

Huiyun Xia
Ying Zhang
Junxia Peng
Yu Fang
Zhongze Gu

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

Received: 17 July 2005
Accepted: 20 December 2005
Published online: 28 March 2006
© Springer-Verlag 2006

H. Xia · Y. Zhang · J. Peng ·
Y. Fang (✉)

Key Laboratory for Macromolecular
Science of Shaanxi Province, School of
Chemistry and Materials Science,
Shaanxi Normal University,
Xi'an 710062,
People's Republic of China
e-mail: yfang@snnu.edu.cn
Tel.: +86-29-85307534
Fax: +86-29-85310097

Z. Gu
National Laboratory of Molecular and
Biomolecular Electronics,
Southeast University,
Nanjing 210096,
People's Republic of China

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 sifts, vesicles, membranes, biomacromolecules, and so on [11–14], the composition and structures of

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 ratio 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 γ -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]. More recently, Zhang et al. 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 [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 sulfide-polymer composite microspheres such as Ag_2S -PNIPAM, CuS-PNIPAM, CdS-PNIPAM, Ag_2S -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 sulfide-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

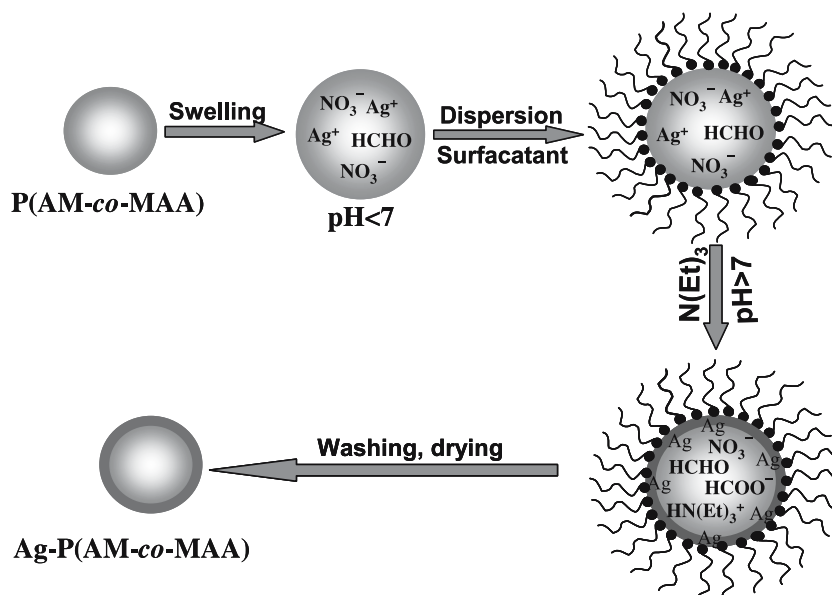
Materials

Acrylamide (AM) was purified by recrystallization in acetone. Methacrylic acid (MAA) was purified by distillation under reduced pressure prior to polymerization. *N,N'*-methylenebisacrylamide (BA), *N,N,N',N'*-tetramethylethylenediamine (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 [$\text{N}(\text{Et})_3$] 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

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



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 AgNO_3 (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 $\text{N}(\text{Et})_3$ 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 NaBH_4 as reducing agent

In a typical synthesis, 0.1 g of P(AM-co-MAA) microgels swollen by 0.3 mol l^{-1} AgNO_3 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 NaBH_4 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.

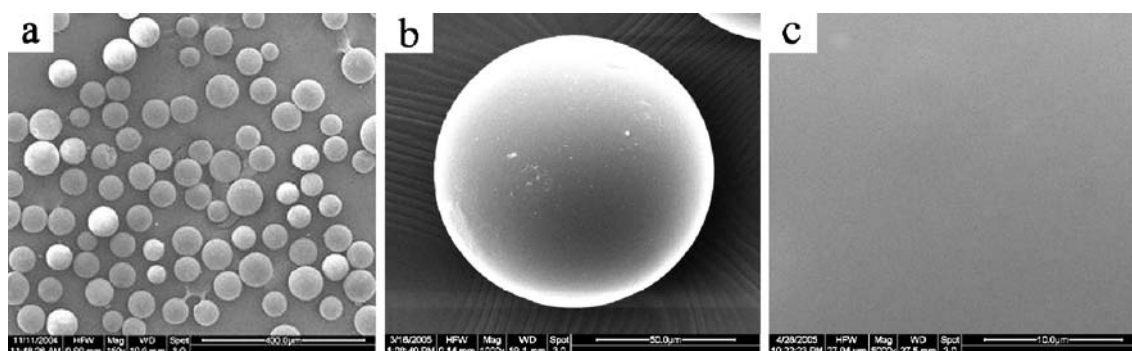
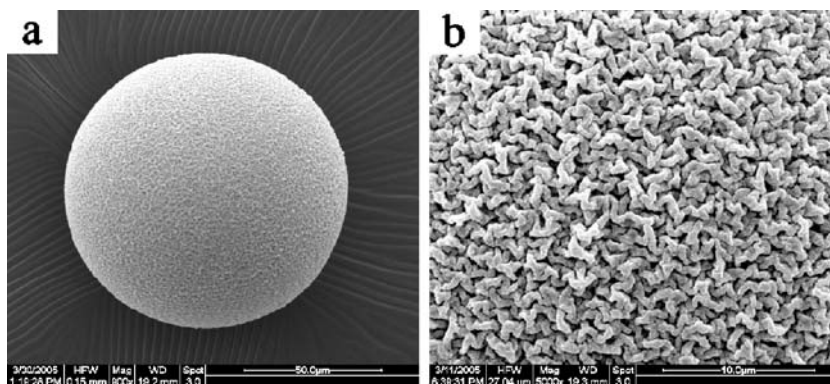


Fig. 2 SEM images of the P(AM-co-10%MAA) microgels. **a** The microgels are easy to be dispersed; **b** They adopt perfect spherical shapes; **c** The structure of their surfaces is uniform

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



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 $0.02^\circ \cdot \text{s}^{-1}$. 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

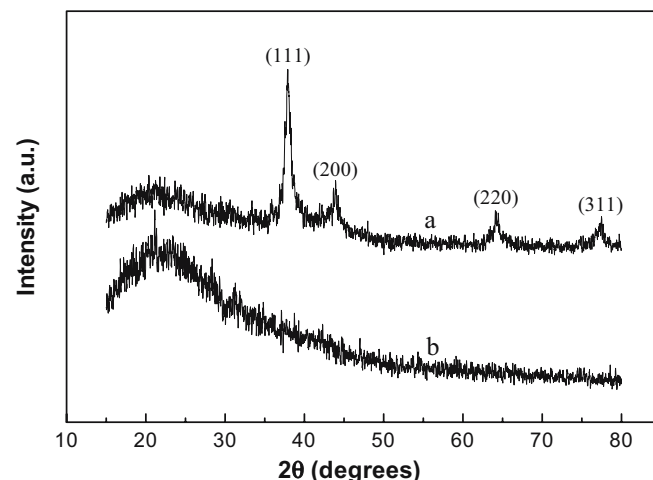
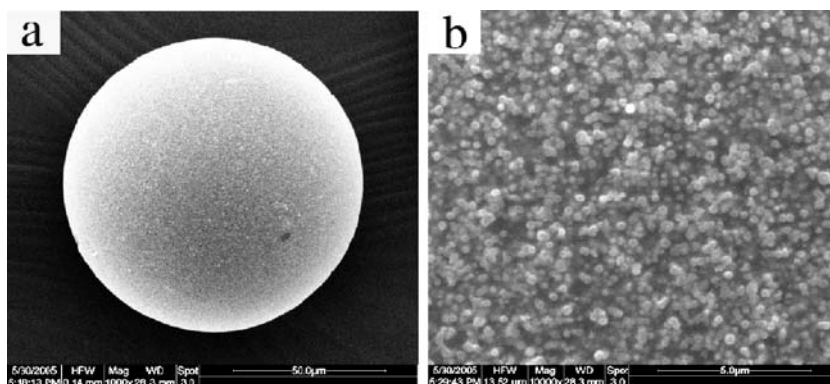


Fig. 4 XRD patterns of a Ag-P(AM-co-MAA), b P(AM-co-MAA)

Fig. 5 SEM image of Ag-P (AM-co-20%MAA) composite microsphere (a) and high-magnification image of it (b)



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

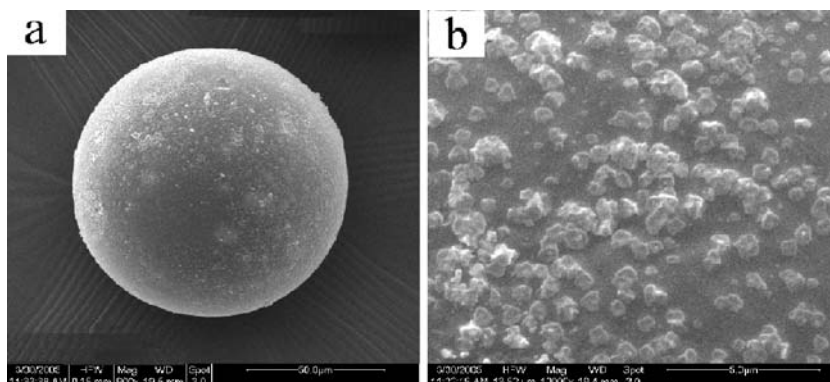
Figure 6 shows the SEM images of the Ag-P(AM-co-10%MAA) composite microspheres prepared in a similar way as that described earlier, but surfactant was not used. Comparing these images with those shown in Fig. 3, it is clear that the presence of surfactant in the preparation system is crucial for the 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.

Fig. 6 SEM image of Ag-P (AM-co-10%MAA) composite microsphere (no surfactant) (a) and high-magnification image of it (b)



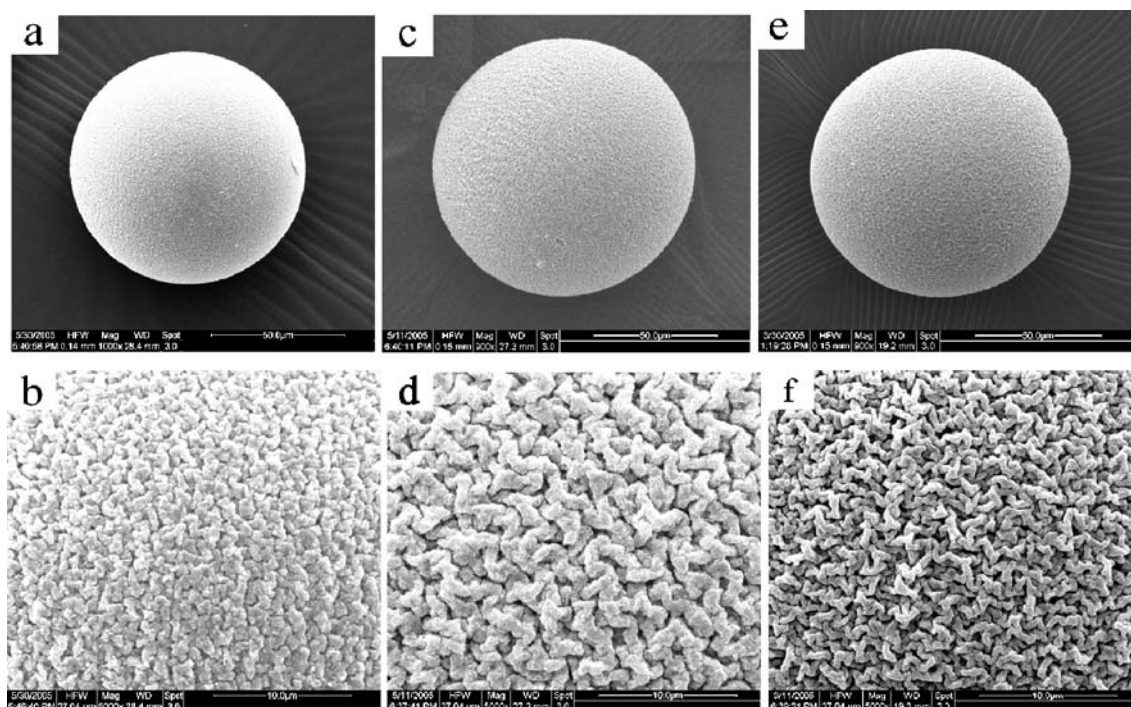


Fig. 7 SEM images of the Ag-P(AM-co-10%MAA) composite microspheres prepared at different dosages of Span-80. **a, b** 0.160 g; **c, d** 0.240 g; **e, f** 0.800 g

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.

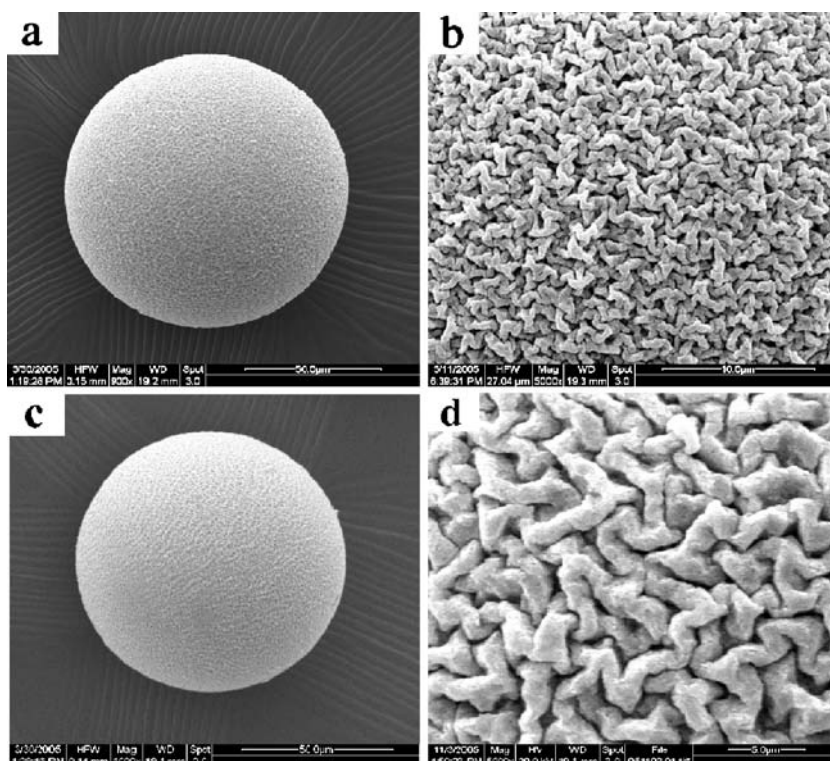
Effect of reducing agents on the surface structures of Ag-P(AM-co-10%MAA) composite microspheres

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

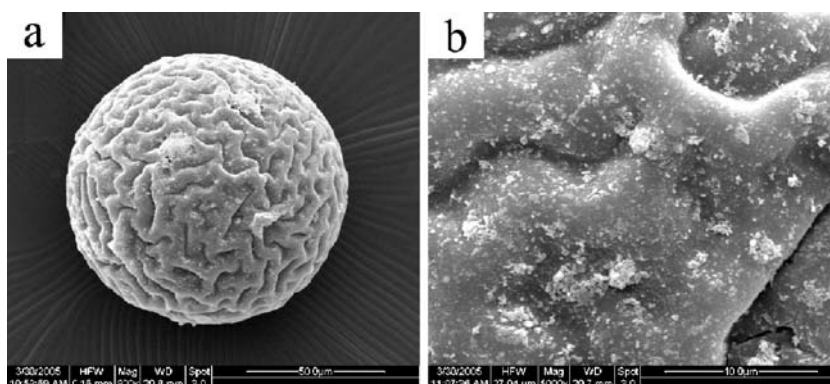
Fig. 8 SEM images of the Ag-P (AM-co-10%MAA) composite microspheres prepared at different initial concentration of AgNO_3 . **a, b** 0.30 M; **c, d** 1.50 M



surface structures. The zigzag-like surface morphologies of the Ag-P(AM-co-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 AgNO_3 and HCHO, the reduction was initiated by introducing $\text{N}(\text{Et})_3$ 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 $\text{N}(\text{Et})_3$ 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

Fig. 9 SEM images of Ag-P (AM-co-10%MAA) composite microspheres with NaBH_4 as a reducing agent



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, includ-

ing 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.

Acknowledgements The authors would like to thank the National Natural Science Foundation of China (20373039, 20543002), the Doctoral Program Foundation of Ministry of Education of China (20040718001), and the Ministry of Science and Technology of China (2003BA310A05) for financial support.

References

1. Antonietti M, Göltner C (1997) *Angew Chem Int Ed Engl* 36:910
2. Winiarz JG, Zhang LM, Lal M, Friend CS, Prasad PN (1999) *J Am Chem Soc* 121:5287
3. Ozin GA (2000) *Chem Commun* 6:419
4. Torrence NJ, Moore CM, Minteer SD (2002) *Langmuir* 18:6254
5. Gill I (2001) *Chem Mater* 13:3404
6. Sopeña F, Cabrera A, Maqueda C, Morillo E (2005) *J Agric Food Chem* 53:3540
7. Weiner S, Addadi L (1997) *J Mater Chem* 7:689
8. Estroff LA, Hamilton AD (2001) *Chem Mater* 13:3227
9. Mann S (2000) *Angew Chem Int Ed Engl* 39:3392
10. Caruso F, Spasova M, Salgueiriño-Maceira V, Liz-Marzán LM (2001) *Adv Mater* 13:1090
11. Davis SA, Burkett SL, Mendelson NH, Mann S (1997) *Nature* 385:420
12. Hubert DHW, Jung M, German AL (2000) *Adv Mater* 12:1291
13. Copper SJ, Sessions RB, Lubetkin SD (1998) *J Am Chem Soc* 120:2090
14. Braun E, Eichen Y, Sivan U, Ben-Yoseph G (1998) *Nature* 391:775
15. Saunders BR, Vincent B (1999) *Adv Colloid Interface* 80:1
16. Antonietti M, Gröhn F, Hartmann J, Bronstein L (1997) *Angew Chem Int Ed Engl* 36:2080
17. Murray MJ, Snowden MJ (1995) *Adv Colloid Interface Sci* 54:73
18. Schärtl W (2000) *Adv Mater* 12:1899
19. Xu SQ, Zhang JG, Paquet C, Lin YK, Kumacheva E (2003) *Adv Funct Mater* 13:468
20. Zhang JG, Xu SQ, Kumacheva E (2004) *J Am Chem Soc* 126:7908
21. Wu DZ, Ge XW, Huang YH, Zhang ZC, Ye Q (2003) *Mater Lett* 57:3549
22. Chen CW, Chen MQ, Seizawa T, Akashi M (1998) *Adv Mater* 10:1122
23. Wang PH, Pan CY (2000) *Eur Polym J* 36:2297
24. Wang PH, Pan CY (2000) *Colloid Polym Sci* 278:245
25. Dong AG, Wang YJ, Tang Y, Ren N, Yang WL, Gao Z (2002) *Chem Commun* 4:350
26. Zhang JH, Liu JB, Wang SZ, Zhan P, Wang ZL, Ming NB (2004) *Adv Funct Mater* 14:1089
27. Lee JE, Kim JW, Jun JB, Ryu JH, Kang HH, Oh SG, Suh KD (2004) *Colloid Polym Sci* 282:295
28. Bai CL, Fang Y, Zhang Y, Chen BB (2004) *Langmuir* 20:263
29. Fang Y, Bai CL, Zhang Y (2004) *Chem Commun* 7:804
30. Zhang Y, Fang Y, Wang S, Lin SY (2004) *J Colloid Interface Sci* 272:321
31. Zhang Y, Fang Y, Lin SY, Liu J, Yang JL (2004) *Acta Phys-Chim Sin* 20:897
32. Bai CL, Wang S, Zhang Y, Fang Y (2003) *J Shaanxi Norm Univ (Nat Sci Ed)* 31:62
33. Yang JX, Fang Y, Bai CL, Hu DD, Zhang Y (2004) *Chin Sci Bull* 49:2026
34. Sondi I, Goia DV, Matijević E (2003) *J Colloid Interface Sci* 260:75
35. Henglein A (1993) *J Phys Chem* 97:5457