# Preparation of Redox Fibers Containing Hydroxy-Alkyl Amino Groups and Their Adsorptive Properties Toward Au(III)

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ABSTRACT: Three kinds of redox fibers (fibers II, III, and IV) are prepared by amination of the reactive chloromethylated poly(vinyl acetate) grafting polystyrene-divinylbenzene fiber (fiber I) with diethanolamine, ethanolamine, or triethanolamine. The Ncontent of the fibers is 2.26, 2.71, and 1.86 mmol  $g^{-1}$ , respectively. Results of static adsorption experiments show that the adsorption amount of fibers II, III, and IV toward Au(III) reaches 550 mg g<sup>-1</sup>, 620 mg g<sup>-1</sup>, and 409 mg g<sup>-1</sup>, respectively, between pH 2.0 and pH 3.0. Some adsorbed Au(III) can be reduced to Au(0). The reduction percentage of Au(III) adsorbed by fiber II increases with rising pH value of the solution and can be as high as 87% at pH 5.0. The amount of Au(III) adsorbed by fiber II increases with solution temperature, but decreases with ionic strength of the solution. The adsorption amount of fibers II and III toward Au(III) is less in ethanol or in acetacetate medium than in water. Kinetic adsorption data indicates that 50 min is needed for fiber II to adsorb half of its saturate adsorption amount of Au(III). It was proved by elemental analysis, infrared spectroscopy, nuclear magnetic resonance, and electron spectroscopy for chemical analysis determinations that the carbon atoms connecting with the hydroxy groups near the nitrogen atoms were easily oxidized into carbonyl ones during redox adsorption reaction of fibers II, III, and IV with Au(III). Some grains of gold adsorbed on fiber II were discovered under scanning electron microscopy. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 47-54, 1999

**Key words:** redox fiber; gold; redox adsorption; preirradiation-induced grafting copolymer; fiber-containing diethanolamine group

#### INTRODUCTION

Fibrous adsorbing materials have a highly developed specific surface area, which is good for increasing adsorption and desorption speeds. On the other hand, they can be used in various forms, such as yarn, fabrics, nonwoven fabrics, and net for satisfying the needs of various exchange ad-

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sorption processes. Since the 1980's, we had been studying fibrous adsorbents, including activated carbon fibers and the organic fibers containing nitrogen, sulfur, or phosphorus atoms.<sup>1,2</sup> We found that some adsorbents strongly adsorbed and reduced noble metallic ions<sup>3,4</sup> and could obtain noble metal directly in a simple recovery process. As a typical weak, basic anion exchange adsorbent, the fibers containing the diethanolamine group should strongly adsorb Au(III) at high level acidity, but adsorb a small amount of Au(III) at low-level acidity. In fact, the poly(vinyl

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acetate) grafting poly(glycidylmethacrylate)-diglycolic acrylate fiber amined with diethanolamine (a fiber containing a diethanolamine group) adsorbs Au(III) strongly at low level of acidity (pH 5.5), and can reduce Au(III) into Au(0).<sup>5</sup> To answer the question of what happens during the adsorption process on the earth, in the present paper, the fibers containing diethanolamine, ethanolamine, and triethanolamine groups were synthesized to study their redox adsorption processes toward Au(III).

### **EXPERIMENTAL**

#### **Preparation of Redox Fibers**

Poly(vinyl acetate) fiber was grafted with 445% (w/w) polystyrene-divinylbenzene (preirradiation induced by  $\gamma$ -ray), then chloromethylated (named fiber I). Fiber I was reacted with diethanolamine in different solvents, such as dioxane, 1,2-dichloroethane, *N*,*N*-dimethylformamide, and toluene, respectively, at different temperatures for a certain time to find out the most favorable reacting condition. Then, the increasing weight percentage of fiber I (*W*%) amined with diethanolamine at different reacting conditions was determined. *W*% was calculated as follows:

$$W\% = rac{W_1 - W_a}{W_a}$$

where  $W_1$  is the weight of the fiber after reaction and  $W_o$  is the original weight of the fiber. Fibers III and IV were obtained by fiber I reacted with ethanolamine and triethanolamine at the most favorable condition, respectively.

# Properties of Fibers II, III, and IV in Adsorbing Au(III)

 Static adsorption experiments: ~ 0.02 g of the fiber was added to 25 mL of the 2 mmol L<sup>-1</sup> Au(III) solution in an iodometric flask, which was placed in the thermostatic vibrator. The flask was shocked for a certain time at the required temperature in different adsorption conditions (such as medium, ionic strength of the solution and temperature). The concentration of Au(III) solution before and after adsorption was determined by a WFC-1C atom absorption spectrum (made by Beijing, the third analytical instrument factory). Adsorption amount (Ea) was calculated as follows,

$$Ea~(g~g^{-1}) = \frac{(M_o - M) * V}{W} * 197$$

where  $M_o$  and M are the concentration of Au(III) solution before and after adsorption (mmol L<sup>-1</sup>), respectively; V is the volume of the solution used for adsorption (L); and W is the weight of the redox fiber used (g).

2. Au ion (Ed) on the fibers was desorbed with a mixture of 90% (v/v) acetone, 5% hydrochloric acid, and 5% distilled water. Reduction adsorption amount of Au(II-I)(Er) on the fibers was calculated as follows,

$$Er = Ea - Ed$$
.

The reduction percentage (Rp) of Au(III) on the fiber was equal to Er over Ea.

3. Adsorption kinetics in a similar situation as static adsorption experiments, 0.05 g of fiber II was added to 50 mL of the 4.5 mmol  $L^{-1}$  Au(III) (pH 2.0) solution, and 0.2 mL Au(III) solution was taken out to determine the amount of Au(III) adsorbed by the fiber for different time intervals at 40°C.

# **Instrument Analyses**

- 1. The content of nitrogen, carbon, and hydrogen atoms in the fibers before and after adsorbing Au(III) was analyzed by a Perkin-Elmer 240C elemental analyzer.
- 2. Fibers before and after adsorbing Au(III) were cut into fine pieces and dried in vacuum, then pressed into pellets with KBr. The infrared absorption spectra of the fibers were recorded on a Nicolet 170SX Fourier transform infrared spectrometer.
- 3. Elemental gold on the fibers was verified with a Rigaku D/max IIIA X-ray diffractometer using a nickel-filtered CuK<sub> $\alpha$ </sub> radiation generated at 40 kV and 30 mA. Diffraction spectra, with diffraction angles from 30° to 80°, were obtained.
- 4. The binding energy data of carbon, nitrogen, and gold atoms in or on fiber II before and after adsorbing Au(III) at pH 2.0 were obtained with an ESCALAB MKII spectrometer (British VG Company).

Medium	Toluene	Ethanol	<i>N,N-</i> Dimethylformamide	1,2- Dichloroethane	Dioxane								
Temperature (°C)		70					80			40	60	70	90
Time (h) W%	11.4	$\begin{array}{c} 4\\11.3\end{array}$	13.1	12.8	2 13.3	$\begin{array}{c} 4 \\ 15.3 \end{array}$	6 15.8	8 15.5	$\begin{array}{c} 10\\ 14.5 \end{array}$	7.2	12.6	$\begin{array}{c} 4\\ 14.5\end{array}$	14.3

 Table I
 Percentage of Increasing Weight of Fiber I (W%) Amined with Diethanolamine in Different Reacting Conditions

- 5. The <sup>1</sup>H-NMR spectrum of the result of *N*benzyl ethanolamine, a model compound of fibers containing the hydroxy-alkyl amino group, oxidized by the 10 mmol  $L^{-1}$  Au(III) solution (pH 2.0) at 40°C, was recorded with a 90 QX NMR spectrometer (Japan; dimethylsulfoxide as a solvent).
- 6. Fibers before and after adsorbing Au(III) were sprayed with gold, then observed, and photographed under a Hitachi S-520 scanning electron microscope.

#### **RESULTS AND DISCUSSION**

#### **Preparation of Redox Fibers**

Table I shows the increasing weight percentage of fiber I (W%) amined with diethanolamine in different reacting conditions. Results show that W% reaches a maximum when the reaction is preformed at 80°C for 6 h in dioxane. It is explained

that dioxane is not only a good swelling agent for fiber I, but also a good solvent for diethanolamine. Thus, the reacting temperature (80°C) and time (4 h) must be moderate to keep the fiber chains and functional groups stable. Diethanolamine, instead of ethanolamine or triethanolamine, was chosen to search for the most favorable reacting condition. The reason is that there are some additional crosslinking bonds when fiber I reacts with ethanolamine, and there is a big space hindrance when using triethanolamine. Amination ratio of the chloromethyl groups in fiber I reaches a maximum when W% is maximum, because W%changes linearly with the amination ratio of the chloromethyl groups in fiber I. The product at this reaction condition is named fiber II. Fibers III and IV are prepared at the most favorable reacting condition. Their N content is 2.26 mmol  $g^{-1}$ , 2.71 mmol  $g^{-1}$ , and 1.86 mmol  $g^{-1}$ , respectively. The reactions are as follows,

$$P-CH_2Cl + H_2NCH_2CH_2OH)_2 = P-CH_2-N(CH_2CH_2OH)_2$$
(fiber II)  
$$N(CH_2CH_2OH)_3 = P-CH_2-N(H)CH_2CH_2OH$$
(fiber III)  
$$P-CH_2-N(H)CH_2CH_2OH$$
(fiber III)

P is the polymer chain. On the other hand, fiber III contains some additional crosslinking structures because ethanolamine contains two N—H bonds for reacting. The infrared spectra of fibers I, II, and IV (Figure 1) show that the stretching vibration (670 cm<sup>-1</sup>) of the C—Cl bond<sup>6</sup> in fiber I disappears or weakens after amination. This means that most of the chloromethyl groups in fiber I are amined.

# Properties of Fibers II, III, and IV in Adsorbing Au(III)

1. Figure 2 is the relationship between the adsorption and reduction amounts of

Au(III) on fiber II and the pH value of the Au(III) solution. Results show that the adsorption amount of Au(III) on fiber II reaches a maximum (550 mg g<sup>-1</sup>) at ~ pH 2.4, but the reduction percentage of Au(III) adsorbed on the fiber increases with rising of the pH value and reaches 87% at pH 5.0. The adsorption amount of fibers III and IV is 620 and 409 mg g<sup>-1</sup> at pH 2.0, and becomes 291 and 266 mg g<sup>-1</sup> at pH 0.3 (2N HCl medium), respectively. The elemental gold adsorbed on the fibers is verified by wide-angle X-ray diffraction (WAXD) (Fig-



**Figure 1** Infrared spectra of fibers I, II, and IV. (a) Fiber I. (b) Fiber II. (c) Fiber IV.

ure 3), proved to have four diffraction peaks of crystal faces of elemental gold in the WAXD graphs. It is very interesting that fiber IV, as a kind of strong basic anion exchange fiber, can reduce Au(III) into Au(0), which is different from our previous work about fiber I amined with trimethylamine<sup>7</sup> to adsorb Au(III) by only an ion exchange process.

2. The amount of Au(III) adsorbed by fibers II and III is 108, 38 mg g<sup>-1</sup> in ethanol and 99, 75 mg g<sup>-1</sup> in acetacetate, respectively; both are less than in water. Results show that the amount of Au ion adsorbed on the fibers changes very little in nonwater solvent though the dielectric constant of acetacetate ( $\epsilon = 4.0$ ), which is much less than that of ethanol ( $\epsilon = 24.1$ ).<sup>8</sup> However, the fibers can reduce Au(III) into Au(0) in ethanol and cannot in acetacetate (proven by



**Figure 2** Effect of the pH value on the adsorption and reduction amounts of fiber II toward Au(III). [Adsorbing condition: 40°C, 24 h, 2.5 mmol L<sup>-1</sup>. ( $\bullet$ ) Adsorption amount. ( $\bigcirc$ ) Reduction amount.]

WAXD). This means that the solvent has a significant effect on the redox adsorption process. It is suggested that the amount of Au(III) reduced by the fibers increases with rising of the dielectric constant of solvent.

3. Figure 4 shows the effect of temperature on the amount of Au(III) adsorbed by fibers II



**Figure 3** WAXD graphs of fibers II and IV after adsorbing Au(III). (a) Fiber II. (b) Fiber IV.



**Figure 4** Effect of temperature on the adsorption amount of the fibers. [Adsorbing condition: pH 2.0, 24 h, 2.5 mmol  $L^{-1}$ . (•) Fiber II. ( $\bigcirc$ ) Fiber IV.]

and IV. Results demonstrate that the amount of Au(III) adsorbed by fibers II and IV increases with rising of the solution temperature at pH 2.0. Higher temperature may be good for the redox adsorption process.

4. Figure 5 shows that the adsorption amount of fiber II toward Au(III) changes with ionic strength of the solution. Results indicate that the adsorption amount of fiber II toward Au(III) decreases with rising ionic strength of the solution (adjusted by sul-



**Figure 6** Relationship between the adsorption amount of fiber II for Au(III) and adsorbing time. (Adsorbing condition: pH 2.0, 40°C, 4.5 mmol  $L^{-1}$ .)

fate of magnesium). It is explained that, because there are more  $HAuCl_4$  molecule formations in high ionic strength solution, there are fewer  $AuCl_4^-$  ions left for ion exchange adsorption with fiber II.

5. In Figure 6, it is discovered that it takes 50 min for fiber II to adsorb half of its saturate adsorption amount of Au(III). The ion exchange adsorption process goes very fast at first, then the chelating and redox processes take place and go very slowly. These processes can be judged by the fiber color during the adsorption process (the fiber becomes dark when the redox adsorption process takes place). It is suggested that the adsorption rate can be determined by the redox adsorption process.





**Figure 5** Effect of ionic strength on the adsorption amount of fiber II toward Au(III). (Adsorbing condition:  $40^{\circ}$ C, pH 2.0, 2.5 mmol L<sup>-1</sup>.)

**Figure 7**  $C_{1s}$  spectra of fiber II before and after adsorbing Au(III). (C1) Before adsorbing. (C2) After adsorbing.



Figure 8  $\,N_{\rm 1s}$  spectra of fiber II before and after adsorbing Au(III). (N1) Before adsorbing. (N2) After adsorbing.

Changes of Carbon, Nitrogen, and Gold Atoms in or on the Fibers after Adsorbing Au(III)

- 1. The electron affinity results show that the N/C value of fiber II before and after adsorbing is 0.044 and 0.042, and those for fiber IV are 0.03 and 0.027, respectively. Thus, nitrogen atoms in the fibers do not lose after redox adsorbing, and the functional groups in the fibers are stable during the redox reaction process.
- 2. The  $C_{1s}$  spectra (Figure 7) of fiber II show that, at pH 2.0, the peak area at ~ 286.3 or 287.4 eV increases, but at 284.6 eV decreases after it has adsorbed Au(III). This indicates that there may be oxidation of C—OH (286.3 eV) or C—H (284.6 eV) bond and formation of the carbonyl or hydroxyl group in the fiber. Meanwhile,



**Figure 9**  $Au_{4f}$  spectrum of Au adsorbed on fiber II. (Dotted line is the simulation result of the curve.)



**Figure 10** <sup>1</sup>H-NMR spectrum of *N*-benzyl ethanolamine oxidized by Au(III).



**Figure 11** Infrared spectra of fibers II and IV before and after adsorbing Au(III). (a) Fiber IV before adsorbing. (b) Fiber IV after adsorbing. (c) Fiber II before adsorbing. (d) Fiber II after adsorbing.



**Figure 12** Scanning electron micrographs of fiber II before and after adsorbing Au(III). (a) Before adsorbing. (b) After adsorbing.

the  $N_{1s}$  spectra (Figure 8) of fiber II show that the  $N_{1s}$  peak shifts from 399 to 401.7 eV after Au(III) is adsorbed [i.e., no N—O bond (403 eV) is formed]. This may be related to the formation of the N—Au coordination bond or protonization of the nitrogen atoms.<sup>9</sup> Figure 9 is the Au<sub>4f</sub> spectrum of Au adsorbed on fiber II. The simulation result of the curve shows that part of Au(III) adsorbed on the fiber is reduced into elemental gold (binding energy is 84 eV).

- 3. Figure 10 is the <sup>1</sup>H-NMR spectrum of *N*-benzyl ethanolamine oxidized by Au(III). Results show that the C—OH bond in the ethanolamine group is oxidized into the C=O bond by Au(III) at pH 2.0. There is a peak of <sup>1</sup>H-NMR at 10 ppm about the chemical shift of the aldehyde group. It is proved again that some C—OH bonds of the fibers containing the hydroxy-alkyl amino group, whose functional structures are similar to N-benzyl ethanolamine, are oxidized into aldehyde groups during the redox adsorption process. However, the N-H bonds remained because the peaks of the N-H bond at 4.3 ppm still appear on the spectrum of <sup>1</sup>H-NMR.
- 4. The infrared spectra (Figure 11) show that the absorption bands of 1670  $\text{cm}^{-1}$  and 1100–1050  $\text{cm}^{-1}$  are formed or reinforced after Au(III) has been adsorbed. This may have resulted from the formation of many

C=O or C-O bonds (i.e., carbon atoms in the fibers are oxidized during the redox adsorption process).

#### Aggregation States of Gold on the Fibers

Elemental gold grains that autoaggregated on the fibers are discovered under scanning electron microscopy (Figure 12). This is due to the easy self-aggregation properties of elemental gold and gold compounds.<sup>10</sup>

# CONCLUSIONS

- 1. Fibers containing hydroxy-alkyl amine groups can reduce Au(III) into Au(0). Carbon atoms connecting with the hydroxy groups instead of the nitrogen ones are oxidized during the redox adsorption process in the fibers.
- 2. The maximum amount of Au(III) adsorbed by fibers II, III, and IV is 550 mg g<sup>-1</sup>, 620 mg g<sup>-1</sup>, and 409 mg g<sup>-1</sup>, respectively. The fibers adsorb fewer Au(III) in nonwater medium and high ionic strength solution than in normal water. The adsorption rate of Au(III) is determined by the slow redox adsorption process.

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