Preparation of silver-poly (acrylamide-co-methacrylic acid) composite microspheres with patterned surface structures

Abstract  Acrylamide (AM) and methacrylic acid (MAA) copolymer microgels were prepared by a reverse suspension polymerization technique. The microgels were used as templates for the preparation of silver-poly (acrylamide-co-methacrylic acid) [Ag-P(AM-co-MAA)] composite microspheres. The surface structures of the microspheres prepared in this way are characterized by zigzag-like structures. It was found that the composition of the microgels, the nature and dosage of surfactants, the quantity of the metal, and even the reduction methods employed have a significant effect upon the surface structures of the microspheres. X-ray diffraction analysis confirmed that Ag formed during the process is in a crystal state of a face-centered cubic structure.

Keywords Microgel · Ag nanoparticles · Composite materials · Template method

Introduction

Organic–inorganic composite microspheres with diameters less than 100 μm have received some interest due to their potential applications in electronics, cosmetics, pharmaceuticals, agriculture, separation, sensors, etc. [1–6]. Among these materials, design and preparation of microspheres with specific surface structures are attracting more attention. This is because the properties of composite microspheres are not only dependent upon their composition but also upon their surface structures [7–9]. For example, metal nanoparticles have been used as building blocks to construct core-shell microspheres and hollow microspheres in micrometer size range, of which the properties can be distinctly different from those of the individual nanoparticles [10]. Furthermore, the composite microspheres may combine the superior properties of the building blocks, the suppleness of organic materials, and the rigidity of inorganic materials, and at the same time, eliminate self-aggregation of nanoparticles in real application.

Composite organic–inorganic microspheres are normally prepared by various template approaches. According to the source, templates can be either artificial materials or natural materials. Compared with other common templates such as sfts, vesicles, membranes, biomacromolecules, and so on [11–14], the composition and structures of

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polymeric microgels can be controlled by choosing monomers, adjusting the composition of reactants, and modulating the reaction conditions [15–17]. The narrow size distribution combined with the inherent steric stabilization makes them ideal templates for preparing spherical micro/nanomaterials [18]. In fact, Antonietti and his coworkers prepared various noble-metal colloids of special shapes by using polystyrene sulfonate microgels as nanoreactors [16]. Xu et al. [19] and Zhang et al. [20] employed the copolymer microgels of N-isopropylacrylamide and acrylic acid and 2-hydroxyethyl acrylate [P(NIPAM-AA-HEA)] as reactors to synthesize Ag and CdS nanoparticles. It was reported that the sizes of the nanoparticles can be altered by varying the molar ration of Cd\(^{2+}\) to COO\(^{-}\) or Ag\(^+\) to COO\(^{-}\) and by changing the cross-linking density of the copolymer. Wu et al. prepared Ag-polystyrene (Ag-PS) composite microspheres by using a \(\gamma\)-radiation technique. However, the structure of the composite microspheres prepared in this way is far from perfect, and the Ag shell is not complete [21]. To improve the structures of composite microspheres, Chen and coworkers grafted poly(N-isopropylacrylamide) (PNIPAM) onto PS microspheres and employed the modified microspheres as new templates [22]. It was found that the surface coverage by Ag was significantly improved, but unfortunately, a complete uniform Ag shell was still not found [22]. Wang and Pan have focused on the studies of polymeric latex for a number of years, and a variety of inorganic-polymer composites in the nanometer size range have been prepared [23, 24]. Chemical reduction of metal ions was used to produce palladium, nickel, and other metals on the surfaces of polymer latexes. As a normal practice, Pd was produced first to catalyze the reduction of other metal ions. Dong and coworkers synthesized a uniform and complete Ag shell with controlled thickness on PS latex via layer-by-layer (LBL) self-assembly of polyelectrolytes and metal nanoparticles [25]. Recently, Zhang et al. explored a solvent-assisted route to preparation of composite microspheres with core (SiO\(_2\))-shell (Ag) structures. The Ag shell formed in this way is also complete and uniform [26]. Furthermore, the same group is also successful in the preparation of composite microspheres with core (SiO\(_2\))-shell (Ag) structures. The Ag shell formed in this way is also complete and uniform [26]. Lee et al. successfully synthesized nanosized Ag particles entrapped in multi-hollow porous poly(methylmethacrylate) (PMMA) microspheres by water-in-oil-in-water emulsion polymerization. It was found that the Ag nanoparticles were impregnated in the inner voids of the microspheres [27]. Recently, our group proposed a polymeric microgel template method and successfully used it in the preparation of various metal sulfiide-polymer composite microspheres such as Ag\(_2\)S-P(NIPAM), CuS-P(NIPAM), CdS-P(NIPAM), Ag\(_2\)S-P(NIPAM-co-MAA), CuS-P(NIPAM-co-MAA), and CdS-P(NIPAM-co-MAA) etc [28–33]. It is to be noted that all the metal sulfiide-polymer composite microspheres reported by our group are all in the tens of micrometer size range, and their surfaces are characterized by a variety of patterns. Furthermore, it was found that the surface morphologies of this kind of composite microspheres are dependent upon various factors, including the nature of templates and sulfides, the molar ratio of the polymers to the inorganic compounds, the way of the inorganic compounds being deposited, and even the reaction conditions.

In this study, the application of the polymeric microgel template method was extended for the preparation of metal-polymer composite microspheres. The purpose of the present study is to investigate whether the method we proposed can be used for the preparation of the metal-polymer composite microspheres and whether the composite microspheres are also characterized by certain patterns. Based upon previous studies and discussions above, we report here the preparation of Ag-P(AM-co-MAA) composite microspheres. Ag was chosen due to its chemical stability, excellent electrical conductivity, nonlinear optical behavior, antibacterial activity, etc. Actually, these properties have aroused people’s interest in the design and preparation of Ag-organic composite materials [34, 35].

**Experimental**

**Materials**

Acrylamide (AM) was purified by recrystallization in acetone. Methacrylic acid (MAA) was purified by distillation under reduced pressure prior to polymerization. \(N,N'\)-methylenbisacrylamide (BA), \(N,N,N',N'\)-tetramethylenediamine (TMED), and sorbitan monooleate (Span-80) were of chemical grade, and ammonium per-sulfate (APS), cyclohexane, acetone, silver nitrate (AgNO\(_3\)), formaldehyde (HCHO), and triethylamine [N(Et)\(_3\)] were of analytical grade. All these chemicals were used without further purification. Water used in the experiment was double-distilled.

Preparation of P(AM-co-MAA) microgels

A typical preparation is as follows: 100 ml of cyclohexane and 0.600 g of Span-80 were added to a 250-ml three-neck boiling flask equipped with a mechanical stirrer, a nitrogen inlet, and a Hirsch funnel. The mixture was stirred under nitrogen purging until the surfactant was uniformly dispersed. At the same time, 1.200 g of AM and MAA (10 and 20 wt% against total monomer weight, respectively), 0.060 g of BA, 0.400 g of NaOH, and 1 ml of APS were dissolved into 6 ml of double-distilled water. Then, the solution was stirred continuously under a nitrogen atmosphere. Reaction was initiated by addition of 1 ml of promoter, TMED solution, and conducted under stirring (380 rpm) at 20 °C for 4 h. The P(AM-co-MAA) microgels are obtained as white precipitates. They were filtered and washed with deionized water and acetone. Finally, the microgels were dried in a vacuum at 80 °C for 24 h.
formed were collected by filtration, washed alternatively with double-distilled water and acetone several times to remove the unreacted monomer and other impurities, and finally dried at room temperature.

Preparation of Ag-P(AM-co-MAA) composite microspheres with formaldehyde as reducing agent

P(AM-co-MAA) microgels (0.1 g) was swollen by a solution containing AgNO₃ (0.3 mol l⁻¹) and HCHO. The swollen microgels were suspended in an oil phase containing cyclohexane and Span-80 under stirring. Then, triethylamine was added drop-wise to the reaction system. The suspension was further stirred for another 3 h before separation by centrifugation. The introduction of N(Et)₃ can raise the pH of the microgels, and the increase in pH should start from the interface between the microgel and the continuous phase, resulting in the initiation of the reduction reaction of Ag⁺ at the position.

Other composite microspheres of different compositions were prepared in a similar way. The preparation process was schematically shown in Fig. 1.

Preparation of Ag-P(AM-co-MAA) composite microspheres with NaBH₄ as reducing agent

In a typical synthesis, 0.1 g of P(AM-co-MAA) microgels swollen by 0.3 mol l⁻¹ AgNO₃ solution was resuspended in an oil phase containing cyclohexane and Span-80 with stirring at 9 °C. Then, the reverse micelle solution (cyclohexane and Span-80) containing NaBH₄ was added. The suspension was further stirred for another 3 h. Finally, the products were collected and washed alternatively with double-distilled water and acetone and dried in air.

Fig. 1 Schematic representation for the preparation of Ag-P(AM-co-MAA) composite microspheres

Fig. 2 SEM images of the P(AM-co-10%MAA) microgels. a The microgels are easy to be dispersed; b They adopt perfect spherical shapes; c The structure of their surfaces is uniform
Characterization

The morphologies of the P(AM-co-MAA) and Ag-P(AM-co-MAA) composite microspheres have been examined by Philips scanning electron microscopy (SEM; Quanta-200). The structure of Ag nanoparticles was confirmed by a Japan Rigaku D/MAX-III X-ray diffractometer. The X-ray diffraction spectra were taken for 2θ angles from 15 to 80° at a scan rate of 0.02°·s⁻¹. Accelerating voltage and electric current are 35 kV and 40 mA, respectively.

Results and discussion

The P(AM-co-10%MAA) microgels prepared by the reverse suspension polymerization technique are spherical, easy to be dispersed, and their surfaces are smooth as shown in Fig. 2. Furthermore, the average diameter of the microgels is about 70 μm. It was also found that the sizes of the microgels may be altered by simply varying the amount of cross-linker, changing the weight ration of the monomers, and adjusting the stirring speed. The images and sizes of PAM and P(AM-co-20%MAA) microgels are similar to those shown in Fig. 2.

Figure 3 shows the SEM images of Ag-P(AM-co-MAA) inorganic–organic composite microspheres obtained by reverse suspension polymerization technique employed HCHO as reducing agent. The composite microspheres exhibited regular spherical morphologies (Fig. 3a). As expected, the average diameter of the microspheres is also about 70 μm, equal to that of the templates, indicating directly the confinement effect of the template to the inorganic reaction. Compared with the microgel template, the surface morphologies of the composite microspheres are characterized by zigzag-like structures, of which almost no variation in the thickness of the wrinkles and any site on the sphere looks similar to any other, although the wrinkles are randomly oriented and arranged (Fig. 3b).

The presence of Ag in the composite microspheres was confirmed by energy dispersive analysis of X-rays (EDX) measurement. EDX measurement also revealed the presence of Au, which might be originated from the spray of the metal before SEM measurement. The presence of Ag in the composite microspheres was further confirmed by X-ray diffraction (XRD) measurement as shown in Fig. 4. In reference to the figure, it is revealed that compared to the XRD pattern of the microgels (cf. Fig. 4b), the XRD pattern of Ag-P(AM-co-MAA) composite is characterized by a number of sharp peaks (cf. Fig. 4a), indicating that some crystalline materials are present within the composite microspheres. Compared to the standard XRD pattern of Ag as shown in the Joint Committee for Powder Diffraction Studies (JCPDS) card (no. 04-0783), it is clear that the sharp peaks may be assigned to the diffractions of the (111), (200), (220), and (311) planes of cubic Ag.

Effect of the composition of the template microgels upon the surface structures of the polymer-inorganic composite microspheres

To study the effect of the composition of the template microgels upon the surface structures of the final composite microspheres, two more Ag-polymer composite microspheres were prepared by employing microgel template

Fig. 3 SEM image of the Ag-P (AM-co-MAA) composite microsphere (a) and high-magnification image of it (b)

Fig. 4 XRD patterns of a Ag-P(AM-co-MAA), b P(AM-co-MAA)
method, taking PAM and P(AM-co-20%MAA) as templates, respectively. It was found that the surface of the Ag-PAM composite microspheres is structureless and almost has no difference with that of the template microgels. In contrast, however, the surface structure of the Ag-P(AM-co-20%MAA) composite microspheres is characterized by crystalline particles, which has been proven to be Ag by XRD and EDX studies (Fig. 5b). Comparing the surface structures of the three inorganic-polymer composite microspheres reveals that the compositions of template microgels have a great effect upon the surface morphologies of the mentioned composite microspheres.

Effect of the dosage of surfactant upon the surface structures of the polymer-inorganic composite microspheres

Figure 6 shows the SEM images of the Ag-P(AM-co-10%MAA) composite microspheres prepared in a similar way as that described earlier, but surfactant was not used. Comparing these images with those shown in Fig. 3, it is clear that the presence of surfactant in the preparation system is crucial for the formation of patterned surface structures. Actually, it was almost impossible to disperse the microgels containing Ag⁺ evenly in the oil phase without surfactant. The “poor” surface structures of the inorganic-polymer composite microspheres might be a result of the uneven suspension of the template microgels in the oil phase.

Figure 7 depicts the SEM images of the Ag-P(AM-co-10%MAA) composite microspheres prepared at different dosages of Span-80 (0.160, 0.240, and 0.800 g) (Fig. 7a,c,e) and their enlarged surface structures (Fig. 7b,d,f). It is clearly shown that not only the presence of surfactants affects the surface structures of Ag-polymer composite microspheres but also its dosages. As shown in the figure, to obtain well-patterned Ag-P(AM-co-10% MAA) composite microspheres, a minimum amount of the surfactant is needed. But at the same time, too much surfactant would make the patterns too fine, which might limit the potential applications of the composite microspheres.

Further observing the images, it may also be found that in contrast to the microspheres in micrometer size range, the fine structures of the surface patterns are in nanometer size range, that is to say that in addition to combining the advantages of inorganic and organic materials, these composite microspheres may also combine the advantages of traditional microparticles in micrometer size range and those in nanometer size range.
Effect of the quantity of the metal on the surface structures of Ag-P(AM-co-10%MAA) composite microspheres

To investigate the dependence of the surface morphology of the microspheres upon the quantity of the metal produced, we have prepared Ag-P(AM-co-10%MAA) composite microspheres with different ratios of the metal to the organic template. The initial concentrations of AgNO₃ in the preparation systems are 0.30 and 1.50 M. Figure 8 shows the SEM images of the microspheres and their enlarged surface structures. It is clearly shown that the increase in the quantity of the metal made the zigzag structure of the composite microsphere more coarse, but the patterned structure is still randomly oriented and arranged. This result may be rationalized by considering that a greater quantity of the metal must correspond to greater initial concentrations of metal ion and the reducing agent. Without a doubt, greater initial concentrations of the reactants will react more rapidly at a proper condition, resulting in greater metal particles, which might be responsible for the coarse surface structures.

Effect of reducing agents on the surface structures of Ag-P(AM-co-10%MAA) composite microspheres

Figure 9 shows the SEM images of Ag-P(AM-co-10%MAA) composite microspheres prepared by the polymeric microgel template method taking NaBH₄ as a reducing agent. It is demonstrated clearly that Ag formed on the template constituted a metal layer with “crude” patterns, a sharp contrast to that formed when HCHO was used as a reducing agent. The difference might be caused by the difference in the nature of the reducing agent and/or by the different method employed to conduct the reducing reaction. As mentioned earlier, the reduction reaction in the microgel system containing AgNO₃ and HCHO was initiated by increasing pH of the system via the introduction of N(Et)₃ in a controlled manner. In contrast, the reaction in the present system was initiated by the introduction of NaBH₄ via a reverse micelle method, in which the reducing agent was first dissolved in an aqueous surfactant solution and then introduced. The reduction reaction started once the microgels containing Ag⁺ come into collision with the micelles containing the reducing agent. Clearly, different reaction method and different reducing agent might be responsible for the difference in the surface structures of the composite microspheres. The impurities remaining on the composite microspheres as shown in Fig. 9 might be Na₃BO₃ produced from the reaction. These studies demonstrated clearly that the patterns formed on the Ag-polymer composite microspheres were also dependent upon the nature of the reducing agent and the method employed to carry out the reaction.

Based upon the results reported above, it might be possible to propose a model to describe the formation of the
surface structures. The zigzag-like surface morphologies of the Ag-P(AM-co-10%MAA) composite microspheres might have resulted from the confinement and guidance of the network structure of the template microgel to the precipitation of reduced product (Ag). For the microgel system containing AgNO₃ and HCHO, the reduction was initiated by introducing N(Et)₃ slowly into the system. This is because the reaction between Ag⁺ and HCHO could be only started when the pH of the system is higher than 8. Clearly, the reduction should start at the interface between the microgel and the continuous phase because the pH of this site is increasing first, and thereby, Ag⁺ and HCHO in the inner part of the microgels would diffuse to the interface to make up the deficiency. These processes continued till Ag⁺ was consumed completely, provided N(Et)₃ was added adequately. The small wrinkles formed on the surface of the composite microspheres might be a reflection of the heterogeneous interface structure (at a molecular level) between the microgel and the continuous phase. Therefore, it can be expected that all the factors affecting the structures and properties of the interfaces would affect the surface structures of the final inorganic-polymer composite microspheres. This is why the composition of the template microgel and the dosage of surfactants have a significant effect upon the surface morphologies of the composite microspheres. Furthermore, the ways for conducting inorganic precipitation reactions and the quantity of Ag deposited also affect the surface morphologies of the composite microspheres [29]. Of course, the interaction between the functional groups in the microgel and the metal ions should also affect the surface...
morphologies, as revealed by the control studies using PAM microgel as a template.

**Conclusions**

In summary, polymeric microgel template method could be extended to the preparation of Ag-P(AM-co-MAA) composite microspheres. Similar to that found in the preparation of metal sulfides-polymer composite microspheres by the mentioned template method, Ag-P(AM-co-MAA) composite microspheres prepared this way also occupy unusual surface morphologies characterized by zigzag-like wrinkles. Furthermore, various factors, including the composition of the template, the dosage of the surfactant, the quantity of the metal, and the reducing agent affect the surface structures of the composite microspheres significantly. It is expected that other noble metal-polymer composite microspheres with patterned surface structures might be also prepared via the proposed polymeric microgel template method.

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