

Synthesis of Tailor-Made Nanoporous Polyaniline Derived with PVA/Alkaline Metal System for Metal Complexation

Chan Woo Lee,¹ Sang Hyop Choi,² Han Mo Jeong,² Sok-Hawn Rhyu,²
Ki-Whan Chi,² Koo Sik Yoon²

¹Department of Chemistry, Hanyang University, Seoul 133-791, Korea

²Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea

Received 20 March 2009; accepted 16 February 2011

DOI 10.1002/app.34376

Published online 22 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Nanoporous polyanilines (PANIs) have attracted attention due to well-defined molecular structures and chemical versatility, which also complicate the mechanisms of interaction between metal ions and PANI. To further understand the complexation with metal ions, tailor-made nanoporous PANIs were synthesized with self-stabilized dispersion polymerization (SSDP) using the poly(vinyl alcohol) (PVA) and various alkaline metals for suitable target metal complexation. The effective complexation results for the removal of Cr ions were obtained by

the nanoporous PANI derived from a PVA/Li system. The synthesized tailor-made PANI-emeraldine base (EB) was easily oxidized by a Cr(VI) oxidant resulting in a pernigraniline form with a rigid polymer template and effective metal ion binding sites, and then the reduced form of Cr(III) can be complexed with the resulting PANI. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2497–2502, 2011

Key words: polyaniline; complexation; PVA; tailor-made; adsorption; stabilizer

INTRODUCTION

Adsorption is an effective and versatile method for the removal of heavy metals when combined with an appropriate desorption and metal recovery step.^{1–4} Among the heavy metals, chromium ions exist in the environment as both trivalent Cr(III) and hexavalent Cr(VI) forms, and the hexavalent form is 500 times more toxic than the trivalent form.⁵ It is well known that amine derivatives form coordinate bonds with positively charged metal ions due to the presence of an electron-rich nitrogen atom. Among polymers, conducting polyaniline (PANI) is useful because of its unique redox or doping/dedoping properties with a chemical reagent or electrochemical technique.⁶ In addition, PANI nanostructures are of great interest as they have a high surface area and a reactive —NH group in the polymer chain flanked on either side by a phenylene ring, which imparts a very high chemical flexibility for the complexation of metal ions. The complexation behavior of PANI was originally investigated for the importance of metal ion sensing in biology, medicine, and environmental fields by Hirao et al.^{7–9} PANI-metal nanoparticle composites also show enhanced sensing and catalytic

capabilities, as compared to those of pure PANI.^{10,11} Although non-nanoporous PANI has been employed for metal complexation, a highly nanoporous PANI system has not been used for transition metal complexation. Recently, we have developed a general chemical route to produce PANI nanofibers using a self-stabilized dispersion polymerization (SSDP) method that occurs at an aqueous/organic interface at low temperature.^{12,13} In this study, PANI nanofibers that formed at an early stage in the polymerization process became scaffolds for the secondary growth of PANI and turned into irregularly shaped agglomerates containing nanofibers and particles. However, if secondary growth could be suppressed, the yield of nanofibers in the final product could be greatly increased. In theory, if all the reactants were consumed during the formation of nanofibers, secondary growth would be suppressed as no reactants would be available for further reaction.

In addition, PANI can be made more processable in the composite form with another water soluble such as PVA and poly(styrene sulfonic acid) which are used as stabilizers. Alternatively, when polymerization proceeds in the presence of a steric stabilizer such as poly(vinyl alcohol) (PVA),¹⁴ microscopic precipitation or aggregation can be prevented and well-dispersed particles are obtained.

For very low temperatures, lithium chloride is the best water-soluble salt due to its low molecular mass and large depression of the freezing point of water. If a combination system of a PVA/alkaline metal could be introduced in this SSDP method, a tailor-

Correspondence to: C. W. Lee (lcw@hanyang.ac.kr) or K. S. Yoon (ksyoon@ulsan.ac.kr).

Contract grant sponsor: University of Ulsan(2002-0042).

made binding site for targeted metal ions size such as Cr(III) ion (0.615 Å) could be derived from the different alkaline metal ion sizes (Li⁺: 0.76 Å K⁺: 1.38 Å, Rb⁺: 1.52 Å, and Cs⁺: 1.67 Å) for complexation.¹⁵ Herein, we report a new robust synthetic method of tailor-made PANI having a high surface area and efficient adsorption properties for the removal of Cr(III) ions based on the combination of metal ions and steric stabilizer prior to ammonium persulfate (APS) initiator addition.

EXPERIMENTAL

Synthesis of tailor-made nanoporous polyaniline

All chemicals were of analytical grade and were used as received. In a typical experiment, the SSDP method was performed in a 2-L jacketed reaction vessel. An aniline monomer (0.1 mol) and 1M HCl (400 mL) were added to the organic phase (chloroform, 200 mL) in a reaction flask equipped with a mechanical agitator. An aqueous solution (200 mL) of LiCl (5.0 g) and PVA (5.0 g) was added to the solution containing monomer at -28°C to produce a dispersed colloidal solution at -25°C. The dispersed colloidal solution was stable for some time, and 0.025 mol APS dissolved in water (100 mL) was quickly added to the colloidal solution. After reaction for 16 h, the resultant PANI was filtered and washed several times with deionized water and ethanol to remove residual reagents. After drying at 50°C for 24 h, the dark green powder of the emeraldine salt (ES) was dedoped with 1M NH₄OH solution, filtered, and dried to produce the EB polymer in high yield (23%). The morphology and structure of PANI were characterized by SEM (FE-SEM, JEOL, LTD; JSM-600F). FT-IR data were acquired using a Thermo Mattson Satellite spectrometer. X-ray diffraction (XRD) measurements were recorded using powder and a diffractometer scanning on a Rigaku generator producing a monochromatized, nickel-filtered CuK α radiation. The ionic metal concentration in the solution was measured using inductively coupled plasma (ICP) analysis.

Sorption experiments

The adsorption of alkaline metals (Li, K, Rb, and Cs) and Cr ion in aqueous solution on the tailor-made nanoporous PANI particles was performed in batch experiments. Aqueous solution (100 mL) containing alkaline metals (Li, K, Rb, or Cs) or Cr ion at a concentration of 2 mM were sonicated and incubated with a given amount of PANI particles (2 eq) at a fixed temperature of 25°C. After a desired treatment period, the PANI particles were filtered from the solution, and then the concentration of metal ion in the filtrate after adsorption was measured by ICP.

RESULTS AND DISCUSSION

Synthesis and characterization of tailor-made PANI

In our experiment, a PVA/alkaline metal system was employed as a stabilizer. Moreover, the various alkaline metals would influence the tailor-made binding site for complexation between Cr(III) ions (0.64 Å) and PANI because of the different ion sizes. To achieve this goal, tailor-made PANI was prepared in a heterogeneous medium composed of aqueous and organic phases in the presence of the stabilizer/alkaline metal for the removal of chromium. First, PVA as a stabilizer and LiCl were added into the aniline monomer water/organic solution, and the initiator APS was added to the monomer solution in one portion. In this reaction, vigorous mixing was achieved with a mechanical shaker to evenly distribute the reactants prior to polymerization. As the polymerization began, the initiator induced the formation of pink (~530 nm, observed color) nanofibers via the slow polymerization of aniline monomers since the aniline monomer and the initiator were effectively separated by a stable colloidal boundary between the aqueous and organic phases. Therefore, polymerization occurred only at the interface where all components interacted for polymerization. The newly formed ES form of the PANI nanofibers was hydrophilic and rapidly moved away from the interface, diffusing into the water layer. In this way, as the nanofibers formed, they were continuously withdrawn from the stabilized colloidal solution, thus avoiding secondary growth and allowing new nanofibers of uniform sizes (~37 nm in diameter, surface area of 45 m²/g) to grow at the interface, as observed by SEM [Fig. 1(a)]. The effect of aniline concentration on the morphology of the polymerization product was observed as an increase in nanofiber diameter to ~49 nm with an increase in aniline concentration (by two times), as shown in Figure 1(b). Thus, a low concentration of aniline was favorable for the synthesis of small diameter fibers. These results are consistent with a recent report of aniline nanofiber synthesis via the seeding method.¹⁵ The cationic metal size also has an influence on the morphology of the resulting PANI. Thus, reactions that are rapidly mixed using PVA as a stabilizer and RbCl or CsCl produce nonpure nanofibers and irregular particles [Fig. 1(c-e)]. When the reaction was performed under similar conditions but without a stabilizer, an irregular morphology of the product was observed [Fig. 1(f)]. Note that since the PANI prepared with stabilizer was in its metal-doped ES form, the affinity of the PANI salt for the solvent depended on the ionic strength and, therefore, moved from the water-containing stabilizer to the organic phase containing chloroform. Accordingly, PANI nanostructures can

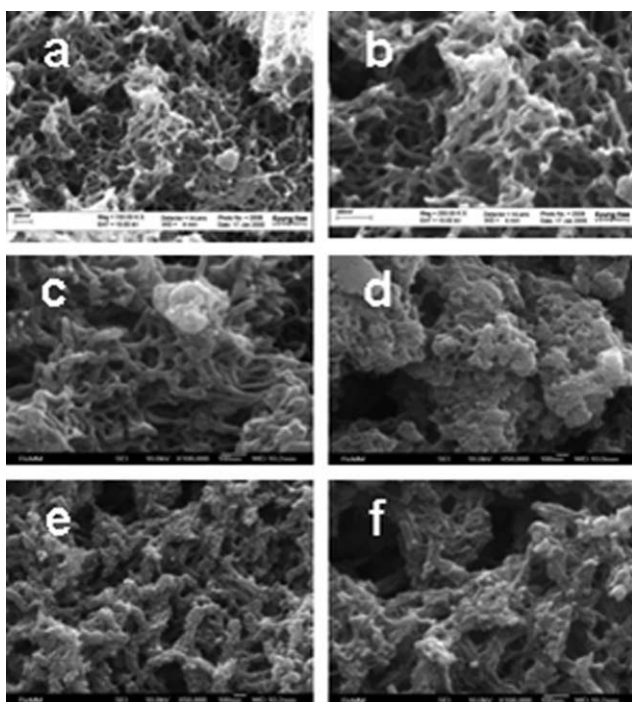


Figure 1 SEM images showing the morphologies of the tailor-made PANI nanofibers synthesized from PVA with (a) LiCl (~ 37 nm in diameter, surface area of $45 \text{ m}^2/\text{g}$, 0.25M), (b) LiCl (0.50M), (c) KCl (~ 50 nm in diameter, surface area of $33 \text{ m}^2/\text{g}$), (d) RbCl, (e) CsCl, and (f) without alkaline metal.

be made by introducing “structural directors” into the chemical polymerization bath. These structural directors include “soft templates” such as surfactants,¹⁶ organic dopants,¹⁷ or polyelectrolytes¹⁸ that assist in the self-assembly of PANI nanostructures. Kaner et al. reported that by using relatively dilute aniline solutions, PANI nanofibers could be obtained when the oxidant was added at a single time, whereas only granular PANI particulates were formed when the oxidant was added dropwise.¹⁹ The mechanism was such that when the oxidant was added dropwise, a secondary growth process competed with fibril formation of the nanofibers, which was favored when the oxidant was added all at once. However, in this study, the dropwise addition method of APS had no influence on the formation of nanofibers. Although the mechanism governing the formation of PANI nanofibers remains unclear at this point, the use of PVA as a steric stabilizer preferably directed the nanofiber structure. The steric stabilizer appears to facilitate the growth of nanofibers along the polymer chains. It is believed that the PVA reduces the formation of the number of nucleation sites on the surface of the nanofibers, allowing PANI to grow into nanofibers. Therefore, it is not surprising that PANI favors more nanoporous and compact morphologies in water with a stabilizer. Pure nanofibers of PANI formed effectively during

chemical oxidative polymerization in aqueous/organic solutions via the stabilizing system of PVA/LiCl.

The next key issue was to illustrate the existence of the potential binding site for the adsorption of Cr(III) in the PANI-EB. To do so, we compared the IR spectra of the PANI-EB obtained with and without a stabilizer. The FT-IR spectrum of the synthesized EB powder is shown in Figure 2. The EB polymer has quinoid (Q) and benzenoid (B) units along with amine and imine functional moieties. The most important peaks in the spectrum of the EB [prepared without stabilizer, Fig. 2(e)] were observed at 1590 (Q), 1487 (B), 1355 (deformation of the C–N bond), 1306 (C–N stretching), 1165 (C–N stretching), and 827 cm^{-1} (C–H deformation). These results indicate that the polymer chain is identical to that of conventional PANI. The obtained IR spectra [Fig. 2(a–d)] prepared with a stabilizer was compared with that of Figure 2(e). For instance, the bands [Fig. 2(a–d)] near 1480 (B), 1370 , 1150 , 815 , and 810 cm^{-1} were red shifted compared with those from Figure 2(e). Additionally, the band at 640 cm^{-1} from the benzenoid ring deformation appeared in the spectra of Figure 2(a–d). Thus, the bands became weak in the pure and regular nanofiber structure due to the flexibility of the benzenoid rings in the random-coil conformation after decomplexation of the alkaline metal from the PANI-metal complex. This indicates that the free volume of the nanofiber sample increased to produce binding sites. In contrast, the compact-coil conformation (or aggregation) of PANI without a stabilizer had a much weaker band near 640 cm^{-1} [Fig. 2(e)], indicating that the free volume decreased. Hence, the IR spectra support the thesis that potential metal ion binding sites existed in the PANI-EB obtained with the stabilizer.

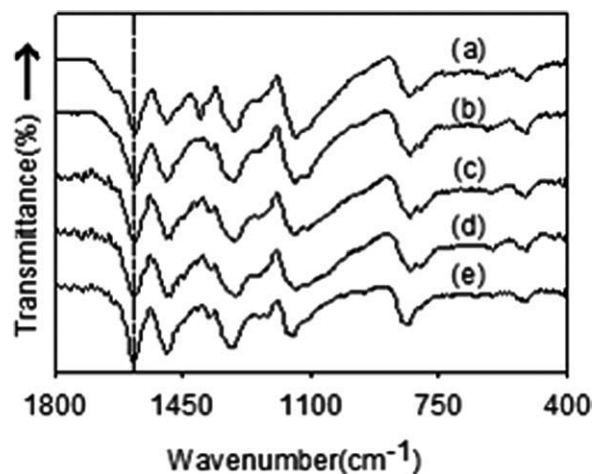


Figure 2 FT-IR spectra of the tailor-made PANI nanofibers synthesized from PVA with (a) LiCl, (b) KCl, (c) RbCl, (d) CsCl, and (e) without alkaline metal.

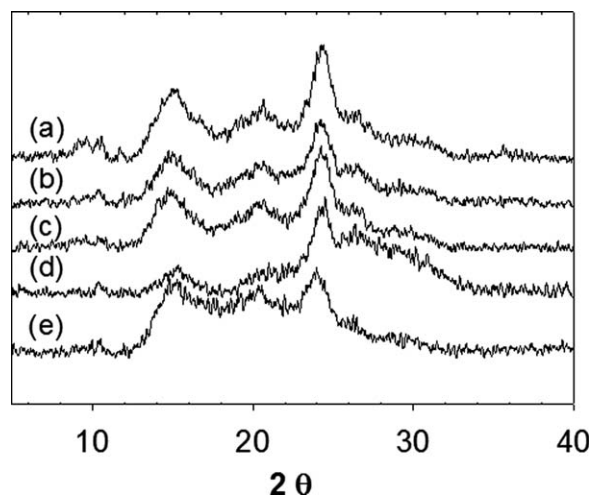


Figure 3 X-ray diffraction powder patterns of the tailor-made PANI nanofibers synthesized from PVA with (a) LiCl, (b) KCl, (c) RbCl, (d) CsCl, and (e) without alkaline metal.

Interestingly, significant differences in the X-ray diffraction (XRD) due to an alkaline metal effect were observed, as shown in Figure 3. XRD of PANI nanofibers (without metal) exhibited only weak and broad peaks, indicating that the nanofibers were primarily amorphous. A weak peak at $2\theta = 24^\circ$ was observed and was ascribed to the periodicity parallel to the ordered polymer chains [Fig. 3(e)].¹⁶ XRD of PANI-metal composites exhibited intense peaks corresponding to the same range for the aggregated PANI structure [Fig. 3(a–d)]. The d -spacing (~ 3.5 Å) associated with the diffraction peak at 24° corresponds to the face-to-face interchain stacking distance between the phenyl rings. Thus, the increase in intensity of the 24° peak along with the decrease in the amorphous phase intensity implies improved π - π interchain stacking due to the regular nanofiber structure. This suggests a more planar chain conformation with reduced torsion angles between the phenyl ring and the plane of the backbone, producing a pronounced channel with binding sites for the effective adsorption of cationic metals such as Cr(III).

Adsorption properties

A useful property of the tailor-made PANI is its three-dimensional branched nature, which could provide cavities for the complexation of many metal ions. The PANI may act as templates for metal complexation with coordination occurring potentially at the interior. Thus, they may serve as useful polyfunctional ligands and metal ion adsorption agents. Generally, the adsorption capacity is affected by the properties of the adsorbent, including its structure, size, and surface chemistry.²⁰ The approach

described for the synthesis of a tailor-made PANI derived from LiCl for the adsorption of Cr(III) should be especially applicable to the adsorption of Cr(III) ions. To achieve this goal, redox chemistry was employed for the subsequent experiment between PANI and hexavalent Cr(VI). Thus, a strong oxidant hexavalent Cr(VI), such as $K_2Cr_2O_7$, which has a dichromate anion form in water, oxidizes the PANI-EB into pernigraniline (PB), and the hexavalent Cr(VI) is reduced to the cationic trivalent form Cr(III). Accordingly, the adsorption or complexation of trivalent Cr(III) can effectively occur with the imine group of PB.

Figure 4 shows the FT-IR spectra of PANI-EB before complexation and Cr(III)/PANI after complexation. Before complexation, the quinoid peak at 1590 cm^{-1} , the benzenoid peak at 1487 cm^{-1} , the C–N stretching near the quinoid ring at 1375 cm^{-1} , and the C–N stretching in the secondary aromatic amine at 1308 cm^{-1} were observed. After complexation, the quinoid peak at 1590 cm^{-1} was stronger due to the oxidation by the $K_2Cr_2O_7$ oxidant. This result was identical to those of the characteristic peaks of the synthesized PB form.²¹ Therefore, the intensity at 1375 cm^{-1} disappeared significantly with the complexation of Cr(III). Furthermore, the corresponding benzenoid, C–N stretching and $CH_{\text{in-plane}}$ bending at 1487 , 1375 , and 1136 cm^{-1} were shifted to 1598 and 1491 cm^{-1} , indicating complexation. It is clear from the FT-IR data that Cr(III) ions had migrated into the PANI and complexed with the interior amine groups. Evidence for the presence of the trivalent chromium species was obtained by adjusting the pH of the solution with NaOH. A white precipitate formed, indicating the presence of Cr(III) and the formation of $Cr(OH)_3$. Thus, the hexavalent Cr was reduced to trivalent Cr to produce an insoluble PANI-Cr(III) complex. Similar FT-IR results

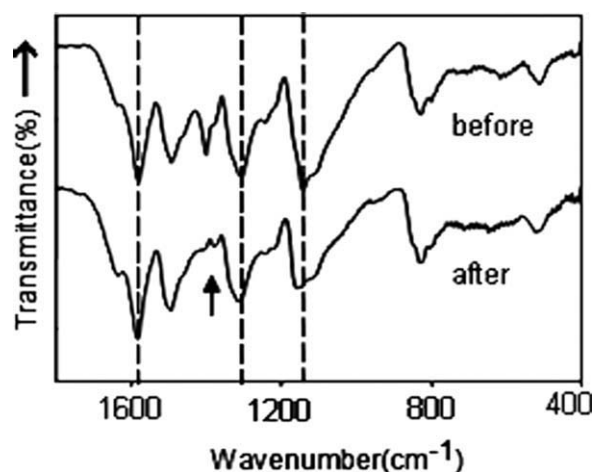


Figure 4 FT-IR spectra of the PANI-EB/Cr ions before and after complexation.

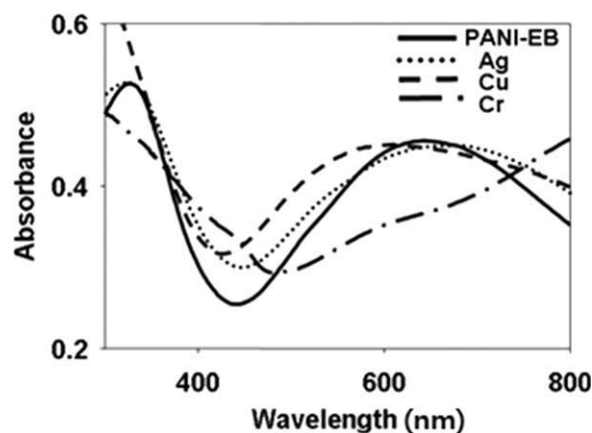


Figure 5 UV spectra of the PANI-EB/metal ions (Ag^+ , Cu^{2+} , Cr^{3+}) before and after complexation.

were obtained with Cr ion complexation in the presence of Ag^+ or Cu^{2+} , and no differences in complexation for each metal ion were observed.

To investigate the difference in complexation for each metal ion, the UV spectral changes were studied via the metal complexation when metal ions were added to the nanoporous PANI-EB solution. The degree of absorbance of the exciton band (near 630 nm) was retained in the presence of Ag^+ or Cu^{2+} , while the exciton band significantly decreased and two new bands, near 430 and 800 nm, increased in the presence of Cr. These peaks are typically assigned to polaron bands originating from the conducting (i.e., doped) EB salts. Furthermore, the metal-complexed solutions were green, indicating that the polaron bands could derive a stronger binding affinity in the form of a PANI-EB-Cr complexation. These phenomena are presumably related to the fact that the more oxidized form or electron-deficient species such as the Cr^{3+} ion can promote the efficient formation of polaron bands due to the classical doping process (Fig. 5).

In addition, the adsorption of Cr(VI) ions on PANI-EB synthesized from various alkaline metal ions (Li, K, Rb, and Cs) were investigated, as shown in Figure 6. In this study, the aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ (VI) (3.3×10^{-4} M) was prepared by successive dilutions of a stock solution (6.8×10^{-2} M). A 20-mL solution (3.3×10^{-4} M) of Cr(VI) as a strong oxidant was tested with 30 mg of PANI EB. After sonication for 5 min at 25°C , the solution was vigorously stirred for 30 min to produce the partially oxidized polymer PANI-PB and the reduced metal Cr(III). The backbone of PB has a quinoid structure which provides rigidity to the polymer, and the amine or imine group of PANI can be used for strongly binding cationic metals. The resulting absorbent was separated from the solution with a syringe filter. The filtered solution containing chro-

mium ion was analyzed using the inductively coupled plasma (ICP) method. As shown in Figure 6, the uptake of Cr(III) ions was initially fast, since the majority of Cr(III) was adsorbed within the first few minutes, and a complete equilibrium between the two phases was established within 50 min for all cases. This initial, fast adsorption occurs due to the relatively small number of adsorbed Cr species compared with the high number of available nanoporous surface sites. A relative change in Cr(III) uptake occurs [Fig. 6(a–d)], i.e., the percentage adsorption increases from 38% to 72%, as the alkaline metal dopant size (or pore size) used in the PANI-EB system was altered (Li^+ : 0.76 Å, K^+ : 1.02 Å, Rb^+ : 1.38 Å, and Cs^+ : 1.52 Å). Thus, a tailor-made PANI/Li system provides the best adsorption result for trivalent Cr (0.615 Å), as shown in Figure 6(a). The absorption capability of the aggregated and irregular compact-coil PANI prepared without stabilizer [Fig. 6(e)] shows only moderate adsorption properties. The increase in adsorption occurs due to the high availability of surface area derived from PANI with a nanofiber structure, as well as the appropriate size of the metal ion adsorbent sites. The adsorption properties for other transition metal ions ($\text{Ag}(\text{NO}_3)$ and $\text{Cu}(\text{NO}_3)_2$) as a nonoxidant in the same adsorption condition were also investigated. However, the adsorption results for the treatment of $\text{Ag}(\text{NO}_3)$ or $\text{Cu}(\text{NO}_3)_2$ in the presence of tailor-made PANI-EB(Li) significantly decreased in the range of 30–40%. As a result, the nonoxidized PANI nanofibers do not provide sufficient adsorption binding sites since the oxidized form (pernigraniline base) of PANI derived from $\text{K}_2\text{Cr}_2\text{O}_7$ (VI) as a strong oxidant has a rigid quinoid structure (imine group), and PANI can provide a polymer template and effective binding sites for the metal ions.

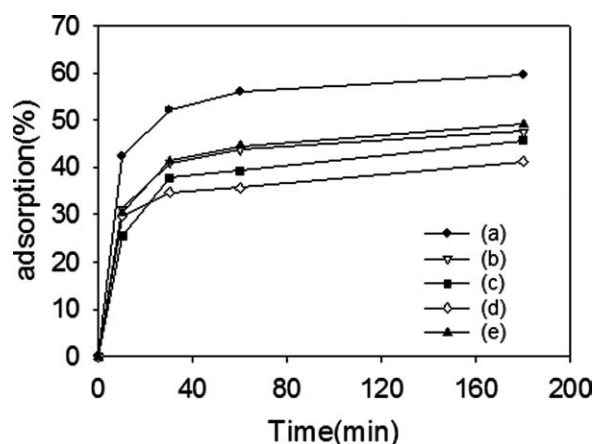


Figure 6 Alkaline metal effect of the tailor-made PANI nanofibers on the total chromium adsorption with (a) LiCl, (b) KCl, (c) RbCl, (d) CsCl, and (e) without alkaline metal.

CONCLUSIONS

In summary, the PVA stabilizer/LiCl system avoids secondary growth and allows for the growth of new nanofibers of uniform size at the water/organic interface. Furthermore, the tailor-made nanofiber PANI synthesized using the SSDP method with the stabilizer system generates matching cavity sizes for the removal of target metals, as was demonstrated for the effective adsorption of Cr(III). This tailor-made PANI-EB was easily oxidized by the Cr(VI) oxidant, $K_2Cr_2O_7$, based on the unique redox properties of PANI, resulting in an oxidized form with a rigid polymer template and effective metal ion binding sites. Application of the designed polymers with tailor-made binding sites to the environment field would enable the efficient adsorption and removal of hazardous metals. The strategy described above for the preparation of effective adsorbents as well as the synthesis of nanofibers should serve as interesting and important contributions to the fields of PANI and environmental chemistry.

References

1. Li, X. G.; Feng, H.; Huang, M. R. *Chem Eur J* 2009, 15, 4573.
2. Li, X. G.; Feng, H.; Huang, M. R. *Chem Eur J* 2010, 16, 10113.
3. Huang, M. R.; Peng, Q. Y.; Li, X. G. *Chem Eur J* 2006, 12, 4341.
4. Lu, Q. F.; Huang, M. R.; Li, X. G. *Chem Eur J* 2007, 13, 6009.
5. Kowalski, Z. *J Hazard Mater* 1994, 37, 137.
6. Chiang, C. K.; MacDiamid, A. G. *Synth Met* 1996, 13, 193.
7. Higuchi, M.; Imoda, D.; Hirao, T. *Macromolecules* 1996, 29, 8277.
8. Dimitriev, O. P. *Macromolecules* 2004, 37, 3388.
9. Izumi, C. M. S.; Ferreira, D. C.; Constanino, R. L.; Temperini, L. A. *Macromolecules* 2007, 40, 3204.
10. Kitani, A.; Akashi, T.; Sugimoto, K.; Ito, S. *Synth Met* 2001, 121, 1301.
11. Drelinkiewicz, A.; Hasik, M.; Kloc, M.; *Catal Lett* 2000, 64, 41.
12. Lee, K. H.; Cho, S. U.; Park, S. H.; Heeger, A. J.; Lee, C. W.; Lee, S. H. *Nature* 2006, 441, 65.
13. Lee, S. H.; Lee, D. H.; Lee, C. W. *Adv Funct Mater* 2005, 15, 1495.
14. Cho, M. S.; Park, S. Y.; Hwang, J. Y.; Choi, H. J. *Mater Sci Eng C* 2004, 24, 15.
15. Shannon, R. D. *Acta Cryst* 1976, A32, 751.
16. Yu, L.; Lee, J. I.; Shin, K. W.; Park, C. E.; Holze, R. *J Appl Polym Sci* 2003, 88, 1550.
17. Qiu, H. J.; Wan, M. X.; Matthews, B. M.; Dai, M. *Macromolecules* 2001, 34, 675.
18. Liu, J. M.; Yang, S. C. *J Chem Soc Chem Commun* 1991, 1529.
19. Huang, J.; Kaner, R. B. *Angew Chem Int Ed* 2004, 43, 5817.
20. Huang, J. X.; Kaner, R. B. *J Am Chem Soc* 2004, 126, 851.
21. Chi, K. W.; Hwang, H. Y.; Park, J. Y.; Lee, C. W. *Synth Met* 2009, 159, 26.
22. Moon, Y. B.; Cao, Y.; Smith, P.; Heeger, A. J. *J Polym Commun* 1989, 30, 196.