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Synthesis of Ag-coated polystyrene colloids by an improved surface seeding and shell growth technique

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Abstract

In this paper, an improved surface seeding and shell growth technique was developed to prepare Ag-polystyrene core shell composite. Polyethyleneimine (PEI) could act as the linker between Ag ions (Ag nanoparticles) and polystyrene (PS) colloids and the reducing agent in the formation of Ag nanoparticles. Due to the multi-functional characteristic of PEI, Ag seeds formed in-situ and were immobilized on the surface of PEI-modified PS colloids and no free Ag clusters coexist with the Ag "seeding" PS colloids in the system. Then, the additional agents could be added into the resulting dispersions straightly to produce a thick Ag nanoshell. The Ag nanoshell with controllable thickness was formed on the surface of PS by the "one-pot" surface seeding and shell growth method. The Ag-coverage increased gradually with the increasing of mass ratio of $AgNO_3$/PS. The optical properties of the Ag–PS colloids could be tailored by changing the coverage of Ag.

Keywords: Core-shell structure; Ag coating; Surface seeding and shell growth; "One-pot" reaction

1. Introduction

Advanced materials with core-shell structure have attracted extensive attention owing to their unique properties and versatile applications [1]. Deposition of metal nanoparticles on dielectric colloids is one of the investigation topic because of their excellent optical, electric and catalytic properties [2–4]. The metal Ag exhibits highest electrical conductivity and thermal conductivity among all of the metals. Also, it is a good substrate for surface-enhanced Raman spectroscopy [5,6] and one of the best candidates for the production of metallodielectric composites in the near-infrared spectral range [7]. In addition, the Mie resonances of the Ag shell can be shifted to much higher wavenumber than that of the corresponding Ag nanosphere [8].

The properties of Ag-colloid complex are dependent on the metal coverage [5,8]. Therefore, control of metal coverage is very important for the applications of this core shell composites. Until now, various approaches, such as the reduction of silver precursor in a dispersion solution containing PS spheres [9], thermal evaporation technique [5], electroless plating [10], polyol process [11], "in situ" formation by dispersion copolymerization of styrene and a polyamine in the presence of metal salts [12] and tollens-soaked process [13], have been developed to deposit Ag on the surface of solid core. However, the uneven distribution or lower metal coverage on the core surface were obtained. The sonochemical method was used to fabricate uniform coating on the core surface [14], but high-intensity ultrasound and removal of oxygen are necessary, otherwise the impurity of Ag_2O can be observed. The layer-by-layer self-assembly technique has been successfully exploited to prepare uniform and thick metal coating on the colloids, but the operation is complex and time-consuming [15].

One of the successful strategies is the surface seeding and shell growth technique that can easily prepare Ag-colloid composites with controllable metal coverage. The procedure involves the activation of the surface of core by

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"seeds" of metals (Ag, Au, Pd) followed by deposition of the metal Ag on the core surface [16–18]. Surface modification followed by the adsorption of pre-prepared metal nanoparticles [16] or Ag^+ ions [17], solvent-assisted route [18] have been adopted to deposit "seeds" onto core surface. However, after "seeding" reaction, free metal particles and/or excessive reductant coexist with metal-colloid composites in the system. To make the shell growth process executable, the impurities must be removed by repetitious centrifugation/wash cycles. Otherwise, additional metal particles can be obtained besides a shell around core surface in the shell growth process. It would be perfect if there are no isolated metal nanoparticles and residual reductant coexists with "seeding" colloids after "seeding" reaction. If that, the shell growth process may be performed directly followed the surface seeding step without centrifugation/wash. That is, a "one pot" surface seeding and shell growth process could be adopted to prepare Ag-colloids composites with controllable coverage.

In this paper, a "one pot" surface seeding and shell growth technique was developed for the preparation of Ag–PS composites. Polyethyleneimine (PEI) could act as the linker between Ag ions (Ag nanoparticles) and polystyrene (PS) colloids and the reductant in the preparation of Ag nanoparticles. Based on the multi-functional characteristic of PEI, Ag seeds formed in situ and were immobilized on the surface of PEI-modified PS colloids and no free Ag clusters coexit with the Ag "seeding" colloids in the system. Thus, without centrifugation and wash cycles, the additional reductant was introduced to produce thick Ag nanoshell. The Ag nanoshell with controllable coverage formed on the surface of PS by the "one-pot" surface seeding and shell growth process. The coverage of metal shell was easily controlled by changing mass ratio of silver nitrate to PS sphere. By changing the coverage of metal shell, the optical properties of the core-shell colloids could be tailored.

2. Experimental details

2.1. Materials

Silver nitrate ($AgNO_3$), polyethyleneimine (PEI, MW 600 000–1 000 000), styrene, ethanol, sodium citrate ($C_6H_5O_7Na_3 \cdot 2H_2O$), formaldehyde (HCHO, 37%), ammonia solution (25%), ascorbic acid were purchased from Shanghai Chemicals Co. Ltd. Water was distilled twice. Prior to use, the styrene was washed with 10% sodium hydroxide to remove the anti-polymerizer.

2.2. Synthesis

2.2.1. Synthesis of PS colloids

The PS colloids with diameter about 400 nm were prepared by emulsion polymerization in water–alcohol system [19]. Specifically, 0.1 g sodium lauryl sulfate and 0.11 g potassium pyrosulphate were dissolved into the 70 ml water–alcohol solution (volume ratio is 2:5). Prior to add styrene, the solution was bubbled with N_2 for 10 min. After this, 4.0 mL styrene was added under nitrogen atmosphere and rapid stirring. The emulsion solution was heated to 343 K and maintained at this temperature for 8 h. After polymerization reaction, the solution was filtrated and washed with ethanol and obtained solid was dried under air at room temperature.

2.2.2. Modification of PS colloids with PEI

Quantitative PS colloids were dispersed into phosphobuffer solutions (solution A), and then, the PEI aqueous solution was added into the solution A. The mass ratio of PEI to PS is about 1:2. Obtained solution was stirred under room temperature for 60 min. After centrifugation/wash cycles, the solids (PEI modified PS colloids) were obtained.

2.2.3. Preparation of Ag-coated PS colloids

Method 1: *reduction with PEI-formaldehyde*. In this method, the PEI that adsorbed on the PS surface act as reductant for the preparation of Ag seeds, the formaldehyde was used to increase coverage of Ag. The experimental details are as follows: quantitative $AgNO_3$ was dissolved into the 100 ml aqueous dispersion solution containing 0.1 g PEI modified PS colloids. The mixture was heated to 373 K for 1 h. The color of the dispersion solution changed from colorless to yellow. After cooling to room temperature, the ammonia, and sodium citrate were added into the dispersion solution. (The molar ratio of $AgNO_3/C_6H_5O_7Na_3 \cdot 2H_2O$ is 2 and the pH of the system is about 10.) Then, the excessive HCHO diluted with ethanol was added dropwise to reduce residual Ag ions.

Method 2: *reduction with PEI-sodium citrate*. In method 2, the PEI are also as reductant to obtain Ag seeds, the sodium citrate was used to produce thick Ag nanoshell. After Ag seeding, the dispersion solution was cooled to 353 K, and then the sodium citrate (the molar ratio of sodium citrate to Ag is 1:1) was added into dispersion. The reaction was additionally carried out 30 min under this temperature.

Method 3: *reduction with PEI-ascorbic acid*. In the method, the function of PEI is the same as that in methods 1 and 2; ascorbic acid was adopted to produce thick Ag nanoshell. After Ag seeding, the dispersion solution was cooled to room temperature and the aqueous solution of ascorbic acid (0.1%,) was added dropwise into the dispersion.

In the synthesis, the mass ratios of Ag/PS were changed from 4 to 1 to control the coverage of the silver shell.

After the reaction, the solids were isolated and cleaned by centrifugation/washing/redispersion cycles.

2.3. Characterization

Transmission electron microscopy (TEM) (JEM-2010 at 200 kV) was used to characterize the particle size and morphology. The samples for TEM were prepared by dropping the particles dispersed in ethanol onto a copper grid that was then dried under ambient condition prior to being introduced into the TEM chamber. X-ray powder diffraction analysis (XRD) was conducted on a Rigaku D/max-IIB X-ray diffractometer at a scanning rate of 4° per minute with 2θ ranging from 5 to 100, using CuKα radiation ($\lambda = 1.5418\,\text{Å}$). XPS (X-ray photoelectron spectroscopy) analysis was performed on a VG ESCALAB MK II with a MgKα (1253.6 eV) achromatic X-ray source. Uv-vis spectra were recorded with a UV-vis spectrophotometer (756CRT). IR spectra were recorded in the range of 400–4000 cm^{-1} on an Alpha Centauri FT/IR spectrophotometer using KBr pellets.

3. Results and discussion

Scheme 1 represents the schematic procedure for the synthesis of Ag–PS core-shell composite by the "one-pot" surface seeding and shell growing technique. The positive charged PEI was adsorbed on the PS colloid surface. Then, silver ions were added into the dispersion of the PEI–PS colloids. After heating the resulting dispersion and then adding formaldehyde into the dispersion, thick silver nanoshell may be obtained on the PS surface.

In step 1, the positive charged PEI is adsorbed on the negative PS surface. The IR spectrum of solid after adsorption of PEI on the PS was given in Fig. 1. The band at 3410 and 1600 cm^{-1} ascribed to the N–H stretching vibration and N–H bending vibration, respectively. After heating the dispersion of Ag$^+$ and PEI–PS, the color of the dispersion solution changed from white to yellow, which indicates the formation of Ag nanoparticles [12]. The component and morphology of as-obtained products were characterized by TEM, XRD and XPS. Fig. 2 shows the TEM images of the products. It can be seen that well-dispersed particles are immobilized on PS spheres. The particle size is about 10 nm as shown in Fig. 2a. The XPS and XRD shown in Fig. 3 were used to examine the component of the particles. The binding energy for Ag3d$_{3/2}$ is located at about 374.6 eV, which is close to the literature value for Ag^0 [12]. In the XRD pattern, five diffraction peaks are observed at $2\theta = 38.2°, 44.3°, 64.5°, 77.6°, 81.6°$, which correspond to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) reflections of cubic structure of metallic Ag, respectively (PDF: 4-783).

The TEM, XPS and XRD results demonstrated that the Ag modified PS spheres were obtained after heating the dispersion system containing Ag$^+$ and PEI–PS. It is well demonstrated that the metal nanoparticles deposited on the surface of core colloids provide nucleation sites for the growth of thick metal nanoshell. Previously, "seeding" colloids were obtained by reducing Ag$^+$–PS with NaH$_2$PO$_2$ [18], reducing Ag$^+$–SiO$_2$ with KBH$_4$ [17] and adsorption of pre-prepared metal nanoparticles on core surface [16]. It is obvious that excessive metal nanoparticles

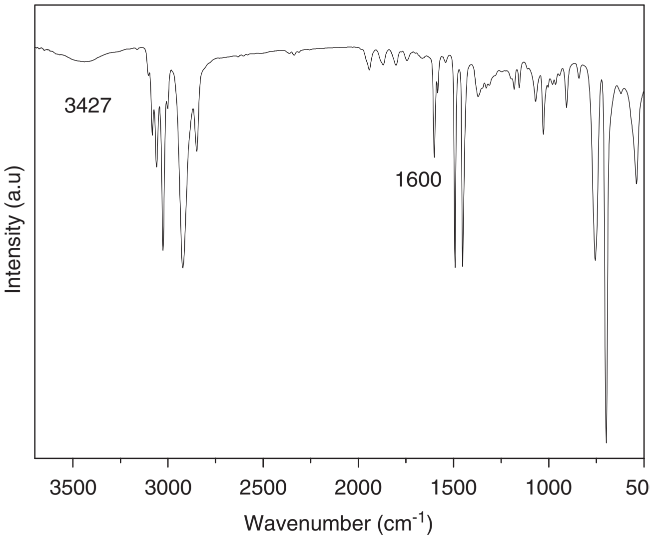


Fig. 1. FTIR spectrum of PEI–PS colloids.

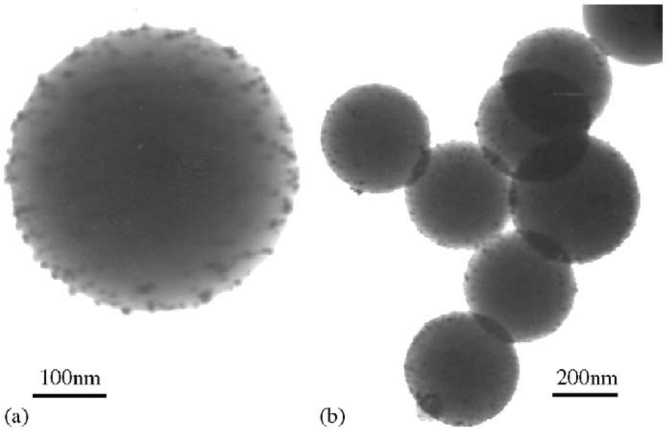
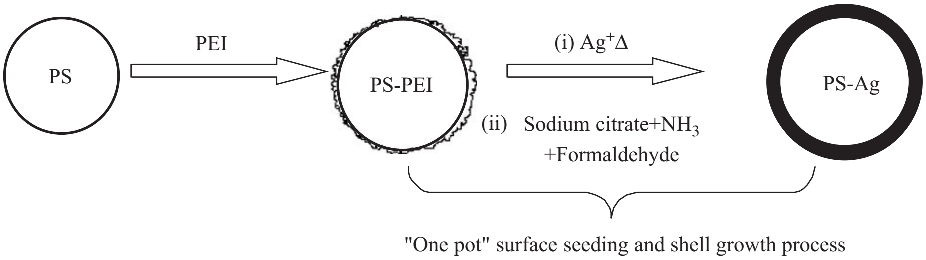


Fig. 2. TEM images of silver "seeding" PS spheres: (a) higher and (b) lower magnification.



Scheme 1. Procedure for the preparation of Ag–PS core-shell composite.

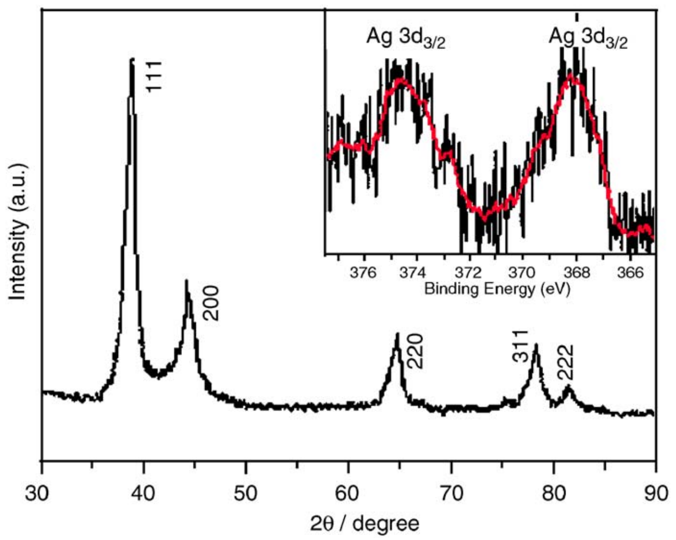


Fig. 3. XRD pattern of the PS spheres after Ag Seeding. XPS of Ag$_{3d}$ is shown in the inset.

and reductant coexists with "seeding" colloids. These impurities must be removed to ensure that the shell growth mainly occur on the core surface. In our experiment, the PEI that adsorbed on the core surface can bond with Ag$^+$ ions [20] and metal nanoparticles [21]. In addition, PEI can also act as a reductant in the preparation of metal nanoparticles [22]. Thus, due to the multi-functional characteristic of PEI, it is probable that all "seed" Ag nanoparticles formed in situ and were immobilized on the core surface. The result was demonstrated by UV-vis absorption spectrum. The UV-vis absorption spectrum of the Ag–PS spheres exhibits two absorption peaks at about 410 and 630 nm, which comes from the plasmon resonance of single Ag nanoparticles and plasmon–plasmon interaction between the silver nanoparticles [23], respectively (Fig. S1). However, the supernatant obtained from the dialyzed resulting solution was colorless and shows no absorption peak in the range of 400–800 nm (Fig. S2). The peak at about 300 nm can be contributed to absorption of excess Ag$^+$ ions [24]. In addition, TEM image of the product shows that only the Ag-modified PS sphere, but no free Ag particles were observed (Fig. 2b).

The above-mentioned results indicate that all the Ag nanoparticles were immobilized on the surface of core and only Ag$^+$ ions coexist with Ag "seeding" PS sphere. Thus, the dispersion solution obtained after the "seeding" reaction could be directly used for shell growth process without centrifugation/wash treatment. After adding ammonia and sodium citrate, the formaldehyde was added dropwise to the dispersion solution, the color of the dispersion changed gradually from yellow ("seeding" PS spheres) to red, or to black based on the different mass ratio of Ag/PS. This indicates the increase of Ag coverage on the surface of PS colloids. Fig. 4 shows the typical TEM images of the silver-coated PS spheres with different metal coverage. From the TEM images we can see that the size of the Ag particles gradually increases on the PS surface. Accordingly, the coverage gradually increases. This gradual growth process also was demonstrated by the XRD patterns as shown in Fig. 5. For contrast, the XRD pattern of Ag "seeding" PS spheres was also given. In the XRD patterns, the XRD peaks become narrower as particle size (metal coverage) gets larger, and the evidence of the increase of metal coverage obtained form XRD patterns match well with that observed from TEM images.

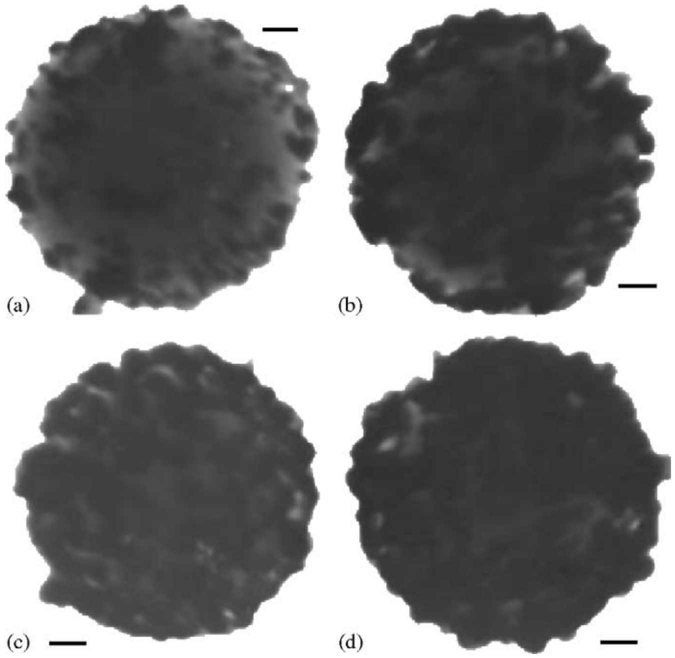


Fig. 4. TEM images of the Ag–PS colloids after shell growth at various mass ratios (AgNO$_3$/PS): 1:1. 2:1, 3:1 and 4:1 for a, b, c and d, respectively. Scale bar: 50 nm.

The optical resonance of single Ag nanoparticles is confined to relatively narrow wavelength ranges and cannot be readily shifted. By tailoring the particle geometry to metal nanoshell, the optical resonance of the Ag nanoparticles may be extended to broader range than that of single Ag particles. The optical properties of the metal shell are dependent on metal coverage (or ratio of the core to shell) [2,17]. Fig. 6 shows the Uv-vis absorption spectra of the Ag-modified PS colloids with different coverage of Ag. The absorption spectra for all samples exhibit two peaks: the peak 1 locates at the range of 400–600 nm, peak 2 at 600–900 nm. Peak 1 is due to Mie plasmon resonance from the single Ag nanoparticles [23]. The emergence of peak 2 may be contributed to the collective absorption behavior of Ag particles on the core (the optical properties of metal shell) [17,21,23]. The two peaks gradually shift to high wavelength when the metal coverage increases. The red-shift may be explained as follows. After shell growth reaction, the size of Ag nanoparticles increases, which resulted in the red shift of the peak 1. On the other hand, metal coverage increases as the particle size of Ag increases, which results in the shift of peak 2 to high wavelength [2,17]. When metal coverage is low, for example, after

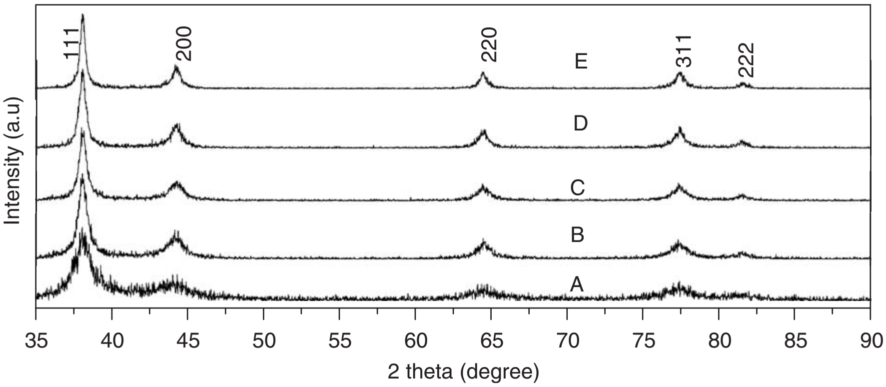


Fig. 5. XRD patterns of the Ag–PS colloids with different coverage of Ag, the curves B–E correspond to the sample shown in Fig. 4a, b, c, and d, respectively; the curves A: PS spheres after "seeding".

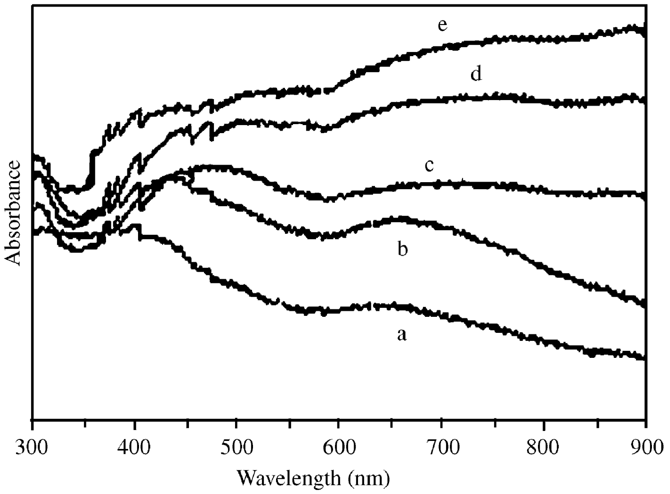


Fig. 6. Uv-vis absorption spectra of the Ag–PS colloids with different coverage of Ag, the curves a–e correspond to the curves A, B, C, D, E shown in Fig. 5, respectively.

"seeding" reaction, the core shell structure mainly shows optical plasmon resonance of single Ag particles. The intensity of peak 2 gradually enhances as the metal coverage increases. Finally, the Ag–PS composites mainly display the optical properties of Ag nanoshell when almost continuous Ag nanoshell was formed. The Uv-vis analysis shows that one can easily tune optical properties of Ag–PS composites by changing the metal coverage.

The effect of metal coverage on the optical properties also was demonstrated by Uv-vis diffuse reflectance spectra (DRS) as shown in Fig. S3. The samples and their corresponding DRS peak were listed in Table S1. The "seeding" PS spheres show three absorption peaks at 410, 520 and 616 nm, which were denoted as peak A, peak B and peak C, respectively (curve a). The peak A locates at 428, 435, 438 and 441 nm for curve b, c, d, and e, respectively. The peak B shifted from 520 nm for curve a to 546, 550, 558 and 570 nm for curve b, c, d, and e, respectively. The peak C locates at 740, 747, 816, 786 for curve b, c, d, and e, respectively. From Fig. S3 and Table S1 we can see that the three peaks shift to high wavelength when the metal coverage increases. In the same time, the intensity of peaks at high wavelength increases as the metal coverage increases. The results are similar to that in the Uv-vis absorption spectra.

The preparation methods have obvious influence on the feature of the core shell structure. In above-mentioned method, the PEI and formaldehyde were used to create Ag seeds and grow thick Ag nanoshell, respectively (method 1). In methods 2 and 3, the PEI that adsorbed on the PS surface still acts as reductant for formation of Ag seeds, whereas the sodium citrate and ascorbic acid were used to grow thick Ag nanoshell, respectively. Fig. 7 shows TEM images of the silvered PS spheres obtained with method 2. It can be observed that the coverage of metal increases with the increase of ratio of Ag–PS. However, it needs to be pointed out that metal ions and excessive reductant coexists in reaction system. When the ratio of $AgNO_3$/PS was high, "free" Ag particles were observed after shell growth process. When ascorbic acid was used, the increase of coverage is inapparent with the increase of ratio of Ag/colloid (Fig. 8). In this case, though ascorbic acid was slowly added, the uneven distribution of Ag particles on the PS surface and many free silver particles were observed. This is due to that the ascorbic acid is a rapid reductant that resulted in a large number of new nuclei in the dispersion system. As a consequence, free Ag nanoparticles formed in dispersion medium besides those around core surface. In method 1, the sodium citrate that acts as chelate agent with Ag ions was added all at a time and reductant (formaldehyde) was added dropwise. Such a "slow" reducing process ensures that reduction of Ag ions mainly takes place on the surface of the core. The results show that the reducing method had obvious effect on feature of the Ag–PS colloids.

4. Conclusion

Ag coated polystyrene spheres were prepared by the "one pot" surface seeding and shell growth technique. Ag seeds formed in situ and were immobilized on the surface

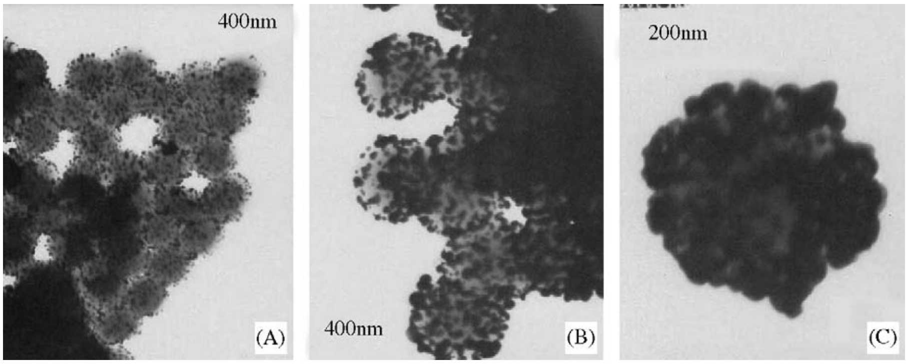


Fig. 7. TEM images of Ag–PS composites prepared by method 2. The ratio of $AgNO_3$ to PS is 1:1, 2:1 and 3:1 for A, B, C, respectively.

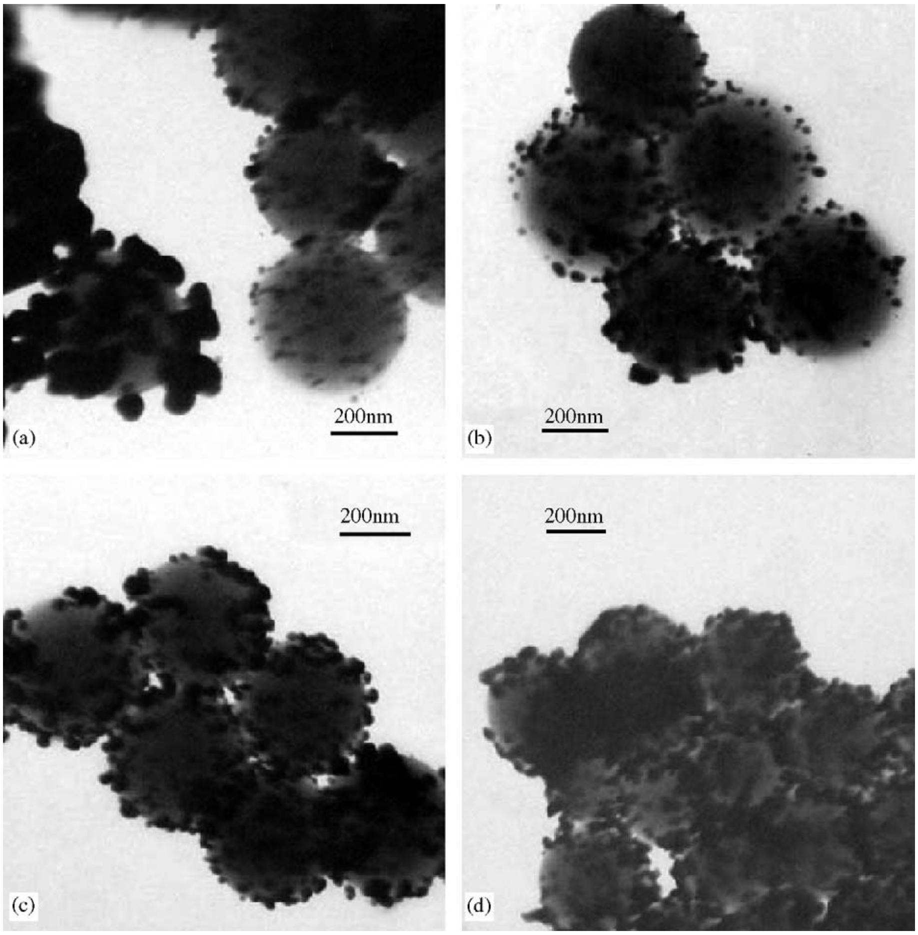


Fig. 8. TEM images of Ag–PS composites prepared by method 3. The ratio of $AgNO_3$ to PS is 1:1, 2:1, 3:1 and 4:1 for a, b, c, d, respectively.

of the PEI modified PS colloids. The dispersion obtained from "seeding' reaction could be directly used for the growth of thick Ag nanoshell without centrifugation/wash treatment. Experimental results showed that Ag nanoshells with controllable thickness were obtained by the "one pot" surface seeding and shell growth process. The optical properties of as-prepared Ag-colloid composites could be tailored by changing the coverage of metal shell. Silver-PS composites are expected to have potential applications in many technological areas such as optical resonance, surface enhanced Raman scattering, catalysis and biochemistry. The immobilization of Ag nanoparticles on microspheres could allow them to retain high activity on recycling, enhance their pH and temperature stability, and enable easy separation from the reaction medium by centrifugation for reuse. This process is promising for the preparation of the composite materials due to its virtue of convenient preparation and easy control of metal coverage.

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Appendix A. Supplementary data

Supplementary Figs. S1–S3 and Table S1 associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.06.022.

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