Preparation of micron-sized polystyrene/silver core–shell microspheres by ultrasonic assisted electroless plating

Junhua Cheng, Guoyou Gan, Junpeng Li, Xianglei Yu, Lin Tang and Chengbin Liu

1 Faculty of Material Science and Engineering, Kunming University of Science and Technology, Kunming 650093, People’s Republic of China
2 State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, Sino-Platinum Metals Co., Ltd, Kunming 650106, People’s Republic of China
* Authors to whom any correspondence should be addressed.

E-mail: ganguoyou@kust.edu.cn and lijunpeng@ipm.com.cn

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Abstract
In the study, PS/Ag composite microspheres with polystyrene (PS) core and silver shell were synthesized by ultrasonic electroless plating. The samples were characterized by SEM, FTIR and XRD. The effects of times of sensitization and silver plating, mass ratio of AgNO₃ to PS microspheres and stirring method on the preparation and dispersion of PS/Ag microspheres were studied. The results show that the more times of sensitization and silver plating, the more uniform the silver deposition on the surface of microspheres. When the mass ratio of AgNO₃ to PS microspheres is 2:1, it can promote the uniform coating of silver shell and reduce the content of free silver. Ultrasonic assisted electroless plating for 10 min can prevent PS/Ag microspheres from agglomerating and improve the speed of electroless plating. The thickness of the silver shell on the surface of the PS microsphere is about 200 nm.

1. Introduction
Recent studies have shown that core–shell organic-inorganic composite particles have attracted much attention due to their wide applications in microelectronics [1–3], catalysis [4–6], magnetism [7], biomedicine applications [8,9] and so on. For example, composite particles with polymer microspheres as a matrix and metal shell have the characteristics of high conductivity, uniform particle size, and high elastic modulus. In particular, composite microspheres with a nickel metal shell have excellent ferromagnetic properties. This type of composite material is widely used in anisotropic conductive adhesive filled particles. The traditional anisotropic conductive adhesive is composed of metal particles or organic-inorganic fillers forming a solid film in polymer matrix [10,11]. Micron sized organic-inorganic composite particles are usually coated with conductive metals such as copper, silver or gold. Because the thermal expansion coefficient of the composite particles is similar to that of the polymer matrix, the composite particles after hot pressing are squeezed into each other, a larger contact area is formed between the two electrodes, and a good conductive path is formed.

Up to now, many synthetic methods of organic-inorganic composite particles have been reported, such as electroless plating [12–17], pulsed laser irradiation [18], sonochemical deposition [19,20], in situ chemical reduction [21–24], ultrasonic irradiation [25], electrodeposition [26], etc.

The electroless plating usually involves the steps of roughening, sensitization, activation, and metals reduction. However, there are still some problems to be solved in the traditional electroless plating process. Because it is difficult to obtain evenly distributed activation centers during the pretreatment process, it is difficult for metal particles to nucleate and grow uniformly on the surface of the microspheres. The obtained shell has poor coating effect and poor dispersion of composite microspheres. Recently, researchers have done a lot of work and tried to optimize this traditional electroless coating. Deng et al [27] reported a method of SiO₂ microspheres with silanol groups with electrostatically adsorbing [Ag (NH₃)₂]⁺ and then reducing and
stabilizing function by polyvinylpyrrolidone (PVP) to fabricate PS/Ag composite. Although the adhesion between the SiO2 microspheres and the silver is improved, the non-uniform [Ag(NH3)2]2+ adsorption results in the uneven thickness of the shell layer on the surface of the SiO2 microspheres. Jiang et al. [28] prepared hollow nickel spheres with the aid of ultrasound and multiple activations. Although hollow and dense nickel spheres were also obtained, the aggregation of PS/Ni microspheres occurred due to the irregularity of the silver shell. Hu et al. [29] Hollow silver spheres are prepared by combining in situ reduction and electroless plating with modified polystyrene as a template. Although hollow and dense silver spheres are obtained, the silver nanoparticles on the surface of the PS core are easy to fall off due to the poor adhesion between the core and the outer silver nanoparticles.

In this paper, combining the advantages of ultrasonic dispersion and electrostatic deposition, monodisperse PS microspheres with sulfonic acid groups were prepared by chemical coarsening, and Sn2+ ions were adsorbed by electrostatic adsorption. Then through multiple sensitization and silver plating, the Ag nanoparticles were further uniformized on PS microspheres, and finally prepare PS/Ag composite microspheres under the method of ultrasonic assisted electroless plating. In this method, multiple sensitization and silver plating play an important role in uniformly depositing Ag nanoparticles on the PS surface. The preparation of PS/Ag composite microspheres was studied by SEM, FTIR and XRD. The morphology of the coated microspheres was characterized by SEM, the modified PS microspheres were characterized by FTIR and the crystal structure of the silver layer was characterized by XRD.

2. Experiments

2.1. Material

Polystyrene microspheres with particle average diameter of 5 μm were purchased from Shanghai Chemical Reagent Co. (China). Chromium trioxide (CrO3), H2SO4 (98%), tin(II) chloride dehydrate (SnCl2·2H2O), aqua ammonia (NH3·H2O), HCl, silver nitrate (AgNO3, 99%), Hydrazine hydrate (N2H4·H2O), absolute ethanol (EtOH) were supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and used as received. All experimental water was ultrapure water.

2.2. Preparation of PS/Ag composite microspheres by ultrasonic assisted electroless plating

The pretreatment process includes three steps: coarsening, sensitization and silver plating. Firstly, PS microspheres were coarsened with roughening solution. 4 g PS microsphere powder was immersed in 400 ml roughening solution (mixed solution of 0.5 mol l−1 CrO3 and 6 mol l−1 H2SO4) at 50 °C for 2 h, and the coarse PS particles were obtained by stirring at a constant speed of 600 rpm. After ultrasonic dispersion, the mixture was washed with absolute ethanol and deionized water for several times and centrifuged (figure 1(a)). Then, the microspheres were redistributed into 400 ml of acidic SnCl2 aqueous solution (0.05 mol l−1 SnCl2 and 1.3 mol l−1 HCl) and sensitized by ultrasound at room temperature for 10 min to obtain PS dispersion of Sn2+. The mixture was dispersed by ultrasonic, washed with absolute ethanol and deionized water for several times, and then centrifuged. Sn2+ ions not absorbed by microspheres were removed (figure 1(b)). Then, 10 ml of fresh [Ag(NH3)2]2+ composite ion aqueous solution (0.2 mol l−1) was added. After the reaction, the product was collected and washed three times with absolute ethanol and deionized water (figure 1(c)). Then the sensitization and silver plating processes were repeated. Finally, the microspheres were centrifugally washed for several times and dried in a constant temperature drying oven at 60 °C (figure 1(d)).

Polystyrene microspheres were introduced into fresh [Ag(NH3)2]2+ composite ion aqueous solution at room temperature, and hydrazine hydrate solution was added dropwise to prepare PS/Ag composite microspheres under ultrasound-assisted (40 HZ) conditions. Avoid removing of silver particles on the surface of microspheres by continuous ultrasonic assisted electroless plating, ultrasonic irradiation was carried out every 30 s. After electroless plating, PS/Ag composite microspheres were filtered and washed several times with deionized water and absolute ethanol. The PS/Ag composite microspheres were dried in a drying oven at 60 °C (figure 1(e)).

2.3. Characterization

The chemically roughened PS microspheres were characterized by FTIR, PS/Ag composite microspheres were observed by SEM and the crystal structure of the coating was determined by x-ray diffraction.

3. Results and discussion

3.1. Effect of multiple sensitization on the morphology of PS/Ag composite microspheres

Scheme 1 describes in detail the preparation process of PS/Ag composite microspheres. In this method, the purchased PS microspheres are used as the core of the composite microspheres, after roughening, multiple
sensitization, silver plating treatments, and then the PS/Ag composite microspheres are obtained by ultrasonic-assisted electroless plating. After treatment with the above scheme, PS/Ag composite microspheres with good coating effect and dispersibility can be obtained.

The SEM image of the selected PS microspheres is shown in figure 1(a). The size of PS particles is relatively uniform, with a diameter of 3 ~ 5 μm. It can be seen from the figure that the microsphere has a good spherical shape and its surface is very smooth.

After chemically coarsening the PS microspheres with a coarsening solution, PS microspheres with -SO₃H groups on the surface are obtained (scheme 1(a)). The morphology of the roughened PS microspheres can be seen by SEM, and the roughening has no obvious effect on the sphere and size of the original PS microspheres (figure 1(b)). FTIR proved the existence of -SO₃H groups on the PS microspheres, as shown in figure 2. Before chemical roughening, the peaks are located at 3065 cm⁻¹, 3038 cm⁻¹, 2958 cm⁻¹, 2885 cm⁻¹ and 1619 cm⁻¹,
1489 cm⁻¹, 1418 cm⁻¹, which can be clearly seen in the FTIR spectrum of PS microspheres (figure 2(a)). These are the infrared characteristic peaks of polystyrene. Under the action of the roughening solution, new peaks appeared at 1181 cm⁻¹ and 1043 cm⁻¹, as shown in the enlarged inset in figure 2. These new peaks can be attributed to the asymmetric and symmetrical vibration of the -SO₃H group. All peaks observed in the spectrum indicate that after the sulfonation reaction, the -SO₃H group was successfully modified on the PS microspheres.

When preparing PS/Ag composite microspheres by electroless plating, the purpose of chemical roughening is to use the oxidation and corrosion effect of strong oxidants to change the microscopic shape of the substrate surface, form micropores or etching grooves on the substrate surface, and remove other impurities on the surface, thereby improving the hydrophilicity of the substrate The surface and form proper roughness to enhance the bonding force between the substrate and the coating metal to ensure good adhesion of the coating. When the roughened PS microspheres are added to the acidic SnCl₂ aqueous solution, Sn²⁺ ions are easily adsorbed to the PS microspheres by the electrostatic adsorption between -SO₃H groups and Sn²⁺ ions on the surface (scheme 1(b)). In this regard, the effects of one-time sensitization, silver plating and multiple sensitization and silver plating on the quality of silver shells were compared through experiments.

Figures 3(a) and (b) show the SEM images of PS/Ag composite microspheres prepared by one-time sensitization, silver plating and multiple sensitization and silver plating with a diameter of 5 µm, respectively. It
can be seen from figure 3(a) that the silver coverage rate of PS/Ag composite microspheres prepared by one-time sensitization silver plating is low, and a large number of silver particles are dispersed outside the PS microspheres. However, under the same other reaction conditions, it can be seen from figure 3(b) that the PS/Ag composite microspheres prepared by multiple sensitization silver plating have uniform silver particles, and the whole composite microspheres still have a good spherical structure. Compared with figures 3(a) and (b), there is less free silver in figure 3(b), but there is still a small amount of free silver agglomerated between PS/Ag composite microspheres, indicating that PS/Ag composite microspheres have poor dispersion.

The experimental results show that multiple sensitization and silver plating can effectively improve the deposition of silver particles on the surface of PS microspheres. The main reason is that after the chemical roughening, the positively charged Sn^{2+} ions and the negatively charged —SO_3H groups on the surface of the PS microspheres produce electrostatic adsorption, so that the Sn^{2+} ions are uniformly distributed on the surface of the PS microspheres. After multiple sensitization and silver plating, Sn^{2+} ions can also be more evenly distributed on the surface of the PS microspheres. When silver ammonia solution is added, the [Ag(NH_3)_2]^+ ions are rapidly reduced to silver nanoparticles by Sn^{2+} ions, and the distribution of silver nanoparticles will be more uniform.

\[ \text{Sn}^{2+} + 2[\text{Ag(NH}_3)_2]^+ \rightarrow 2\text{Ag} + \text{Sn}^{4+} + 4\text{NH}_3\uparrow \]

These silver nanoparticles as nucleation sites promote the in situ reduction of silver ammonia particles by hydrazine hydrate and promote the growth of silver nanoparticles. Due to the uniform surface modification of PS microspheres after chemical coarsening, Sn^{2+} ions are uniformly adsorbed on the surface of PS microspheres in the sensitization process. After adding silver ammonia solution, Ag nanoparticles will be formed, which provides the basis for uniform deposition, growth and formation of dense Ag shell on the surface of PS microspheres by subsequent electroless plating of Ag.

3.2. Effect of AgNO_3 and PS microsphere mass ratio on preparation of PS/Ag composite microspheres

In order to analyze the effect of the mass ratio of AgNO_3 and PS microspheres on the deposition of silver nanoparticles on the surface of PS microspheres, three typical mass ratios of AgNO_3 and PS microspheres (1:1, 2:1 and 4:1) were selected to investigate the effect of the mass ratio of AgNO_3 and PS microspheres on the deposition of silver nanoparticles on the surface of PS microspheres. Figure 4 shows the SEM images of PS/Ag composite microspheres prepared by three different mass ratios of AgNO_3 and PS microspheres. It can be seen from figure 4(a) that when the mass ratio of AgNO_3 to PS microspheres is 1:1, the surface of PS microspheres is not completely covered by Ag nanoparticles, and a complete silver shell is not formed. When the mass ratio of AgNO_3 to PS microspheres is 2:1, silver nanoparticles tightly cover the surface of polystyrene microspheres, as shown in figure 4(b). When the mass ratio of AgNO_3 to PS microspheres increased to 4:1, the silver particles deposited on the surface of the PS microspheres increase significantly, and a large number of silver particles cover the PS microspheres and PS/Ag composite microspheres reunite, as shown in figure 4(c).

In general, the effect of the mass ratio of AgNO_3 and PS microspheres on PS/Ag composite microspheres is: when the mass ratio of AgNO_3 and PS microspheres is relatively low, the coating of Ag particles on the surface of PS/Ag composite microspheres is incomplete; with the increase of the mass ratio of AgNO_3 to PS microspheres, a complete and thicker Ag coating layer can be formed gradually, but when the silver nitrate is excessive, the PS/Ag composite microspheres will agglomerate. The influence of the mass ratio of AgNO_3 to PS microspheres on the coating effect is mainly related to the number of silver active sites formed on the surface of the PS...
microspheres. After several times of sensitization and silver plating, uniform Ag nanoparticles were formed on the surface of the microspheres, which provided nucleation center for the subsequent growth of Ag nanoparticles. The silver ammonia solution in the solution is reduced to Ag particles by hydrazine hydrate and grows preferentially in the nucleation center of Ag. With the increase of the mass ratio of AgNO₃ and PS microspheres, the more silver ammonia ions adsorbed on the surface of the microspheres, the more Ag particles were generated, and the coverage rate was improved. When the mass ratio of AgNO₃ to PS microspheres is too high, the growth rate of Ag on the surface of the microspheres is different, which leads to the uneven growth of Ag particles. These results indicate that the coverage rate of Ag nanoparticles on the surface of PS microspheres can be controlled by adjusting the mass comparison of AgNO₃ and PS microspheres.

3.3. Preparation of monodisperse PS/Ag spheres by ultrasonic electroless plating

In this experiment, we choose 40 Hz ultrasonic wave as the stirring method of electroless plating. Polystyrene microspheres with a diameter of 5 μm are sensitized and silver-plated multiple times, and then added to a silver ammonia solution with a mass ratio of AgNO₃ to PS microspheres of 2:1, and hydrazine hydrate is added at a constant rate. It was found that the bubbles generated in the reaction could be completely released in a shorter time by ultrasonic wave than by mechanical stirring. The effect of ultrasound on the preparation of PS/Ag composite microspheres was studied by comparing the micro morphology of PS/Ag composite microspheres prepared by mechanical stirring and ultrasonic.

As shown in figure 5(a), under the ultrasonic condition, the surface of PS/Ag composite microspheres is evenly coated with silver, and the dispersion is good; carefully observe the PS/Ag composite microspheres in
figure 5(a), as shown in figure 5(b), the silver plating effect on the surface of the composite microspheres is good, the surface of the PS microspheres has a complete silver shell, and the PS/Ag composite microspheres have good dispersibility, the particle size range of silver from 200 nm to 890 nm, and the thickness of the silver shell on the surface of the PS microsphere is about 200 nm. Figure 5(c) shows PS/Ag composite microspheres under mechanical stirring. Only part of the silver shell was intact and agglomerated. Compared with figure 5(b), the coating rate of PS microspheres in figure 5(d) is significantly reduced under the condition of mechanical stirring, and the coating is uneven and the dispersion is poor. The reason is that ultrasonic cavitation accelerates the transmission of materials in the plating solution and makes polystyrene microspheres evenly dispersed. The results show that the PS/Ag microspheres prepared by ultrasonic assisted electroless plating have good dispersion and can deposit complete silver shell on the surface of PS microspheres.

Figure 6 shows the XRD patterns of PS/Ag composite microspheres prepared by ultrasonic assisted electroless plating and pure PS microspheres. Curve (a) shows that pure PS microspheres are amorphous, corresponding to the wide reflection peak at $2\theta = 13.5^\circ$. Curve (b) shows the x-ray diffraction patterns of PS/Ag composite microspheres prepared by ultrasonic assisted electroless plating. The results show that the crystallization peaks are 38.04°, 44.24°, 64.38°, 77.32° and 81.46° respectively, corresponding to (111), (200), (220), (311) and (222) Bragg’s reflections of the FCC structure of Ag (JCPDS no.04-0783). As shown in figure 6 curve (b), the disappearance of strong reflection at $2\theta = 13.5^\circ$ of PS/Ag composite microspheres prepared by ultrasonic assisted electroless plating, indicating that the coverage rate of silver nanoparticles on the surface of PS microspheres is very high. The results show that Ag nanoparticles with good crystallinity were successfully deposited on the surface of PS Core after multiple sensitization and silver plating and electroless silver plating with hydrazine hydrate.

4. Conclusions

In conclusion, Ag/PS microspheres were prepared by ultrasonic electroless plating using polystyrene microspheres as template. In this study, multiple sensitization and silver plating play an important role in the uniform deposition of silver nanoparticles on the surface of PS template; The coating rate of silver nanoparticles on PS surface can be controlled by the mass ratio of PS microspheres to silver nitrate. When the mass ratio of PS microspheres to AgNO$_3$ is 1:2, the coverage of Ag nanoparticles deposited on PS is complete and uniform; In addition, compared with mechanical stirring, ultrasonic assisted electroless plating is more beneficial to the dispersion of PS/Ag microspheres under different stirring conditions. SEM and XRD confirmed the formation of PS/Ag composite microspheres.

Furthermore, this method based on multiple sensitization, silver plating and ultrasonic electroless plating also provides a new method for depositing different metallics (Cu, Au, Ag, and Ni, etc) onto various polymer material surfaces. Based on this technology, the preparation of various inorganic-organic composite materials can be realized. At present, it has been widely used in optical, magnetic, antibacterial, conductive and catalytic...
applications. However, with the continuous emergence of new organic materials, such composite particles will have a wider range of applications.

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ORCID iDs

Junhua Cheng ORCID iDs https://orcid.org/0000-0003-0154-896X
Lin Tang https://orcid.org/0000-0002-3920-0400
Chengbin Liu https://orcid.org/0000-0001-9835-6045

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