

Electrically controllable perchlorate removal based on poly(aniline-co-*o*-aminophenol) doped with *p*-toluene sulfonate

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ABSTRACT: Poly(aniline-co-*o*-aminophenol) (PANOA) was synthesized via electrochemical copolymerization of *o*-aminophenol and aniline using *p*-toluene sulfonate (TSA⁻) as the counterion. The redox transformation of PANOA is accompanied by the exchange of anions into and out of the copolymer, and the feasibility of perchlorate (ClO₄⁻) removal via an electrically switched ion exchange process was evaluated in this study. The results of electrochemical quartz crystal microbalance (EQCM), electrochemical impedance spectroscopy (EIS), and Fourier transform infrared spectroscopy (FTIR) demonstrated the successful release of TSA⁻ upon reduction and uptake of ClO₄⁻ upon reoxidation of the copolymer. Also, in this work, the possible ion-exchange mechanism of PANOA was proposed. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41895.

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INTRODUCTION

The efficient removal of perchlorate from the environment has attracted great attention due to its significant health concern,^{1,2} however, ClO₄⁻ is difficult to be removed because of its solubility and nonreactivity. Among various ClO₄⁻ remediation treatments, ion exchange is a commonly used approach owing to its simplicity and high efficiency.³ Recently, conducting polymers have been widely applied as ion exchanger because of their reversible redox character,⁴⁻⁶ and the electrochemical reduction and oxidation of conducting polymers is usually accompanied by the release and uptake, respectively, of dopant anions for the maintenance of electro-neutrality in the polymer films.

Conducting polymer-based hybrid materials have been developed as novel ion exchangers.^{7,8} Poly(aniline-co-*o*-aminophenol) (PANOA), a copolymer of aniline and *o*-aminophenol, has been synthesized and applied for different purposes such as wastewater purification^{9,10} and electrocatalytic oxidation and reduction.^{11,12} Recently, Zhang *et al.*¹³ synthesized PANOA using Cl⁻ as the counterion and applied it as an electrically switched ion exchanger for ClO₄⁻ removal, and a molar ratio (ClO₄⁻/Cl⁻) of 0.53 was obtained during this ion-exchange

process. However, the films of conducting polymers will keep the memory of the size of the counterion once it is dedoped and be only redoped by comparable or smaller anions according to the reported “size-memory” effect.¹⁴ In other words, large counterions can be easily replaced by small anions; and the reverse exchange can also occurs but presents a low efficiency. And it should be pointed out that for anion exchange, the molecular size of counterion is not the bigger the better, because cation exchange is primarily found to be dominant in the presence of large counter anions, for example, polyvinyl-sulfonate (PVSⁿ⁻) and dodecylsulfate (DS⁻), due to the immobility of these large counterions in the polymer matrix.^{4,15-18} Thus, the molecular size of counterion has a great influence on the anion-exchange efficiency of conducting polymers.

Herein, we first report on the synthesis of PANOA using *p*-toluene sulfonate (TSA⁻) as the counterion. Because the molecular size of TSA⁻ is much larger than that of ClO₄⁻, the PANOA-TSA⁻ can be used as an electrically switched ion exchanger for the efficient removal of ClO₄⁻. Also in the present work, the associated ion-exchange behaviors are systematically characterized by means of electrochemical quartz crystal microbalance (EQCM), electrochemical impedance spectroscopy (EIS), cyclic

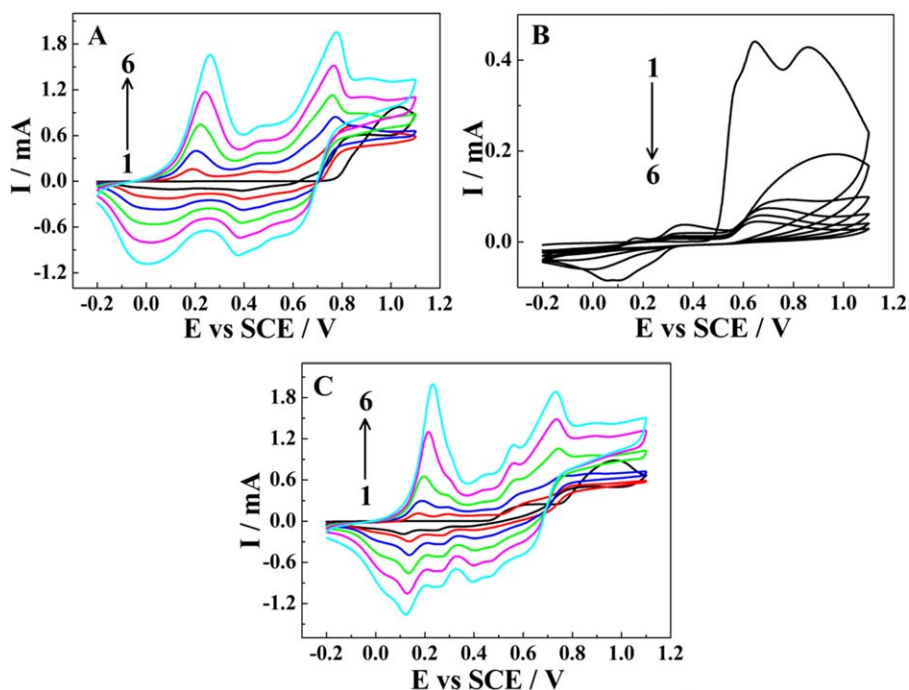


Figure 1. Cyclic voltammograms for the electro-synthesis of polyaniline (A), poly(*o*-aminophenol) (B) and PANOA (C) in 0.8M *p*-toluene sulfonic acid: (1) first cycle, (6) sixth cycle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

voltammetry (CV), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials and Reagents

Aniline, *o*-aminophenol, and *p*-toluene sulfonic acid were purchased from Sinopharm Chemical Reagent Co. Ltd. (China), and aniline was distilled under reduced pressure before use. All other reagents were of analytical grade and used without further purification. All solutions were prepared using doubly distilled water.

Electrosynthesis of PANOA-TSA⁻

Electrodeposition of PANOA-TSA⁻ was conducted in a 0.8M *p*-toluene sulfonic acid solution containing 0.25M aniline and 0.01M *o*-aminophenol in an electrolytic cell consisting of a glassy carbon (3 mm diameter) working electrode, a platinum foil auxiliary electrode, and a saturated calomel reference electrode (SCE). CV was carried out for the electro-synthesis of PANOA-TSA⁻ at a scan rate of 60 mV s⁻¹, and the electrolysis was finished after 10 repeated cycles.

Ion Exchange Between TSA and Perchlorate

The ion exchange between TSA⁻ and ClO₄⁻ was investigated by immersing the PANOA-TSA⁻ working electrode in a solution of 0.3M HClO₄, and CV was carried out between -0.4 and 0.6 V at 10 mV s⁻¹ for different cycles. The scan was started cathodically during the CV, and the reduction peak and the oxidation peak on the reverse scan due to the redox of the copolymer were accompanied by the dedoping and redoping of counterions. EQCM was conducted to evaluate the release of TSA⁻ upon reduction and uptake of ClO₄⁻ upon reoxidation, in

which the PANOA-TSA⁻ films were deposited on a 7.995 MHz Au-coated quartz crystal for five cycles.

Characterization and Measurements

EQCM was conducted on a CHI 420B electrochemical workstation (CH Instruments, China), and CV and EIS measurements were carried out on a CHI 660D electrochemical analyzer (CH Instruments, China). FTIR spectra of PANOA before and after ion exchange, that is, PANOA-TSA⁻ and PANOA-ClO₄⁻, were recorded on a FTIR-8400S spectrometer (Shimadzu, Japan). The SEM images of PANOA-TSA⁻ and PANOA-ClO₄⁻ were obtained with a model JSM-6360LA scanning electron microscope (JEOL, Japan). The

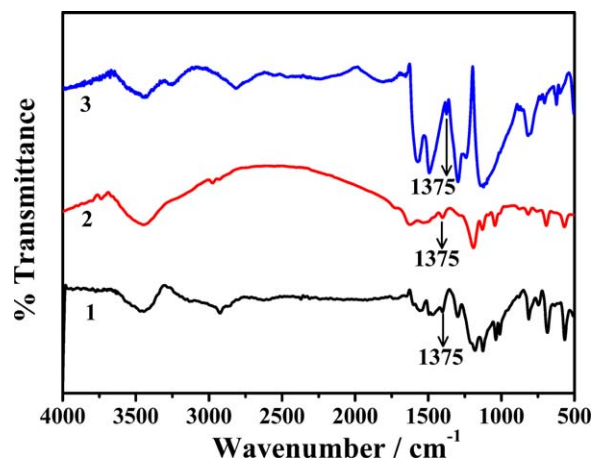


Figure 2. FTIR spectra of polyaniline (1), poly(*o*-aminophenol) (2), and the copolymer (3) synthesized in 0.8M *p*-toluene sulfonic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Solubility of PANOA, Polyaniline, and Poly(*o*-aminophenol) in Different Solvents

	PANOA	Polyaniline	Poly- <i>o</i> -aminophenol
Water	×	×	×
Ethanol	×	×	×
Acetone	×	×	×
Petroleum ether	×	×	×
N-Methyl pyrrolidone	√	√	√

×: insoluble; √: soluble.

conductivity of PANOA, polyaniline, and poly(*o*-aminophenol) were measured with a model SZT-2A four-probe instrument (Suzhou Tong-Chang Electronics Company Ltd., China).

RESULTS AND DISCUSSION

Electrosynthesis of PANOA-TSA⁻

Figure 1 shows the CVs for the electrosynthesis of polyaniline, poly(*o*-aminophenol) and PANOA, respectively, in 0.8M *p*-toluene sulfonic acid solution. The shape of CVs for PANOA [Figure 1(C)] is similar to that of polyaniline [Figure 1(A)]; however, three obvious differences can still be observed: (1) two oxidation peaks appear at 0.64 and 0.97 V on the first cycle on Figure 1(C), but only one oxidation peak at 1.04 V is found on the counterpart on Figure 1(A). The two oxidation peaks on Figure 1(C) are attributed to the oxidation of hydroxyl groups in phenyl ring of *o*-aminophenol (0.64 V) and the oxidation of amino groups from both monomers (0.97 V), respectively,¹⁹ and the oxidation peak at 1.04 V on Figure 1(A) is due to the irreversible oxidation of aniline to form polyaniline²⁰; (2) four pairs of redox peaks appear on the CVs of Figure 1(C) from the second cycle, and only three pairs of redox peaks can be observed on Figure 1(A); (3) dark green films are deposited on the electrode surface after ten repeated cycles on Figure 1(C), however, the films corresponding to Figure 1(A) are light green. The color differences between PANOA and polyaniline mean that their structures may be different from each other, which may be attributed to the different polymerization mechanisms.¹⁹ All these evidences indicate that PANOA is obtained via the copolymerization of aniline and *o*-aminophenol. It is noteworthy that during the synthesis of PANOA, electroneutrality can be preserved by doping TSA⁻ into the copolymer, so the obtained copolymer is denoted as PANOA-TSA⁻. In addition, it can be seen from Figure 1(B) that the repetitive potential scan during *o*-aminophenol polymerization leads to the decay of current, which is due to the electrode fouling during the polymerization of phenolic compounds.^{21,22}

Table II. Conductivity Data of PANOA, Polyaniline, and Poly(*o*-aminophenol)

	PANOA	Polyaniline	Poly(<i>o</i> -aminophenol)
Conductivity (S cm ⁻¹)	0.056	0.019	< 1.0 × 10 ⁻⁵

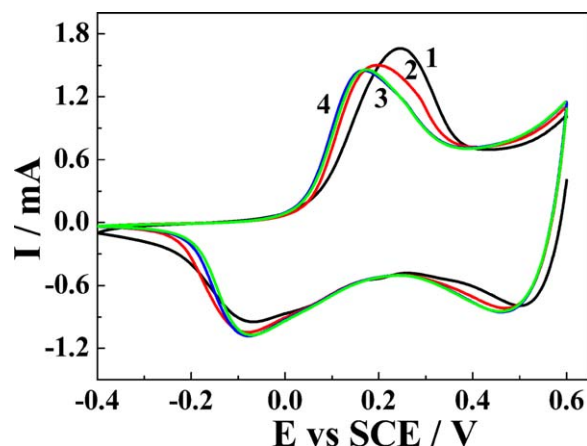


Figure 3. Cyclic voltammograms of PANOA-TSA⁻ in 0.3M HClO₄ solution: (1) first cycle, (2) second cycle, (3) 50th cycle, and (4) 100th cycle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The FTIR spectra of polyaniline, poly(*o*-aminophenol), and PANOA are provided for comparison (Figure 2). As can be seen, these FTIR spectra are different from each other especially at the wave number below 1400 cm⁻¹, indicating that the structure of the copolymer is different from those of polyaniline and poly(*o*-aminophenol). However, the peak at 1375 cm⁻¹ attributed to the stretching vibrations of TSA⁻ is observed for all the three spectra. It is reasonable since TSA⁻ is adopted as the counterion during the electrosynthesis of the three polymers. In addition, for a better comparison, the solubility and the conductivity data of PANOA, polyaniline and poly(*o*-aminophenol) are presented in Tables I and II, respectively.

Ion Exchange Between TSA⁻ and Perchlorate

Figure 3 shows the CVs of PANOA-TSA⁻ in 0.3M HClO₄ solution, and the scan was started cathodically. On the first cycle, a

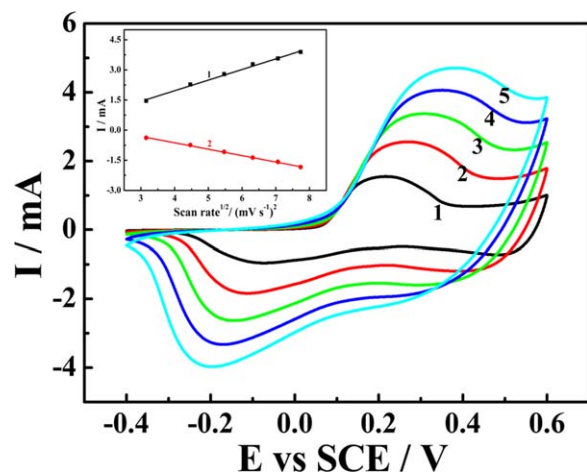


Figure 4. Cyclic voltammograms of PANOA in 0.3M HClO₄ solution at varying scan rates: (1) 10, (2) 20, (3) 30, (4) 40, and (5) 50 mV s⁻¹. Inset: Plots of the oxidation and the reduction peak current versus the square root of scan rate: (1) oxidation peak current and (2) reduction peak current. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

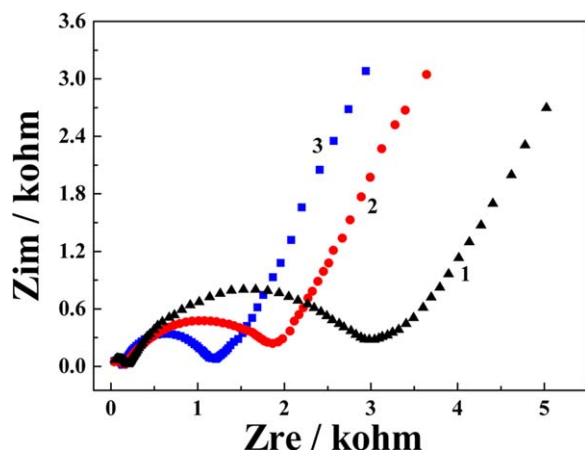


Figure 5. Nyquist plots of PANOA-TSA⁻ in 0.1M KCl solution containing 5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] before (1) and after its ion exchange with ClO₄⁻ in 0.3M HClO₄ for 10 (2) and 50 cycles (3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pair of well-defined redox peaks appear at -0.07 and 0.25 V, which are caused by the redox reaction of PANOA, and the exchange of counterions in the polymer (TSA⁻ in this work) with anions in solution (ClO₄⁻ used here) occurs as a result of this redox reaction.²³ It is evident that the process of reduction and oxidation is reversible, and the TSA⁻ unloading and ClO₄⁻ loading can be controlled by potential modulation. With the consecutive cycling till the 50th cycle, the oxidation peak shifts negatively and decreases little by little. Since the anion exchange capacity can be estimated by comparing the charge passed, that is, the area under the curve for each potential scan,²⁴ it is shown that the anion exchange capacity of the copolymer decays with potential scanning.

The redox process of conducting polymers accompanied by the dedoping/redoping of counterions is significantly influenced by kinetics. The CVs of PANOA-TSA⁻ in 0.3M HClO₄ at varying scan rates with a negative initial scan are shown in Figure 4. As can be seen, the reduction and the oxidation peak of PANOA,

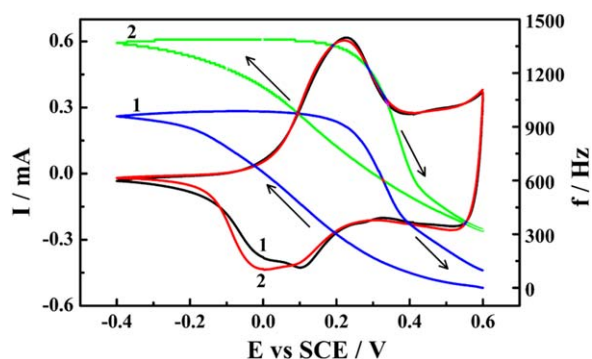
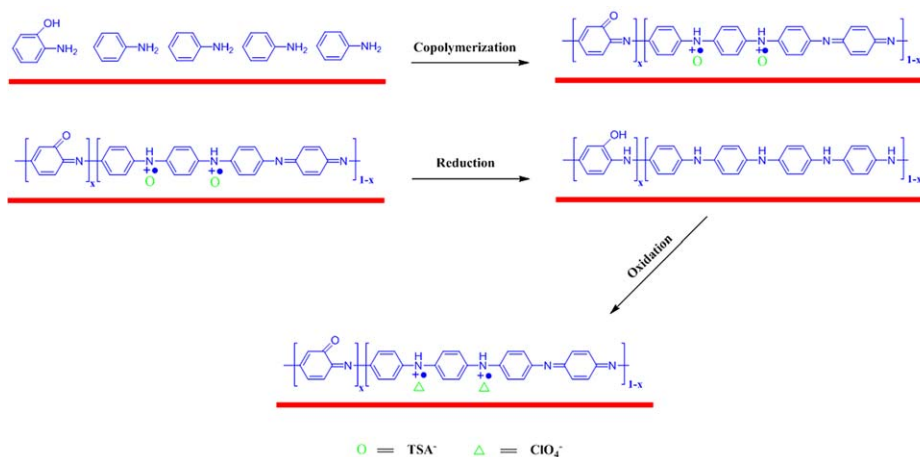


Figure 6. Cyclic voltammograms and simultaneous EQCM responses of PANOA-TSA⁻ in 0.3M HClO₄ at a scan rate of 10 mV s⁻¹: (1) first cycle, (2) 10th cycle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

corresponding to the TSA⁻ unloading and ClO₄⁻ loading, shift to a more negative and positive potential, respectively, with an increase in the scan rate from 10 to 50 mV s⁻¹. This indicates that a high dedoping/redoping reversibility of PANOA can be obtained at a relatively low scan rate. Also, it is shown that the reduction and the oxidation peak current of PANOA is proportional to the square root of scan rate in the given range of scan rate (inset of Figure 4), indicating that the ion exchange between TSA⁻ and ClO₄⁻ within PANOA is a partially diffusion control process.

EIS Characterization

EIS is an important approach for the analysis of surface changes of conducting polymer films.²⁵ The Nyquist plots of PANOA-TSA⁻ before and after its ion exchange with ClO₄⁻ in 0.3M HClO₄ for different cycles are shown in Figure 5. Frequency sweeps extended from 10⁵ to 0.1 Hz, and it was operated at the open circuit potential (0.2 V) using a sine wave potential of 5 mV. All the three impedance spectra consist of a depressed semicircle at high frequency and a straight line at low frequency. The diameter of the depressed semicircle is equivalent to the charge transfer resistance (R_{ct}), which is a sensitive and directive



Scheme 1. Schematic illustration of electrically switched anion exchange between TSA⁻ and ClO₄⁻. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

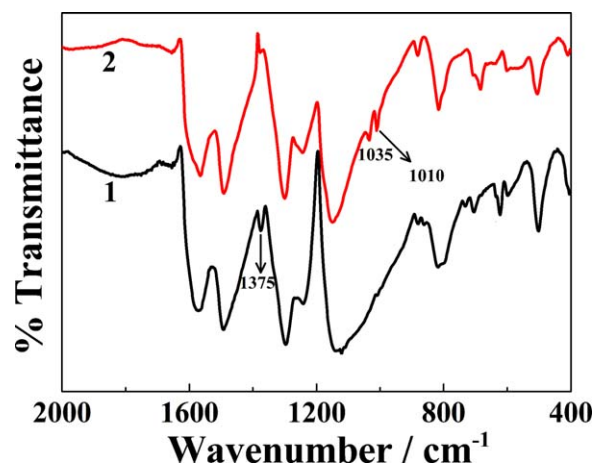


Figure 7. FTIR spectra of the copolymer (1) before ion exchange, and (2) after 50 cycles of ion exchange with ClO_4^- . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

factor indicating the changes at the electrode-solution interfaces.²⁶ Before the ion exchange with ClO_4^- , PANOA-TSA⁻ has the largest R_{ct} . After the dedoping/redoping process is conducted in 0.3M HClO_4 for 10 cycles, R_{ct} is greatly decreased; and a further decrease in R_{ct} is observed after the ion exchange is extended to 50 cycles. The significant decrease in the R_{ct} of PANOA is attributed to the gradual replacement of TSA⁻ by ClO_4^- , since the exchange of counter anions in a film of conducting polymer such as polyaniline could influence the conductivity of the films.⁵

EQCM Analysis

Because mass change (Δm) can be monitored by recording the resonant frequency shift (Δf),²⁷ EQCM can be used for in-situ investigation of ion-exchange process. To avoid viscoelastic effects in EQCM measurements,²⁸ the PANOA-TSA⁻ films were deposited on Au-coated quartz crystal for only five cycles. The conversion of Δf and Δm is based on the Sauerbrey equation: $\Delta m = -\Delta f / C_f$, where C_f is the sensitivity factor of the quartz resonators (737 $\text{Hz } \mu\text{g}^{-1}$ in the present work). The CVs of PANOA-TSA⁻ in 3 mL 0.3M HClO_4 at a scan rate of 10 mV s^{-1} and the corresponding frequency responses were recorded simultaneously (Figure 6). The frequency increases as the potential is scanned negatively, and a sharp increase is observed from about 0.3 V (curve 1). This change in frequency agrees well

with the corresponding CVs, in which the reduction peak attributed to the dedoping of TSA⁻ begins to form at 0.3 V. On the reverse scan (from -0.4 to 0.6 V), an obvious decrease in the frequency occurs at about 0.2 V, which is due to the redoping of ClO_4^- into the copolymer films. This sharp oscillation of the frequency at 0.2 V is consistent with the CVs, because the oxidation peak due to the uptake of anions appears at about 0.2 V on the CVs.

The redoping of ClO_4^- into the copolymer films can result in the removal of ClO_4^- from the solution. The accurate mass of TSA⁻ dedoped and ClO_4^- removed can be obtained according to the Sauerbrey equation, and the molar ratio of ClO_4^- to TSA⁻ is calculated to be 1.51, which is much larger than previously reported value of 0.53.¹³ The significantly improved molar ratio of ClO_4^- to the counterion is due to the fact that the selected counterion in the present work is TSA⁻, which molecular size is larger than that of ClO_4^- ; however, a small anion, Cl^- , is chosen as the counterion in Ref. [13]. Based on the “size-memory” theory,¹⁴ the PANOA-TSA⁻ has a more high affinity for ClO_4^- than PANOA- Cl^- . After 10 repeated dedoping/redoping cycles, the mass of PANOA decreases by 0.2 μg by comparing the terminal points of curves 1 and 2. The decrease in the net mass of the copolymer is mainly attributed to the replacement of TSA⁻ by ClO_4^- , since the molar mass of the former is much larger than that of the latter. The electrically switched anion exchange between TSA⁻ and ClO_4^- can be summarized as Scheme 1. Here, it should be pointed out that although TSA⁻ is also harmful to human as ClO_4^- , it can be adsorbed effectively by graphene owing to its large molecule size and benzene ring.²⁹ Moreover, the purpose of this work is to introduce an idea that large counterions doped in conducting polymers can be easily replaced by anions in solution compared with counterions of small molecular size. So TSA⁻ is still adopted as the counterion in this work.

FTIR and SEM Characterizations Before and After Ion Exchange

The FTIR spectra of PANOA-TSA⁻ before and after ion exchange with ClO_4^- are shown in Figure 7. Before ion exchange (curve 1), a small but sharp peak at 1375 is attributed to the stretching vibrations of sulfoxide,³⁰ revealing the presence of TSA⁻ in the copolymer films. After 50 repeated dedoping/redoping cycles in 0.3M HClO_4 , the characteristic peak of TSA⁻ decreases remarkably, indicating that most TSA⁻ are dedoped

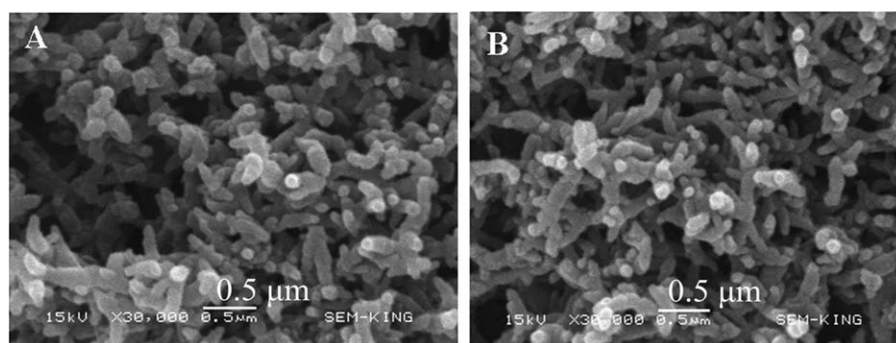


Figure 8. SEM images of the copolymer before (A) and after 50 cycles of ion exchange with ClO_4^- (B).

from the copolymer (curve 2). Another two small peaks are observed at 1035 and 1010 cm^{-1} after the ion exchange with ClO_4^- , and these two peaks are assigned to the characteristic adsorption of ClO_4^- .¹³ The results from FTIR can demonstrate that ClO_4^- is incorporated into the copolymer instead of TSA^- after the ion exchange.

However, there are no obvious differences in the morphologies of PANOA- TSA^- after its ion exchange with ClO_4^- for 50 cycles, as shown in Figure 8. This indicates that the anion exchange does not affect the morphology of the copolymer, which might be attributed to the “morphology-memory” effect of conducting polymers.⁵

CONCLUSIONS

The anion-exchange property of PANOA is utilized for the electrically controllable removal of perchlorate. TSA^- , an anion with larger molecular size compared with perchlorate, is chosen as the counterion in the electrosynthesis of PANOA by considering the “size-memory” effect of conducting polymers. The anion-exchange behaviors of the copolymer are further evidenced by EQCM, CV, FTIR, and EIS measurements. The morphologies of the copolymer change little after 50 cycles of ion exchange due to the “morphology-memory” effect, indicating excellent stability during multiple ion exchange. The electrically switched and efficient perchlorate removal ability of PANOA makes it a good candidate for future designing of water purification systems.

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REFERENCES

1. Dasgupta, P. K.; Martinelango, P. K.; Jackson, W. A.; Anderson, T. A.; Tian, K.; Tock, R. W.; Rajagopalan, S. *Environ. Sci. Technol.* **2005**, *39*, 1569.
2. Srinivasan, R.; Sorial, G. A. *Sep. Purif. Technol.* **2009**, *69*, 7.
3. Gu, B.; Ku, Y. K.; Brown, G. M. *Environ. Sci. Technol.* **2005**, *39*, 901.
4. Weidlich, C.; Mangold, K. M.; Juttner, K. *Electrochim. Acta* **2005**, *50*, 1547.
5. Hao, Q. L.; Lei, W.; Xia, X. F.; Yan, Z. Z.; Yang, X. J.; Lu, L. D.; Wang, X. *Electrochim. Acta* **2010**, *55*, 632.
6. Kong, Y.; Sha, Y.; Xue, S. K.; Wei, Y. *J. Electrochem. Soc.* **2014**, *161*, H249.
7. Lin, Y. H.; Cui, X. L.; Bontha, J. *Environ. Sci. Technol.* **2006**, *40*, 4004.
8. Lin, Y. H.; Cui, X. L. *Chem. Commun.* **2005**, *17*, 2226.
9. Zhang, Y.; Li, Q.; Tang, R.; Hu, Q. C.; Sun, L.; Zhai, J. P. *Appl. Catal. B: Environ.* **2009**, *92*, 351.
10. Zhang, Y.; Liu, X. M.; Li, Q. *J. Appl. Polym. Sci.* **2013**, *128*, 1625.
11. Mu, S. L. *Biosens. Bioelectron.* **2006**, *21*, 1237.
12. Mu, S. L. *Electrochem. Commun.* **2009**, *11*, 1519.
13. Zhang, Y.; Mu, S. L.; Deng, B. L.; Zheng, J. Z. *J. Electroanal. Chem.* **2010**, *641*, 1.
14. Lapkowski, M.; Vieil, E. *Synth. Met.* **2000**, *109*, 199.
15. Naoi, K.; Lien, M.; Smyrl, W. H. *J. Electrochem. Soc.* **1991**, *138*, 440.
16. Michalska, A.; Wojciechowski, M.; Jedral, W.; Bulska, E.; Maksymiuk, K. *J. Solid. State. Electrochem.* **2009**, *13*, 99.
17. Weidlich, C.; Mangold, K. M.; Juttner, K. *Electrochim. Acta* **2001**, *47*, 741.
18. Tamm, J.; Alumaa, A.; Hallik, A.; Sammelselg, V. *J. Electroanal. Chem.* **1998**, *448*, 25.
19. Mu, S. L. *Synth. Met.* **2004**, *143*, 259.
20. Mu, S. L.; Chen, C. X.; Wang, J. M. *Synth. Met.* **1997**, *88*, 249.
21. Yang, X. Y.; Kirsch, J.; Fergus, J.; Simonian, A. *Electrochim. Acta* **2013**, *94*, 259.
22. Yang, X. Y.; Kirsch, J.; Olsen, E. V.; Fergus, J. W.; Simonian, A. L. *Sensor. Actuat. B. Chem.* **2013**, *177*, 659.
23. Mu, S. L.; Zhang, Y.; Zhai, J. P. *Electrochim. Acta* **2009**, *54*, 3923.
24. Lilga, M. A.; Orth, R. J.; Sukamto, J. P. H.; Haight, S. M.; Schwartz, D. T. *Sep. Purif. Technol.* **1997**, *11*, 147.
25. Chen, W. C.; Wen, T. C.; Gopalan, A. *Synth. Met.* **2002**, *128*, 179.
26. Zhao, D. M.; Zhang, X. H.; Feng, L. J.; Jia, L.; Wang, S. F. *Colloids Surf. B* **2009**, *74*, 317.
27. Kong, Y.; Li, X. Y.; Ni, J. H.; Yao, C.; Chen, Z. D. *Electrochem. Commun.* **2012**, *14*, 17.
28. Weidlich, C.; Mangold, K. M.; Juttner, K. *Synth. Met.* **2001**, *119*, 263.
29. Wu, T.; Cai, X.; Tan, S. Z.; Li, H. Y.; Liu, J. S.; Yang, W. D. *Chem. Eng. J.* **2011**, *173*, 144.
30. Stuart Tipson, R. J. *Am. Chem. Soc.* **1952**, *74*, 1354.