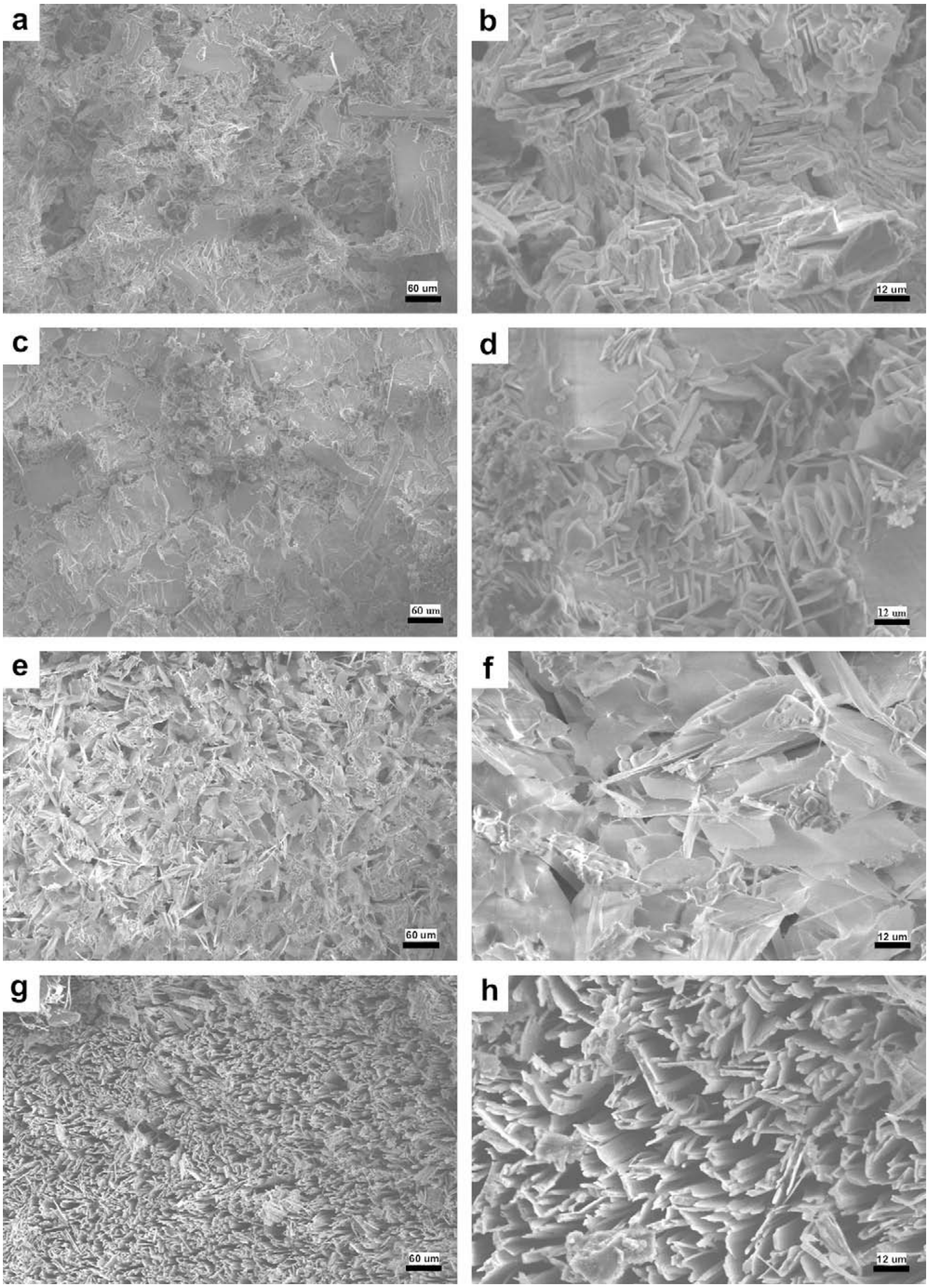

Fig. 3. SEM images of PANI prepared with different [ANI]: (a) and (b) 2.64×10^{-2} M; (c) and (d) 3.48×10^{-2} M; (e) and (f) 4.13×10^{-2} M; (g) and (h) 7.78×10^{-2} M. The 16.5 ml HCl (1 M) was desired.

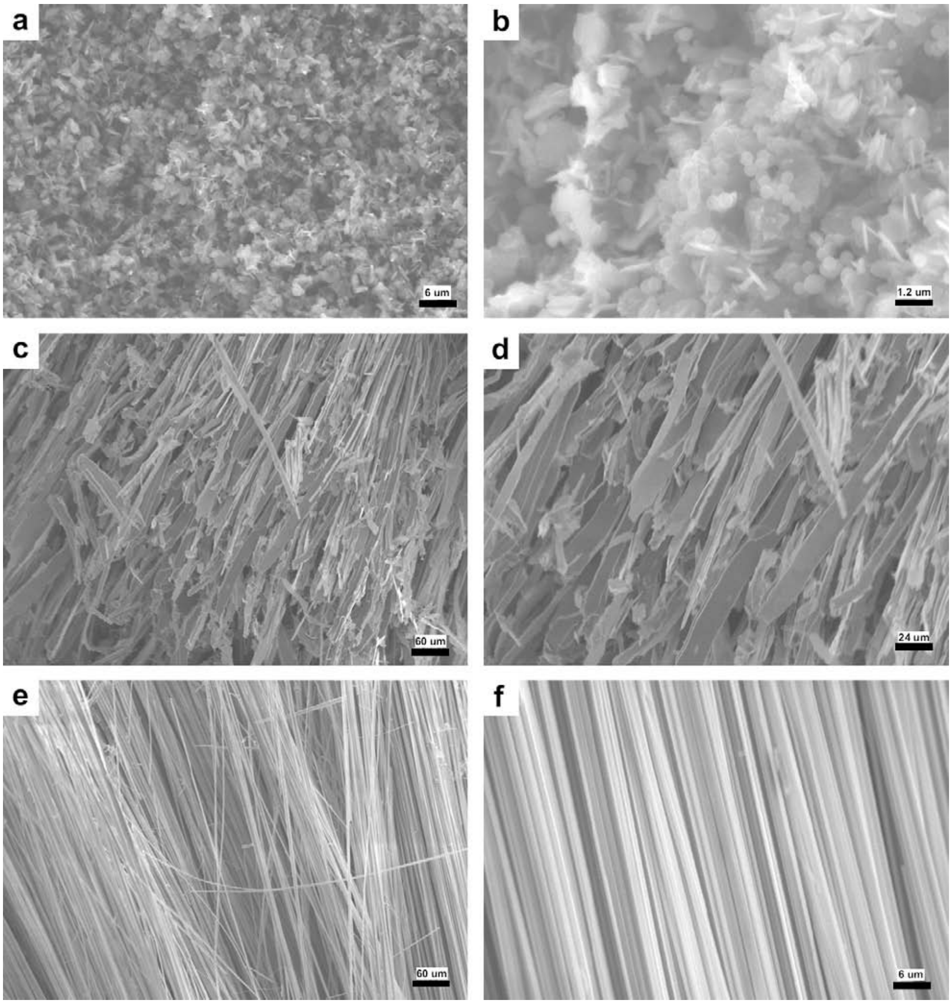

Fig. 4. SEM images of PANI synthesized with different [HCl]/[ANI]: (a) and (b) 1.14; (c) and (d) 1.50; (e) and (f) 9.09. 250 ml distilled water and HCl aqueous solution of 1 M was desired.

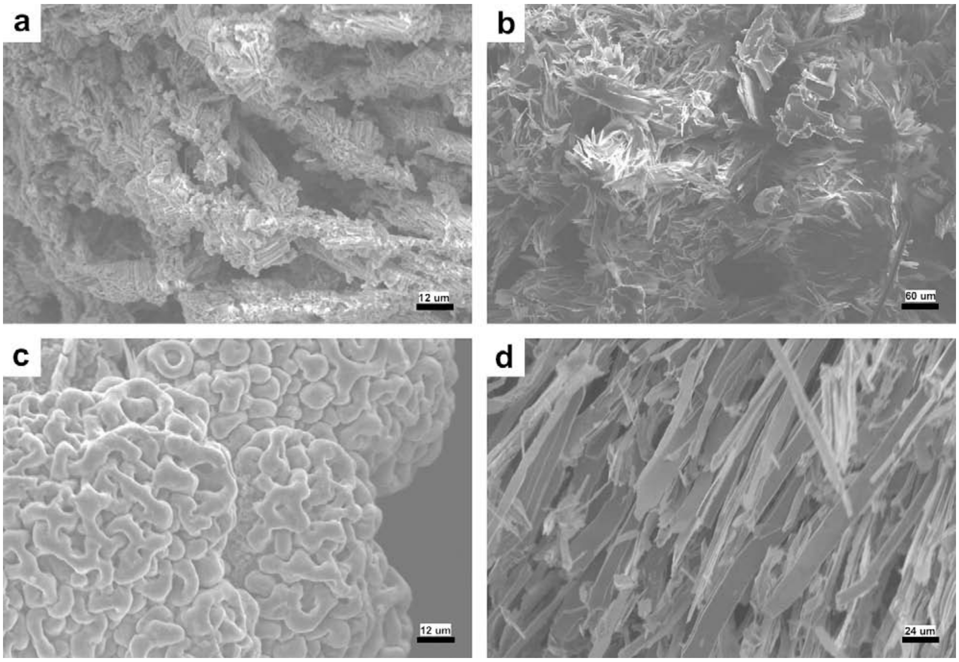

Fig. 5. SEM images of PANI prepared with different inorganic acids: (a) HNO_3; (b) H_2SO_4; (c) H_3PO_4 and (d) HCl. [Acid]/[ANI] = 1.5, [ANI] = 7.78×10^{-2} M.

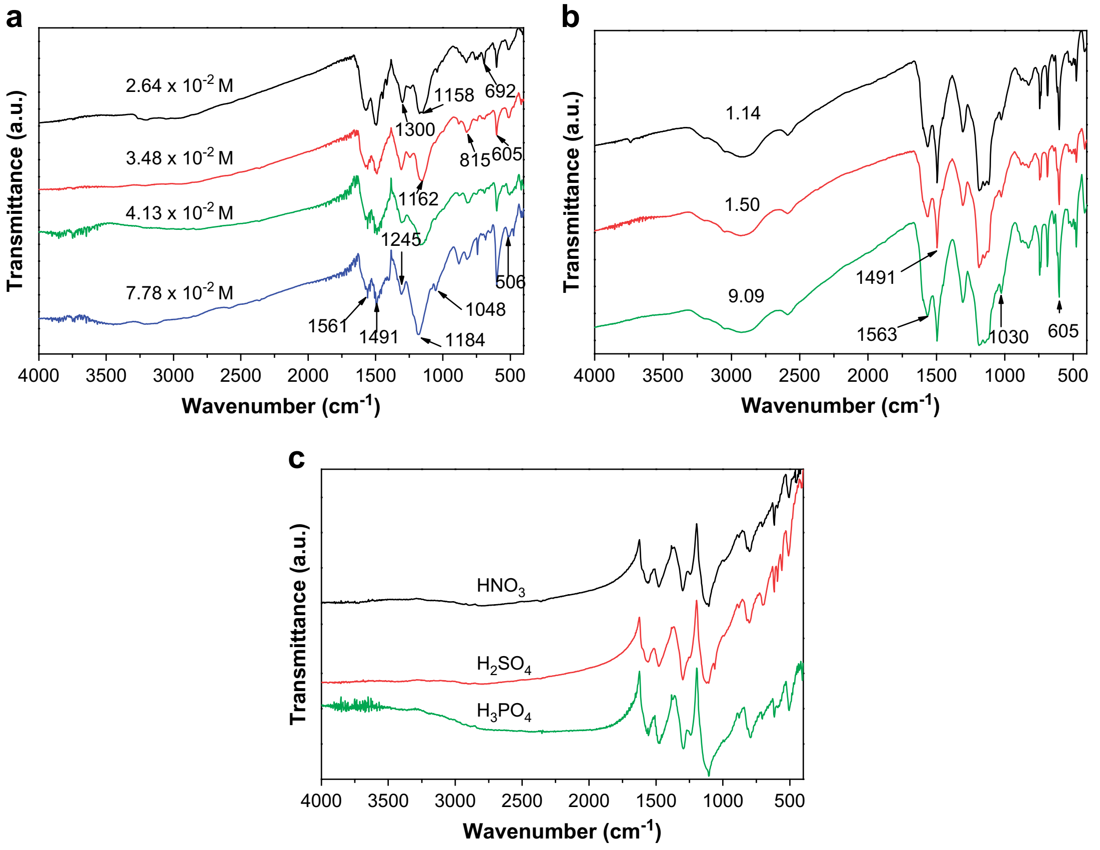

Fig. 6. FTIR spectra of PANI prepared with different [ANI] (a) (sample conditions are the same as in Fig. 3), [HCl]/[ANI] (b) (sample conditions are the same as in Fig. 4), and dopants (c) (sample conditions are the same as in Fig. 5).

3.5. *Molecular structure*

The FTIR spectra of PANI prepared with different [ANI] are shown in Fig. 6a. The characteristic bands at 1561 and 1491 cm^{-1} are attributed to C=C a stretching deformation mode of the quinoid and benzenoid rings, the 1300 cm^{-1} band is assigned to the C–N stretching of the secondary aromatic amine. The band at 1245 cm^{-1} could be interpreted as a C–N–C stretching vibration in the polaron structure. Aromatic C–H in-plane bending vibration mode is formed during protonation [26]. Bands at 1048 and 692 cm^{-1} are the results of C–H out-of-plane bending of 1,2,4-ring and C–H out-of-plane bending of 1,2-ring, respectively. Out-of-plane deformations of C–H on 1,4-disubstituted rings are located at 815 cm^{-1}, and the absorption peak at 605 cm^{-1} is caused by the excitation absorption of the quinoid ring [27]. The peaks at 800–900 cm^{-1} are the characteristic peaks of para-substitution of the aromatic ring, which indicate that the polymerization proceeds via a head-to-tail mechanism. Upon acid protonation of emeraldine base, the quinoid units are believed to be converted to benzenoid units by a proton-induced spin unpairing mechanism and without absorption band at 1380 cm^{-1}. In the case of protonated emeraldine, the long absorption tail above 2000 cm^{-1}, which masks the

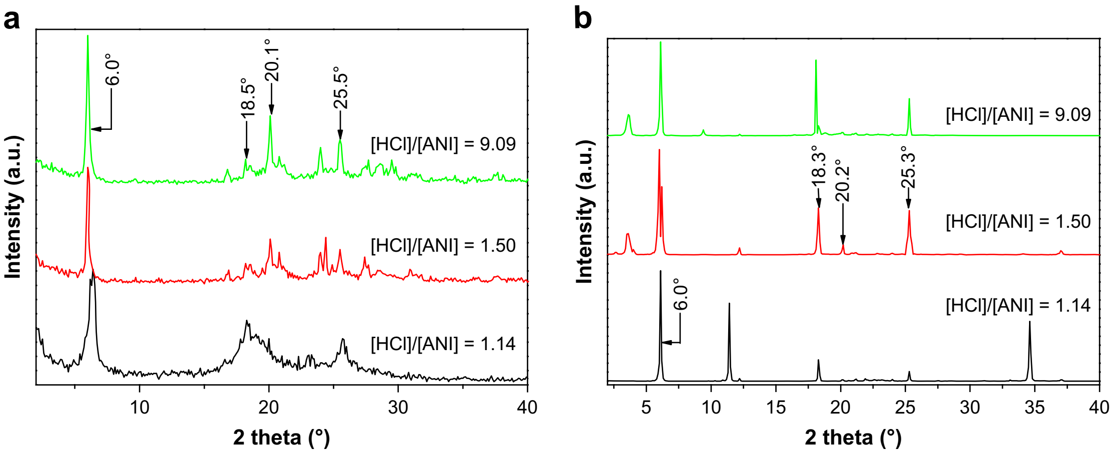

Fig. 7. XRD patterns of PANI arrays (a) and anilinium cations (b) with different [HCl]/[ANI] ratios.

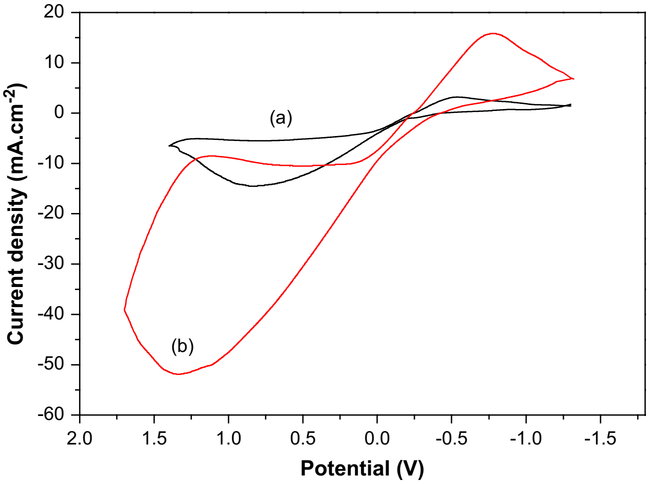

Fig. 8. CV curves of traditional PANI powders (a), and the oriented PANI fibers (b).

N–H stretching vibration in the 3100–3500 cm^{-1} region, and the appearance of the intense broad band at about 1160 cm^{-1}, have been associated with high electrical conductivity and a high degree of electron delocalization in PANI [28,29]. These characteristic peaks are identical to those of PANI particles prepared by common method [26]. The results indicate that the backbone structures of PANI arrays obtained by us are identical to the PANI particles synthesized using traditional method. The shifts of the vibration bands (shifts from 1590 to 1561 cm^{-1} and from 1502 to 1491 cm^{-1} for stretching deformation of quinoid) [30] of the oriented PANI indicates a longer effective conjugation length.

FTIR spectra of PANI prepared with different [HCl]/[ANI] are shown in Fig. 6b. The presence of the peaks at 1563 and 1491 cm^{-1} is a common feature of the all PANI products. Interestingly, the peak intensities at 1030 and 605 cm^{-1} change with different [HCl]/[ANI] ratios in the feed, the different peak intensities maybe coming from the different conjugated quinoid rings due to [HCl]/[ANI] ratio, which indicates that all the samples are doped by HCl [31]. Fig. 6c shows the FTIR spectra of HNO_3, H_2SO_4, H_3PO_4 doped PANI prepared by self-assembly method. It is found that the FTIR spectra of these three PANI are similar, and identical with other inorganic and organic acids doped PANI products exclusive of the absorption bands of dopants [16,18,25,31].

The XRD patterns of oriented PANI arrays at different [HCl]/[ANI] ratios are shown in Fig. 7a. The XRD patterns of the oriented PANI arrays show four typical diffraction peaks at $2\theta = 6.0, 18.5, 20.1$, and $25.5°$ (d-spacing = 14.71, 4.79, 4.41, and 3.49 Å, respectively). The peak centered at $2\theta = 20.1°$ is ascribed to periodicity parallel to the polymer chain, while the peak at $2\theta = 25.5°$ is caused by the periodicity perpendicular to the polymer chain [32]. The three peaks at 18.5, 20.1 and 25.5° are generally observed in conventionally synthesized PANI products, but the peak at around $2\theta = 6.0°$ is only observed for highly ordered PANI in which PANI chain distance increases by effective interdigitations of dopant molecules [33]. The increase in the peak intensity ($2\theta = 6.0°$) indicates that the HCl doped PANI ordering in the molecular chains increases with increase in the micron-sized fibers length [31].

Concerning the formation mechanism of PANI, the XRD patterns of the anilinium cation salts precipitated at [HCl]/[ANI] = 1.14, 1.50, and 9.09 are shown in Fig. 7b. The anilinium cation salts are crystals and their sharp peaks at $2\theta = 6.0, 18.3, 20.2$ and $25.3°$ are observed, which are all the characteristic peaks of the anilinium cation salts [17]. The sharp peaks mentioned above still remained in the resulted oriented PANI arrays. This further confirms that the anilinium cations might act as the template in the formation of PANI arrays.

3.5.1. Electrical property

The conductivity of the oriented PANI array was measured by a typical four-probe method as 1.79 S cm^{-1}. The conductivity value is of the same order as that of other PANI fibers by other methods. The cyclic voltammetry (CV) curves of the oriented PANI array were measured and are shown in Fig. 8. Compared with traditional PANI powders, the oriented PANI array has higher redox current density, which reveals a remarkable electrochemical catalysis activity for the PANI array.

4. Conclusions

Highly oriented PANI array was synthesized by a self-assembly method in the presence of inorganic acids as dopants. Controllable shapes and sizes of PANI products can be obtained by changing the [ANI], [H$^+$]/[ANI] ratio and dopant kinds. The resulted PANI products are characterized by SEM, FTIR and XRD; it is found that the main chain structures of PANI arrays are identical to those of the emeraldine salt by traditional methods, which is expected to show unique electrical and electrochemical properties.

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References

[1] Lu W, Fadeev AG, Qi BH, Smela E, Mattes BR, Ding J, et al. Science 2002;297:983–7.
[2] Kim BJ, Oh SG, Han MG, Im SS. Langmuir 2000;16(14):5841–5.
[3] Kaul PB, Day KA, Abramson AR. J Appl Phys 2007;101(8):83507–13.
[4] Zhu Y, Li J, Wan M, Jiang L. Polymer 2008;49(16):3419–23.
[5] Yang C, Huang L, Chi Y, Lin W, Liu F, Wang T. Polymer 2007;48(11):3237–47.
[6] Li G, Zhang Z. Macromolecules 2004;37(8):2683–5.
[7] Huang J, Kaner RB. J Am Chem Soc 2004;126(3):851–5.
[8] Sudha JD, Sasikala TS. Polymer 2007;48(1):338–47.
[9] Wu T, Lin Y. Polymer 2006;47(10):3576–82.
[10] Li G, Pang S, Xie G, Wang Z, Peng H, Zhang Z. Polymer 2006;47(4):1456–9.
[11] Wu CG, Bein T. Science 1994;264:1757–9.
[12] Cepak VM, Martin CR. Chem Mater 1999;11(5):1363–7.
[13] Skotheim TA, Elsenbaumer RL, Reynolds JR. Handbook of conducting polymers. 2nd ed.. New York: Marcel Dekker; 1997. p. 423–35.
[14] Zhang XY, Manohar SK. Chem Commun 2004;4(20):2360–1.
[15] Huang J, Wan MX. J Polym Sci A Polym Chem 1999;37(2):151–7.
[16] Huang K, Wan MX. Chem Mater 2002;14(8):3486–92.
[17] Wei ZX, Zhang ZM, Wan MX. Langmuir 2002;18(3):917–21.
[18] Zhang ZM, Wei ZX, Wan MX. Macromolecules 2002;35(15):5937–42.
[19] Liang L, Liu J, Windisch C, Exarhos G, Lin Y. Angew Chem Int Ed 2002;41(19):3665–8.
[20] Stejskal J, Sapurina I, Trchova M, Konyushenko EN, Holler P. Polymer 2006;47(25):8253–62.
[21] Cram DJ, Hammond GS. Organic chemistry. New York: McGraw Hill; 1964. p. 210–1.
[22] Zimmermann A, Kunzelmann U, Dunsch L. Synth Met 1998;93(1):17–25.
[23] Madathil R, Ponrathman S, Byrne HJ. Polymer 2004;45(16):5465–71.
[24] Wang YY, Jing XL. J Phys Chem B 2008;112(4):1157–62.
[25] Xia HB, Narayanan J, Cheng DM, Xiao CY, Liu XY, Chan HSO. J Phys Chem B 2005;109(26):12677–84.
[26] Kang ET, Neoh KG, Tan KL. Prog Polym Sci 1998;23(2):277–324.
[27] Xia HB, Chan HSO, Xiao CY, Cheng DM. Nanotechnology 2004;15(12):1807–11.
[28] Tang J, Jing X, Wang B, Wang F. Synth Met 1988;24(3):231–8.
[29] Lu FL, Wudl F, Nowak M, Heeger AJ. J Am Chem Soc 1986;108(26):8311–3.
[30] Wang Y, Rubner MF. Synth Met 1992;47(3):255–66.
[31] Anilkumar P, Jayakannan M. Langmuir 2006;22(13):5952–7.
[32] Li W, Zhu M, Zhang Q, Chen D. Appl Phys Lett 2006;89(10):103110–2.
[33] Liu J, Wan MX. J Mater Chem 2001;11(2):404–7.