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Preparation of metal sulfide–polymer composite microspheres with patterned surface structures†

Yu Fang,* Chaoliang Bai and Ying Zhang
School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, P. R. China. E-mail: yfang@snnu.edu.cn; Fax: +86 29 5307025; Tel: +86 29 5307534(L)

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CuS–poly(*N*-isopropylacrylamide), CuS–poly(*N*-isopropylacrylamide-*co*-methacrylic acid), Ag_2S–poly(*N*-isopropylacrylamide) and Ag_2S–poly(*N*-isopropylacrylamide-*co*-methacrylic acid) composite microspheres exhibiting complex surface morphologies were prepared by employing the minigel template method.

Recently, inorganic–organic composite microspheres have become the focus of intensive research due to their importance in potential wide-ranging applications.[1–3] Moreover, the combination of organic and inorganic compounds in the nano-size range can yield new materials which may combine the advantages of inorganic, organic and nano-materials.[4] Many recent efforts have been focused on the integration of inorganic nano-particles into the interior of polymer microspheres, which would offer opportunities to explore their novel collective mechanical, thermal, optical, magnetic, and electronic properties.[5,6]

Various approaches have been designed to prepare composite materials in order to obtain the required properties and structures. Among them, the template approach is particularly useful due to the ability to construct highly ordered materials in a controllable manner.[7,8] Both artificial and natural materials have been used as templates.[9,10] Minigels are crosslinked sponge-like polymeric particles.[11] Compared with other templates, particularly natural templates, the size, composition, charge nature, and even cross-linking density of minigels are easily controlled.[12] Their narrow size distribution combined with their inherent stability makes them ideal templates for preparing spherical inorganic–organic composite materials. Antonietti and his colleagues[13] prepared various noble-metal colloids of special shapes by using polymeric minigel as microreactors. Snowden, Silver and co-workers[14] used minigels of poly(*N*-isopropylacrylamide-*co*-acrylic acid) to stimulate the formation of spherical Y_2O_3 : Eu phosphors. Shen *et al.*[15] have reported the synthesis of PbS and ZnS nanocomposites *via* minigels of Pb- or Zn-methacrylate, which were then copolymerized into a polystyrene matrix. Pan and Wang[16] have focused on the studies of polymeric latex for a number of years, and a variety of polymer–inorganic composites in the nanometre range have been prepared. Kim *et al.*[17] embedded ZnO nanoparticles into poly(methyl methacrylate) microspheres by *in situ* suspension polymerization. Recently, Ge and coworkers[18] prepared Ag–polystyrene and CdS–polystyrene microspheres by using a γ-radiation technique. To the best of our knowledge, however, inorganic–polymer composite microspheres with patterned surface structures have not been reported.

In this contribution, we synthesized CuS–poly(*N*-isopropylacrylamide-*co*-methacrylic acid) (PNIPAM-MAA) composite microspheres with patterned surface structures by a polymeric minigel template method. The minigels were prepared by reverse suspension polymerization of the aqueous solution of NIPAM and MAA initiated by ammonium persulfate (APS) in *n*-heptane. It was expected that the network structure of minigels might control and direct the precipitation of metal sulfides, and thereby controlling the final size and morphology of the composites.

In a typical synthesis, to a 250 mL flask, 75 mL of *n*-heptane and 0.6 g of a neutral surfactant mixture formed by Span-80 and Tween-80 (5 : 1 volume ratio) were added. The mixture was stirred vigorously under a nitrogen atmosphere, giving a fully emulsified surfactant solution. At the same time, 1.0 g of NIPAM, 0.2 g of MAA, 0.02 g of *N*,*N*′-methylenebisacrylamide (BA), and 0.3 mL of APS (216 mg mL^{-1} in aqueous phase) were dissolved in 6 mL of doubly distilled water. To the organic phase, the monomer solution was added *via* a funnel. Polymerization was initiated by addition of 0.5 mL of a promoter, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED), solution (50 mg mL^{-1}). The reaction was lasted for 3 h at 20 °C with stirring (360 rpm), resulting in PNIPAM-MAA minigels. The minigels thus obtained were collected by filtration, washed alternately with doubly distilled water and acetone several times, and then dried at room temperature. For the preparation of the composite microspheres, 0.3 g of the minigels were swelled in 1.2 mL of 0.2 mol L^{-1} aqueous $Cu(Ac)_2$ solution. Then, the minigels containing Cu^{2+} were re-suspended in 75 mL of *n*-heptane with mild stirring. 40 min after the addition of metal-containing minigels, H_2S was introduced slowly for 25 min with constant stirring, since the formation of CuS in the system is found to be practically complete after this period. The system was further stirred for 3 h before separation by centrifugation. The CuS–PNIPAM-MAA microspheres thus obtained were further treated in the same way as for the treatment of the minigels. CuS–PNIPAM composite microspheres were prepared in a similar way.

Fig. 1 shows typical SEM images of the obtained CuS–PNIPAM and CuS–PNIPAM-MAA microspheres, which range from 50 to 65 μm in size (Fig. 1a, 1c), and have complex, but regular surface morphologies (*cf.* Fig. 1b, 1d). On further examination of the

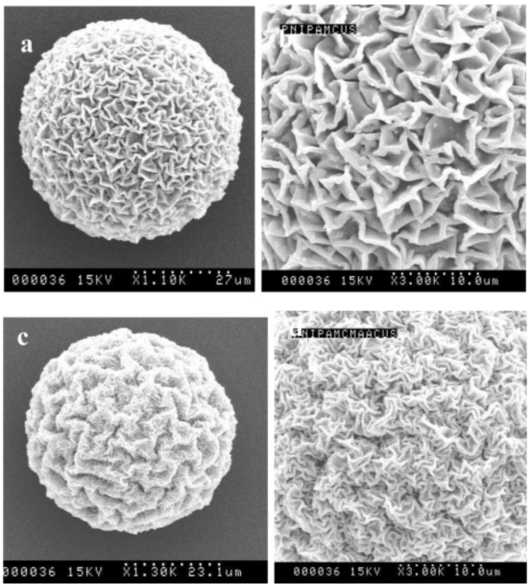

Fig. 1 SEM images of the composite microspheres: (a) CuS–NIPAM, (c) CuS–PNIPAM-MAA, (b) and (d) high magnification images of a and c, respectively. Precipitation reaction lasted for 25 min.

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† Electronic supplementary information (ESI) available: more SEM images and XRD patterns of the composite microspheres and PNIPAM-MAA minigels. See http://www.rsc.org/suppdata/cc/b3/b314533f/

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images, it can be observed that the surface of the CuS–PNIPAM composite microspheres is unique and full of wrinkles, which look as though they have been folded artificially. In contrast, the surface structure of the CuS–PNIPAM-MAA microspheres looks like waste cotton yarn. The difference in the surface structures of the two composites may be a result of utilization of different templates. The interactions, mainly association and coordination, between MAA and Cu^{2+} should be stronger than those between NIPAM and Cu^{2+}due to the presence of carboxylic groups in MAA, and thereby the distribution and diffusion of Cu^{2+} within the two minigels should be different, resulting in different precipitation behavior of the sulfide or different surface patterns of the precipitated sulfide (The IR spectra of the two templates are given in the ESI†).

The wrinkles in the surface of the CuS–PNIPAM microspheres may be a result of the effect of the network structure of the PNIPAM minigels on the precipitation of CuS, which might proceed gradually from the surface of the minigels into the inner part. It is the Cu^{2+} ions situated at the outer part of the minigels that meet H_2S first, and thereby precipitate locally. As the precipitation reduces the local concentration of the ion, free Cu^{2+} ions in the minigels will diffuse to make up the deficiency. These processes continue till the ions are consumed completely provided the precipitating agent is introduced adequately. Clearly, the precipitation may stop at positions other than the center of the minigels due to the limited amount of metal ions available. This implies that the composite microspheres prepared in this way may adopt a core–shell structure. This speculation has been confirmed by the studies of the PbS–PMAA system.[19] In fact, formation of the patterned surface structures of the composite microspheres is a gradual process. This theory was confirmed by introduction of a limited amount of H_2S into the system (as an example, Fig. S1 in the ESI shows an SEM image of CuS–PNIPAM-MAA composite microspheres and their enlarged surface structure. In this case, the precipitation lasted for only 5 min). As for the formation of the patterned surface structures of the composite microspheres, the interaction between the metal ions and the monomer units of the template may play a crucial role. It is this interaction that may affect the distribution and diffusion of Cu^{2+}, and result in microspheres with patterned surface structures. Clearly, different minigels may have different network structures, and thereby yield different surface patterns.

The surface structures of metal sulfide–polymer composite microspheres depend not only on the nature of the template, but also on the nature of the sulfide since the interaction depends both on the nature of the template, and also on the nature of the polymer. Fig. 2 shows the SEM images of Ag_2S–PNIPAM and Ag_2S–PNIPAM-MAA composite microspheres, and their enlarged surface structures. The preparation procedures for these composites are the same as those described in the experimental section, but the salt used is $AgNO_3$, and the molar number of this salt is double that of $Cu(Ac)_2$. It can be seen that the surface structure of Ag_2S–PNIPAM is more or less similar to that of CuS–PNIPAM. The surface structure of Ag_2S–PNIPAM-MAA, however, is very different from that of CuS–PNIPAM-MAA, and looks like closely arranged *Hovenia dulcis* (Japanese raisin tree) flowers.

In summary, for the first time, CuS–PNIPAM, CuS–PNIPAM-MAA, Ag_2S–PNIPAM and Ag_2S–PNIPAM-MAA composite microspheres exhibiting patterned surface structures have been prepared by employing a minigel template method. It has been revealed that the surface structures of these composite microspheres depend not only on the nature of the template, but also on the nature of the metal sulfide. It is speculated that the minigels mainly play roles of confinement and guidance in the precipitation of the sulfides.

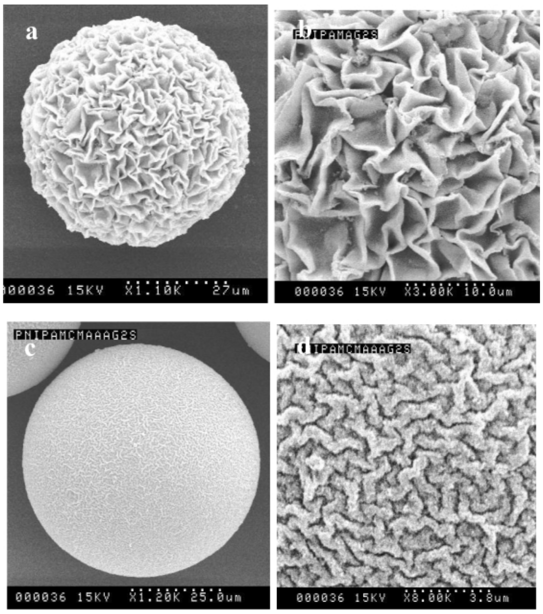

Fig. 2 SEM images of Ag_2S–PNIPAM and Ag_2S–PNIPAM-MAA composite microspheres (a, c) and high magnification images of part of the surfaces of the microspheres (b, d). The precipitations lasted for 25 min.

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