

Syntheses of PAM Microgel Surfaced Covered with Alkyl Quaternary Ammonium Surfactant/Keggin-Type Polyoxometalate Complexes

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ABSTRACT: The composite microspheres of poly(lacrylamide) microgels (PAM) surfaced covered with [2-(methacryloyloxy)ethyl]dodecyldimethylammonium (MEDDAB)-tungstophosphate (HPW) complexes (MEDDAB-HPW) were synthesized by using ion-exchange reaction between MEDDAB located within the porous PAM microgels and HPW in aqueous solution. The morphology and component of the composite microspheres were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis, respectively. The results indicated that PAM/MEDDAB-HPW composite microsphere with different hierarchical surface structures could be obtained by controlling the weight ratio of MEDDAB to HPW in the microgels and cross-linking degree of PAM microgels. Although the surface morphologies of the composite microspheres prepared in different conditions were different, a general feature was that the composite microspheres have the core-shell structure and the wrinkly surface covered with the particles of MEDDAB-HPW complexes. The formation of the wrinkly

surface is attributed to the difference in shrinkage between inside and outside of PAM microgel frameworks due to deposition of MEDDAB-HPW on the surface, and the formation of MEDDAB-HPW small particles originates from the reaction between MEDDAB aggregation and HPW. For this composite microsphere, PAM hydrogel core is suitable to store water-soluble substances, and the shell composed of the surfactant/Keggin-type polyoxometalate complexes is not only amphiphilic but also catalytic. Additionally, PAM/MEDDAB-HPW composite microspheres with big size and MEDDAB-HPW particles with small size make the composite microspheres not only easy for separation but also beneficial for catalysis. This material provides an example to construct microreactors with new structure used in diphasic catalytic reaction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 4000–4010, 2009

Key words: PAM microgels; polymerizable surfactant; Keggin-type polyoxometalate; core-shell composite materials

INTRODUCTION

Polyoxometalates (POMs), as a unique class of metal-oxide clusters, have many properties that make them attractive for applications in catalysis, medicine, and materials science. One application is related to H₂O₂-based catalytic oxidation. H₂O₂-based catalytic oxidation has received much attention from an environmental point of view, and soluble transition metal-based catalysts have been devel-

oped for the oxidation with an aqueous H₂O₂.^{1–3} Although many efficient procedures based on the tungsten catalysts for the oxidation with H₂O₂ have been developed, most of them are homogeneous systems and share common drawbacks, that is, catalyst/product separation and catalyst reuse are difficult. The immobilization of catalytically active species onto solid supports can solve the catalyst recovery and recycle.^{4–8} For the development, some heterogeneous systems such as insoluble polyoxotungstates,⁵ immobilized peroxotungstates,⁹ triphasic phosphotungstate,¹⁰ or pseudo-heterogeneous systems,¹¹ have been reported. Yamada and his cooperators prepared the insoluble catalysts based on self-assembly process of non-cross-linked amphiphilic copolymer ligands and inorganic species. This process would promote the cross-linking of the copolymer by the inorganic species to provide networked, supramolecular, and insoluble complexes.^{12–14} They might possess many mesopores where the inorganic species would be tightly supported by many ligands

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not to be dissociated. The amphiphilic copolymers and the inorganic species might construct effective catalytic sites with high affinity to both hydrophobic and hydrophilic reagents. Compared with traditional heterogeneous catalyst, these materials used as the catalyst in diphasic reaction possess the obvious advantages. However, the distribution of the catalytically active species in heterogeneous catalysts reported in literatures is not analogous to that of the emulsion droplets with core/shell structure.

On the basis of this point of view, improvement of triphasic catalysts is necessary. Hence, we planned to develop composite material with core/shell structure to meet the requirement mentioned earlier. Our concept is using a polymer hydrogel as core for storage of water-soluble reactant and catalyst polyoxotungstates as shell to construct the structural composite material.

More recently, our group proposed a polymeric microgels template method for preparation of composite microsphere materials. Employing microgels including poly(*N*-isopropyl acrylamide-*co*-acrylic acid), poly(*N*-isopropylacrylamide-*co*-methacrylic acid), polyacrylamide, and poly(*N*-isopropylacrylamide) as templates, several interesting polymeric composite microspheres with core-shell structure have been successfully synthesized.^{15–19} On the basis of these results, a composite microsphere material with a hydrogel core and polyoxotungstates/alkyl quaternary ammonium surfactant complexes shell can be not only feasible but also profitable. To our knowledge, however, the composite microsphere material with hydrogel core and polyoxotungstates/alkyl quaternary ammonium surfactant complexes shell has never been reported. The overall synthetic procedure we proposed is shown in Scheme 1.

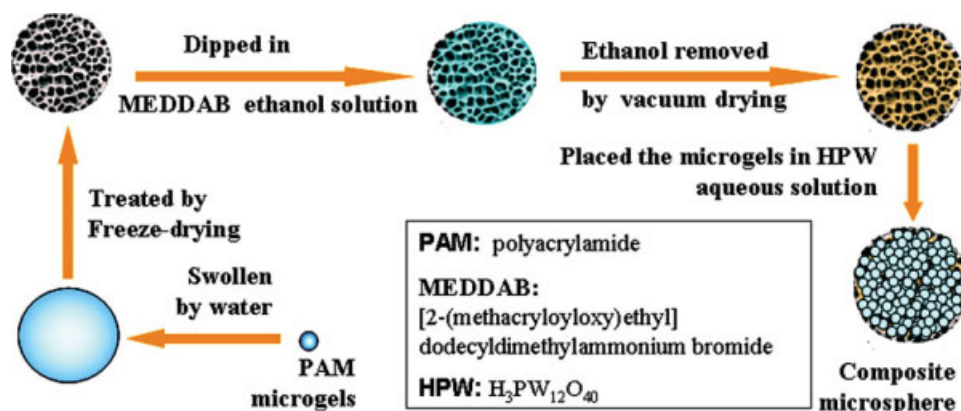
Polyacrylamide (PAM) microgels were first prepared by inverse emulsion polymerization, and then the porous PAM microgels were prepared by the freeze-drying treatment of water-swelled PAM

microgels. The porous PAM microgels were immersed in ethanol solution of [2-(methacryloyloxy)ethyl]dodecyl-dimethylammonium bromide (MEDDAB), then, the dipped microgels were immersed in solution of $H_3PW_{12}O_{40}$ (HPW). The core-shell composite microspheres (PAM/MEDDAB-HPW) with hierarchical surface morphologies were obtained. The remarkable features of these composite microspheres are that the core-composed hydrogel is suitable to store the water-soluble substance, and the shell can be a potential catalyst in H_2O_2 -based catalytic oxidation due to it being surfactant/Keggin-type polyoxometalate complexes. So, this nature makes it interesting, for example, the composite microspheres could be used as a recoverable catalysis microreactor. Additionally, the particles size on the surface of the composite microsphere with submicrometer or nanometer scale makes it has high specific surface area, and the composite microsphere with micrometer scale makes it separation easy. The method proposed in this study gives an example for preparing core-shell composite microspheres that are potentially used as recoverable triphasic catalyst.

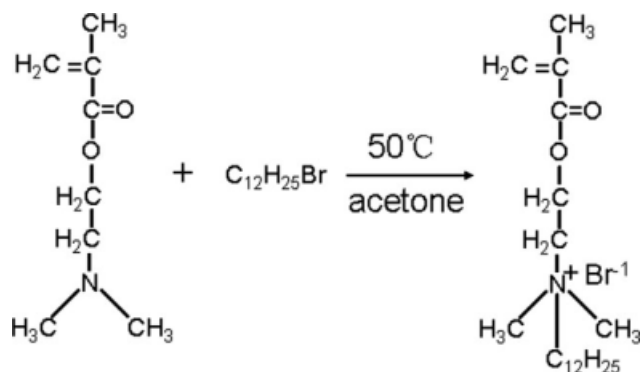
EXPERIMENTAL SECTION

Materials

[2-(Methacryloyloxy)ethyl]dodecyl dimethylammonium bromide was synthesized by the reaction between dodecyl bromide ($C_{12}H_{25}Br$) and 2-(dimethylamino)ethyl methacrylate (DM). Dodecyl bromide 2-(dimethylamino)ethyl methacrylate were purified by vacuum distillation. The monomer acrylamide (AM) was purified by recrystallization in acetone and dried under vacuum. The following chemicals including *N,N,N',N'*-tetramethylethylenediamine (TMEDA), *N,N*-methylenebisacrylamide (BA), Span-80 were of chemical grade. Ammonium persulfate (APS), cyclohexane, and phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) were of



Scheme 1 Procedure for the preparation of PAM/MEDDAB-HPW composite microsphere. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 2 Synthesis of MEDDAB.

analytical grade. Water used in the experimental was doubly distilled.

Synthesis of (2-(methacryloyloxy)ethyl) dodecyl dimethyl ammonium bromide

[2-(Methacryloyloxy)ethyl]dodecyl dimethyl ammonium bromide (MEDDAB) was synthesized according to the literature.²⁰ The corresponding procedure is shown in Scheme 2.

The reaction conditions are as follows. The concentration of reactants in acetone is about 15–17%; the ratio of DM to $C_{12}H_{25}Br$ is 1 : 1.2 at 50°C; The reaction time is 48 h. For purification, MEDDAB was recrystallized three times by anhydrous ether from acetone. A typical synthesis is as follows. 2-(Dimethylamino)ethyl methacrylate (DM) acetone solution was treated with dodecyl bromide under nitrogen at 50°C for 48 h. The concentration of DM in acetone is about 15–17%, and the ratio of DM to $C_{12}H_{25}Br$ is 1 : 1.2. The resulting product MEDDAB was obtained after purification by recrystallization three times in mixture of anhydrous ether and acetone. The product is analyzed by infrared spectrum (IR) and 1H -NMR ($CDCl_3$, 300 MHz, δ in ppm): 6.14d (*trans*- $CH_2=C$, 1H), 5.67d (*cis*- $CH_2=C$, 1H), 4.67t ($COOCH_2$, 2H), 4.17m ($\alpha-CH_2-N$, 2H), 3.67t ($N-\alpha-CH_2$, 2H), 3.51s ($N(CH_3)_2$, 6H), 1.95d ($CH_3-C=$, 3H), 1.76m ($N-\beta-H_2$, 2H), 1.26–1.47m ($-(CH_2)_9-$, 18H), 0.88t ($-CH_3$, 3H).²⁰

Preparation of PAM microgels

PAM microgels were synthesized via an inverse suspension polymerization technique according to the literature.¹⁸ The typical procedure is as follow: 70 mL of cyclohexane and 0.52 g of Span-80 were added to a 150 mL three-neck flask equipped with a mechanical stirrer and a nitrogen inlet. The mixture was stirred under nitrogen purging until the surfactant was uniformly dispersed. At the same time, 1.20 g of AM, 0.06 g of cross-linker BA (To get the different cross-linking degree of PAM microgels, 0.06 g

and 0.04 g BA were selected in the experiment), and 0.5 mL of 18% APS dissolved into 5 mL of double-distilled water were added to the mixture. The mixture was then stirred continuously under a nitrogen atmosphere. The polymerization was initiated by the addition of the promoter, which was 1 mL of the 5% TMEDA aqueous solution, and the resulting mixture was stirred (380 rpm) at 20°C for 4.5 h. The PAM microgels were collected and washed alternatively with double-distilled water and acetone, and the white product was dried overnight under ambient conditions.

Preparation of porous PAM microspheres

PAM microspheres with porous structure were prepared by the freeze-drying treatment. A preparation procedure was similar to the literature.¹⁹ PAM microgels (0.1 g) was swollen by adding 8 mL of double-distilled water and then the sample being quenched in liquid nitrogen was dried by an ALPHA1-2 freeze-drying instrument at $-55^\circ C$ for 24 h. The PAM microgels with porous structures were finally obtained. The porous PAM microgels with different pore sizes were gained when PAM microgels prepared in different amounts of the cross-linker (BA) were treated by freeze-drying. In the experiment, the amounts of BA selected were 0.04 g, 0.06 g, and 0.08 g in 5 mL aqueous phase.

Preparation of PAM/MEDDAB microgels

According to Scheme 1, the preparation of PAM/MEDDAB microgels is as follow. At room temperature, 0.1 g of the porous PAM microgels was saturated with MEDDAB ethanol solution in a laboratory dish to make all of the microgels uniformly immersed, and this dish was then placed in a desiccators with stopcock to be vacuumed so that ethanol was uniformly volatilized from all immersed microgels. PAM/MEDDAB microgels were finally obtained. The PAM/MEDDAB microgels loaded different amount MEDDAB were gained by altering concentration of MEDDAB in ethanol solution. In the experiment, the ratios of the MEDDAB to freeze-dried PAM microgels in weight were 2.5 : 97.5, 5 : 95, 10 : 90, 20 : 80, 30 : 70, and 40 : 60, respectively.

Preparation of PAM/MEDDAB-HPW composite microspheres

PAM/MEDDAB-HPW composite microspheres were prepared employing the ion-exchange between phosphotungstate anions (HPW) in a solution and [2-(methacryloyloxy)ethyl]dodecyl dimethyl ammonium bromide cations (MEDDAB) loaded on PAM/MEDDAB microgels. The typical procedure is as follow:

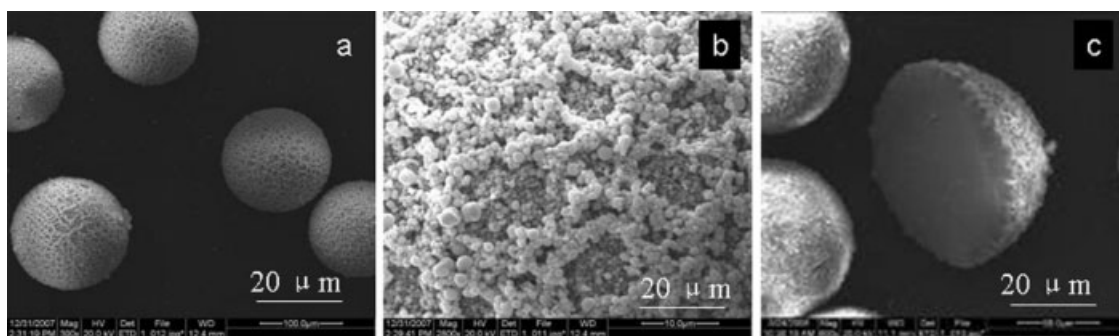


Figure 1 The typical SEM images of the PAM/MEDDAB-HPW composite microspheres prepared using the freeze-dried PAM microgels as templates.

A given amount of PAM/MEDDAB microgels reacted with HPW aqueous solution reacted at 40°C for a week in swinging bed. The composite microspheres were washed with water by ultrasonication for several times, and then washed with acetone for another several times. The PAM/MEDDAB-HPW composite microspheres were obtained. The composite microspheres with different surface morphologies were prepared by using PAM microgels prepared in different conditions as mentioned in the section "Preparation of porous PAM microspheres," and using PAM/MEDDAB microgels prepared in different conditions as mentioned in section "Preparation of PAM/MEDDAB microgels." Additionally, the concentration of HPW in aqueous solution was another factor to affect the surface morphology of PAM/MEDDAB-HPW composite microspheres.

In the experiment, the mole ratio of HPW to MEDDAB being 5, 15, and 25 were selected.

Characterization

The morphologies of the PAM microgels, the freeze-dried PAM microgels, PAM/HPWA composite microspheres, and the PAM/MEDDAB-HPW composite microspheres were examined by Philips scanning electron microscopy (SEM) using an accelerating voltage of 20 kV. Before imaging, the samples were sputtered with thin layers of gold. The elements in the samples were probed by an energy-dispersive X-ray spectrophotometer (EDX) attached to a Hitachi S-570 electron microscope. The IR spectra were recorded on an AVTAR360 Nicolet Fourier transform infrared (FT-IR) spectrometer using a KBr

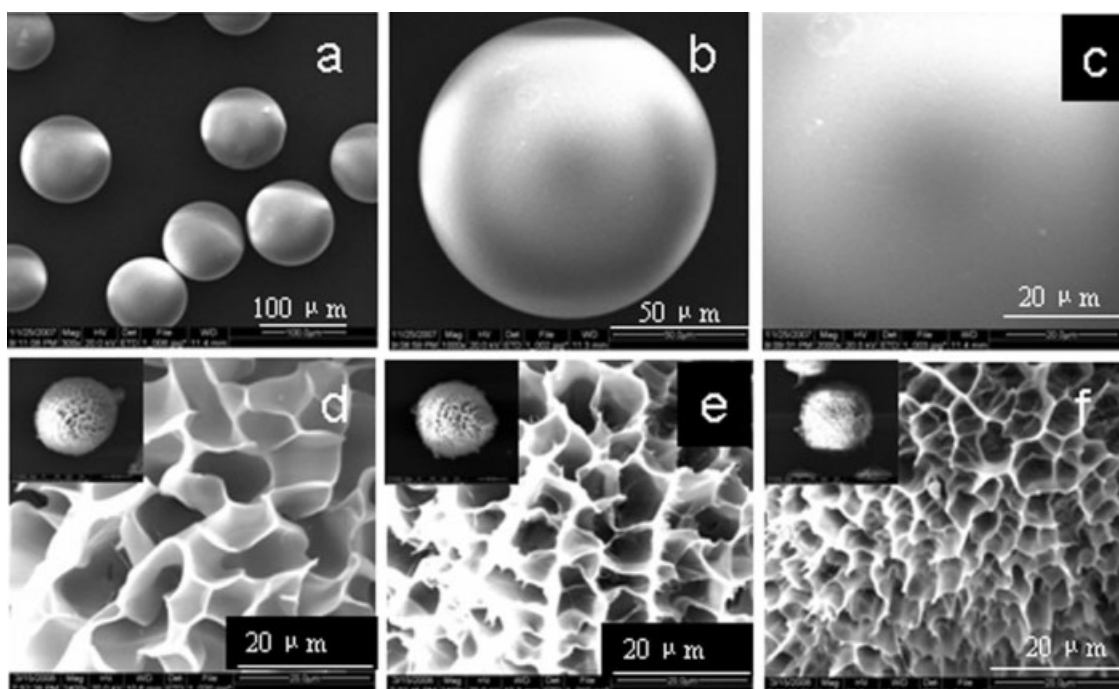


Figure 2 SEM images of the water-swollen PAM microgels after treated with acetone (a–c) and after treated by freeze-drying in the case of BA dosage 0.04 g (d), 0.06 g (e), and 0.08 g (f) used in preparation of PAM microgels.

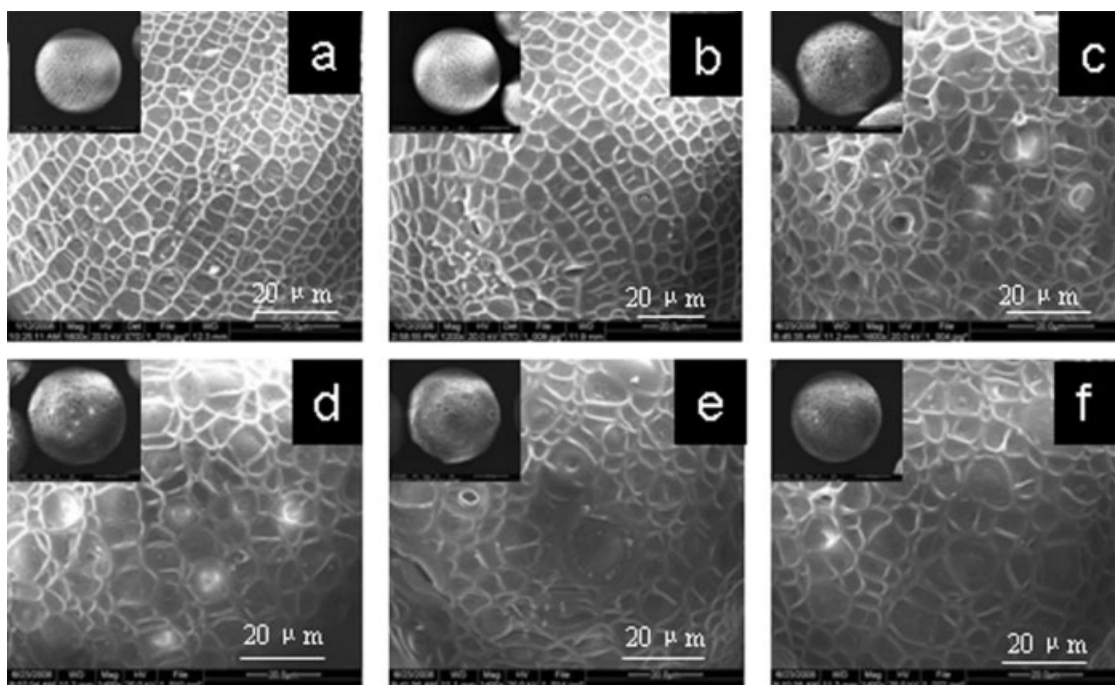


Figure 3 SEM images of the PAM/MEDDAB microspheres prepared using the freeze-dried PAM microgels (BA, 0.06 g) as templates. [The weight ratio of MEDDAB to the freeze-dried PAM microgels: (a) 2.5%; (b) 5%; (c) 10%; (d) 20%; (e) 30%; (f) 40%].

pellet. Thermogravimetric analyses (TGA) were performed using a Perkin–Elmer TGA-7 instrument. The composite powders were heated to 800°C in air at a scan rate of 10°C/min.

RESULTS AND DISCUSSION

The structural feature of the PAM/MEDDAB-HPW composite microspheres

According to the protocol we proposed to prepare PAM/MEDDAB-HPW composite microspheres with core/shell structure, the ion-exchange between phosphotungstate anions (HPW) in aqueous solution and MEDDAB loaded on PAM/MEDDAB microgels was used to form insoluble MEDDAB-HPW complexes on the surface of the PAM microgels. The typical SEM images are shown in Figure 1. It is obviously indicated that the well-distributed PAM/MEDDAB-HPW composite microspheres have the hierarchical surface structure. The feature of the composite microspheres is the wrinkled surface densely covered with small particles, and the composite microspheres have the core/shell structure.

Evolution in surface morphology of the composite microspheres

To gain a deeper understanding of the formation of the composite microspheres with hierarchical structure, the changes in morphology of microspheres along preparation process are investigated.

Influence of BA dosage on the surface morphology of the freeze-dried PAM microgels

On the basis of PAM microgels as templates to prepare the composite microspheres, it is necessary to explore the differences in the morphology of the PAM microgels prepared or treated in different conditions. Figure 2 shows SEM images of the water-swollen PAM microgels after being washed with alcohol and after being treated by freeze-drying.

It can be seen in Figure 2(a–c) that PAM microgels have a narrow distribution in size and the surface of the water-swollen PAM microgels after treated with acetone is smooth. For the water-swollen PAM microgels after treated by freeze-drying, the microgels are porous [refer Fig. 2(d–f)]. R.P. Washington has reported on the hydrogels with porous structures after freeze-drying treatment.²¹ The formation of hydrogels with porous structure is attributed to the nonergodic behavior of kinetic concentration fluctuations before forming hydrogels, phase separation, and instantaneous thermodynamic concentration fluctuations. The amide groups on the polymeric chains of PAM microgels have a favorable ability to form stronger hydrogen bonds with water. Additionally, the capillarity of the pores in PAM microgels could strengthen the ability to absorb water. The hydrogen bonds between the water molecules and amide groups on the PAM polymeric chains were weakened when the water-swollen PAM microgels were treated by acetone. As a result, water left the pore wall of the polymer network and

the hydrogen bonds among the amide groups on the polymeric chains simultaneously formed, this effect finally resulted in the collapse of the porous structures and the microsphere surface becoming smooth. For the water-swollen PAM microgels after treated by freeze-drying, the water in PAM microgels was instantaneously solidified because of the liquid nitrogen quencher. The solidified water left the microspheres by turning from a solid state into a gas state when the water-swollen PAM microgels were treated by freeze-drying. As a result, the microgels with porous structures could be obtained.¹⁹ As for a decrease in pore size of PAM microgels with BA dosage, it can be explained by the fact that the swelling behavior of PAM microgels strongly depends on the cross-linking degree. The more BA in preparation of PAM microgels is used, the less the resulting PAM microgels are swelled. Consequently, porous size of the freeze-dried PAM microgels decreases with BA dosage.

Influence of the weight ratio of MEDDAB to PAM microgels on the surface morphology of PAM/MEDDAB composite microspheres

According to the procedure for preparation of the PAM/MEDDAB-HPW composite microspheres shown in Scheme 1, the second step is to introduce MEDDAB into the porous PAM microgels. So, the effect of the weight ratio of MEDDAB to PAM microgels on the morphology of PAM/MEDDAB composite microspheres should be considered.

Figure 3 shows the SEM images of PAM/MEDDAB microspheres prepared in the different weight ratio of PAM microgels to MEDDAB. The surface of PAM/MEDDAB microspheres has a grid pattern, and the surface morphology of PAM/MEDDAB microspheres regularly changes with increase of the weight ratio of MEDDAB to PAM microgels. It is clear that the grid size increases with increasing the weight ratio ranging from 2.5 to 40% but the grid density decreases. The resulting surface patterns are related to the following factors. It is found from Figure 2(e) and Figure 3 that the grid pattern on the surface of the PAM/MEDDAB microspheres derived from PAM microgels pores filled by MEDDAB. MEDDAB would remain in PAM microgels pores after the ethanol evaporated from MEDDAB ethanol-immersed porous PAM microgels. The more MEDDAB introduced, the more MEDDAB in porous of PAM microgels stayed. Compared with bigger pores, the smaller pores are easily permeated. As a result, the decrease in smaller pores is more marked than in bigger pores with increase of MEDDAB. In the light of the above explanation, the surface morphologies shown in Figure 3 could be understood.

Influence of the weight ratio of MEDDAB to PAM microgels on the surface morphology of PAM/MEDDAB-HPW composite microspheres

The third step for preparation of the PAM/MEDDAB-HPW composite microspheres is to introduce HPW to the PAM/MEDDAB microspheres. Figure 4

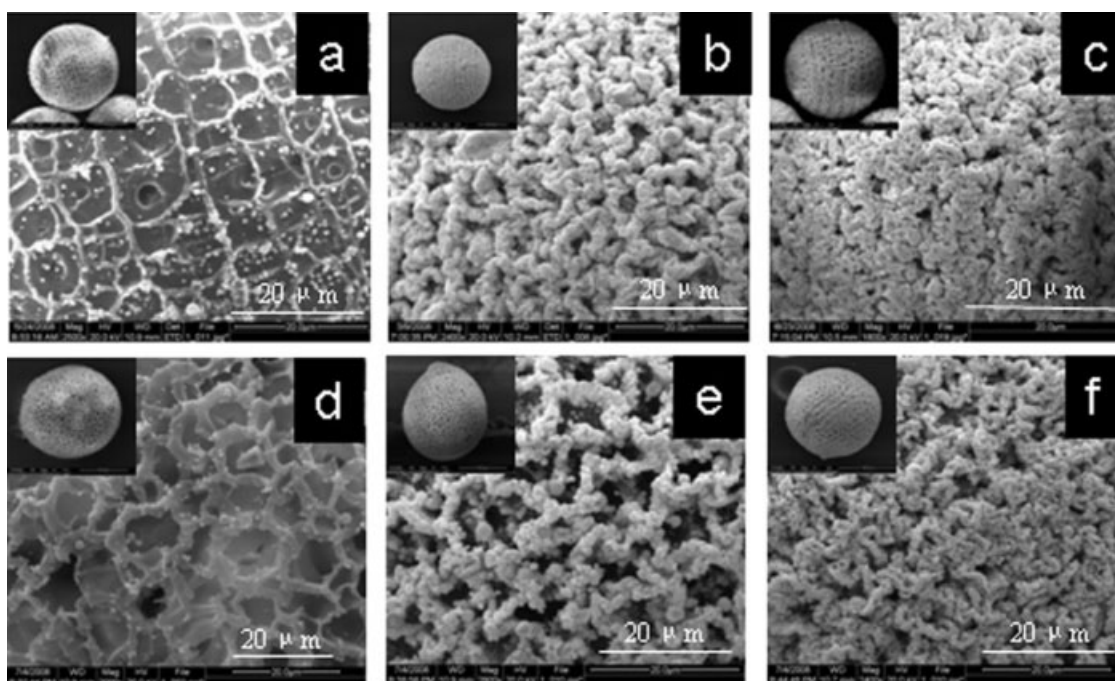


Figure 4 SEM images of the PAM/MEDDAB-HPW composite microspheres [the weight ratio of MEDDAB to PAM microgels: (a,d) 2.5%, (b,e) 5%, (c,f) 10%]; (d–f): the water-swelled the PAM/MEDDAB-HPW composite microspheres after treatment by freeze-drying.

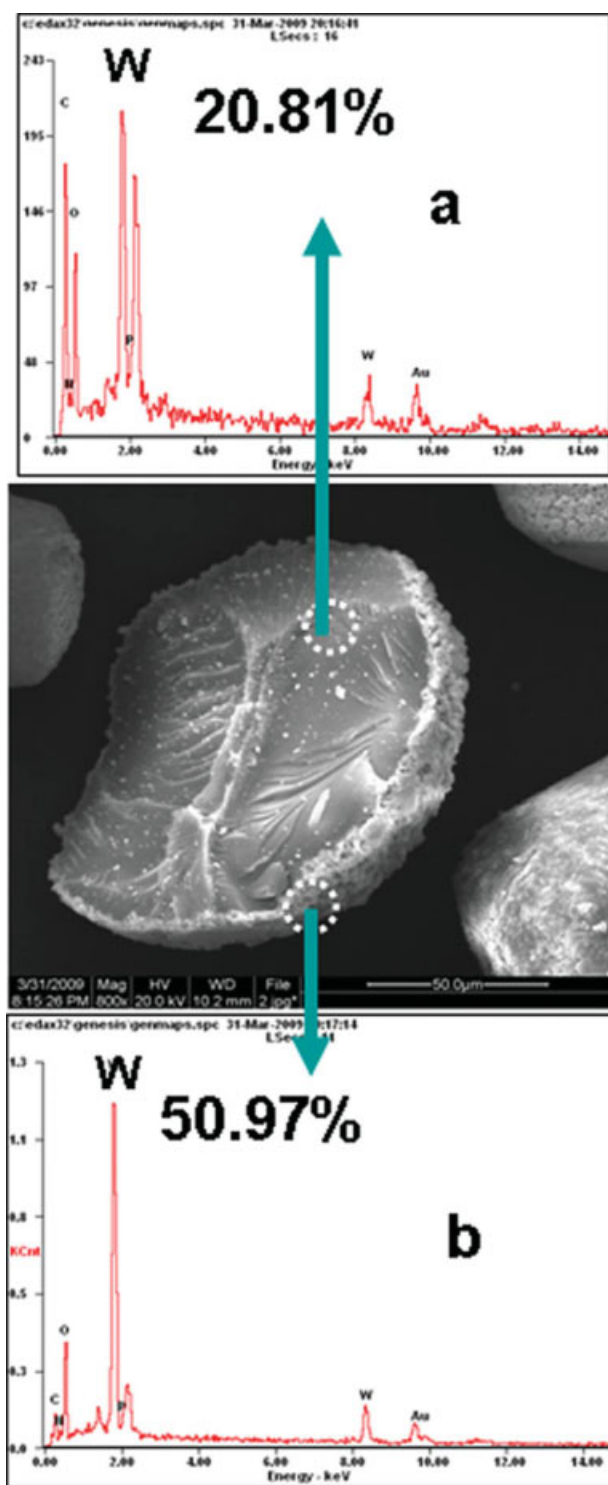


Figure 5 SEM image and EDX of the PAM/MEDDAB-HPW composite microspheres with different W amount in core (a) and shell (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shows the SEM images of PAM/MEDDAB-HPW composite microspheres prepared in different weight ratios of MEDDAB to PAM microgels. Making a comparison between the SEM images shown in Figure 4(a–c), it is obviously found that the surface

morphology of PAM/MEDDAB-HPW composite microspheres strongly depends on the weight ratio of MEDDAB to PAM microgels. The surface wrinkles became denser with increase in weight ratio of MEDDAB to PAM microgels. The above results indicate that surface morphology of PAM/MEDDAB-HPW composite microsphere could be controlled by varying the weight ratio of MEDDAB to PAM microgels.

The experimental result regarding the formation of the surface wrinkles can be attributed to the following reasons. For pure PAM microgels as shown in Figure 2(a–c), the water-swollen PAM microgels would contract uniformly as PAM microgels are washed with acetone. However, PAM microgels frameworks can contract unevenly when some substance unevenly deposited on the frameworks. The flexibility of PAM microgels frameworks between inside and outside of PAM microgels would be different when MEDDAB-HPW formed on the frameworks located at the surface of PAM microgels. The areas of frameworks deposited MEDDAB-HPW became relatively rigid, and the more MEDDAB-HPW some areas of the frameworks had, the more rigid those areas of the frameworks became. As a result, the frameworks with different rigidity would unevenly shrink to make the surface of composite microspheres distorted when the water-swelled composite microspheres were washed with acetone. The similar results were found in our previous researches.^{15–19} The above statements also strongly supported by a set of SEM images as shown in Figure 4. The surface wrinkles of the water-swelled composite microspheres treated with acetone [Fig. 4(a–c)] are evidently more dense than that treated by freeze-drying [Fig. 4(d–f)], and the more MEDDAB-HPW the composite microsphere loaded, the less the composite microspheres shrank. EDX analysis indicated that the characteristic peaks for W elements on face were more obvious than that in side (Fig. 5), indicating that HPW was mainly deposited on the surface of the composite microspheres. In addition, the core of the mechanically cracked water-swollen freeze-drying composite microspheres shown in Figure 6 is porous, indicating that the core of PAM/MEDDAB-HPW could be swelled by water. On the basis of the explanation aforementioned, the regular change in the surface wrinkles of the composite microspheres shown in Figure 4 and the composite microspheres having core/shell structure shown in Figure 1 can be understood.

Influence of cross-linking degree on the surface morphology of the composite microspheres

To confirm the dependence of the generated surface pattern on the pore structure of the PAM microgels,

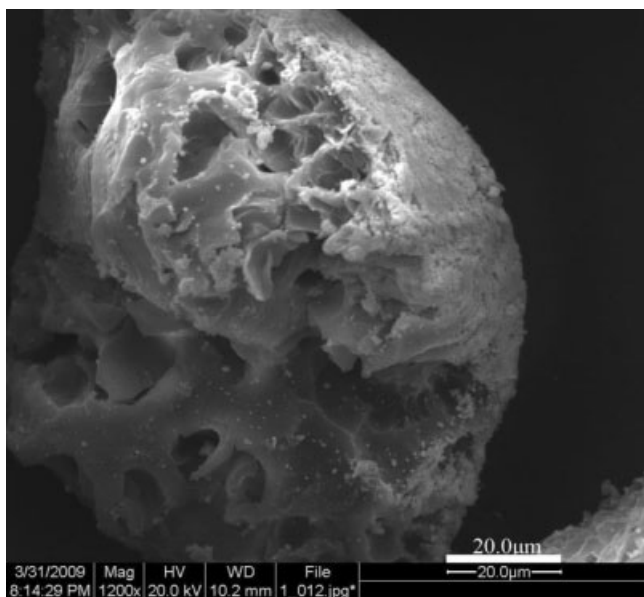


Figure 6 SEM image of the mechanically cracked water-swollen PAM/MEDDAB-HPW composite microspheres treated by freeze-drying.

PAM microgels with different pore size were used in the preparation of the PAM/MEDDAB-HPW composite microspheres. The results are showed in Figure 7.

It can be seen in Figure 7 that the grid on the surface of the PAM/MEDDAB microspheres with the increase of cross-linking degree became dense. The regular change in the grid shown in here is not difficult to understand. Making a comparison between

Figure 2(d–f) and Figure 7(a–c), it can be found a evident correlation between the regular change in the grid shown in Figure 7(a–c) and the regular change in the pore size shown in Figure 2(d–f). The bigger the pore size of PAM microgels is, the bigger the grid size of PAM/MEDDAB microspheres is. Taking a given weight ratio of MEDDAB to PAM microgels into account, the results shown in Figure 7(a–c) are completely acceptable.

The appearance regarding the orderly change in wrinkle shown in Figure 7(d–f) is also related to the regular change in the pore size of PAM microgels. The increase of BA used in preparation of PAM microgels makes not only the pore size small but also the pore framework rigid. These effects lead to the increase in amount of MEDDAB-HPW located on the surface with the increase of BA dosage. As a result, the MEDDAB-HPW particles on the surface of the composite microsphere become dense with the increase of BA dosage. This conclusion could be verified by the results from TG. The amounts of HPW in the composite microspheres prepared by changing amount of BA can be calculated from the TG curves shown in Figure 8(a–c). On the basis of the calcined residue of HPW being a mixture of WO_3 and P_2O_5 ,²² and the residue percentages of 10.967%, 31.003%, 49.462%, the calculated amounts of HPW in the composite microspheres are 11.071%, 31.296%, 49.930%, respectively. These results obviously indicate the increase of HPW with BA amount.

The formation of MEDDAB-HPW in small particles on the composite microspheres is related to reaction

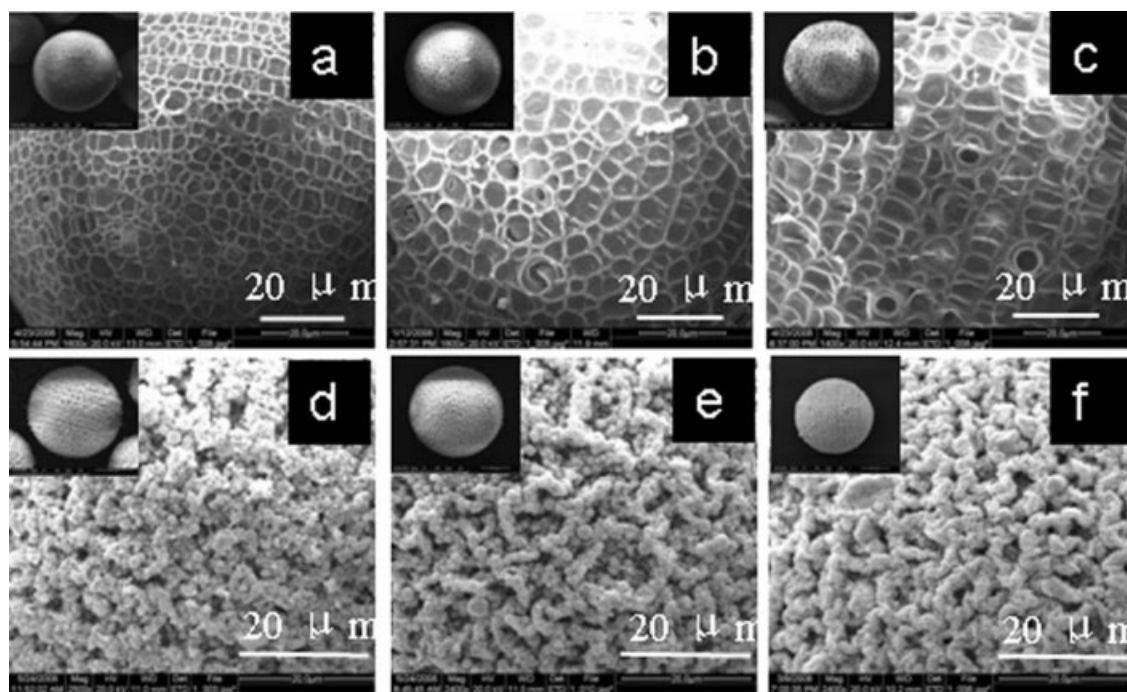


Figure 7 SEM images of PAM/MEDDAB microspheres (a–c) and PAM/MEDDAB-HPW composite microspheres (d–f) as the pore size of PAM microgels were controlled by changing amount of BA: 0.08 g (a,d), 0.06 g (b,e), and 0.04 g (c,f).

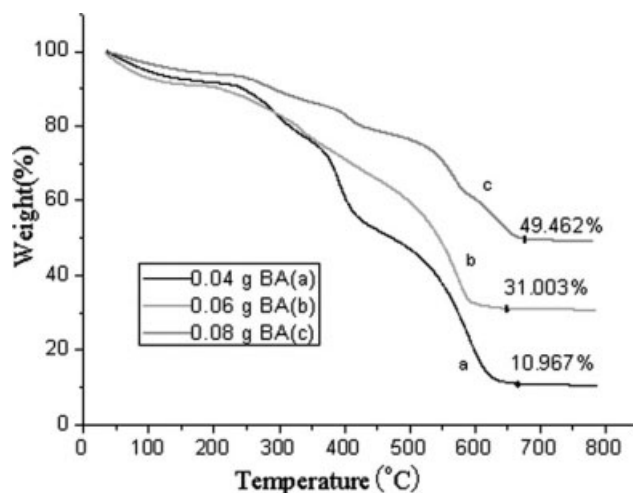


Figure 8 The TG curves of PAM/MEDDAB-HPW composite microspheres prepared in different amount of BA: 0.04 g (a), 0.06 g (b), and 0.08 g (c).

between the aggregation of MEDDAB and HPW. MEDDAB is a kind of quaternary ammonium surfactants, so, the formation of the small particles is likely related to the aggregation of MEDDAB. Although aggregation of MEDDAB has not been reported, the analogous compound has been investigated. Zana and coworkers have studied the aggregation behavior of the polymerizable surfactant dimethylhexadecyl-(2-acrylamidoethyl) ammonium bromide (AM16) with time-resolved fluorescence quenching (TRFQ) and viscometry.²³ The results indicated that AM16 could form the aggregation in aqueous solution and aggregation number increased with increasing surfactant concentration. Charles L. McCormick synthesized a novel water-soluble monomer, dimethyldodecyl (2-acrylamidoethyl) ammonium bromide (DAMAB), and the resulting compound had an amphiphilic structure analogous to cationic surfactants, hence it would form micelles at concentrations above the critical micelle concentration (cmc).²⁰ These results clearly indicate that some polymerizable surfactants as mentioned earlier possess ability to form aggregates. To get some information on aggregation of MEDDAB, Figure 9 depicts the steady-state fluorescence emission spectra of pyrene in water and in aqueous solution containing MEDDAB. For MEDDAB aqueous solution, an obvious excimer emission centering around 470 nm appeared. This feature implies that MEDDAB molecules may form O/W aggregates in a manner analogous to typical surfactant in bulk water, and pyrene as a hydrophobic molecule is incorporated into the hydrophobic core of the aggregate.^{24,25} It is worthy of remark that the profile of the excimer emission of pyrene depends on the structure of surfactant. Compared with ordinary surfactant, the hydrophilic group in MEDDAB locates between the two hydrophobic groups. Pyrene molecules in the aggregates

formed by MEDDAB are difficult to reorient, and both the imperfectly and perfectly stacked conformations of pyrene molecules coexist in the aggregates. As a result, both fluorescence emissions at 425 nm and 470 nm rather than the typical simultaneously appear.²⁶ Therefore, the distorted emission spectrum of pyrene in the aggregates formed by MEDDAB appeared. On the basis of the above results on formation of MEDDAB aggregation, the small particles on the surface of the composite microspheres are possibly derived from the reaction between the aggregation of MEDDAB and HPW. To verify this conclusion, the reaction between MEDDAB and HPW in aqueous solution was carried out. The SEM image of the resulting product is shown in Figure 10. As expected, the product is of microspheres. The surfactant-encapsulated clusters (SECs) have the general tendency to assemble into spherical aggregates, which is attributed to the rearrangement of surfactants on the exterior of the polyoxometalate, and the stable assemblies of surfactant-encapsulated polyoxometalate complexes could be obtained as spheres.²⁷ Therefore, the small particles located at the surface of PAM/MEDDAB-HPW are MEDDAB-HPW complexes.

Analysis of components of the composite microsphere

The techniques including FT-IR and EDX were used for the analysis of composite microspheres. The results as an example to show the general information on components of the composite microspheres are as follows.

FT-IR analysis

Figure 11 shows the typical FT-IR spectra of PAM microgels (a) and the composite microspheres (b).

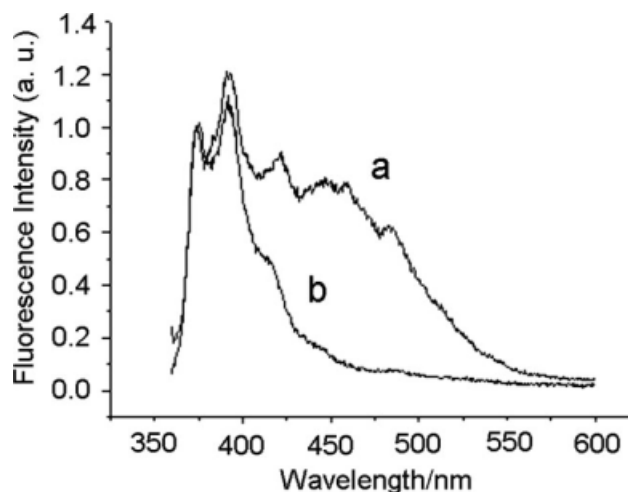


Figure 9 Fluorescence spectra of pyrene in aqueous solution containing MEDDAB (a) and water (b).

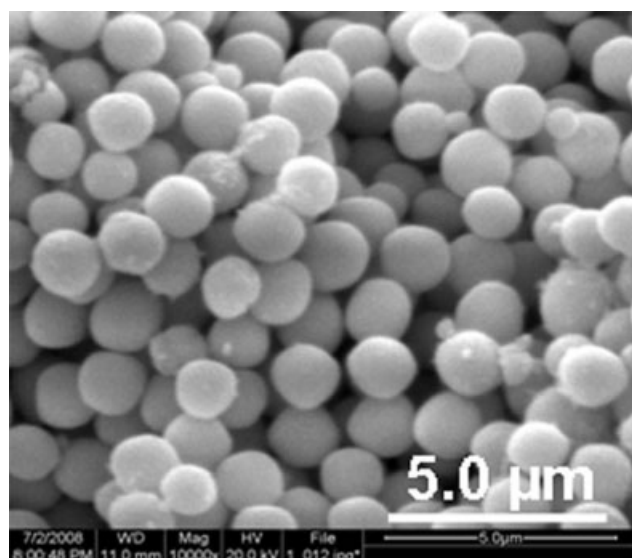


Figure 10 SEM images of MEDDAB-HPW particles formed in aqueous solution.

The characteristic absorption bands for PAM are clearly observed. The peaks at 1658 cm^{-1} ($\nu_{\text{C=O}}$), 2944 cm^{-1} (ν_{CH_2}), and $3500\text{--}3300\text{ cm}^{-1}$ (ν_{NH})²⁸ appeared in the FT-IR spectrum of the composite microspheres confirm that PAM exists in the composite materials. The set of peaks at 1079 cm^{-1} , 987 cm^{-1} , 889 cm^{-1} , and 809 cm^{-1} related to the asymmetric stretching of the P—O bond, the asymmetric stretching of the W—O bond, the symmetric and asymmetric stretching of the W—O—W bridge, respectively.²⁹ Weaker peaks related to the Keggin structure are present at 604 and 526 cm^{-1} . These are in perfect agreement with FT-IR data reported by Prasad.³⁰ The presence of W in the composite microspheres was verified by EDX as shown in Figure 12.

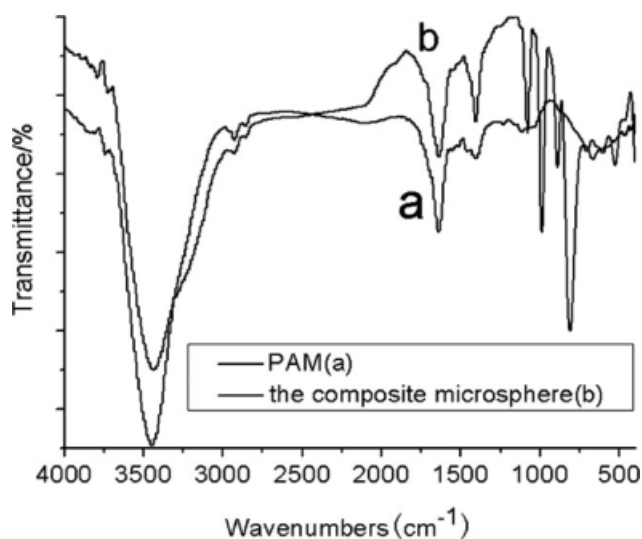


Figure 11 FT-IR spectra of PAM microgels (a) and the PAM/MEDDAB-HPW composite microsphere (b).

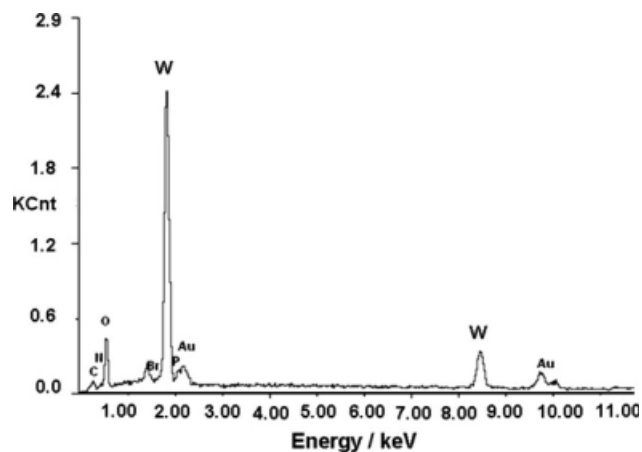
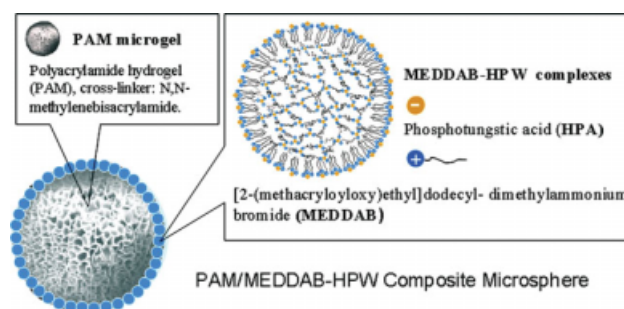


Figure 12 EDX spectrum of typical PAM/MEDDAB-HPW composite microspheres.

The feature of PAM/MEDDAB-HPW composite microspheres

The formation of surfactant-encapsulated polyoxometalate complexes by the self-assembling has been extensively investigated,²⁶ suggesting that the supermolecular interactions between cationic surfactants and polyoxometalates at air/water interface or bulk phase to form aggregates are common. These results allow us to prepare various interesting composite materials of surfactants and inorganic complexes for different purposes. Compared with some composite materials of surfactants/inorganic complexes reported in literature, PAM/MEDDAB-HPW composite material reported here is a first example for the composite material with hydrogel core and surfactant/polyoxometalate complexes shell. On the basis of the results and discussion in this article, the component and the structure of composite microspheres are illustrated in Scheme 3. The features of PAM/MEDDAB-HPW composite material are briefly summarized as follows. PAM/MEDDAB-HPW composite material possesses the core/shell structure, and PAM hydrogel core makes the composite material suitable for storage of water-soluble substances.



Scheme 3 The illustration indicated the component and the structure of PAM/MEDDAB-HPW composite microspheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The shell with particle aggregates of MEDDAB-HPW complexes is not only amphiphilic but also catalytic. PAM/MEDDAB-HPW composite microspheres with big diameter and MEDDAB-HPW aggregates with small diameter make the composite microspheres not only easy for separation but also beneficial for catalysis. Interestingly, owing to the weak hydrophobic interactions between alkyl chains in the MEDDAB-HPW aggregates, the alkyl chains could be conformationally disordered to rearrange their relative positions under different medium.²⁶ Therefore, these natures make composite microspheres interesting, for example, the globular aggregates stably suspended either in water or a hydrophobic solvent, and spontaneous assembling at the water-hydrophobic solvent boundary, which is especially suitable to use them as catalytic microreactors in diphasic catalysis.

CONCLUSIONS

PAM/MEDDAB-HPW composite microspheres with controllable surface morphology were synthesized by the reaction between MEDDAB located within the porous polyacrylamide (PAM) microgels and HPW in aqueous solution. The composite microspheres have the hydrogel core and the potential catalysis shell. The features of this composite microsphere are summarized as follows. (1) The hydrogel core is suitable to store water-soluble substances, and the shell formed in surfactant/Keggin-type polyoxometalate complexes makes it not only amphiphilic but also catalytic. (2) PAM/MEDDAB-HPW composite microspheres with big diameter and the MEDDAB-HPW globular aggregates with small diameter make the composite microspheres not only easy for separation but also beneficial for catalysis. (3) The MEDDAB-HPW globular aggregates are amphiphilic, which makes PAM/MEDDAB-HPW composite material especially beneficial for their application in diphasic catalysis. To our knowledge, PAM/MEDDAB-HPW composite material is the first example material to have the hydrogel core and the polyoxotungstates/alkyl quaternary ammonium complexes shell. To construct this kind of material is significant to develop new catalytic materials used in phase-transfer catalytic reaction.

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