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MESOSTRUCTURED MATERIALS

Synthesis and characterization of wormhole-like mesostructured polyaniline

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Abstract Wormhole-like mesostructured polyaniline (PANi) has been synthesized by using sodium dodecyl benzene sulfonate (SDBS) as a structure directing agent and iron trichloride ($FeCl_3 \cdot 6H_2O$) or ammonium persulfatee (APS, $(NH_4)_2S_2O_8$) as an oxidant in an acidic solution. The formation mechanism and structure of polyaniline was studied by powder X-ray diffraction, transmission electron microscopy and FT-IR spectroscopy. It was indicated that aniline (AN)/SDBS would form lamellar structure in an acidic solution, then after introducing oxidant, the wormhole like mesostructures would be formed. The reaction conditions, such as oxidant, oxidant/AN molar ratio, HCl/AN molar ratio, and the reaction temperature had influence on the formation of mesostructures.

Introduction

Due to its wide range of conductivity from insulating to metallic regime, unique redox tunability, good environmental stability, low cost, ease of synthesis, and promising applications in various fields, polyaniline has attracted more and more attention as one of the organic conductive polymers since it was first discovered by Letheby in 1862. Polyaniline with different substituting groups or doping proton acid on its chain, different structure and appearance can expand its application and properties. In recent years, nanostructured polyaniline had received special attention because of its potential application and novel constitutive properties [1–5]. Nanostructured polyaniline, such as nanotubes, nanofibers, etc., can be prepared by chemical or electrochemical oxidative polymerization of aniline monomers [6, 7] in the presence of soft-templates, e.g., surfactants, polyelectrolyte, or hard-templates, e.g., anodic aluminum oxide (AAO). Li [8] also reported the nanostructured PANi synthesized without template and surfactant.

Porous polymer materials had become active materials because of its novel properties in recent years. The porous polymers were mainly focused on poly-furfuryl alcohol or phenol–formaldehyde resin by template method [9, 10]. Recently, porous PANi was also synthesized by some approaches. Wang [11] synthesized macroporous polyaniline inverse opals by using an ordered colloidal assemblies of polyethylene (PS) as template. Vinu [12] reported the synthesis of novel hexagonally ordered nitrogen-doped mesoporous carbon with polyaniline as precursor and SBA-15 as the hard template. Yu [13] reported that an ordered honeycomb structure of 4-dodecylbenzenesulfonic acid (DBSA)-doped polyaniline (PANI) was fabricated in a humid atmosphere. The PANi-DBSA chloroform solution was coated on the hydrophilically treated substrates and then self-assembled honeycomb patterned films. Qin [14] reported that ordered mesoporous polyaniline film had been fabricated by electrodepositing from the hexagonal lyotropic liquid crystalline (LCC). Nandi [15] reported that a new method to synthesize nanostructured polyaniline by using the self-assembly of a mixture of an anionic surfactant sodium dodecylsulfate (SDS) and a non-ionic surfactant, Brij 35 ($C_{12}H_{25}$–$(OC_2H_4)_{23}$–OH) as the structure directing agents (SDA). The in situ polymerization of aniline was carried out at 277–278 K in the presence of SDS with ammonium persulfate as the oxidant. As we

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know, the formation mechanism and the influence of the reaction conditions on the mesostructure were not studied systematically till now. In this article, the wormhole-like polyaniline was prepared by the chemical oxidization with anionic surfactant, sodium dodecyl benzene sulfonate (SDBS) as the structure directing agents. The formation mechanism and the influence of the reaction conditions on mesostructure were systematically characterized by power XRD, TEM and FT-IR.

Experiment

Chemicals

Sodium dodecyl benzene sulfonate (SDBS), ammonium persulfate (APS), and aniline (AN) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. Ferric trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was bought from Shanghai Sinopharm Chemical Reagent Co. Ltd. All the agents were analytical grade and used without further purification.

Preparation

Synthesis of the wormhole-like polyaniline

The wormhole-like polyaniline was prepared by chemical oxidation with two different oxidants by using SDBS as the structure directing agent. In a typical synthesis, 48.0 g of dilute aqueous solution of HCl (4.08% wt) and 1.13 g of SDBS were added to a flask. After stirring for half an hour till SDBS dissolved completely, 1.00 g of aniline was added to the above solution and stirred for 1 h to form a white precipitate. This white precipitate denoted as AN–SDBS–HCl can be filtrated. For polymerization, $FeCl_3 \cdot 6H_2O$ or $(NH_4)_2S_2O_8$ was used as the initiator for the polymerization of aniline and the initiator aqueous solution was added to the above suspended mixture drop by drop and stirred for 24 h, then the green product was filtrated and washed with a great deal of water for many times till the filtrate was neutral, and finally dried at room temperature for 24–48 h under vacuum. When $FeCl_3 \cdot 6H_2O$ was used as the initiator, the product was denoted as PANi–SDBS–HCl–$FeCl_3$ (PSHF). When $(NH_4)_2S_2O_8$ was used as the initiator, the product was denoted as PANi–SDBS–HCl–APS (PSHA). The samples washing with ethanol were denoted as PSHF–ethanol or PSHA–ethanol. The mole ratio of the constituents in the reaction mixture was SDBS:HCl:AN:$FeCl_3 \cdot 6H_2O$ (APS):H_2O=0.25:5.00:1.00:1.82 (0.90):272.

Characterization of the wormhole-like mesostructured polyaniline

X-ray diffraction patterns of all the samples were recorded on a Rigaku D/max-2550VB/PC X-ray diffractometer with Ni filter and Cu Kα radiation at 40 kV and 30 mA. FT-IR spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer. Before measurements, the solid samples were mixed with KBr and performed to pellet, the fluid samples was coated on the KBr disc.

Results and discussions

In our study, when aniline monomer was added to the acidic SDBS solution, the white precipitate was formed immediately, so the macromolecular composite salts may be formed between the dodecyl benzene sulfonate anion and the protonated aniline. When the composite salt was washed with ethanol, the precipitate was dissolved in ethanol and formed a transparent solution. The different oxidants were added to this white precipitated, suspended mixture to form the wormhole-like mesostructures. The formation mechanism and the influence of oxidation potential on the mesostructure of resulted polyaniline were studied. Then, the effect of other reaction factors on mesostructured polyaniline were systematically studied with two different oxidants.

The influence of oxidants on the mesostructure of PSH

Powder XRD and TEM

Figure 1 shows the low angle XRD patterns of the different samples with $FeCl_3$ or $(NH_4)_2S_2O_8$ as the oxidant. Two peaks are observed from the XRD pattern (Fig. 1a) of sample ASH, a composite salt formed by dodecyl benzene sulfonate anion and protonation aniline, which were centered at $2\theta = 3.6°$ and 6.1°, respectively, the corresponding interplanar spacing d value were 2.4 and 1.4 nm, respectively. The strong peak centered at $2\theta = 3.6°$ showed ordered lamellar mesostructure for the composite salts. TEM image further confirmed this lamellar structure (Fig. 2a). The peak centered at $2\theta = 6.1°$ had been assigned to the periodic distance between the dopant and N atom of aniline [16]. The lamellar mesostructure of ASH was illustrated in Scheme 1. The d value (2.4 nm) of the reflection peak of ASH is smaller than the estimated basal spacing (>2.7 nm) [17], which can be due to the overlap between the dodecyl benzene sulfonate anion and the static interaction of the dodecyl benzene sulfonate anion and protonated aniline.

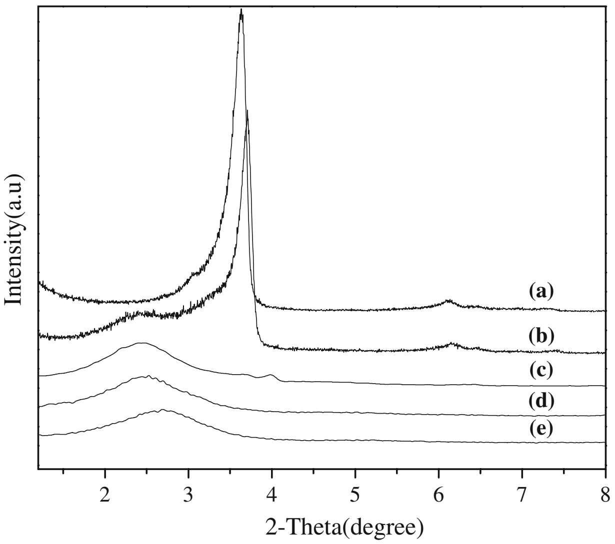


Fig. 1 Low angle XRD patterns of samples with $FeCl_3$ and $(NH_4)_2S_2O_8$ as oxidants. (a) ASH; (b) PSHF; (c) PSHF–ethanol; (d) PSHA; (e) PSHA–ethanol

When $FeCl_3$ was used as the oxidant to polymerize the composite salt, a broad diffraction peak cantered at $2\theta = 2.3°$ appeared from the XRD pattern (Fig. 1b), and the strong diffraction peak centered at $2\theta = 3.6°$ was still existed in sample PSHF, polyaniline without washing with ethanol. After washing with ethanol, the strong diffraction peak centered at $2\theta = 3.6°$ disappeared and only the broad peak centered at $2\theta = 2.3°$ existed from the XRD pattern (Fig. 1c). As we known that the composite salt can be dissolved completely in ethanol, so the mixture of the composite salt and mesostructured material co-existed in PSHF before washing with ethanol; while only the mesostructured material was obtained after washing with ethanol. So in the case that $FeCl_3$ was used as the oxidant, aniline cannot be polymerized totally. When $(NH_4)_2S_2O_8$ was used as the oxidant to polymerize the composite salt, the XRD patterns in Fig. 1d and e show that only one broad peak centered at $2\theta = 2.3°$ existed before and after washing with ethanol, indicating the total polymerization of aniline with $(NH_4)_2S_2O_8$. The polymerization of aniline made the peak shift to low angle and the *d* value increase, and the rigidity and linearity destroyed the lamellar mesostructure and made the peak broaden. From the TEM image in Fig. 2b, we can obviously find mixed phase in sample PSHF. Combined the XRD pattern in Fig. 1b, the blank area is the lamellar mesostructure of composite salts, ASH and the light-colored area was the wormhole-like mesostructure of polyaniline. The sample PSHA–ethanol showed disordered wormlike-like mesostructure from TEM image (Fig. 2c). The different phenomenon would come from the different oxidant ability. The oxidation potential of $FeCl_3$ and $(NH_4)_2S_2O_8$ were $E\Theta\ (Fe^{3+}/Fe^{2+}) = 0.771$ V and $E\Theta\ (S_2O_8{}^{2-}/S_2O_4{}^{2-})$=2.010 V, respectively. Therefore, when $FeCl_3$ was used as the oxidant, the product contained two components, which were composite salts with lamellar structure and polyaniline with wormhole-like mesostructure because of its weak oxidation. $(NH_4)_2S_2O_8$ (APS) has high oxidation ability, so all aniline monomers took part in polymerization and the product was mainly disordered wormhole-like polyaniline because of the rigidity and linearity of polyaniline, which destroyed the lamellar structure. Table 1 showed the weight loss of all samples before and after washing with ethanol, which confirmed our analysis.

The wide angle XRD patterns of samples polymerized with $FeCl_3$ and $(NH_4)_2S_2O_8$ as the oxidant were shown in Fig. 3. The XRD patterns of sample ASH (Fig. 3a) showed many sharp peaks, indicating the composite salt had higher crystallinity. When $FeCl_3$ was used as the oxidant, the XRD pattern of sample PSHF (Fig. 3b) was almost the

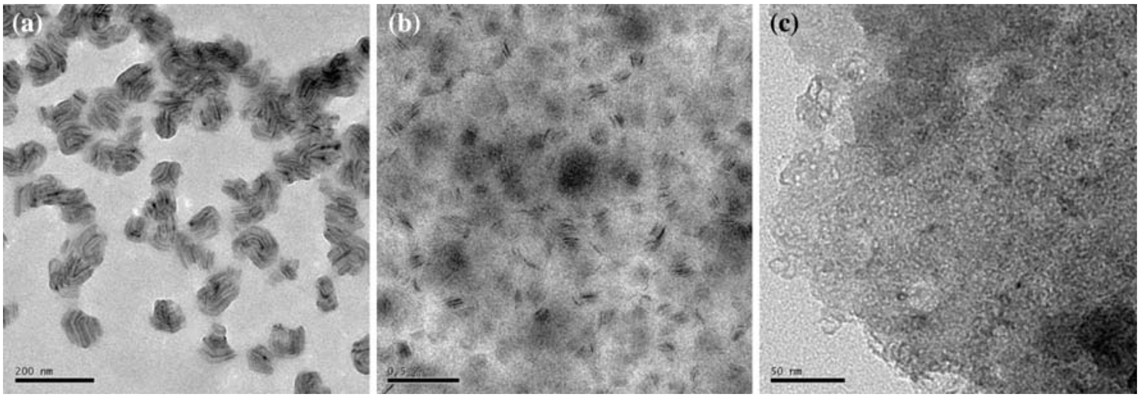
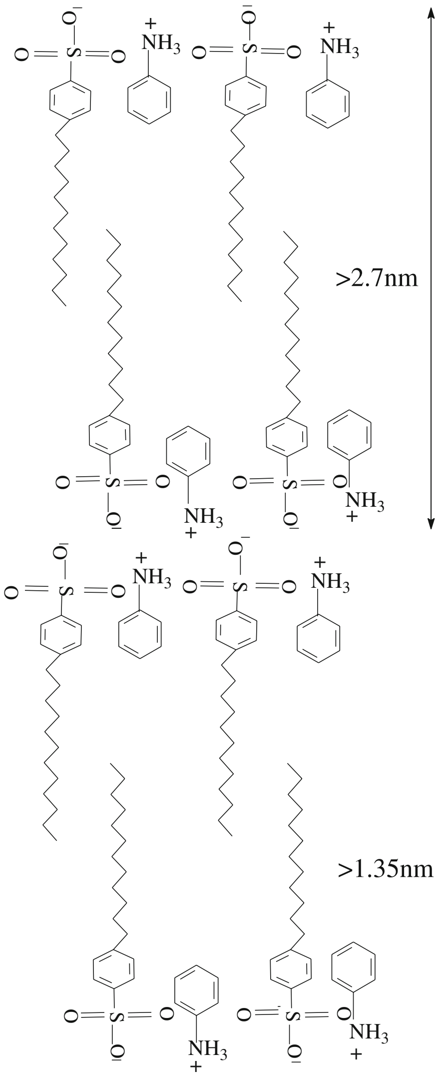


Fig. 2 TEM images of different samples. **a** ASH dispersed with water; **b** PSHF dispersed with water; and **c** PSHA–ethanol dispersed with ethanol



Scheme 1 Schematic illustrations of the lamellar mesostructure of ASH

Table 1 The mass loss of different samples before and after washing with ethanol

Sample	The mass loss (%)
AN–SDBS–HCl	100%
PANi–SDBS–HCl–FeCl$_3$	68.9%
PANi–SDBS–HCl–APS	9.5%

same with the XRD pattern of sample ASH. After washing PSHF with ethanol, the two broad peaks centered at $2\theta = 20°$ and $2\theta = 25°$ still existed, while other sharp peaks disappeared, indicating the sharp peaks were attributed to the composite salt, ASH. When $(NH_4)_2S_2O_8$ was used as the oxidant, the XRD pattern in Fig. 2d and e showed two broad peaks which also centered at about $2\theta = 20°$ and $2\theta = 25°$ for sample PSHA before and after washing with ethanol. The peaks centered at $2\theta = 20°$ and $2\theta = 25°$ had been ascribed to the periodicity parallel and perpendicular to the polymer chains of PANI, respectively [18]. From all these results, we can know that the product contained two components which were composite salts with higher crystallinity and polyaniline with weaker crystallinity when FeCl$_3$ as oxidant, the product was mainly polyaniline when $(NH_4)_2S_2O_8$ as oxidant. These results agree with the results of low angle XRD.

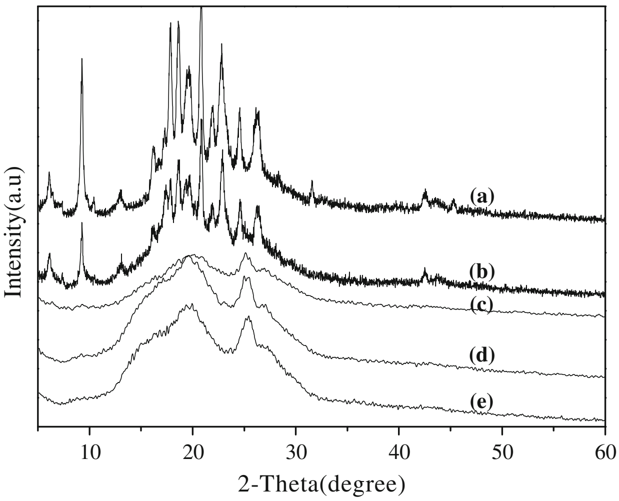


Fig. 3 Wide angle XRD patterns of samples with FeCl$_3$ and $(NH_4)_2S_2O_8$ as oxidant. (a) ASH; (b) PSHF; (c) PSHF–ethanol; (d) PSHA; (e) PSHA–ethanol

FT-IR spectra

Figure 4A shows the FT-IR spectrum of AN, SDBS, and composite salt. For the composite salt, the adsorption peak at 743.4 cm^{-1} was due to the characteristic peaks of adjacent five hydrogen atom of aniline, and the peaks centered at 2924.1 cm^{-1} and 2853.2 cm^{-1} were attributed to the symmetry and asymmetry stretching vibration of methyl and methylene of SDBS, which indicated that the compound salt was composed of SDBS and aniline.

Figure 4B shows the FT-IR spectra of different samples with FeCl$_3$ and $(NH_4)_2S_2O_8$ as the oxidant. The two peaks at 1042.6 cm^{-1} and 1011.5 cm^{-1} were due to the asymmetric stretching of $SO_3{}^{-}$. The C=C stretching vibration of the quinoid and benzenoid rings centered at 1557.5 cm^{-1} and 1480.0 cm^{-1}, respectively. The adsorption peak at 1291.6 cm^{-1} was due to the C–N stretching vibration of quinoid and benzenoid rings. The characteristic bands at 1102.8 cm^{-1} was due to the stretching vibration of N=Q=N (Q represents the quinoid ring) and the aromatic C–H in-plane bending. The head-to-tail coupling of the monomer which produced linear polymeric chains was indicated by the peak at 793.1 cm^{-1}. All these of characteristic peaks were in good agreement with the emeraldine salt form of PANI [19–21]. There FT-IR spectra were identical to these

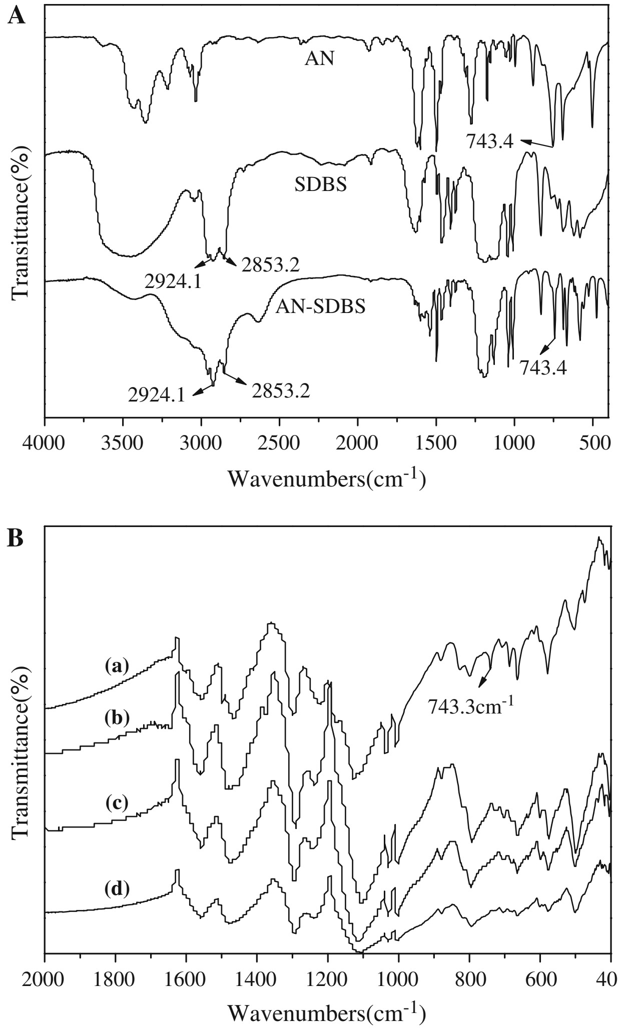


Fig. 4 FT-IR spectra of different samples. (a) PSHF; (b) PSHF–ethanol; (c) PSHA; (d) PSHA–ethanol

samples and were mainly the characteristic adsorption peaks of emeraldine salt form of SDBS–HCl co-doped PANI. Only sample PSHF had the adsorption peak at 743.3 cm^{-1} which was due to the adjacent five hydrogen atom of aniline, so we can conclude that the sample PSHF contains part of aniline which did not take part in the polymerization reaction. The results agree with the above discussion of XRD patterns.

Mechanism of the formation of mesostructured polyaniline

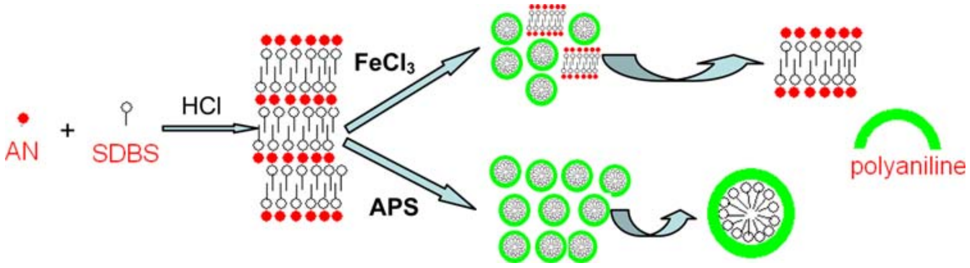
From above discussion, the possible mechanism was illustrated in Scheme 2. The dodecyl benzene sulfonate anion and protonated aniline formed the macromolecular composite salts with lamellar structure. When $FeCl_3$ was used as the oxidant, the product contained two components, which were composite salts with lamellar structure and polyaniline with wormhole-like mesostructure because of its weak oxidation. $(NH_4)_2S_2O_8$ (APS) had high oxidation ability, so all aniline monomers took part in the polymerization reaction and the product was mainly disordered wormhole-like polyaniline because of the rigidity and linearity of polyaniline, which destroyed the lamellar structure.

Influence of the reaction conditions on the mesostructure

When $FeCl_3$ was used as the oxidant, the influence of the reaction temperature on the composition and mesostructure was studied and the XRD patterns were shown in Fig. 5. When the reaction temperature increased from 35 °C to 50 °C, one broad peak centered at about $2\theta = 2.7°$ and one small peak centered at $2\theta = 6.4°$ appeared and the sharp diffraction peak centered at $2\theta = 3.6°$ disappeared. When the reaction temperature increased further, the outline of the XRD pattern kept the same. Higher temperature can increase the performance of oxidation and make more aniline to take part in polymerization, therefore, the XRD patterns of composite salts ASH weaken and even disappear. In another hand, the increase of temperature can increase the polymerization rate of aniline and lead to more oligomer because of the exothermic reaction of aniline polymerization, which will lead to the broaden of the diffraction peak and the mesostructure of the product was disordered and wormhole-like.

The influence of the ratio of $FeCl_3$/AN and the HCl/AN on the mesostructure were also studied, but they had a little influence on the composition and mesostructure. So, when the oxidant with lower oxidation potential was used as the initiative, the reaction temperature can seriously affect the composition and mesostructure of the final product.

Scheme 2 Possible mechanism of polymerization of aniline



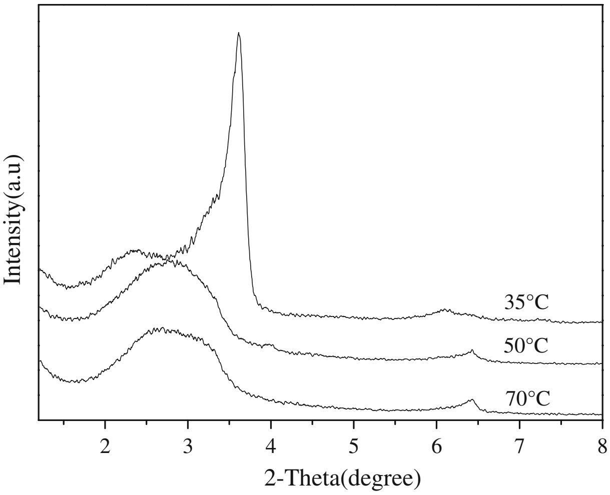


Fig. 5 The XRD patterns of different samples with different temperature. The molar ratio of SDBS:HCl:AN:$FeCl_3$:H_2O was 0.25:5.00:1.00:1.82:272

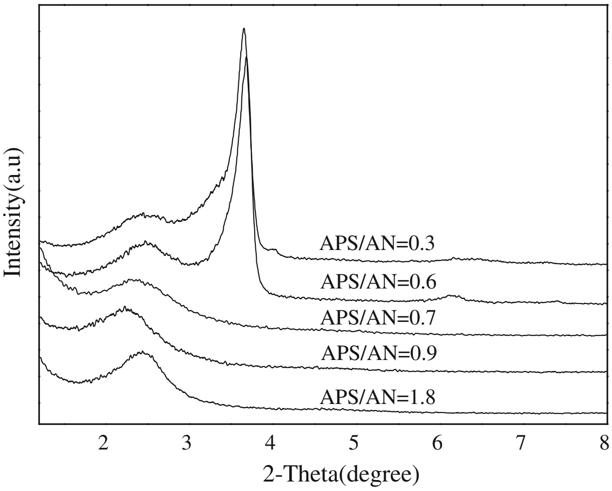


Fig. 6 XRD patterns of PSHA with different APS/AN molar ratios by using $(NH_4)_2S_2O_8$ as the oxidant. The molar ratio of SDBS:HCl:AN:H_2O was 0.25:5.00:1.00:272

When $(NH_4)_2S_2O_8$ was used as the oxidant, the molar ratio of APS/AN had a big influence. Figure 5 shows the influence of the amount of $(NH_4)_2S_2O_8$ on the mesostructure. From the XRD patterns in Fig. 6, when the APS/AN molar ratio was below 0.6, the XRD patterns of sample PSHA showed the mixed phase, lamellar composite salt and mesostructured polyaniline. So we can know that lower mass of oxidant was not enough to polymerize the aniline monomers completely. When the APS/AN molar ratio were higher 0.7, the XRD patterns showed only one broad diffraction peak. However, more oligomers will be produced when the APS/AN molar ratio were increased to 1.8, and this will lead to the framework shrinkage and the 2θ shift to higher angle.

To improve the order of the mesostructured polyaniline, the influence of HCl/AN molar ratio and temperature were also investigated, but, they had no influence on the mesostructure.

Conclusion

The wormhole-like mesostructured polyaniline was prepared by chemical oxidation with $FeCl_3$ or $(NH_4)_2S_2O_8$ as the oxidant and SDBS as the directing agent in the HCl solution. The analysis from powder XRD, TEM, and FT-IR showed that the product was mixed phases and contained two components which were polyaniline with wormhole like mesostructure and composite salt with lamellar mesostructure when $FeCl_3$ was used as oxidant at 35 °C. While the product was mainly mesostructured wormhole-like polyaniline when the strong oxidant APS was used as oxidant at 35°C.

When $FeCl_3$ with lower oxidation potential was used to oxidize the aniline, the reaction temperature had a predominate effect on the composition and mesostructure of the final product, while the $FeCl_3$/AN and HCl/AN molar ratio had a little influence on the mesostructure of the product. When the $(NH_4)_2S_2O_8$ was used as oxidant, the molar ratio of APS/AN was the main factor which influence the composition and mesostructure.

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