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ORIGINAL CONTRIBUTION

Ag-polymer composite microspheres with patterned surface structures

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Abstract Novel silver-poly(acrylamide-*co*-methacrylic acid) [Ag-P(AM-*co*-MAA)] composite microspheres, in tens of micrometer size range, with patterned surface and core/shell structures were prepared by chemical reduction of Ag_2CrO_4-P(AM-*co*-MAA) composite microspheres in ethanol. Characterization with various techniques revealed that the chemical composition of the "shell" is dominated by Ag, but the "core" is dominated by the template, P(AM-*co*-MAA). It was also demonstrated that the surface morphology of the Ag-polymer composite microspheres is similar to that of their precursors and can be controlled to a certain extent by varying the composition of template copolymer, approaches, and amount of Ag_2CrO_4 deposited. This morphology transfer technique is also applicable for other silver salts-polymer composite microspheres. The same silver-polymer composite microspheres with very different morphology have also been prepared by utilizing this technique, but the different precursor microspheres, Ag_3PO_4-P(AM-*co*-MAA), were used.

Keywords Silver · Silver chromate · Silver phosphate · Composite microspheres · Chemical conversion

Introduction

The last decade has witnessed an exponential growth of research activities on inorganic-polymer composite materials due to their application in many fields, such as catalysis, biochemistry, separation, sensing, and biomaterials, which is attributed to their unique physicochemical properties [1–3]. Among the composites, silver-based materials, in particular, silver-polymer composite microspheres are of special interest. This is because silver has the properties of chemical stability, electrical conductivity, a broad spectrum of antimicrobial activities, and lower toxicity in human beings [4–6]. Several methods have been established for the preparation of various silver-polymer composite microspheres, including physical techniques such as thermal evaporation and laser sputtering and chemical techniques such as in-situ chemical reduction, sonochemical deposition, radiation reduction, electroless plating and layer-by-layer (LBL) assembly, etc. [6–20]. For example, Zhang et al. [7] prepared Ag nanoparticles in situ by the reduction of Ag^+ deposited in sulfonated polymeric microspheres, resulting in negatively charged Ag-polymer composite microparticles. This can be assembled into films by alternating deposition with the cationic polyelectrolyte. Sonochemical method, a method usually employed for the preparation of inorganic nano-composite micropheres [8–9], was also used for anchoring metallic nanocrystals (Ag, Au, Pd, and Pt) into the surface of polystyrene (PS) spheres [10]. Radiation reaction was another commonly used technique for the preparation of Ag-polymer composite microspheres [11–14]. Unlike other techniques, the radiation reaction can be conducted at room temperature and at ambient pressure. Furthermore, the reaction is free of reducing agents. The surface coverage of Ag, however, is low. To increase surface coverage, electroless plating [15–18] was exploited to coat

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polymer microspheres and has been successfully used for the preparation of composite microspheres with polymethyl methacrylate (PMMA) as a core and Ni, Co, or some metal alloys (CoNiP, NiFeP, and CoFeP) as a shell. Recently, Dong et al. [19] synthesized an even and complete Ag shell with controlled thickness on PS latex, via a LBL self-assembly of polyelectrolyte and metal nanoparticles. In this case, a complete and homogeneous metal shell is realized; unfortunately, the operation is complex. More recently, Zhang et al. [20] explored a solvent-assisted route to coat Ag or Au on the surface of PS latexes. The metal shell formed in this way is complete and uniform. Our group [21] prepared Ag-P (AM-*co*-MAA) [poly(acrylamide-*co*-methacrylic acid)] composite microspheres with patterned surface structures by combining a chemical reduction technique and a polymer microgel template method, which has been used for the preparation of various inorganic-polymer composite microspheres [22–30].

On the basis of previous studies [21, 26–30], novel Ag-P (AM-*co*-MAA) composite microspheres, of which the surface structure is completely different from that of the one reported earlier [21], were prepared by chemical conversion of Ag_2CrO_4-P(AM-*co*-MAA), which had been previously prepared by the combination of a polymer microgel template method and a reverse micelle technique [29].

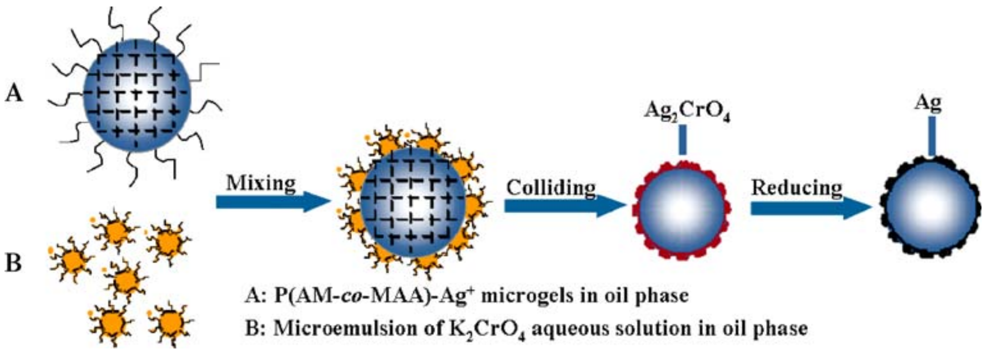
Morphology transfer has recently become one of the important methodologies for the preparation of materials of desired structures or morphologies [31]. Imprinting, templating, and molding are some of the commonly employed morphology transfer methods, but they are limited with respect to the available geometries and sizes [32]. Techniques for morphology transfer on nanoscale have so far remained a challenge. Dloczik et al. [31, 33] synthesized a series of semiconductors (ZnS, Cu_2S, Ag_2S, etc) based on ZnO, using first an exchange of oxygen by sulfur in the gas phase and subsequently a metal ion exchange in solution. Jeong et al. [34] successfully prepared Se@CdSe core-shell particles by using spherical core-shell colloids of Se@Ag_2Se as a chemical template. Inspired by the study on the formation of hollow nanocrystals of cobalt oxide and chalcogenides by cobalt nanocrystal templating through the nano-scale Kirkendall effect [35], Yang et al. [36] extended this strategy to fabricate silver microstructures exhibiting a well-defined, rhombododecahedral exterior morphology by self-assembly coupled with templating of the precursor crystals.

As we know, however, there have been no reports on the preparation of metal-polymer composite microspheres with patterned surface structures via a morphology transfer technique. The present work shows that the morphology of Ag_2CrO_4-P(AM-*co*-MAA) composite microspheres can be successfully transferred to Ag-P(AM-*co*-MAA), another kind of composite microspheres, via a chemical conversion technique. The preparation was completed in three steps and is schemetically shown in Scheme 1. Firstly, AM and MAA copolymer microgels with different compositions were prepared by a reverse suspension polymerization technique. Secondly, the salt-polymer composite microspheres were prepared by combination of a polymer microgel template method and a reverse micelle technique [29]. Finally, the microspheres were transferred into Ag-P (AM-*co*-MAA) via chemical reduction of the silver salt with $N_2H_4 \cdot H_2O$. The details of the preparation are shown in the following experimental section.

Experimental section

Materials

Acrylamide (AM) was purified by re-crystallization in acetone. Methacrylic acid (MAA) was distilled under reduced pressure before polymerizaton. Sorbitan monooleate (Span-80), *N*,*N*′-methylenebisacrylamide (BA), and *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMED) were of chemical grade, and ammonium per-sulfate (APS), cyclohexane, acetone, ethanol, silver nitrate ($AgNO_3$), sodium phosphate ($Na_3PO_4 \cdot 12H_2O$), potassium chromate (K_2CrO_4), and hydrazine ($N_2H_4 \cdot H_2O$) were of analytical grade. All these chemicals were used without further purification. Water used in the experiment was double distilled.



Scheme 1 Schematic representation for the preparation of Ag-polymer composite microspheres

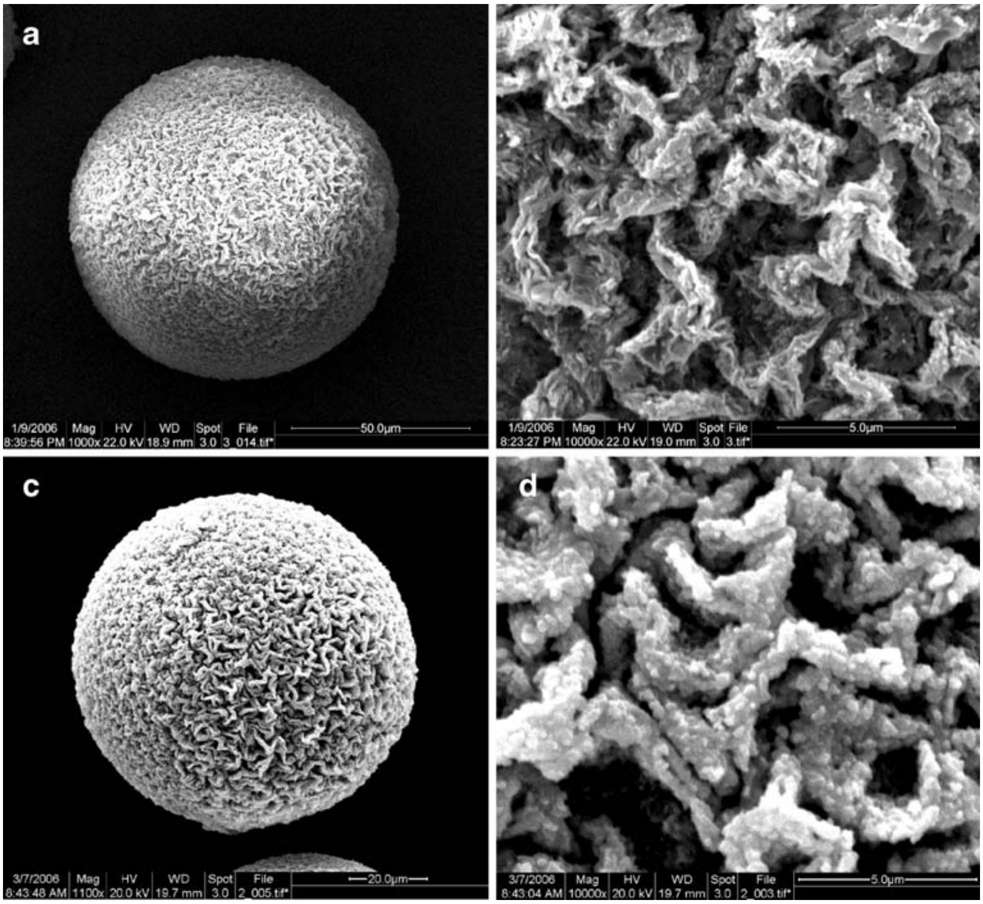


Fig. 1 SEM images of the Ag_2CrO_4-P(AM-*co*-20%MAA) (**a**), Ag-P(AM-*co*-20%MAA) microspheres (**c**), and high magnification images of them, respectively (**b**, **d**) (initial $AgNO_3$ concentration, 0.30 M)

Preparation of P(AM-*co*-MAA) microgels

The P(AM-*co*-MAA) microgels were prepared and characterized in the way as reported in the former report [21].

Preparation of Ag_2CrO_4-P(AM-*co*-MAA) composite microspheres

For a specific preparation, 0.20 g of P(AM-*co*-MAA) microgels in dry state was immersed in a certain volume of 1.00 M $AgNO_3$ solution overnight, allowing Ag^+ to diffuse into the interior of the polymer microgels. Then, the microgels containing Ag^+ were directly added into the organic phase consisting of 30 ml of cyclohexane and 0.30 g of Span-80. The system containing P(AM-*co*-MAA)-Ag^+ microgels was stirred for 40 min at room temperature. In addition, the mixture of 0.10 g Span-80 and 10 ml cyclohexane was sonicated for 1 min to form a primary emulsion. Meanwhile, according to the consumption of the amount of $AgNO_3$, a certain volume of K_2CrO_4

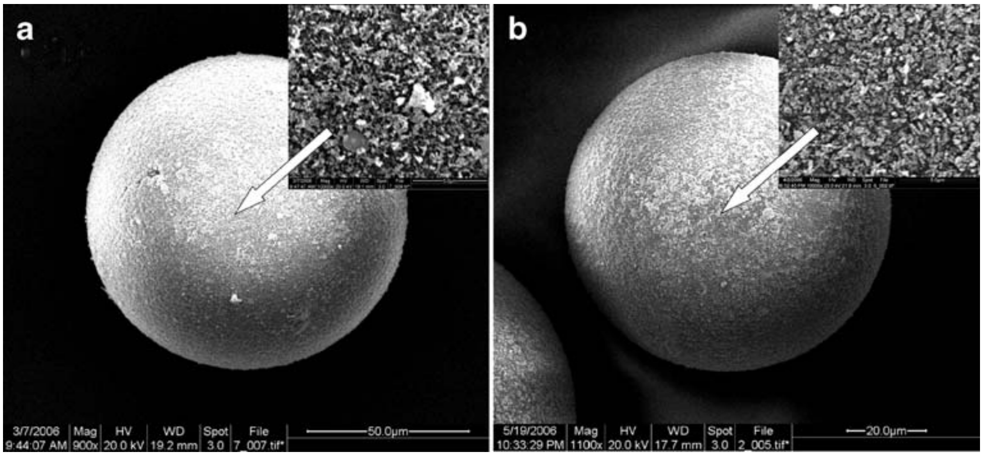


Fig. 2 SEM images of Ag_2CrO_4-PAM (**a**) and Ag-PAM (**b**). The *insets* are the higher magnification images of the surface structures of the corresponding microspheres

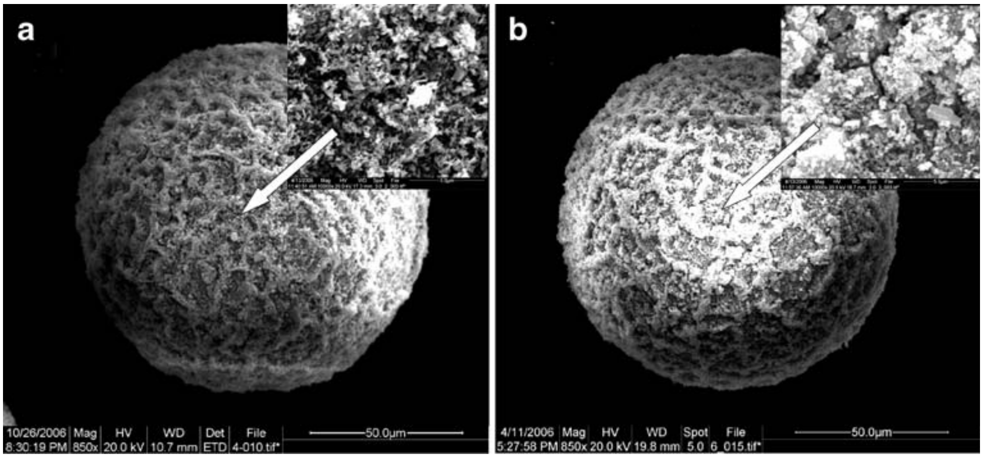


Fig. 3 SEM images of Ag_2CrO_4-P(AM-*co*-10%MAA) (**a**) and Ag-P(AM-*co*-10%MAA) (**b**). The *insets* are the higher magnification images of the surface structures of the corresponding microspheres

solution (0.10 M in water) was added to the primary emulsion so that the molar ratio of $[Ag^+]$ to $[CrO_4^{2-}]$ was 2:1. The emulsion was sonicated for another 1 min and was then transferred to the inverse suspension system, containing the above-mentioned microgels. The system was stirred for 4 h to let Ag^+ in the microgels and CrO_4^{2-} in the reverse micelles to react and form Ag_2CrO_4. The dark red Ag_2CrO_4-P(AM-*co*-MAA) microspheres were collected and washed alternatively with double distilled water and acetone and then dried in air at room temperature.

Other Ag_2CrO_4-P(AM-*co*-MAA) composite microspheres were prepared in a similar way, but different starting compositions had been utilized.

Preparation of Ag-P(AM-*co*-MAA) composite microspheres

The Ag_2CrO_4-P(AM-*co*-MAA) composites (0.10 g) were dispersed in ethanol (40 ml), according to the amount of Ag_2CrO_4 precipitated, a certain volume of $N_2H_4{\cdot}H_2O$ and ethanol (5 mL) was added drop-wise to the suspension system. The system was stirred at 10 °C for 10 h, to ensure that Ag_2CrO_4-P(AM-*co*-MAA) was completely transferred to Ag-P(AM-*co*-MAA). The dark Ag-P(AM-*co*-MAA) microspheres were collected, washed, and dried in a similar way as described above.

Characterization

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) measurements were performed with a Philips, Quanta-200 scanning electron microscope. X-ray powder diffraction (XRD) analysis was carried out by using a Japan Rigaku D/max-III X-ray diffractometer with Cu Kα radiation at 35 kV and 40 mA. The scan rate of 0.02 °/s was applied to record the pattern in the 2θ range of 15–70 °. Thermo-gravimetric analyses were performed using a Perkin-Elmer TGA-7 instrument. The measurement was conducted in an atmosphere of air at a scan rate of 10 °C/min. The microspheres, used as samples, were dried at 50 °C overnight before measurement.

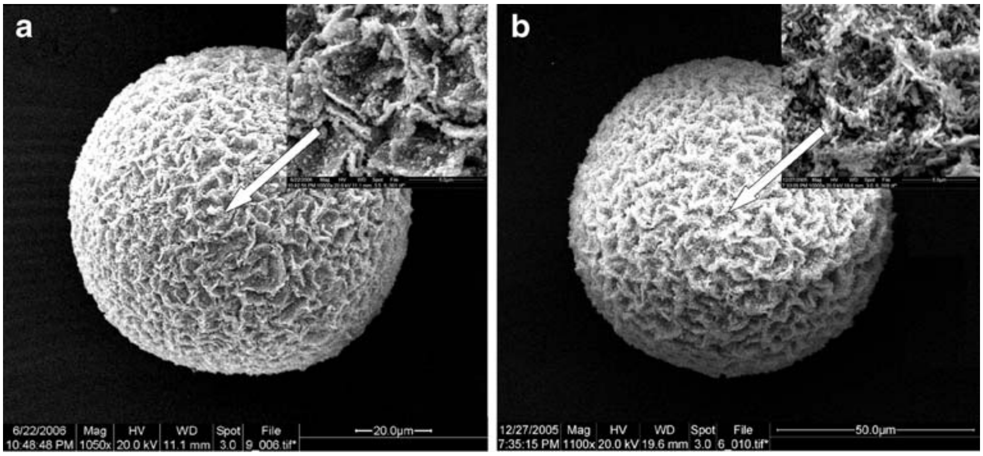


Fig. 4 SEM images of Ag_2CrO_4-P(AM-*co*-20%MAA) prepared with different initial concentrations of $AgNO_3$: **a** 0.60 M, **b** 1.00 M. The *insets* are the higher magnification images of the surface structures of the corresponding microspheres

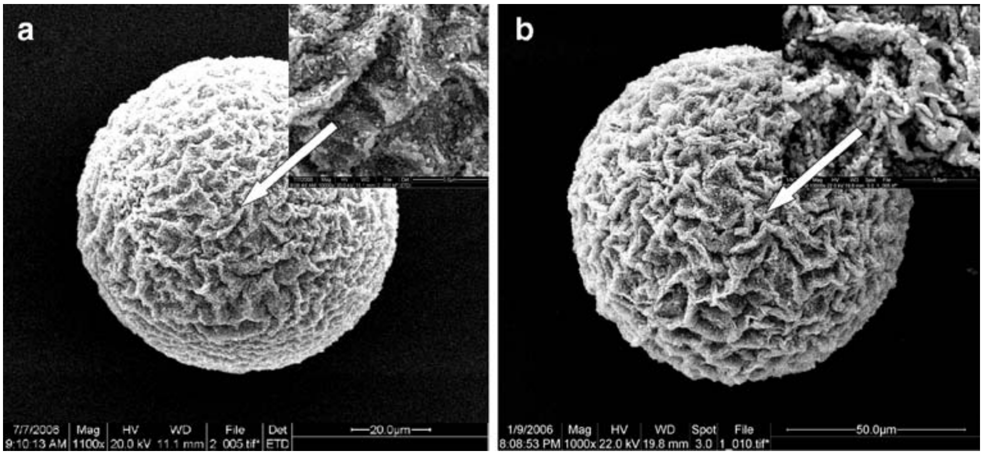


Fig. 5 SEM images of Ag-P(AM-*co*-20%MAA) composite microspheres produced by reducing Ag_2CrO_4-P(AM-*co*-MAA) with different initial concentrations of $AgNO_3$: **a** 0.60 M, **b** 1.00 M. The *insets* are the higher magnification images of the surface structures of the corresponding microspheres

Results and discussion

Surface structures of Ag-P(AM-*co*-MAA) and its precursor

Figure 1 shows the SEM images of a typical Ag_2CrO_4-P(AM-*co*-20%MAA) microsphere (Fig. 1a,b) and a Ag-P(AM-*co*-20%MAA) microsphere (Fig. 1c,d). It can be seen that the sizes of both microspheres are about 100 μm in diameter (Fig. 1a,c), and their surface structures are characterized by similar zigzag patterns (Fig. 1b,d). With further examination of the image shown in Fig. 1d, it is clear that the surface is composed of interconnected, irregularly shaped, primary particles, about a few hundred nanometers in size. In contrast, the surface of the precursor composite microspheres is characterized by a macroscopically ordered, but microscopically disordered collection of small crystals. Furthermore, the surface of the metal-polymer composite microsphere is denser than that of its precursor. The observation of morphology preservation and density increasing after the chemical conversion may be understood by considering the Kirkendall effect [37], which deals with the movement of the interface of reaction between a diffusion pair, being a fundamental solid-state phenomenon. In the present case, hydrazine and Ag_2CrO_4 can react with each other and form a diffusion pair. Encounter of the diffusion pair, at the composite and solution interface, could lead to the quick formation of an interconnected silver shell around the external surfaces of the composite microspheres. This process is followed by a continuous outward flow of the silver salt providing the reducing agent being supplied continuously and forms a relatively compact shell, as well as some individual silver particles being precipitated outside the surface. In this way, the morphology of the salt-polymer composite was maintained. Similar phenomena have also been observed by other groups in the preparation of hollow nanocrystals and rhombododecahedral silver cages [33–36].

It should be noted that the silver content in the metal-polymer composite is about 6 wt% determined by thermo-analysis (supporting information, Fig. S1) and that the composite microspheres are very stable, with no silver particles coming off from the surface during the post-treatment of them.

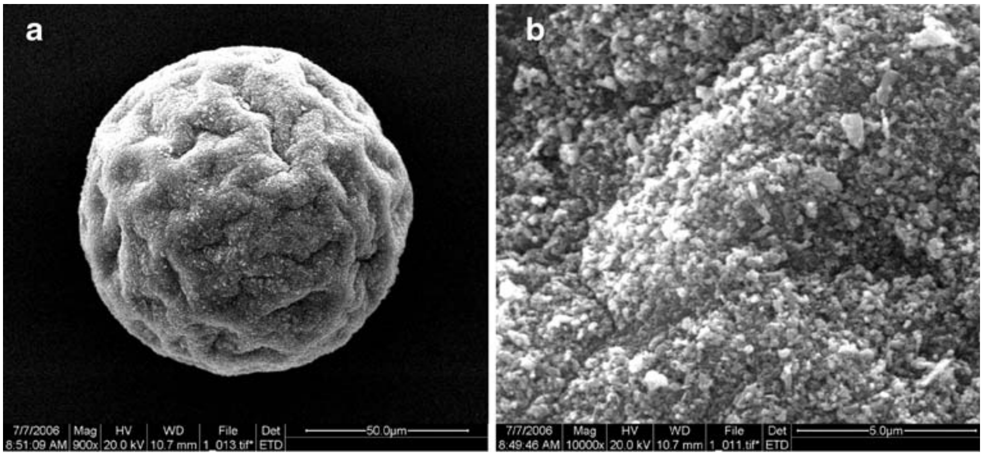


Fig. 6 SEM images of Ag-P(AM-*co*-20%MAA) composite microspheres prepared via a faster chemical reduction of Ag_2CrO_4-P(AM-*co*-20%MAA) (initial $AgNO_3$ concentration, 0.60 M) (**a**) and its high magnification image (**b**)

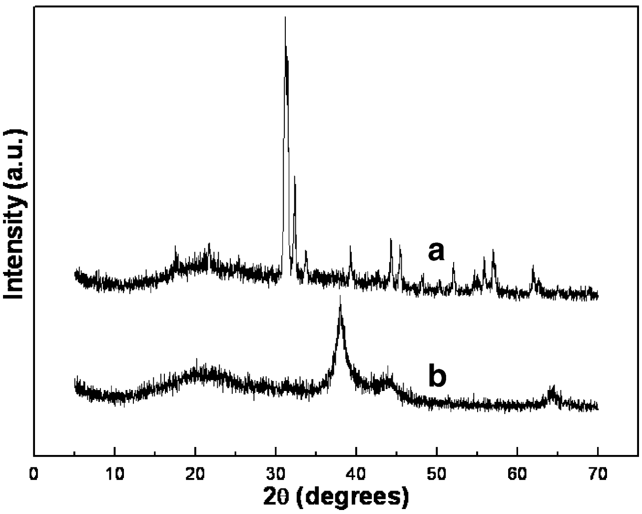


Fig. 7 XRD patterns of the Ag_2CrO_4-P(AM-*co*-20%MAA) (**a**) and Ag-P(AM-*co*-20%MAA) composite microspheres (**b**)

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

The effect of template composition upon the surface structures of the Ag-polymer composite microspheres has been studied by preparing two more Ag-polymer composite microspheres of different template compositions with the same method as described already. In the preparations, PAM and P(AM-*co*-10%MAA) microgels had been used as templates. The typical SEM images of the surface structures of them are depicted in Figs. 2 and 3, respectively.

In reference to Fig. 2, it can be found that the surface structures of both the silver salt-PAM and the Ag-PAM microspheres are very different from those shown in Fig. 1 and are characterized by crystalline particles (Fig. 2b). In contrast, for the copolymer systems (Fig. 3), two-dimensional network structures can be observed on the surfaces of the two composite microspheres. Examination of the insets reveals that the surfaces of the composite microspheres are composed of irregular inorganic particles. Comparing the morphologies of the silver salt-polymer composite microspheres shown in Figs. 1, 2, and 3, it can be concluded that the composition of the template microgels has a great effect upon the surface structures of the composite microspheres. Further, comparing the morphologies of the silver-polymer composite microspheres with those of their corresponding salt-polymer composite microspheres, it may be also concluded that the morphologies of the precursors can be well preserved during the chemical conversion of the surface components.

Effect of the amount of silver on the surface structures of the metal-polymer composite microspheres

To investigate the dependence of the surface morphology of the microspheres upon the quantity of the metal deposited, we have fabricated Ag-P(AM-*co*-20%MAA) composites with different ratios of the metal to the organic template. Here, the ratios were controlled by adjusting the amount of the insoluble silver salts precipitated on the precursor microspheres. The initial concentrations of $AgNO_3$ in the preparation systems are 0.30, 0.60, and 1.00 M, respectively. Figure 4 shows the SEM images of the Ag_2CrO_4-P(AM-*co*-20%MAA) composite microspheres (Fig. 4a,b; initial $AgNO_3$ concentration: 0.60 and 1.00 M, respectively), and the insets reveal the higher magnification images of them. Upon inspection of the images shown in Fig. 1 and those shown in Fig. 4, it can be seen that the surface patterns of the composite microspheres became less distinctive, less ordered, and the irregular salt crystals became larger along with increasing the amount of the insoluble salt deposited. The observation may be rationalized by considering the interaction between the carboxyl groups in the template microgels and the Ag^+. The insoluble Ag_2CrO_4 would deposit in a deeper position of the surface of the template when the concentration of $AgNO_3$ is low. This is because association between the carboxyl groups and the metal ions must inhibit the outward diffusion of the metal ions,

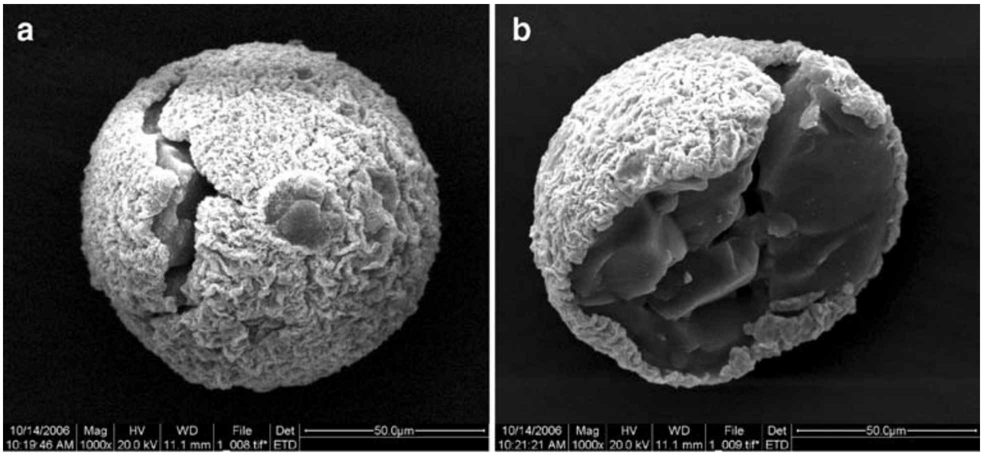


Fig. 8 SEM images of the "exploded" Ag-P(AM-*co*-20%MAA) composite microspheres (**a**) and the hemispheres (**b**)

and this makes the interface of the deposition reaction ($2Ag^{+}+CrO_4^{2-}=Ag_2CrO_4\downarrow$) shift gradually to the inner part of the template microgels, resulting in a surface with distinctive structures. On the contrary, more and more silver ions will stay in a free state with increasing $AgNO_3$ concentration and react with the externally introduced CrO_4^{2-} at a relatively outer part of the microgels. Clearly, the way of the deposition would be more affected by the template microgel networks when the ratio of $AgNO_3$ to the template is low. This may explain why the surface structure of the Ag_2CrO_4-P(AM-*co*-20%MAA) composite microspheres is more distinctive when the deposition amount of the insoluble salt is low. Similarly, it would not be difficult to understand why the surface patterns of the composite microspheres of Ag_2CrO_4-PAM and Ag_2CrO_4-P(AM-*co*-10%MAA) are less distinctive if compared with that of Ag_2CrO_4-P(AM-*co*-20%MAA; cf. Figs. 1a and b, 2a, and 3a).

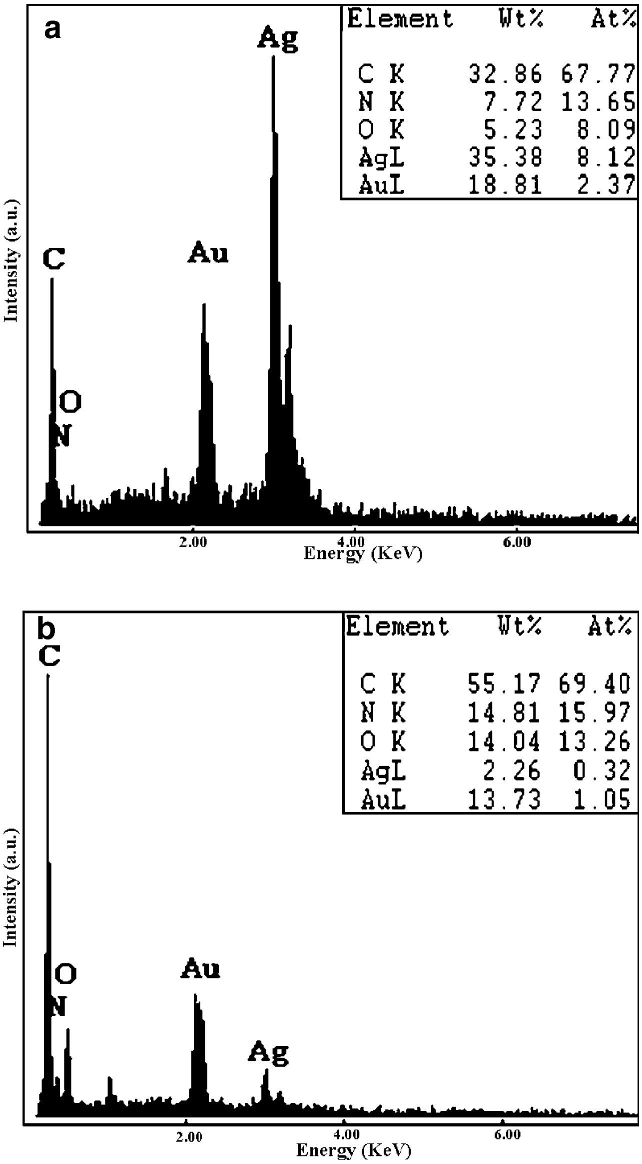
The SEM images of the Ag-P(AM-*co*-20%MAA) composite microspheres of greater silver content, which was prepared by using the corresponding Ag_2CrO_4-P(AM-*co*-20%MAA) microspheres as the template, are shown in Fig. 5. Clearly, the surface structures of these are almost the same as those of their precursors (cf. Fig. 4), indicating again that for the present systems, morphology transfer can be successfully performed by using the proposed chemical conversion technique.

Effect of introduction rate of the reducing agent upon the surface structures of the silver-polymer composite microspheres

Figure 6 depicts the SEM images of the Ag-P(AM-*co*-20% MAA) composite microspheres, prepared via a faster chemical reduction of Ag_2CrO_4-P(AM-*co*-20%MAA) (initial $AgNO_3$ concentration, 0.60 M) and its enlarged surface image (Fig. 6b). In the studies, the reducing agent was introduced by using an isobaric funnel. For the microspheres shown in Figs. 6 and 5a, the introduction of the reducing agent had been finished within 20 and 70 min, respectively. Comparing these images, shown in the two figures, it is clear that slower introduction of the reducing agent is favorable for the formation of clear surface patterns. This is not a surprising result, considering the chemical conversion rate. It can therefore be considered that a faster introduction of the reducing agent must result in a faster reduction of Ag_2CrO_4 and a faster diffusion of the salt from the inner part of the microspheres to the outer part of them, thus resulting in a faster deposition of Ag at the outer part of the microspheres. This must diminish the template effect of the microgels and produce composite microspheres with indistinctive surface structures.

Characterization of the composite microspheres

The surface components of the composite microspheres have been characterized by using an X-ray analysis (XRD) technique. The XRD patterns of the composites are shown in Fig. 7. It is revealed that for curve a in the figure, all of the sharp diffraction peaks can be indexed to orthorhombic crystalline Ag_2CrO_4 as shown in the Joint Committee for Powder Diffraction Studies (JCPDS) card (No. 26-0952), while the broad band around 21 ° in the curve is assigned to amorphous P(AM-*co*-MAA). These results indicate that the composite consists of two phases, i.e., the crystalline Ag_2CrO_4 characterized by the intense peaks with 2θ values of 31.06 °, 31.14 °, 31.43 °, 32.30 °, 39.29 °, and 44.24 ° etc., corresponding to the diffractions from the (220), (031),



Element	Wt%	At%
C K	32.86	67.77
N K	7.72	13.65
O K	5.23	8.09
AgL	35.38	8.12
AuL	18.81	2.37

Element	Wt%	At%
C K	55.17	69.40
N K	14.81	15.97
O K	14.04	13.26
AgL	2.26	0.32
AuL	13.73	1.05

Fig. 9 The EDX spectra of the shell part (**a**) and core part (**b**) of the Ag-P(AM-*co*-20%MAA) composite microspheres

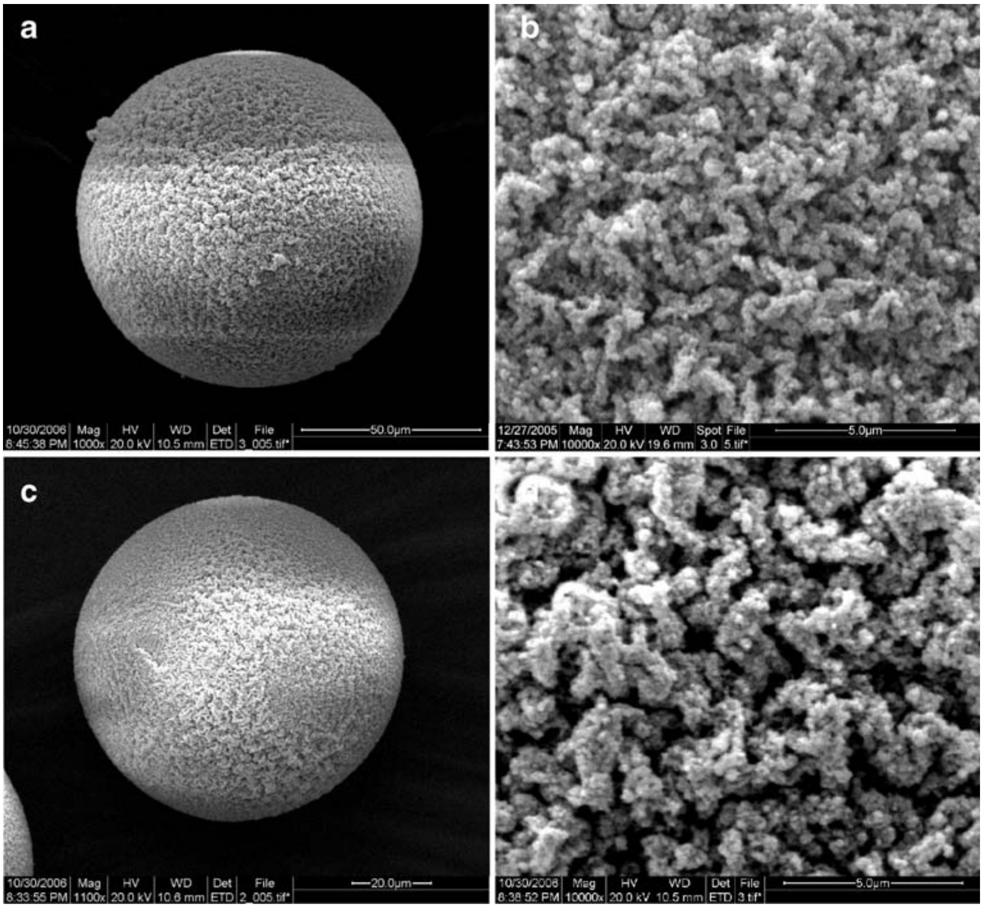


Fig. 10 SEM images of the Ag_3PO_4-P(AM-*co*-20%MAA) (**a**), Ag-P(AM-*co*-20%MAA) composite microspheres (**c**), and high magnification of them, respectively (**b**, **d**)

(211), (002), (122), (240) faces of the crystals, respectively, and the amorphous P(AM-*co*-MAA). In the examination of curve b in the figure, it can be found that the sharp diffraction peaks for Ag_2CrO_4 disappeared, and some new ones appeared. In reference to the JCPDS card (No.04-0783), it is concluded that the new peaks can be assigned to the face-centered cubic Ag crystals. No Ag_2CrO_4 signal in the XRD pattern of Ag-P(AM-*co*-MAA) indicates that the salt had been completely converted to Ag. This conclusion is further supported by the EDX analysis (Supporting information, Fig. S2). EDX analysis reveals that the atomic ratio of Ag to Cr in the salt-polymer composite microspheres is nearly 2:1 (Supporting information, Fig. S2a), which is in agreement with the composition of Ag_2CrO_4. For the composite of Ag-P(AM-*co*-MAA), there is no signal of Cr (5.40 KeV) in the EDX spectrum, but the peak of Ag (2.99 KeV) still exists (Supporting information, Fig. S2b).

To confirm the inner structure of the Ag-P(AM-*co*-MAA) composite microspheres, some "exploded" microspheres were prepared by fast-freezing them in liquid nitrogen (Fig. 8a,b). It is clearly shown that the composite microspheres adopt a typical core-shell structure. Further examination of the shell and the core via EDX analysis shows that the chemical natures of each of them are different. The shell of them is composed mainly of silver with less organic polymer (carbon and nitrogen; Fig. 9a). In contrast, the core is dominated by the polymer with a few percentage of silver (Fig. 9b). This is in accordance with the analysis discussed earlier.

The method established in the present work is not only limited to the transformation of Ag_2CrO_4-P(AM-*co*-MAA) to Ag-P(AM-*co*-MAA) but also to the transformation of Ag_3PO_4-P(AM-*co*-MAA) to Ag-P(AM-*co*-MAA). As an example, Fig. 10 shows one of the typical results (other information related with this composite is shown in the Supporting information, Figs. S3 and S4).

Conclusion

In summary, the special structures (patterned surface and core/shell structures) of the Ag-P(AM-*co*-MAA) composite microspheres have originated from the structures of their precursor composite microspheres, Ag_2CrO_4-P(AM-*co*-MAA), of which the structures are determined by the method, the composition of the templates and the amount of the insoluble salt are deposited in the microgel template. It is also safe to say that morphology preservation is possible during chemical conversion of Ag_2CrO_4 to Ag, provided the reaction is conducted in a sufficiently slow way. The advantages of the method designed for the preparation of Ag-P(AM-*co*-MAA) composite microspheres, with special surface structures, are obvious. To name just a few: (1) pretreatment of the core surface is unnecessary and the metal is produced in situ; (2) surface structure of the metal-polymer composite microspheres and the depositing amount of the metal can be controlled by simply adjusting the insoluble salts and amount precipitated; and (3) method of chemical conversion was versatile, which can be also applied in the preparation of other metal-polymer composite microspheres.

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