Powerful Reactive Sorption of Silver(I) and Mercury(II) onto Poly(o-phenylenediamine) Microparticles

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The strong adsorbability of Ag(I) and Hg(II) ions onto fine poly(o-phenylenediamine) (PoPD) microparticles synthesized through a chemically oxidative polymerization of o-phenylenediamine was systematically examined and PoPD/Ag nanocomposites were facilely prepared through the reactive sorption method. The effect of the (NH₄)₂S₂O₈ oxidant/o-phenylenediamine monomer ratio on the polymerization yield, macromolecular structure, conductivity, and insolubility of the PoPD microparticles was studied. The Ag(I) adsorbability of the microparticles was significantly optimized by varying the oxidant/monomer ratio, doping state, Ag(I) concentration, sorption time, and solution pH. The Ag(I) adsorbance steadily increases with changing oxidant/monomer molar ratio from 3/1 to 1/1, reaching up to the highest Ag(I) adsorbance of 533 mg·g⁻¹ at the oxidant/monomer ratio of 1/1. The sorption process fits the pseudosecond-order kinetics. The adsorption is rapid because both the adsorbance and adsorptivity within 30 min reach up to 76% of the final values. The initial sorption rate of silver ions obtained from the pseudosecond-order equation is 12.9 mg·g⁻¹·min⁻¹. The highest adsorptivity of silver ions is up to 99.1%. The optimal solution pH for Ag(I) sorption is around 5.0. The sorption mechanism may include the chelation and redox reaction between Ag(I) ions and amine/amine groups on the PoPD chains. Similarly, the microparticles also have powerful Hg(II) adsorbility with 96.7% adsorptivity at an initial Hg(II) concentration of 4 mM. Competitive sorption between Ag(I) and Hg(II) in their mixture solution onto the microparticles was studied, exhibiting a preferential sorption toward Ag(I). The microparticles as a cost-effective sorbent demonstrate a promising application in the removal and even recovery of heavy-metal ions from wastewater. The PoPD/Ag nanocomposites possess (1) high Ag content of 34.8 wt %, (2) small diameter of Ag nanoparticles of around 10−20 nm, (3) narrow size distribution, (4) intrinsic electrical conductivity that is much higher than that of original PoPD microparticles without Ag.

1. Introduction

The pollution of heavy-metal ions from many industries, such as metal plating, mining, painting, smelting, car radiator manufacturing, petroleum refining and agricultural activities, has already become a worldwide serious problem that endangers the environment and health of human beings.1,2 Various established technologies, including chemical precipitation,3 electrolysis,4 membrane separation,5,6 ion exchange,7 flotation,8 and sorption,9 have been employed for the recovery and removal of hazardous metal ions from wastewater. Among all of these treatment processes, sorption using suitable sorbents is considered one of the most effective and economical methods in terms of the simplicity of design and easiness of operation. Great efforts have been contributed to the development of new sorbents like activated carbon,9,10 chelating resin,11,12 hydroxypatite,13 silica gel,14 zeolite,15 clay,16 goethite,17 modified mineral sorbent,18 and polymer.19,20 The widely studied sorbent is activated carbon with a large surface area, which is produced by heating carbon in the absence of air. In spite of its prolific application, activated carbon remains an expensive sorbent that is employed more frequently for sorption of organic compounds rather than heavy-metal ions. Therefore, further attention and research are required to develop novel sorbents for heavy-metal ions with high efficiency and low cost.

Recently, aromatic amine polymers have attracted much interest of researchers due to their unique multifunctionality, involving variable conductivity, strong electroactivity, colorful electrochromism, good optical and magnetic activity, and high environmental and thermal stability.21,22 Moreover, some aromatic diamine polymers show highly reactive sensitivity to some metal...
ions, including Ag(I), Cu(II), Hg(II), Pb(II), and Cr(III), through chelation or redox reaction with the amino/imino groups on the polymer chains. Poly(1,8-diaminonaphthalene) prepared by electrolypolymerization of 1,8-diaminonaphthalene has been successfully applied to sense and detect Pb2+ ions, and electrosynthesized poly(1,8-diaminonaphthalene) film could rapidly and efficiently extract heavy-metal ions from their aqueous solution without having to apply any potential. Noticeably, the aromatic diamine polymers with strong binding ability to heavy-metal ions have shown a promising application as cost-efficient sorbents because they can be simply and productively synthesized by chemically oxidative polymerization. Particularly, poly(1,8-diaminonaphthalene) microparticles synthesized by chemically oxidative polymerization were found to exhibit high Ag(I) adsorbance of 1924 mg g⁻¹. Novel copolymer microparticles from 4-sulfonic diphenylamine and 1,8-diaminonaphthalene were proved to possess an even higher Ag(I) adsorbance of up to 2000 mg g⁻¹, which might be the highest Ag(I) adsorbance reported thus far. However, the high price of 1,8-diaminonaphthalene monomer might restrict the extensive application of poly(1,8-diaminonaphthalene) as economic sorbents. As one more important aromatic diamine polymer, polyphenylenediamine microparticles synthesized from inexpensive monomers also possess a strong capability to adsorb Pb(II) ions through a possible chelation between Pb(II) ions and -NH₂/-NH-≡N- groups on the macromolecular chains, indicating a great potential as a cost-effective sorbent. However, the sorption of other heavy-metal ions such as Ag(I) and Hg(II) onto the polyphenylenediamines, especially on poly(o-phenylenediamine) (PoPD) microparticles, has not been investigated systematically. Conducting polymer/metal nanocomposites have been extensively applied in various important fields, such as electroiminescence; nonlinear optics, sensor, catalysis, biochemistry, and digital memory devices because of their novel functionality, including outstanding intrinsic semiconductivity, excellent reactive catalysis, and powerful anticorrosion properties. The oxidative polymers from phenylenediamines, which bear even more functional amino/imino groups than poly(1,8-diaminonaphthalene), have become an important subject of active investigation owing to their better performances just like reversible redox reactivity, chelation, electroactivity, electrochromism, and permselectivity. The incorporation of metal nanoparticles into polyphenylenediamine has not only remained as part of the intrinsic properties of the polymers but also has enhanced their electric and catalytic activities to chemical and biological substances. The biosensors based on polyphenylenediamine/metal nanocomposites exhibited excellent performance, especially remarkably enhanced sensitivity and anti-interference ability in the detection and determination for biosubstances. The biosensors based on polyphenylenediamine/metal nanocomposites exhibited excellent performance, especially remarkably enhanced sensitivity and anti-interference ability in the detection and determination for biosubstances.

2. Experimental Section

2.1. Materials. o-Phenylenediamine (oPD), ammonium persulfate (NH₄)₂S₂O₈, glacial acetic acid, silver nitrate, mercury nitrate, chloroform (CHCl₃), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and N-methylpyrrolidone (NMP) of analytical reagent grade were commercially obtained and used as received.

2.2. Preparation of Fine PoPD Microparticles. Fine PoPD microparticles were synthesized through chemical oxidative polymerization of the oPD in boiling glacial acetic acid at 118 °C using ammonium persulfate as an oxidant. A typical procedure for the preparation of PoPD microparticles was as follows: o-phenylenediamine (oPD, 6.48 g, 60 mmol) was dissolved in 114 mL of warm glacial acetic acid at 40 °C in a 1 L three-necked glass flask. The oxidant solution of (NH₄)₂S₂O₈ (13.68 g, 60 mmol) dissolved in 6 mL water was added dropwise to the warm oPD solution at a rate of one drop (around 60 μL) every 3 s for 40 min (oxidant/monomer molar ratio = 1/1). Immediately after the first few drops, the solution turned dark brown and became black with the continuous dropwise addition of the oxidant. The reaction mixture was then refluxed at 118 °C for 72 h. The resulting polymer microparticles were filtered and rinsed thoroughly with distilled water to remove the residual oxidant and monomer and water-soluble oligomers. Half of the resulting black products were left to dry in air for 3 days for the obtaining of virgin PoPD salt microparticles. The rest half of products were treated with 0.1 M NaOH for 3 h first and then dried for 3 days to obtain the PoPD base microparticles. The PoPD salt and base microparticles were prepared to investigate the effect of doping state on the Ag(I) sorption on the PoPD. The PoPD microparticles with the other two oxidant/monomer molar ratios of 2/1 and 3/1 were also prepared in a similar way through changing the amount of oxidants.

2.3. Sorption of Ag(I) and Hg(II) onto the PoPD Microparticles. The sorption of Ag(I) and Hg(II) ions onto two types of PoPD microparticles was performed in a batch experiment. For batch tests, a given amount of PoPD microparticles (50 mg) was added into AgNO₃ or Hg(NO₃)₂ aqueous solution (25 mL) at a known concentration and constant temperature of 30 °C in a dark environment. After a desired period of sorption, the microparticles were filtered from the solution and the concentration of metal ions
in the filtrate was measured by a molar titration at a residual metal-ion concentration of higher than 10 mM or by inductively coupled plasma at a residual metal-ion concentration of lower than 10 mM. The adsorbance and adsorptivity of metal ions onto the microparticles were calculated according to the equations.25 The initial pH value of AgNO₃ aqueous solution was carefully adjusted between 1.0–9.0 by adding a certain amount of HNO₃ or NaOH solutions with different pH values. Two linearized sorption models on Langmuir and Freundlich isotherms were applied to analyze sorption equilibrium.26 The sorption kinetics of Ag(I) ions onto the microparticles was studied by using the pseudofirst-order and pseudosecond-order kinetic equations.

2.4. Measurements. The IR spectra were recorded on KBr pellets on a Nicolet Magna-IR 550 spectrometer at 2 cm⁻¹ resolution. Wide-angle X-ray diffraction of the microparticles was performed with a Bruker D8 Advance X-ray diffractometer made in Germany with Cu Kα radiation at a scanning rate of 0.888° min⁻¹. The size and morphology of the PoPD particles were observed by Jol TEM-2010 high-resolution transmission electron microscopy. The size and distribution of the as-prepared particles in water were analyzed on Beckman Coulter LS230 laser particle-size analyzer. The bulk electrical conductivity of the PoPD microparticles was measured by a two-disc method using a UT 70A multimeter at ambient temperature. The insolubility of the particles was evaluated using the following method: Polymer powders (5 mg) were added into the solvent (1 mL) and dispersed thoroughly. After the mixture was swayed continuously for 24 h at room temperature, the insolubility was characterized semiquantitatively. X-ray photoelectron spectra were performed with a PHI 5000C ESCA system XPS analyzer and the spectra were calibrated by assuming a 284.6 eV binding energy for aromatic carbons.

3. Results and Discussion

3.1. Synthesis of Fine PoPD Microparticles. The chemical oxidative polymerization of the oPD monomer with (NH₄)₂S₂O₈ as an oxidant in boiling glacial acetic acid afforded fine, uniform, and black PoPD microparticles as products. During the polymerization process, the stable oPD dimers and trimers were formed immediately after the first few drops of oxidants, and then more energy was required for these oligomers to be oxidized or lose electrons to continue the chain growth at 118 °C. The PoPD finally synthesized exhibits a rigid rodlike structure containing phenazine units with some open rings (Scheme 1). The number-average diameter of the microparticles without ultrasonic treatment is 4.572 μm. As listed in Table 1, the polymerization yield and electrical conductivity of the microparticles are significantly dependent on the oxidant/monomer ratio, demonstrating the maximum at the oxidant/monomer molar ratio of 2/1. At lower oxidant content, the oxidant was consumed very quickly; consequently, insufficient oxidant was left to oxidize the residual monomers for further chain propagation and polymerization, resulting in much lower yield and conductivity. When more oxidant was added, more monomers could be oxidized and activated to form radical cations and then more continual chain propagation would occur, leading to the formation of more polymers with higher conductivity. However, too much oxidant would produce more soluble oligomers in the initial polymerization stage and might cause the denitrogenation of polymers during the later polymerization process, finally lowering polymerization yield and conductivity. Apparently, the optimal oxidant/monomer molar ratio should be 2/1 for the synthesis of PoPD with the maximal yield and conductivity.

It can be seen from Table 1 that the oxidant/monomer ratio and doping state greatly influence the solubility of PoPD microparticles in different solvents excluding DMSO. The microparticles obtained are substantially insoluble in 10 mM HCl and NaOH aqueous media and some organic solvents such as CHCl₃ and THF, implying that the microparticles can be a chemical-resistant sorbent in the four media. The gradually enhanced solubility of PoPD in DMSO with increasing oxidant/monomer ratio is attributed to gradually decreased molecular weight, indicating that a lower oxidant/monomer ratio is favorable for the formation of PoPD with higher molecular weight.

3.2. Structure of PoPD Microparticles. The macromolecular structure of the PoPDs formed with different oxidant/monomer ratios was studied by IR spectroscopy (Figure 1). The broad bands at 3379 and 3218 cm⁻¹ are due to the characteristic stretching vibration of N–H bond in amino (–NH₂) and imino (–NH) groups, respectively, strongly suggesting the presence of a large amount of amino and imino groups in the chains of PoPD salts. The two peaks at 1620 and 1514 cm⁻¹ are attributed to the stretching of quinoid and benzenoid rings, respectively. Another two weak bands at 1355 and 1232 cm⁻¹ are attributable to the C–N stretching vibration in the quinoid and benzenoid units, respectively. The band at 849 cm⁻¹ is attributed to the C–H out-of-plane bending vibration of the 1,2,4,5-tetrasubstituted benzene ring, implying that the polymer has the basic phenazine skeleton. The peaks at 616 and 1134 cm⁻¹ are ascribed to respective out-of-plane and in-plane bending vibrations of the 1,2,4-trisubstituted benzene rings, indicative that the PoPD is not fully ladder polymers. The sharp and strong peak at 763 cm⁻¹ might be assigned to C–H out-of-plane bending of aromatic nuclei. The IR spectral results suggest that the PoPD synthesized by chemical oxidative polymerization exhibits a rigid rodlike structure containing phenazine units with some open rings.51

It is found that the oxidant/monomer ratio affects the intensity and wavenumber of IR bands, as shown in Figure 1. With
indicate an increased quinoid content but a decreased benzenoid intensity at 1620 cm⁻¹ increasing oxidant/monomer ratio from 1/1 to 3/1, the band Figure 2.

![Figure 1. IR spectra of PoPD salt and base microparticles prepared at different oxidant/monomer molar ratios of 1/1, 2/1, and 3/1 in boiling glacial acetic acid for 24 h.](image1)

is much weaker at an oxidant/monomer ratio of 3/1, probably suggesting lower molecular weight. It is noteworthy that there is no major difference in the IR spectra between salt and base microparticles prepared at different oxidant/monomer molar ratios of 1/1, 2/1, and 3/1 in boiling glacial acetic acid for 24 h.22 Accordingly, it could be concluded that the PoPD synthesized at an oxidant/monomer molar ratio of 1/1 has a higher molecular weight that has been confirmed by its lowest solubility in DMSO in Table 1. It is noteworthy that there is no major difference in the IR spectra between salt and base states of PoPD microparticles at the same oxidant/monomer ratio.

The supramolecular structure of the PoPD salt microparticles has been characterized by wide-angle X-ray diffraction technique. It is seen from Figure 2 that the microparticles exhibit a broad peak at a Bragg angle of 26°, a weak peak at 18°, together with a possible diffraction at around 5°. The broad diffractogram indicates that the particles possess an amorphous structure piled in a loose and disordered way, which is favorable for the sorption/penetration of metal ions onto/into them.

3.3. Sorption and Its Mechanism of Ag(I) onto PoPD Microparticles. To prove the occurrence of sorption and further clarify the sorption mechanism, several typical techniques such as XRD, TEM, IR, and XPS were employed together. Two kinds of sorption mechanisms were disclosed: redox and chelation sorptions. The redox sorption could be verified by these four techniques. It is found from Figure 2 that Ag(I) has been reduced to Ag(0) by the amino/imino(−NH/−NH−) groups on the PoPD chains after sorption because the Ag(I)-adsorbing PoPD microparticles illustrate three additional sharp peaks at 38°, 44°, and 64° corresponding to the diffraction of (111), (200), and (220) lattice planes of Ag crystals, respectively. TEM images in Figure 3 validate the existence of a large amount of Ag particles on the microparticles. The diameter of most Ag particles is between 10–50 nm after adsorbing Ag(I) at the initial Ag(I) concentration of 10.77 mM for 24 h, as revealed in parts a and b of Figure 3. It is of interest that these Ag nanoparticles were well dispersed on the surface of the microparticles. Some Ag particles that dropped from the surface of PoPD were larger with a diameter of over 100 nm in parts c–e and g of Figure 3, and these larger Ag crystals seem to be single crystals that are proved by electron diffraction patterns in parts f and h of Figure 3.

The occurrence of redox sorption can be further confirmed by obvious variation of IR spectra of PoPD before and after the Ag(I) sorption. It is seen from Figure 4 that the intensity of nearly all of the peaks weakened after adsorbing Ag(I), especially the peak at 3392 cm⁻¹ corresponding to amino and imino groups, because the amount of N−H bonds must become less after the amino/imino groups as major redox active sites have been used to reduce Ag(I) into Ag(0). The presence of Ag(0) particles in the PoPD microparticles could also weaken the IR absorption peaks.

To ascertain the occurrence of chelation sorption, the XPS method was employed to characterize the element composition and its corresponding valency composition, which are summarized in Figure 5 and Table 2. It is found that there are both Ag(I) and Ag(0) on the PoPD microparticles. The silver compositions on PoPD salt and base particles are obviously different after adsorbing Ag(I). The Ag(I) percentage on the PoPD base is higher than that on the PoPD salt, whereas the Ag(0) percentage on the salt is higher than that on the base. This implies that the redox capability of Ag(I) on the salt is stronger than that on the base, whereas the latter chelation capability toward Ag(I) is stronger than the former because one major difference between the PoPD salt and base is the content of neutral amino/imino groups and positively charged amino/imino groups. It appears that chelation sorption mainly happens on neutral amino/imino groups, whereas redox sorption mainly happens on positively charged amino/imino groups.

After adsorbing Ag(I) ions of 100.15 mM for 24 h, the Ag contents on the PoPD salt and base obtained at oxidant/monomer molar ratio of 1/1 are respectively 29.2 and 24.4 wt % based on calculation from the element composition on the surface of PoPD under the hypothesis that the molar content of H is equal to that of C. Both of them are less than those obtained by the titration method, indicating that more Ag element exists within the interior of the PoPD microparticles, which could be attributed to looser structure of PoPD particles.

To gain some deep insights into the sorption process of Ag(I) onto PoPD particles, the XPS method in Figure 6 was also applied to characterize the influence of sorption time on PoPD structure and composition. It is calculated from Figure 6 that the Ag(I) and Ag(0) contents are 56% and 44% respectively in the PoPD salt particles adsorbing Ag(I) for the sorption time of 30 min,
whereas Ag(I) and Ag(0) contents become 39% and 61% respectively for the sorption time of 24 h, suggesting that the chelation sorption is predominant at the initial sorption stage but redox sorption is gradually becoming predominant with increasing sorption time. On the basis of XPS spectra in Figure 6, the neutral –N, –NH, –NH2, and protonated –N+, –NH+,– correspond respectively to 398.1, 399.3, 400.2, 401.2, and 405.7 eV.36,37 The molar ratio of protonated –N+ and –NH+ groups decreased from 18.4 to 13.9 mol %, indicating that the process of Ag(I) sorption is accompanied by the dedoping and then H+ transfer from the protonated amino/imino groups into solution. This has been verified by the decrease in pH value of AgNO3 solution with an increase in the sorption time (Table 3). The higher the Ag(I) adsorbance, the more pH value decreases.

Several important factors such as oxidant/monomer ratio, doping state, initial Ag(I) concentration, and sorption time have been confirmed by the fact that the redox sorption is stronger for the PoPD salt for all oxidant/monomer ratios.

On the basis of all of these discussions above, the sorption mechanism was proposed as follows:

(1) In a short-term sorption, neutral amine/imine groups participate in the intermolecular or even intramolecular chelation with Ag(I) ions (parts a and b of Scheme 2), and physical sorption very rapidly happens simultaneously.

(2) Only a small amount of protonated amine/imine groups take part in redox sorption at an initial stage of Ag(I) sorption because the redox sorption process is relatively time consuming. With the sorption proceeding, Ag(I) ions are reduced by protonated amino (–NH2) and imino (–NH–) groups (part c of Scheme 2). Accompanying the sorption of Ag(I) ions, H+ and doped cations were released from the PoPD chains, resulting in a decrease in pH value. The more the Ag(I) ions are reduced, the more the pH value decreases.

Figure 3. TEM images (a–c, g) and electron diffraction patterns (f, h) of PoPD salt microparticles (oxidant/monomer ratio = 1/1) after adsorbing Ag(I) at a concentration of 10.77 mM at the original pH 5.51 for 24 h at 30 °C. (f) and (h) correspond to (e) and (g), respectively.

Figure 4. IR spectra of PoPD salt and base particles (synthesized at oxidant/monomer ratio = 1/1) before and after sorption of Ag(I) of 100.15 mM at the original pH 5.38 for 24 h at 30 °C.

Figure 5. Ag 3d5/2 and N 1s core-level spectra from XPS of PoPD/Ag composites of the PoPD salt (a, b) and PoPD base (c, d) adsorbing Ag(I) at 100.15 mM at the original pH of 5.38 for 24 h. The PoPD salt and base were both prepared with oxidant/monomer molar ratio of 1/1.


Figure 6. Ag 3d5/2 and N 1s core-level spectra from XPS of PoPD/Ag composites of the PoPD salt (synthesized at oxidant/monomer molar ratio of 1/1) adsorbing Ag(I) at 43.09 mM at the original pH of 5.41 for 0.5 h (a, b) and 24 h (c, d).

Figure 7. Effects of oxidant/monomer molar ratio and doping state on Ag(I) adsorbance of the PoPD microparticles at an initial Ag(I) concentration of 100.15 mM at the original pH 5.38, and 43.09 mM at the original pH 5.41 with a sorbent dosage of 50 mg for a sorption time of 24 h at 30 °C.

The polymerization yield at different oxidant/monomer molar ratios might be utilized to assess the preparation cost of sorbents. Therefore, we introduce a parameter $Q$ (mg·g$^{-1}$) to represent the adsorbance of per gram oPD monomer, which can be obtained by multiplying the sorption capacity of PoPD and the polymerization yield. Corresponding to the oxidant/monomer molar ratio of 1/1, 2/1, and 3/1, the calculated $Q$ values are 213, 353, and 267 mg·g$^{-1}$, respectively. Apparently, the oxidant/monomer molar ratio of 2/1 is the optimal polymerization condition to synthesize PoPD microparticles that would be served as the most cost-effective sorbents.

3.5. Effect of Doping State. As shown in Figure 7, it is surprisingly found that the dedoping process has a different effect on the Ag(I) sorption onto PoPD particles synthesized at different oxidant/monomer ratios. The Ag(I) adsorbability of PoPD salt particles is much stronger than that of PoPD base particles at the same lower oxidant/monomer molar ratio of 1/1, but the difference between the two states becomes smaller as the oxidant/monomer ratio increases, and finally the PoPD base particles even have stronger 43.09 mM Ag(I) adsorbability than PoPD salt particles at the same higher oxidant/monomer molar ratio of 3/1. As proposed in the above discussion about the sorption mechanism, there exist two sorption behaviors including the redox sorption between protonated amine/imine groups and Ag(I) ions as well as the chelation sorption between neutral amine/imine groups and Ag(I) ions. The dedoping process has turned more protonated amine/imine groups into neutral groups, causing an enhanced chelation sorption but a decreased redox sorption. As shown in Scheme 2, two chelation groups are needed, whereas only one reduction group is needed to reactively adsorb one Ag(I) ion. In other words, the enhancement of chelation adsorbance cannot counteract the decline of redox adsorbance. As a result, the PoPD particles synthesized at the same oxidant/monomer ratio of 1/1 demonstrate much lower total Ag(I) adsorbance in a base state than in a salt state. However, the PoPD particles synthesized at oxidant/monomer molar ratio of 3/1 possess so high of an oxidation state that the redox reaction hardly happens. Then the more neutral amine/imine groups produced by dedoping process are beneficial to the chelation sorption that dominates the Ag(I) sorption at an oxidant/monomer molar ratio of 3/1, ultimately

Table 2. Element Content of Total Ag as well as N, Ag(0), and Ag(I) on the Surface of PoPD Prepared at Oxidant/Monomer Molar Ratio of 1/1 by XPS and Titration after Adsorbing Ag(I) for Different Sorption Times and Initial Ag(I) Concentrations

<table>
<thead>
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<th>PoPD state</th>
<th>sorption time (h)</th>
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<th>Ag content by XPS (wt %)</th>
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The great diversity in sorption behaviors of Ag(I) ions on the particles should originate from the difference in their molecular structure. As confirmed by the analysis of the solubility and IR spectra of the polymers, the PoPD synthesized at a lower oxidant/monomer ratio contains more $-NH-$ groups in the molecular chain due to stronger band at 3218 cm$^{-1}$ and thus possesses higher molecular weight, both of which are conducive to a stronger adsorbability through providing more chelation and redox active sites with Ag(I) ions. Moreover, increased quinoid content at a higher oxidant/monomer ratio results in the rise in the oxidation state of the polymer, which is not favorable for the PoPD to reduce Ag(I) ions. Therefore, the PoPD particles prepared at an oxidant/monomer molar ratio of 1/1 exhibit the strongest Ag(I) adsorbability as revealed in Table 3.

3.4. Optimization of Oxidant/Monomer Ratio. The influence of oxidant/monomer ratio on Ag(I) adsorbance onto the PoPD particles was investigated to optimize the synthetic condition of the particles with powerful Ag(I) adsorbability. As shown in Figure 7, the adsorbance and adsorptivity of Ag(I) onto the PoPD salt and base particles decrease with increasing oxidant/monomer ratio.

The polymerization yield at different oxidant/monomer molar ratios might be utilized to assess the preparation cost of sorbents. Therefore, we introduce a parameter $Q$ (mg·g$^{-1}$) to represent the adsorbance of per gram oPD monomer, which can be obtained by multiplying the sorption capacity of PoPD and the polymerization yield. Corresponding to the oxidant/monomer molar ratio of 1/1, 2/1, and 3/1, the calculated $Q$ values are 213, 353, and 267 mg·g$^{-1}$, respectively. Apparently, the oxidant/monomer molar ratio of 2/1 is the optimal polymerization condition to synthesize PoPD microparticles that would be served as the most cost-effective sorbents.

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<td>43.09</td>
<td>20.3</td>
<td>61/39</td>
<td>29.3</td>
</tr>
<tr>
<td>salt</td>
<td>0.5</td>
<td>43.09</td>
<td>19.7</td>
<td>44/56</td>
<td>24</td>
</tr>
</tbody>
</table>
leading to slightly higher Ag(I) adsorbance onto the base particles at a lower Ag(I) concentration. It can be concluded that the salt particles synthesized at the oxidant/monomer molar ratio of 1/1 possess the most powerful Ag(I) adsorbability with the highest adsorbance of 533 mg·g⁻¹ at an initial Ag(I) concentration of 100.15 mM in this study.

3.6. Effect of Initial Ag(I) Concentration and Sorption Isotherm. The effect of the initial Ag(I) concentration on sorption of Ag(I) onto the PoPD microparticles is shown in Figure 8. The Ag(I) adsorbance rises significantly with an increase in Ag(I) concentration, whereas the adsorptivity declines. At a lower initial Ag(I) concentration, especially in the range of 0–10 mM, abundant active groups on the surface of microparticles can react with Ag(I) ions, resulting in a significantly increased adsorbance of Ag(I). Then the sorption process gradually becomes slow with increasing initial Ag(I) concentration. Therefore, both the Ag(I) sorption capacity and adsorptivity reach a high level at the optimal initial Ag(I) concentration of around 10 mM. The highest adsorptivity achieved in this study is 99.1% at the initial Ag(I) concentration of around 1 mM. That is to say, almost all Ag(I) ions will be adsorbed onto the microparticles if the initial Ag(I) concentration is lower than 1 mM.

Two mathematical models proposed by Langmuir and Freundlich were used to describe and analyze the sorption isotherm. The sorption data in the concentration range from 0.5 to 10 mM were selected to be modeled, considering that the sorption of Ag(I) onto the microparticles basically reaches equilibrium in 24 h in this concentration range. The modeled quantitative relationship between Ag(I) concentration and the sorption process is shown in Figure 8 (inset) and the calculated correlation coefficients and standard deviations are listed in Table 4. It can be seen that the sorption isotherm behavior of Ag(I) onto the microparticles does not fit the Langmuir or Freundlich model very well with the correlation coefficients of less than 0.99. This may result from the two concurrent sorption processes of Ag(I) onto PoPD. The chelation sorption is reversible, whereas the
redox sorption during which the Ag(I) is reduced to Ag(0) is irreversible.

3.7. Sorption Kinetics of Ag(I) onto the PoPD Microparticles. Sorption kinetics is studied to determine the time required to reach the equilibrium sorption of Ag(I) ions. Figure 9 shows representative plots of the Ag(I) sorption capacity and adsorptivity versus sorption time for the PoPD salt microparticles. The Ag(I) adsorbability on the microparticles rises nonlinearly with increasing the sorption time. The sorption process can clearly be divided into two steps: an initial rapid step and a subsequent slow step. The sorption of Ag(I) ions onto the microparticles is very rapid during the initial 30 min, for which the sorption capacity and adsorptivity reach up to 316 mg g⁻¹ and 13.6% respectively, that are 76% of the sorption capacity and adsorptivity for 24 h. During the sorption time from 0.5 to 24 h, the sorption rate becomes quite slow. The sorption capacity in the secondary long-term step contributes to a small part of the total Ag(I) sorption.

The initial rapid step of Ag(I) sorption may be attributed to the physical and surface reactive sorption due to a facilely immediate interaction between Ag(I) ions and the active −NH−/−NH₂ groups based on the surface of the microparticles. However, the subsequent slow step is attributable to the reactive sorption inside the microparticles, representing the diffusion of Ag(I) ions into the inner of the microparticles over a long period, besides the time-consuming redox sorption contributes to the long-term sorption as well. The Ag(I) ions chelated and Ag(0) reduced on the surface of the microparticles would further hamper the diffusion of Ag(I) ions, resulting in a rather long time to reach the equilibrium sorption. It can be predicted from Figure 9 that an even higher adsorptivity might be achieved if the sorption time were longer, indicating a great potential in the sorption of Ag(I) ions.

The pseudofirst-order and pseudosecond-order kinetic equations were employed to analyze the sorption kinetics of Ag(I) ions onto the microparticles. The curves of log (Qₑ − Qₜ) versus t and t/Qₜ versus t based on the experiment data are shown in Figure 9 (inset). From the corresponding parameters summarized in Table 5, it is observed that the kinetic behavior of Ag(I) sorption onto the particles is more appropriately described by the pseudosecond-order model because of a much higher correlation coefficient and a much lower standard deviation. The pseudosecond-order model was developed based on the assumption that the determining rate step may be chemisorption promoted by covalent forces through the electron exchange, or valency forces through electrons sharing between sorbent and sorbate, indicating that the sorption of Ag(I) on PoPD is mainly the chemically reactive sorption. The obtained initial sorption rate of Ag(I) ions onto the microparticles is 12.9 mg g⁻¹ min⁻¹. The loading half-time is calculated to be only 16 min. The kinetic data would be very useful for the fabrication and design of systems of wastewater treatment and noble metal recovery.

3.8. Effect of Solution pH. The effect of Ag(I) solution pH 1.0–9.0 on Ag(I) sorption onto the microparticles has been illustrated in Figure 10. Both the sorption capacity and the adsorptivity of Ag(I) ions increased significantly with a pH rise from 1.23 to 3.98 but increased slightly with a further pH rise from 3.98 to 8.32. This could be attributable to a competitive sorption between Ag(I) and H⁺ ions due to deprotonation of amine/imine groups on the PoPD chains. At low pH value, the sorption of Ag(I) ions is greatly weakened because the abundant competitive H⁺ ions occupy the sorption sites, whereas the protonated amine/imine groups are deprotonated with increasing pH value, enhancing Ag(I) adsorbatbility. However, only a slight elevation of Ag(I) adsorbatbility was observed in the pH range of 3.98–8.32, suggesting that the Ag(I) adsorbatbility on the particles approaches saturation gradually. Therefore, the solution pH around 5.0 could be optimal for the practical application of the PoPD microparticles as efficient Ag(I) sorbent.

3.9. Sorption of Hg(II) Ions onto the PoPD Microparticles. The adsorbatbility of Hg(II) ions onto the PoPD microparticles was also explored for the first time in this study. It is notable from Table 6 that the microparticles perform a much stronger adsorbatbility of Hg(II) ions than Ag(I) ions under similar conditions, with the adsorbatbility of Hg(II) up to 96.7%. The great diversity in the adsorbatbility of two heavy-metal ions should result from their different sorption characteristics. It is reported that both the Hg(II) and Ag(I) can be chelated and reduced by the −NH−/−NH₂ groups in the polymer chains. However, two electrons are needed for the PoPD to reduce the Hg(II) into Hg(0), whereas the Ag(I) needs only one electron. Moreover, it is found that the Hg(II) ions were also reduced into the oxidation state of Hg(I) during the sorption process. So, it is more difficult

<table>
<thead>
<tr>
<th>mathematical model</th>
<th>equation</th>
<th>correlation coefficient</th>
<th>standard deviation</th>
<th>rate constant k or initial sorption rate h</th>
</tr>
</thead>
<tbody>
<tr>
<td>pseudofirst-order</td>
<td>( \log (Q_e - Q_t) = -0.000834t + 2.189 )</td>
<td>-0.7079</td>
<td>0.25689</td>
<td>( k = 0.00192 \text{ min}^{-1} )</td>
</tr>
<tr>
<td>pseudosecond-order</td>
<td>( t/Q_e = 0.00242t + 0.07754 )</td>
<td>0.9976</td>
<td>0.0964</td>
<td>( h = 12.9 \text{ mg g}^{-1} \text{ min}^{-1} )</td>
</tr>
</tbody>
</table>

Table 6. Comparison of Sorption Capacity for Hg(II) and Ag(I) Ions on the PoPD Salt (Synthesized at Oxidant/Monomer Ratio of 1/1) at 30°C in a Sorption Solution of 25 mL with a Sorbent Dosage of 50 mg for 24 h

<table>
<thead>
<tr>
<th>metal ion</th>
<th>ion concentration (mM)</th>
<th>capacity (mg g⁻¹)</th>
<th>adsorptivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(I)</td>
<td>4.977</td>
<td>169</td>
<td>62.9</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>4.065</td>
<td>394</td>
<td>96.7</td>
</tr>
</tbody>
</table>

Figure 9. Effect of sorption time on Ag(I) sorption onto PoPD (oxidant/monomer ratio = 1/1) salt particles at 30 °C in AgNO₃ solution of 25 mL at an initial Ag(I) concentration of 43.1 mM at the original pH of 3.4. Inset: The pseudofirst-order and pseudosecond-order plots of the sorption data.
for the Hg(II) ions to be reduced into Hg(0) than the Ag(I) ions. Both Hg(II) and Hg(I) can be chelated by the amine/imine groups on the PD salt particles. Therefore, it seems that the chelation sorption accounts for the main sorption for Hg(II) ions. During the Ag(I) sorption, Ag(0) reduced on the surface of the microparticles could hinder the diffusion of Ag(I) ions and the further contact between Ag(I) ions and reactive groups inside the microparticles. However, there does not exist such an influence in the sorption process of Hg(II) ions, and the Hg(II) ions can be completely chelated by the amine/imine groups on the polymer chains, resulting in a much stronger adsorbability than Ag(I) ions.

3.10. Competitive Sorption of Ag(I) and Hg(II) onto the PoPD Microparticles. Figure 11 shows the competitive sorption kinetics of Ag(I) and Hg(II) onto the PoPD salt particles (synthesized at oxidant/monomer ratio of 1/1) at 30 °C in 25 mL solution at the same initial Ag(I) and Hg(II) concentrations of 4.1 mM with a sorbent dosage of 50 mg.

Figure 10. Effect of solution pH on Ag(I) sorption onto the PoPD salt particles (synthesized at oxidant/monomer ratio of 1/1) at 30 °C in AgNO₃ solution of 25 mL at an initial Ag(I) concentration of 2.84 mM with a sorbent dosage of 50 mg for 24 h.

Figure 11. Competitive sorption kinetics of Ag(I) and Hg(II) onto the PoPD salt particles (synthesized at oxidant/monomer ratio of 1/1) at 30 °C in 25 mL solution at the same initial Ag(I) and Hg(II) concentrations of 4.1 mM with a sorbent dosage of 50 mg.

adsorptivity in pure Hg(II) solution in Table 6. Apparently, the PoPD microparticles are more sensitive to Ag(I) than Hg(II) because Ag(I) is preferentially adsorbed onto the microparticles when both ions coexist in their mixture solution. Nevertheless, PoPD microparticles are still efficient to adsorb both Ag(I) and Hg(II) ions from their binary solutions with an adsorptivity of higher than 50%.

3.11. PoPD/Ag Nanocomposites. The PoPD/Ag nanocomposites were facilely obtained through the reactive sorption process discussed above, as well as the uptake of Ag(I) ions from aqueous solution. Figure 12 shows the size and distribution of PoPD/Ag nanocomposites obtained after the reactive sorption with Ag(I) ions at 1.24–21.55 mM. The number-average diameter is 1.525 µm for PoPD microparticles in stirred pure water without Ag(I) ions. The diameter declined dramatically with reactively adsorbing Ag(I). All PoPD/Ag nanocomposites possess a number-average diameter (Dₐ) of below 170 nm and a small size polydispersity index (Dₐ/Dₜ) from 1.18 to 1.29, indicating a narrow size distribution of the nanocomposites. In particular, the nanocomposite prepared at the initial Ag(I) concentration of 10.77 mM exhibits a minimal Dₐ value of 77 nm and a minimal size polydispersity index of 1.18. In addition, it can be found in parts a and b of Figure 3 that Ag nanoparticles with a diameter between 10–50 nm were well dispersed on the surface of PoPD particles, and the smallest diameter of Ag particles can reach as small as 10–20 nm. Some larger Ag nanoparticles with a diameter of over 100 nm have dropped from the surface of PoPD, as shown in parts c–e and g of Figure 3. Thus, it should be noted that the reactive sorption method could also be considered as one new method to prepare Ag single nanocrystals, which have been proved by electron diffraction pattern. The highest content of Ag element in the nanocomposite can reach 34.8 wt %, as evaluated by titration. It has been confirmed that some Ag(I) ions were chelated by PoPD in the sorption process. A possible mechanism of the formation of PoPD/Ag nanocomposites is proposed that the Ag(I) ions on PoPD could serve as an internal stabilizer that can provide strong static repulsion among the particulates and efficiently stabilize the as-formed Ag nanoparticles by preventing them from conglomerate. The conductivity of the nanocomposites was enhanced by 100–1000 times compared with the as-prepared PoPD salt particles, and even an increased conductivity of more than 4 orders of magnitude has been realized for the PoPD base particles after adsorbing Ag(I) ions. These results strongly suggest that the introduction of Ag crystals into polymers through the sorption method can enhance the conductivity of conducting polymers. Moreover, it has been reported that the biosensors based on the polyphenylenediamine/metal nanocomposites...
exhibited excellent performance in the detection and determination for biosubstances.\textsuperscript{33-35} The highly effective anchor for enzymes by the metal nanoparticles and the excellent permselectivity of polyphenylenediamine both contributed to their remarkably enhanced sensitivity and anti-interference ability.\textsuperscript{34,35} Therefore, it could be believed that the prepared PoPD/Ag nanocomposites with high purity through a simple and effective sorption method would have a promising application in biosensors and other microelectronics devices and their other properties deserve further research and development.

4. Conclusions

Both synthetic yield and electrical conductivity of fine PoPD microparticles by a chemical oxidation polymerization of \(o\)-phenylenediamine in boiling glacial acetic acid simultaneously exhibit the maximum at a \((\text{NH}_4)_2\text{S}_2\text{O}_8\) oxidant/oPD monomer molar ratio of 2/1. The sorption behavior of Ag(I) onto PoPD microparticles strongly depends on the oxidant/monomer ratio, doping state, and the content of amine/imine groups. A lower oxidant/monomer molar ratio of 1/1 will produce PoPD chains with more imino (\(-\text{NH}^-\)) groups, higher molecular weight, and lower oxidation state, and accordingly higher Ag(I) adsorbance. At a fixed oxidant/monomer ratio of 1/1, the Ag(I) adsorbance onto the PoPD salt particles is higher than that of corresponding base particles, but the difference between the two states becomes smaller with increasing oxidant/monomer ratio, and finally the Ag(I) adsorbance on the base particles even surpasses the adsorbance on the salt particles at the oxidant/monomer ratio of 3/1. The Ag(I) adsorptivity of the microparticles can further be optimized by regulating the initial Ag(I) concentration, sorption time, and solution pH, demonstrating the highest Ag(I) adsorbance and adsorptivity of 533 mg·g\(^{-1}\) and 99.1%, respectively. The optimal solution pH for Ag(I) sorption is around 5.0. The sorption process well fits the pseudosecond-order kinetics with a very rapid initial sorption rate of 12.9 mg·g\(^{-1}\)·min\(^{-1}\). The sorption process mainly includes the fast chelation between Ag(I) and neutral amine/imine groups and the physical sorption in the initial stage of sorption, as well as the long-term sorption ascribed to a relatively time-consuming redox sorption between Ag(I) and protonated amine, imine, and free amine. The PoPD microparticles also demonstrate a powerful Hg(II) adsorbability with an adsorptivity of 96.7% at an initial Hg(II) concentration of 4 mM. Competitive sorption of Ag(I) and Hg(II) mixture solution reveals a preferential sorption of Ag(I) onto the microparticles. Having a powerful adsorbability of Ag(I) and Hg(II) ions and good cost effectiveness, the PoPD microparticles perform a wide application prospect in the removal and even recovery of heavy-metal ions from their aqueous solutions or wastewater. The PoPD/Ag nanocomposites containing Ag nanoparticles of 34.8 wt % and 10–20 nm were facilely prepared through a simple reactive sorption. A small amount of Ag single crystals with the diameter over 100 nm were also observed in the nanocomposites. The conductivity of the nanocomposites increased by 100–1000 times compared with the as-prepared PoPD salt without Ag and even by more than 4 orders of magnitude compared with the PoPD base. The nanocomposites could possibly serve as novel electroactive materials in chemical sensors and microelectronic devices.

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