Preparation of Nano-Porous Silver by Electroless Plating

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Abstract. A preparation method of nanoporous silver was introduced. First, polystyrene (PS) was pretreated. Then silver was deposited on the surface of PS. And finally, PS was removed to obtain porous silver by extraction. The effects of different reaction conditions on the reaction rate and silver deposits were studied. The reaction conditions include silver nitrate concentration, sodium hydroxide concentration, glucose concentration and temperature. The best reaction condition is 0.074 mol·L\textsuperscript{-1} AgNO\textsubscript{3}, 0.22 mol·L\textsuperscript{-1} glucose, 0.05mol·L\textsuperscript{-1} NaOH and the reaction temperature is 20°C.

1. Introduction
Nano-porous metal materials are the most attractive research objects in the field of nanotechnology and porous material science in recent years. With the excellent properties of both nanomaterials and metallic materials, nano-porous metals have great application prospects in the fields of catalysis, sensors, optics, biological filtration and separation [1-3]. The template method is one of the commonly used methods for preparing nano-porous metals. Polystyrene (PS) is the most common used material due to its controllable diameter and easy removal [4]. Electroless and electro-depositon are normally the two methods for metal deposition [5]. Because the PS microspheres are insulated, the nano-porous metals are usually prepared by electroless plating.

In this paper, PS/Ag core-shell structure was synthesized by electroless silver plating with PS as the templates. The effect of reaction conditions on the amount of silver deposits was investigated.

2. Experiments
2.1. Materials
PS microspheres prepared by our laboratory (730nm in diameter size). Ethanol, potassium dichromate, sulfuric acid (98%), stannous chloride, palladium chloride, hydrochloric acid (36%–38%), Silver nitrate, ammonium hydroxide, sodium hydroxide, glucose, tartaric acid (AR, Beijing Tongguang Chemical Co., Ltd.) were used as received.

2.2. Experimental Methods
The PS was preprocessed by three steps before electroless plating, including roughness, sensitization and activation. First, PS was soaked in roughing solution (10.00mL H\textsubscript{2}SO\textsubscript{4}, 12.00g K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} and 100.0mL H\textsubscript{2}O) for 30 min at 75°C with high speed stirring and washed with deionized water for three times by vacuum filtering subsequently. Then, the roughened PS was dispersed in sensitized solution (40.00 g·L\textsuperscript{-1} SnCl\textsubscript{2}, 20.00 mL·L\textsuperscript{-1} HCl, 200.0 mL·L\textsuperscript{-1} C\textsubscript{6}H\textsubscript{5}OH and a few Sn Grains) for 15min under...
ultrasonic. PS was collected by centrifugation and washed with deionized water. Next, the sensitized PS was dispersed in activation solution (0.50 g·L⁻¹PdCl₂, 10.00 mL·L⁻¹ HCl and 200.0 mL·L⁻¹ C₂H₅OH) for 10 min under ultrasonic, and then dried in vacuum after filtering and washing by deionized water.

The electroless plating silver solution consists of silver salt solution (20 g·L⁻¹ AgNO₃, appropriate amount of ammonium hydroxide and NaOH) and reducing solution (100.0 mL·L⁻¹ C₂H₅OH, 8 g·L⁻¹ glucose and 4 g·L⁻¹ tartaric acid). The two solutions were mixed in equal volume and the preprocessed PS was immersed into it for 4 h under ultrasound. The PS/Ag composite was obtained by centrifugation washing for 3 times and dried in vacuum oven at 50°C. Finally, the PS template was removed by extraction.

2.3. Analytical Method
The Ag⁺ concentration was measured by inductively coupled plasma optical emission spectrometer (ICP-OES, PE OPTIMA 7000DV, USA).

3. Result and Discussion

3.1. Silver Deposition onto the Surface of PS
It is widely accepted that electroless plating is a redox reaction occurred selectively on the active surface. As for the reduction reaction of Ag⁺, reaction equation is as follows:

\[2[Ag(NH₃)₂]OH+CH₂OH(CHOH)₄CHO→2Ag↓+H₂O+3NH₃+CH₂OH(CHOH)₄COONH₄\]

The deposition amount of Ag refers to the amount of Ag⁺ reduced per unit volume, which can be obtained by calculating the difference between the initial Ag⁺ concentration of the solution and the real-time Ag⁺ concentration. The concentrations of Ag⁺ at different times were measured by ICP.

3.2. Effect of Silver Nitrate Concentration on Silver Deposits
Figure 1 shows the dependence of the amount of silver deposition on deposition time at different silver nitrate concentrations. AgNO₃ was used as the main salt in the electroless silver plating. Both the deposition rate and the amount of silver deposits increased first and then decreased slightly as the concentration of silver nitrate increases from 0.058 mol·L⁻¹ to 0.103 mol·L⁻¹. As the concentration of silver nitrate increases, the silver ions in the bath gradually increase and the reaction speed becomes faster. Therefore, the amount of silver deposition increases continuously. However, when the concentration of silver ions is too high, the silver ammonia solution will have a self-decomposition reaction, making the stability of the bath worse and the amount of silver deposition less. So the optimal silver nitrate concentration is 0.074 mol·L⁻¹.

![Figure 1](image_url)

**Figure 1.** The deposition amount of silver at different silver nitrate concentration varies with deposition time.
3.3. Effect of Sodium Hydroxide Concentration on Silver Deposits

Figure 2 shows the variation of silver deposits with deposition time at different sodium hydroxide concentrations. Both the deposition rate and the amount of silver deposits increased as the concentration of sodium hydroxide increases from 0.0125 mol·L⁻¹ to 0.05 mol·L⁻¹.

![Figure 2](image)

**Figure 2.** The deposition amount of silver at different sodium hydroxide concentration varies with deposition time.

3.4. Effect of Glucose Concentration on Silver Deposits

Figure 3 shows the deposition amount of silver at different glucose concentration varies with deposition time. The amount of silver deposition increases as the concentration of glucose increases from 0.014 mol·L⁻¹ to 0.038 mol·L⁻¹. But when the glucose concentration is too high, the initial reaction rate is too fast, which may result in silver being deposited directly into the solution rather than on the PS surface. Therefore, from the perspective of controlling the amount of silver deposit and saving raw materials, it is advisable to select the concentration of glucose at 0.22 mol·L⁻¹.

![Figure 3](image)

**Figure 3.** The deposition amount of silver at different glucose concentration varies with deposition time.

3.5. Effect of Temperature on Silver Deposits

Figure 4 shows the deposition amount of silver at different temperature varies with deposition time. When the reaction temperature is above 35℃, both the deposition rate and the amount of silver deposition are much higher than normal. When the temperature is higher than 35℃, although the rate and amount of silver deposition are greatly increased, it will lead to the deposition of silver directly in the bath rather than on the PS surface. So the optimum reaction temperature is 20℃.
4. Conclusion
Electroless plating can successfully deposit silver onto PS surface and changing the reaction conditions will have an important impact on the amount of silver deposited. As the concentration of silver nitrate increases, the amount of silver deposits increased first and then decreased slightly and the best reaction condition is 0.074 mol·L⁻¹. As the concentration of sodium hydroxide increases, the amount of silver deposits increased. As for the glucose, the best reaction condition is 0.22 mol·L⁻¹. The reaction temperature has an important influence on the reaction rate of electroless plating and the best reaction temperature is 20°C.

5. Reference
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