Original Research

Polyaniline nanostructures tuning with oxidants in interfacial polymerization system

Fanxin Zeng[a], Zongyi Qin[a,*], Banglei Liang[b], Tao Li[b], Na Liu[b,*], Meifang Zhu[a,b]

[a]*State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China*
[b]*College of Material Science and Engineering, Donghua University, Shanghai 201620, China*

Abstract

Three kinds of nanostructured polyanilines (PANIs) were prepared through interfacial polymerization by using ammonium persulfate (APS) as a single oxidant, and APS/FeCl$_3$, APS/K$_2$Cr$_2$O$_7$ as composite oxidants, respectively. It is observed that faster formation process and higher yield of nanostructured PANIs could be achieved in the presence of FeCl$_3$ and K$_2$Cr$_2$O$_7$. The as-prepared PANIs were characterized by field emission scanning electron microscopy, ultraviolet–visible absorption spectroscopy, Fourier transform infrared and Raman spectroscopy, X-ray diffraction analysis and electrochemical measurements including cyclic voltammetry and galvanostatic charge/discharge measurement. The influence of composite oxidants on the morphology, microstructure, and electrical and electrochemical properties of PANIs was discussed. Interestingly, when APS/K$_2$Cr$_2$O$_7$ was used as the composite oxidants, PANI exhibited petal-like structure with high yield of 57.35% instead of general nanofibrous morphology formed in interfacial polymerization. Compared with those nanofibrous PANIs obtained by using APS as a single oxidant or APS/FeCl$_3$ as composite oxidants, petal-like PANIs exhibited the largest specific capacitance (692.4 F/g at scan rate of 5 mV/s) and highest cycle stability among them. It provides a new insight into the control of PANI nanostructures with high yield and energy storage ability by simply selecting suitable composite oxidants in interfacial polymerization.
© 2015 Chinese Materials Research Society. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: Nanostructured polyaniline; Interfacial polymerization; Composite oxidants; Microstructure; Capacitive property

1. Introduction

Nanostructured conducting polymers have received great attention due to their remark"able properties and promising applications in nanomaterials and nanodevices. Among them, polyaniline (PANI) has been extensively studied owing to its mild reaction condition in the synthesis, excellent chemical stability, appropriate conductivity, and unique proton doping–dedoping properties [1–3]. Recently, PANI has been designed to a variety of nanostructures, such as nanofibers, nanospheres, hollow nanocapsules, nanosheets, nanorods and nanotubes [1,4–7]. Because of the peculiar small size effect, the nanostructured

PANIs have been promising in widely potential applications, such as electrochemical supercapacitors, batteries, metallic anti-corrosion coatings, sensors, electrochromic devices, light emitting diodes and so on [1,2,6]. These nanostructured PANIs can be prepared by electrochemical polymerization, hard or soft-template polymerization, rapid-mixing and dilute solution routes and radiolytic synthesis, as well as interfacial polymerization [1,3]. Among these methods, interfacial polymerization is one of the most effective approaches, which produces high-quality PANI nanofibers in large quantities [7–13].

Previously work about interfacial polymerization has been expended toward the effect of doping acids, solvents, polymerization temperature, and monomer concentration on the morphology of nanostructured PANIs. However, less attention has been paid to the effect of the oxidant especially composite

---

*Corresponding authors. Fax: +86 2167792855.
E-mail addresses: phqin@dhu.edu.cn (Z. Qin), liuna@dhu.edu.cn (N. Liu).

oxidants on the morphology, microstructure and electrochemical properties of PANIs. In traditional chemical system, the oxidant can only affect the yield and conductivity of PANI owing to the bulk reaction where aniline monomer and oxidant are completely contacted. However, during the process in interfacial polymerization, the reaction between monomer and oxidant only occurs where they encounter. Moreover, the morphology and dimension of nanostructured PANIs can be efficiently controlled by just adjusting the redox potential of the oxidants [14]. It has been reported that ammonium persulfate (APS), ferric chloride (FeCl$_3$), potassium permanganate (KMnO$_4$), potassium dichromate (K$_2$Cr$_2$O$_7$), as well as some composites such as Fe^{3+}/hydrogen peroxide (H$_2$O$_2$) and Cu^{2+}/O$_2$ could be used as the efficient oxidants for the synthesis of PANI [2,11,15–20]. Furthermore, when K$_2$Cr$_2$O$_7$ or FeCl$_3$ was used as oxidant for aniline polymerization, the conversion was very low. Fortunately, when they were used with APS as a composite oxidant, higher conversion was obtained. However, in interfacial polymerization system, the composite oxidants especially that with the most common used oxidant, APS, as one of the component was scarcely studied. Meanwhile the adjustment on the morphology and property of final products is limited to some degree when the single oxidant would be designated oxidizability. Fortunately, the composite oxidants system can exhibit more widely controllable oxidizability depending on the nature and amount of the second component of the oxidants, which can be expected to obtain more complicated nanostructures of PANIs [15,21,22].

Since the oxidants play an important role in controlling the formation of PANIs, it is necessary to study the effects of the oxidants especially the composite oxidants to prepare high-quality nanostructured PANIs. In this article, three kinds of nanostructured PANIs were prepared through interfacial polymerization by using APS and APS-based composite oxidants. The influence of composite oxidants on the morphological structure, chain structure, crystallinity, and electrical and electrochemical properties were investigated.

2. Experimental

2.1. Materials

Aniline monomers with an average molecular weight of 93 g/mol, APS, FeCl$_3$, K$_2$Cr$_2$O$_7$, carbon tetrachloride (CCl$_4$) and hydrochloric acid (HCl) were purchased by Sinopharm Chemical Reagent Co., Ltd. and used without further purification. The deionized water was used for all the experiment.

2.2. Preparation

The typical procedure for the synthesis of PANI via interfacial polymerization was carried out as follows: aniline monomers were dissolved in 100 mL CCl$_4$ and various oxidants including APS, APS/FeCl$_3$ (molar ratio of 2:1) and APS/K$_2$Cr$_2$O$_7$ (molar ratio of 1:1) were dissolved in 100 mL 1 M HCl solution, respectively. The molar ratio of aniline monomer to oxidant was 4:1, 1:3 and 2:1 for APS, APS/FeCl$_3$ and APS/

K$_2$Cr$_2$O$_7$, respectively. Then aniline monomer and oxidant solutions were carefully transferred to a 250 mL beaker to form a static interface of the two phases. After reaction for 12 h at room temperature, the resulting precipitates were filtered and rinsed with deionized water for several times, and the products were dried under vacuum at 60 °C for 24 h.

2.3. Characterization

Field emission scanning electron microscopy (HITACHI S–4800, Tokyo, Japan) was employed to observe the morphology of as-prepared PANIs. Ultraviolet–visible spectra (UV–vis) were recorded on a Shimadzu UV-2550 ultraviolet–visible spectrophotometer in the wavelength region of 200–900 nm with a scan rate of 100 nm/min. Fourier transform infrared spectra (FT-IR) were recorded from KBr sample pellets using a Nicolet 8700 FT-IR spectrometer over a wavenumber range of 2000–400 cm^{-1} with a resolution of 4 cm^{-1} at room temperature, and Raman spectra on a Renishaw invia-Refle micro-Raman Spectroscopy System using a 532 nm Nd:YAG laser with the output power of 20 mW. X-ray diffraction (XRD) patterns were obtained by a Philips PX1500 X-ray diffractometer by using Cu Kα X-rays with a voltage of 40 kV and a current of 30 mA.

The electrical conductivity of compressed PANI pellets was measured by a two-point probe method at room temperature by using an Agilent 34401A digital multi-meter linked to the computer. The electrochemical measurements were tested on CHI 660D workstation (Chenhua, Shanghai, China) by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements in 1.0 M H$_2$SO$_4$ electrolyte. The experiments were carried out on a three-electrode mode with platinum wire as counter electrode, Ag/AgCl as reference electrode and glassy carbon electrode as working electrode, respectively. The working electrode was prepared by dropping a concentrated PANI onto a glassy carbon electrode with a diameter of 3 mm. Typically 2 mg of the product was ultrasonically dispersed in 1 mL deionized water to form a uniform concentrated solution. Finally, 10 μL of the above solution was dropped onto the glassy carbon electrode using a pipet gun and dried at room temperature. The typical CV measurements were carried out at the scan rate of 5, 10, 20, 30, 50, 80 and 100 mV/s within the potential window of −0.2–0.8 V. Subsequently, the GCD plots were measured in the potential range of −0.2–0.8 V at a current density of 0.5, 1 and 2 A/g. Furthermore, the long-term cycle stability was evaluated by repeating the cyclic voltammetry at a scan rate of 5 mV/s for 1000 cycles.

3. Results and discussion

3.1. Formation process

PANI is typically synthesized by oxidative polymerization of aniline in strong acidic solution using APS as oxidant via a variety of approaches. The reaction is characterized by an induction period followed by bulk precipitation of a dark-green electrical conducting powder called emeraldine salt. In interfacial polymerization, it is believed that the self-assembly of aniline
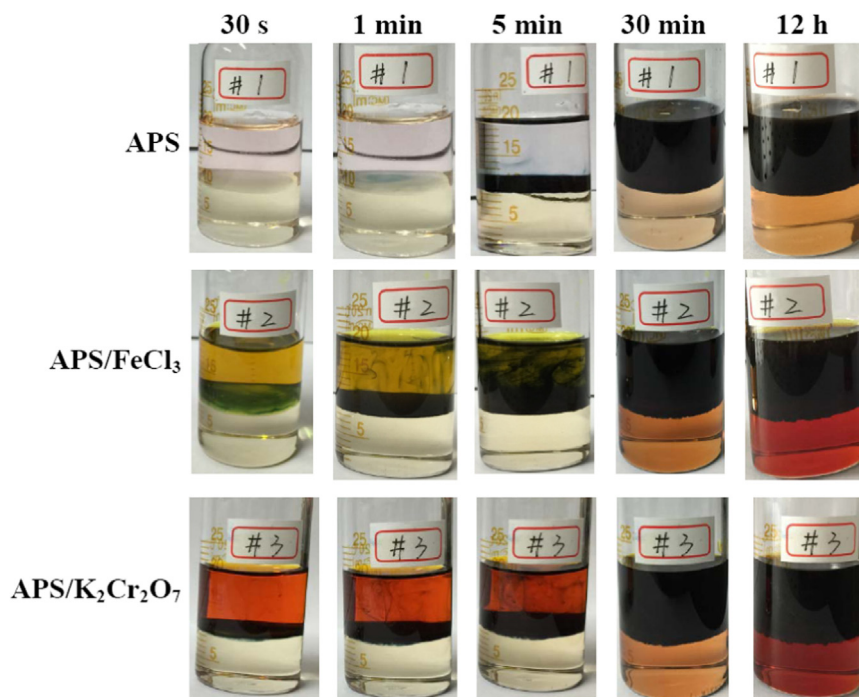
Fig. 1. Formation processes of nanostructured PANIs through interfacial polymerization by using APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ as the oxidant.

oligomers can guide the growth of polymeric structures, and furthermore, aniline oligomers with high concentration would assemble into more complicated nanostructures [22,23]. The formation process of PANI in the interfacial polymerization system by using various oxidants was illustrated in Fig. 1. With the extension of time, the color of the reaction system changed from transparent to blue and then deep green once PANIs were formed at the interface, meanwhile, the product would diffuse into aqueous phase due to their hydrophilic property. As seen in Fig. 1, the formation of PANI in the presence of the composite oxidants became rapider than that for single oxidant. Moreover, the fastest formation process of PANIs could be achieved with the composite oxidants of APS/K$_2$Cr$_2$O$_7$. After the reaction time of 12 h, the aqueous phase was filled with PANI products. Furthermore, the yield was 9.02, 33.32 and 57.35% for APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$, respectively. Clearly, the PANI prepared with APS/K$_2$Cr$_2$O$_7$ possessed the highest yield owing to the strongest oxidizability, far higher than that carried out with single oxidant. Meanwhile, the yield of PANI prepared by APS/FeCl$_3$ also exceeded that in single oxidant system. It demonstrated that the combination of different oxidants can effectively improve the reaction rate together with the yield. The effect of the oxidant on the conductivity of the PANI was also investigated. The conductivity of products prepared with APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ was measured to be 1.27, 1.46 and 1.02×10^{-2} S/cm, respectively. These results show that the nature of the oxidants is not very important in determining the electrical property of PANIs prepared in interfacial polymerization system.

3.2. Morphology

Fig. 2 shows the SEM images of PANIs synthesized through interfacial polymerization with APS as a single oxidant, APS/

FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ as composite oxidants, respectively. It is found that similar nanofibrous morphology of PANI could be observed when FeCl$_3$ was introduced as the second component compared with that for APS as single oxidant. What's more, the average diameters of PANI nanofibers slightly increased from 70 nm to 80 nm. However, as-prepared PANI did not exhibited nanofibrous nanostructure as observed in general interfacial polymerization system in the presence of K$_2$Cr$_2$O$_7$ as the second component in composite oxidants. In more details, the product exhibited a special petal-like structure with the sphere diameters of 500 nm. It has been reported that the combination of Fe^{2+}/APS can effectively initiate the synthesis and enhance the reaction rate during the chemical reaction, with the conclusion that the addition of Fe^{2+} in conventional polymerization system plays an important role in changing the bulk morphologies of PANI from irregular particle agglomerates to nanofibers [24]. Herein, the composite oxidants of APS with FeCl$_3$ or K$_2$Cr$_2$O$_7$ had the similar influence on the formation of nanostructured PANI. According to the formation mechanism of PANI, the homogeneous nucleation is beneficial for the nanofibers and the heterogeneous nucleation is inclined to the irregular morphologies [10,25]. From the reaction process during the polymerization, it includes the induction period, the formation of pernigraniline oxidation state and the reduction of pernigraniline to the emeraldine oxidation state [1,3]. In the induction period, the formation of the oligomers depended greatly on the oxidizability of the reaction system. Owing to the combination of different components, the oxidizability of the system with composite oxidants became too strong, leading to the generation of large amount of oligomers at the initial period [15,24,26]. Then the oligomers could form the petal-like morphology through the self-assembly [4,5]. Thus, the SEM images elucidate that the reactions could be remarkably affected by the oxidants in the system. In the
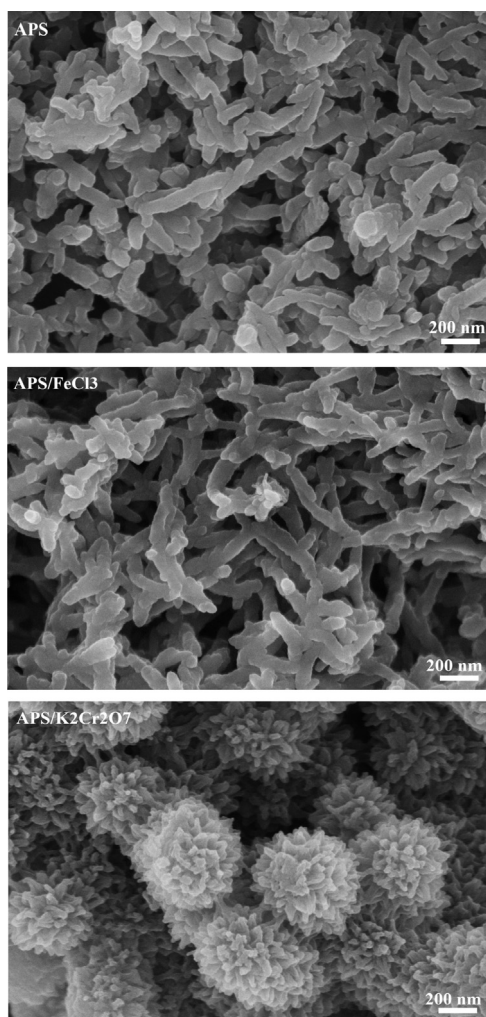
Fig. 2. SEM images for nanostructured PANIs prepared by interfacial polymerization by using APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ as the oxidant.

other word, the morphology of PANIs could also be efficiently tuned by simply introducing a suitable second oxidant, providing a new insight into the synthesis of nanostructured PANIs.

3.3. Optical structure

Fig. 3 shows the UV–vis absorption spectra of nanostructured PANIs prepared by using APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ as the oxidants, respectively. The absorption bands at 330, 430 and 750 nm for PANI prepared with APS as single oxidant indicated PANI was in the emeraldine salt form. At the same time, the characteristic bands were assigned as follows: the lowest wavelength band around 330 nm was often related to the presence of cation radical and corresponded to a π–π* transition in the benzenoid structure, the mediate band was related to the n–π* transition and on behalf of the doping degree on polymer chains, while the band around 750 nm was attributed to π–n transition and it is also ascribed to exciton formation in the quinonoid rings [22,27,28]. As previously reported [4,29], the blue-shift of the π–n transition band was in
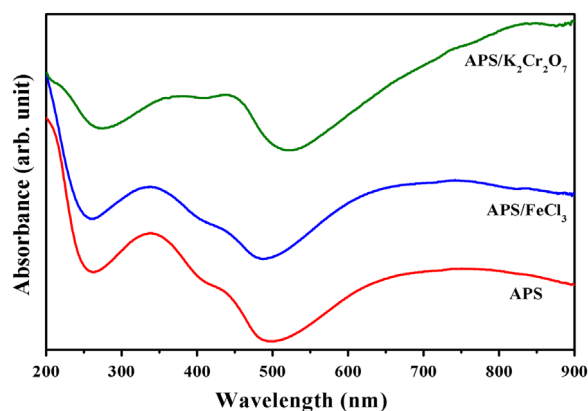

Fig. 3. UV–vis spectra for nanostructured PANIs prepared through interfacial polymerization by using APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ as the oxidant.
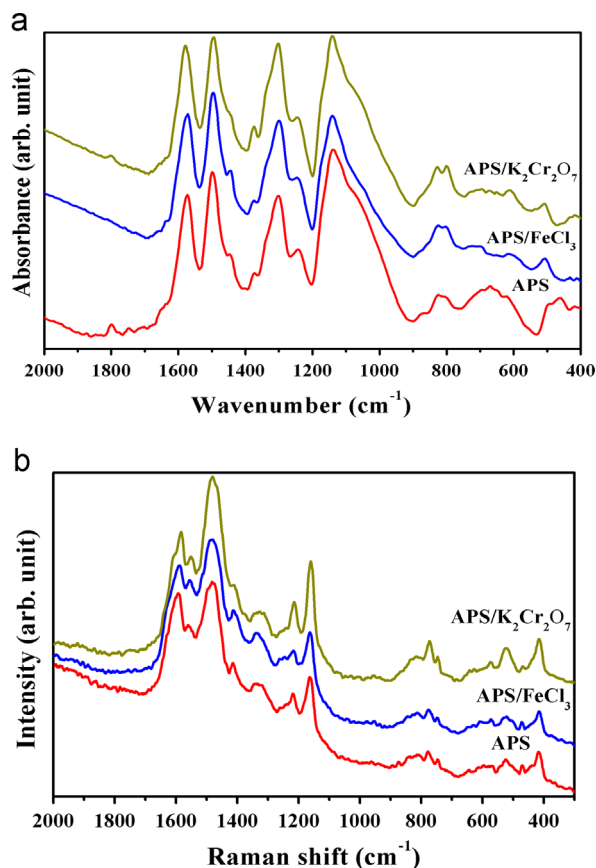

Fig. 4. FT-IR (a) and Raman (b) spectra for nanostructured PANIs prepared through interfacial polymerization by using APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ as the oxidant.

accord with a decreasing extent of conjugation due to the presence of the phenazine-like unites and the aniline oligomers. As shown in Fig. 3, in the presence of FeCl$_3$, similar bands appeared as observed for APS as single oxidant. However, there is an obvious different in the absorption curves between nanofibrous and petal-like structure. For PANI obtained with composite oxidants of APS/K$_2$Cr$_2$O$_7$, the band at 330 nm appeared a tiny red shift compared with that for single APS oxidant. Meanwhile, the characteristic band at long

wavelength red-shifted to 830 nm compared to the nanofibrous PANIs, implying the existence of large conjugation length along polymer chains. For further understanding the optical property of PANIs, the direct optical energy gap (E_g) was determined from the Tauc Formula: $\alpha h\nu = A(h\nu - E_g)^n$, where A is a constant, α the absorption coefficient, $h\nu$ the incident photon energy, and the index n related to the distribution of the density of states and equals to 1/2 for direct band gap semiconductor [26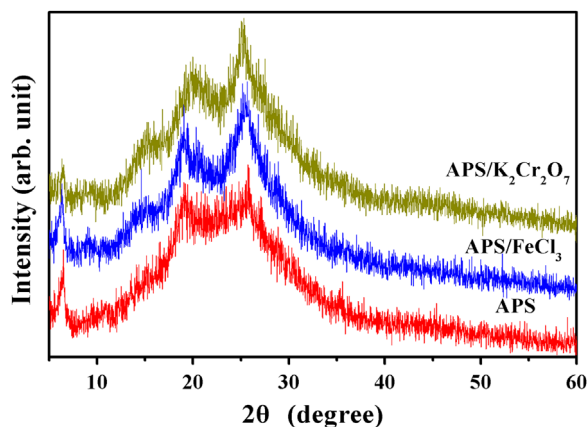,30]. The calculated values were within the range of 2.45–2.55 eV and quite approximate for all the PANIs. This result indicates that there is no obvious difference on the intrinsic conductivity of the PANIs, being consistent with the results from conductivity measurements.

3.4. Chemical structure

Fig. 4(a) shows the FT-IR spectra of PANI synthesized with various oxidants through interfacial polymerization. It can be seen that no remarkable differences could be observed, indicating the main components of each nanostructured PANI possessed similar chemical structures. The characteristic peaks at 1577 and 1492 cm^{-1} could be assigned to the C=C stretching vibration of the quinoid ring and benzenoid ring, respectively [12,22,24,28]. Strong band at 1301 cm^{-1} was attributed to the C–N stretching of the secondary aromatic amine, and the high intensity meant the long conjugated length along polymer chains. The typical band around 1250 cm^{-1} was corresponded to a C–N$^+\bullet$ stretching vibration in the conducting form [9,29]. Meanwhile, the strong band at 1140 cm^{-1} was attributed to the C–H aromatic in-plane bending vibration mode, which could be described as an "electronic-like band", demonstrating all the PANIs were in the doped state [8,16]. In addition, the conductivity of PANIs can be estimated from the area ratio of the characteristic quinoid and benzenoid peaks at 1577 and 1492 cm^{-1}, respectively. The oxidation degree of PANIs

Fig. 5. XRD patterns for nanostructured PANIs prepared through interfacial polymerization by using APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ as the oxidant.
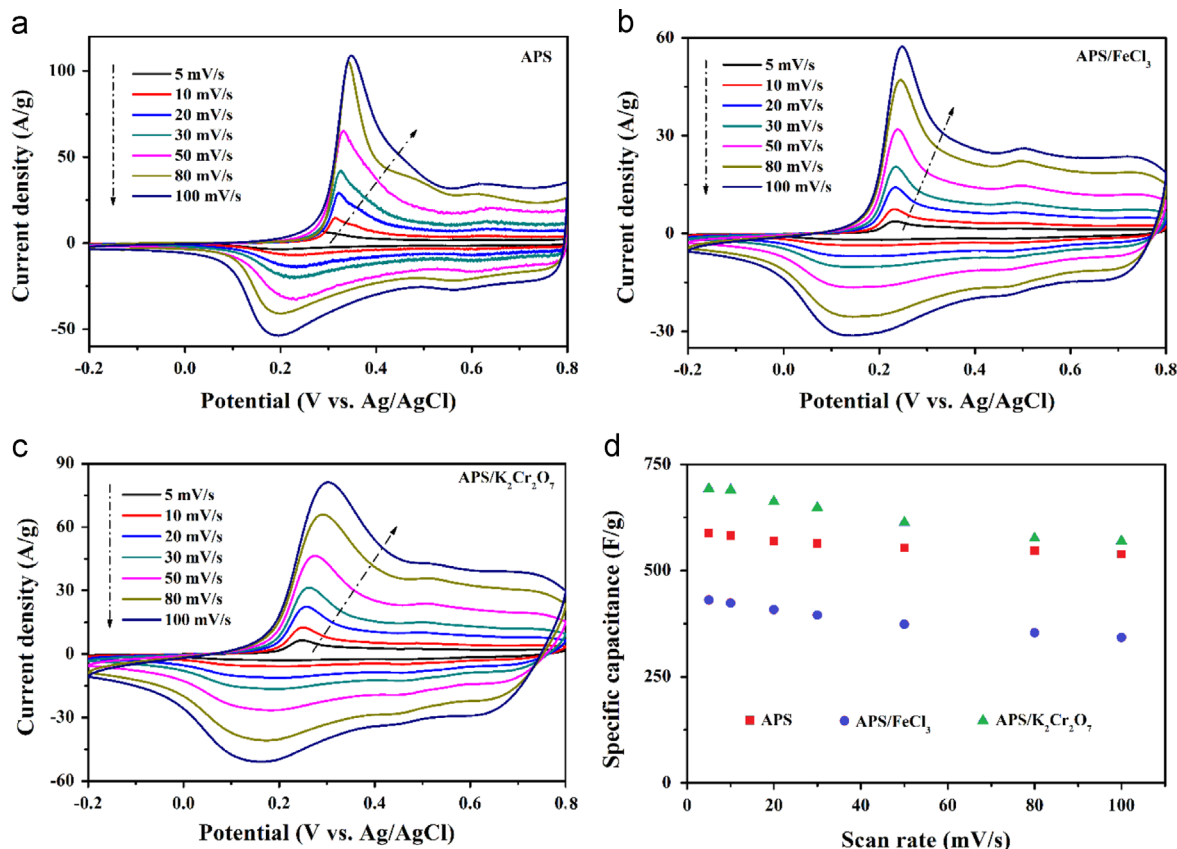

Fig. 6. CV curves (a–c) and specific capacitance (d) as a function of scan rates for nanostructured PANIs prepared through interfacial polymerization by using APS (a), APS/FeCl$_3$ (b) and APS/K$_2$Cr$_2$O$_7$ (c) as the oxidant.

increases with increasing the ratio, hence, the number of quinoid rings in the molecular structure of the conducting polymer also increases [22]. The infrared results indicate that the effect of oxidant on the electrical property of PANIs could be neglected.

On the other hand, Raman spectroscopy shows a more comprehensive reflection about the change of the molecular chain structure of PANI. As observed in Fig. 4(b), there are seven characteristic absorption peaks at 1590, 1480, 1330, 1160, 775, 520 and 414 cm^{-1}. The bands at 1590 (νC$=$C) and 1480 cm^{-1} (νC$=$N) were due to bipolaronic units, and at about 1160 cm^{-1} (βC–H) to polaronic units. The bands at 1330 and 775 cm^{-1} were attributed to C–H stretching vibration and C–N wagging vibration in benzene ring, respectively [10,15,27]. What's more, the bands from 1324 to 1375 cm^{-1} were associated to νC–N of polarons with different conjugation lengths and the bands from 1450 to 1500 cm^{-1} were correlated to νC$=$N modes associated with quinoid units with different conjugation lengths [3,10]. As similar to the infrared results, no obvious difference on chemical structure could be observed for three nanostructured PANIs.

3.5. Crystalline structure

In general, conducting polymer is a semicrystalline material and the crystallinity can be attributed to the systematic alignment of the polymer chains by chain folding or the formation of single or multiple helices. Fig. 5 shows the XRD patterns of PANI synthesized through interfacial polymerization with three kinds of oxidants. As shown in Fig. 5, all the PANIs mainly exhibited two characteristic peaks at $2\theta=19.5°$ and $25.8°$, which could be ascribed to the (100) and (110) plane of PANI, and to periodicity parallel and periodicity perpendicular to the polymer chain, respectively [16,27,31]. Meanwhile, the presence of the peak at about $6.8°$ revealed the short range ordering between the chiral counter anion and the polymer chains, and the enhancement in intensity indicated the ordered nanostructures [10,28]. Therefore, PANIs synthesized with APS/FeCl$_3$ and APS exhibited high ordering owing to the regular nanofibrous morphology, whereas the petal-like PANI prepared with APS/K$_2$Cr$_2$O$_7$ possessed weak peaks, implying that the macroscopic arrangement weakened original ordering of PANI chains [5]. For further investigation on the crystalline property of nanostructured PANIs, the domain length (D) can be calculated by the Debye Scherrer's formula: $D=K\lambda/\beta\cos(\theta)$, where D is the grain size, K the Scherrer constant (1.00 for equatorial reflections of rod-like or needlelike crystallites), λ the X-ray wavelength used, β the angular line width at half-maximum intensity in radians and θ Bragg's angle [26,30]. The value for (110) reflection for PANIs prepared with APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ was 40.3, 33.6 and 36.6 Å, respectively. Obviously, all these values were within the range of 20–70 Å in the case of emeraldine salt form. It is clear that the introduction of the second oxidant into the interfacial
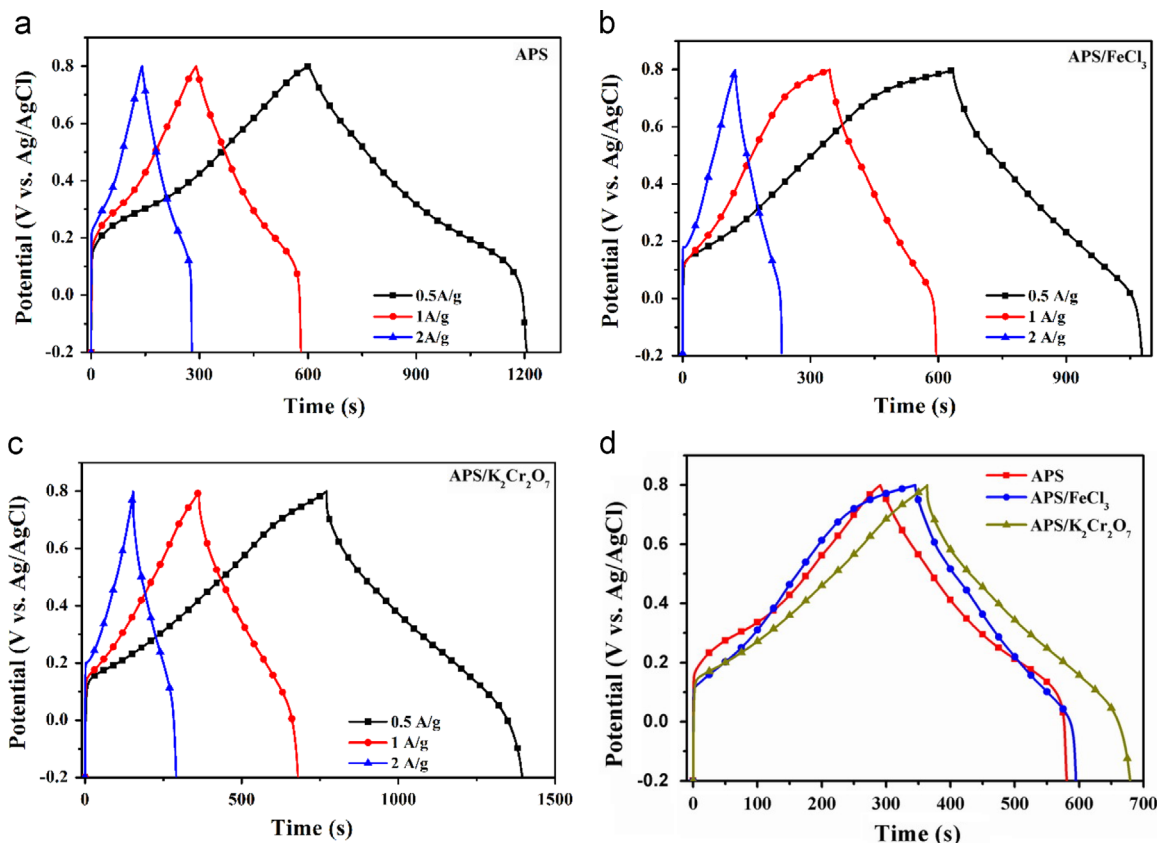

Fig. 7. GCD curves (a–c) at various current densities and at current density of 1 A/g (d) for nanostructured PANIs prepared through interfacial polymerization by using APS (a), APS/FeCl$_3$ (b) and APS/K$_2$Cr$_2$O$_7$ (c) as the oxidant.
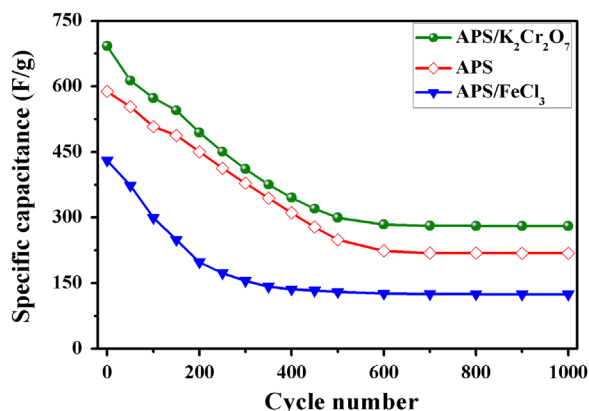
Fig. 8. Cycle stabilities for nanostructured PANIs prepared through interfacial polymerization by using APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ as the oxidant.

polymerization system could greatly improve the crystalline property of PANIs compared with that for APS as single oxidant.

3.6. Electrochemical properties

To evaluate energy storage capability of as-prepared nanostructured PANIs as the electrode material, their electrochemical behaviors were studied by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurement in a three-electrode system with 1.0 M H$_2$SO$_4$ electrolyte. As shown in Fig. 6 (a–c), each curve exhibited a similar shape with two pairs of redox peaks at the scan rate ranging from 5 mV/s to 100 mV/s. These characteristic peaks could be attributed to redox transitions between leucoemeraldine form and polaronic emeraldine and the Faradaic transformation of emeraldine to pernigraniline [10,32]. It is noticeable that the cathodic peaks shifted positively and the anodic peaks shifted negatively with the increase of scan rates. On the other hand, the area of the curves could reflect the capacitance and corresponding values were calculated and plotted in Fig. 6(d). Clearly, the values of specific capacitance for all the PANIs decreased upon the increase of scan rates. It is worth to point out that the capacitance for petal-like PANIs was larger than those for PANI nanofibers. In general, the specific capacitance at a relative slow scan rate is closest to that of full utilization of the electrode material [2,22]. At slow scan rate of 5 mV/s, the specific capacitance for PANIs prepared with APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ was 588.4, 430.6 and 692.4 F/g, respectively. With the increase of the scan rates, only the outer layers of active materials could contribute and the values deduced to some degree due to either depletion or saturation of the protons in the electrolyte inside the electrode during the redox course [16,33]. At the scan rate of 100 mV/s, the specific capacitance for PANIs prepared with APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ decreased to 538.0, 342.6 and 569.5 F/g, respectively.

Fig. 7(a–c) presents the GCD plots of nanostructured PANIs prepared with various oxidants at a gravimetric current density of 0.5, 1 and 2 A/g, respectively. All the nanostructured PANIs exhibited nearly symmetric charge–discharge curves, featuring that the potential of charge/discharge was a linear response to time, which could be believed as a good capacitance behavior

[10,16,32]. Moreover, the discharge time was accordance with the specific capacitance. To clearly obtain the difference on the specific capacitance among three nanostructured PANIs, the GCD plot at a current density of 1 A/g was presented at Fig. 7(d). The specific capacitance for PANIs prepared with APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ was 290.3, 349.8 and 315.7 F/g, respectively. The change trend was consistent with that obtained from CV curves.

The cycling stability of nanostructured PANIs prepared with various oxidants was tested at the scan rate of 50 mV/s for 1000 cycles. As shown in Fig. 8, all the PANIs exhibted a decrease in the capacitance with the cycling number to some extent. The reduction in the capacitance was due to the swelling and shrinkage during the Faradic reaction process [2,22,33]. After the cycling of 1000 numbers, the specific capacitance of PANIs prepared with APS, APS/FeCl$_3$ and APS/K$_2$Cr$_2$O$_7$ decreased to 218.3, 124.3 and 280.6 F/g, respectively. It is obvious that petal-like PANI possessed the best cycle stability among three kinds of nanostructured PANIs. Obviously, the highest electrochemical performance could be achieved when K$_2$Cr$_2$O$_7$ as the second oxidant was introduced into traditional interfacial polymerization system.

4. Conclusions

Three kinds of nanostructured PANIs were prepared through interfacial polymerization by using of traditional APS and APS-based composite oxidants, respectively. The influence of the composite oxidants on the morphology, microstructure and electrochemical properties of nanostructured PANIs was discussed. It is found that in the presence of FeCl$_3$ and K$_2$Cr$_2$O$_7$, as-prepared PANIs exhibited faster formation process and higher yield as compared with that obtained with APS as a single oxidant, but all the as-prepared PANIs possessed similar conductivity. Especially, for the composite oxidants of APS/K$_2$Cr$_2$O$_7$, PANI exhibited petal-like structure instead of nanofibers in general interfacial polymerization system. Moreover, petal-like PANI exhibited the best capacitive property and cycle stability among three kinds of nanostructured PANIs. This work provides a new insight into PANI nanostructures tuning by simply selecting the suitable composite oxidants in interfacial polymerization system, meanwhile high yield and well electrochemical performance can be greatly achieved.

References

[1] G. Ciric-Marjanovi, Recent advances in polyaniline research: polymerization mechanisms, structural aspects, properties and applications, Synth. Met. 177 (2013) 1–47.

[2] R.S.R. Ramya, M.V. Sangaranarayanan, Conducting polymers-based electrochemical supercapacitors – progress and prospects, Electrochim. Acta 101 (2013) 109–129.

[3] S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, Progress in preparation, processing and applications of polyaniline, Prog. Polym. Sci. 34 (2009) 783–810.

[4] Y. Wang, J.L. Liu, H.D. Tran, M. Mecklenburg, X.N. Guan, A.Z. Stieg, B.C. Regan, D.C. Martin, R.B. Kaner, Morphological and dimensional control via hierarchical assembly of doped oligoaniline single crystals, J. Am. Chem. Soc. 134 (2012) 9251–9262.

[5] J. Tao, M. Yang, H. Gao, J. Yu, G. Wang, Synthesis and assembly of oligoaniline for hierarchical structures within stable and mild acid system, Colloid. Surf. A 451 (2014) 117–124.

[6] H. Park, T. Kim, J. Huh, M. Kang, J. Lee, H. Yoon, Anisotropic growth control of polyaniline nanostructures and their morphology-dependent electrochemical characteristics, ACS Nano 6 (2012) 7624–7633.

[7] J. Huang, R.B. Kaner, A general chemical route to polyaniline nanofibers, J. Am. Chem. Soc. 126 (2004) 851–855.

[8] X.W. Xue, Z. Wang, Y. Wu, L. Bao, H. Wang, Interfacial synthesis of polyaniline nanostructures induced by 5-sulfosalicylic acid, Mater. Lett. 64 (2010) 1865–1867.

[9] R. Li, Z. Chen, J. Li, C. Zhang, Q. Guo, Effective synthesis to control the growth of polyaniline nanofibers by interfacial polymerization, Synth. Met. 171 (2013) 39–44.

[10] W. Yang, Z. Gao, N. Song, Y. Zhang, Y. Yang, J. Wang, Synthesis of hollow polyaniline nano-capsules and their supercapacitor application, J. Power Sources 272 (2014) 915–921.

[11] L. Zhang, M. Wan, Y. Wei, Nanoscaled polyaniline fibers prepared by ferric chloride as an oxidant, Macromol. Rapid Commun. 27 (2006) 366–371.

[12] G. do Nascimento, P. Kobata, M. Temperi, Structural and vibrational characterization of polyaniline nanofibers prepared from interfacial polymerization, J. Phys. Chem. B 112 (2008) 11551–11557.

[13] X. Zhang, J. Zhu, N. Haldolaarachchige, J. Ryu, D. Young, S. Wei, Z. Guo, Synthetic process engineered polyaniline nanostructures with tunable morphology and physical properties, Polymer 53 (2012) 2109–2120.

[14] H. Ding, M. Wan, Y. Wei, Controlling the diameter of polyaniline nanofibers by adjusting the oxidant redox potential, Adv. Mater. 19 (2007) 465–469.

[15] M. Bláha, M. Riesová, J. Zedník, A. Anžlovar, M. Žigon, J. Vohlídal, Polyaniline synthesis with iron(III) chloride–hydrogen peroxide catalyst system: reaction course and polymer structure study, Synth. Met. 161 (2011) 1217–1225.

[16] L. Ren, G. Zhang, J. Wang, L. Kang, Z. Lei, Z. Liu, Z. Liu, Z. Hao, Z. Liu, Adsorption–template preparation of polyanilines with different morphologies and their capacitance, Electrochim. Acta 145 (2014) 99–108.

[17] M. Ayad, W. Amer, M. Whdan, In situ polyaniline film formation using ferric chloride as an oxidant, J. Appl. Polym. Sci. 125 (2012) 2695–2700.

[18] M. Ayad, M. Shenashin, Polyaniline film deposition from the oxidative polymerization of aniline using $K_2Cr_2O_7$, Eur. Polym. J. 40 (2004) 197–202.

[19] A. Rahy, M. Sakrout, S. Manohar, S. Cho, J. Ferraris, D. Yang, Polyaniline nanofiber synthesis by co-use of ammonium peroxydisulfate and sodium hypochlorite, Chem. Mater. 20 (2008) 4808–4814.

[20] X. Bai, X. Li, N. Li, Y. Zuo, L. Wang, J. Li, S. Qiu, Synthesis of cluster polyaniline nanorod via a binary oxidant system, Mater. Sci. Eng. C 27 (2007) 695–699.

[21] Y. Wang, X. Jing, J. Kong, Polyaniline nanofibers prepared with hydrogen peroxide as oxidant, Synth. Met. 157 (2007) 269–275.

[22] T. Li, Z. Qin, B. Liang, F. Tian, J. Zhao, N. Liu and M. Zhu, Morphology-dependent capacitive properties of three nanostructured polyanilines through interfacial polymerization in various acidic media, Electrochim. Acta 177, 2015, 343-351.

[23] S. Surwade, S. Agnihotra, V. Dua, N. Manohar, S. Jain, S. Ammu, S. Manohar, Catalyst-free synthesis of oligoanilines and polyaniline nanofibers using H_2O_2, J. Am. Chem. Soc. 131 (2009) 12528–12529.

[24] G. Li, C. Zhang, Y. Li, H. Peng, K. Chen, Rapid polymerization initiated by redox initiator for the synthesis of polyaniline nanofibers, Polymer 51 (2010) 1934–1939.

[25] Y. Wan, X. Jing, Formation of polyaniline nanofibers – a morphological study, J. Phys. Chem. B 112 (2008) 1157–1162.

[26] P. Chutia, A. Kumar, Electrical, optical and dielectric properties of HCl doped polyaniline nanorods, Physica B 436 (2014) 200–207.

[27] S. Banerjee, J.P. Saikia, A. Kumar, B.K. Konwar, Antioxidant activity and haemolysis prevention efficiency of polyaniline nanofibers, Nanotechnology 21 (2010) 19–63.

[28] L. Zhang, G.I.N. Waterhouse, L. Zhang, Coaxially aligned polyaniline nanofibers doped with 3-thiopheneacetic acid through interfacial polymerization, J. Nanomater 2011 (2011) 1–7.

[29] H.R. Tantawy, A.T. Weakley, D.E. Aston, Chemical effects of a solvent-limited approach to HCl-doped polyaniline nanopowder synthesis, J. Phys. Chem. C 118 (2014) 1294–1305.

[30] İ.A. Kariper, Synthesis and characterization of cerium sulfide thin film, Prog. Nat. Sci. 24 (2014) 663–670.

[31] J.P. Pouget, M.E. Jozefowicz, A.J. Epstein, X. Tang, A.G. Macdiarmid, X-ray structure of polyaniline, Macromolecules 24 (1991) 779–789.

[32] W. Wu, D. Pan, Y. Li, G. Zhao, L. Jing, S. Chen, Facile fabrication of polyaniline nanotubes using the self-assembly behavior based on the hydrogen bonding: a mechanistic study and application in high-performance electrochemical supercapacitor electrode, Electrochim. Acta 152 (2015) 126–134.

[33] Y. Zhao, H. Wei, M. Arowo, X. Yan, W. Wu, J. Chen, Y. Wang, Z. Guo, Electrochemical energy storage by polyaniline nanofibers: high gravity assisted oxidative polymerization vs. rapid mixing chemical oxidative polymerization, Phys. Chem. Chem. Phys. 17 (2015) 1498–1502.