Attapulgite@polymer Particles with Double-layer Polymer Shell via Soapless Seeded Emulsion Polymerization

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ABSTRACT: Attapulgite needle encapsulated with double-layer polymer shell (ATP@DP) were prepared by the soapless seeded emulsion polymerization of the second monomer styrene in the dispersion of the attapulgite needle encapsulated with poly(methyl methacrylate) (ATP@PMMA), which was also conducted by the soapless seeded emulsion polymerization of the first monomer methyl methacrylate with the cetyltrimethylammonium bromide (CTAB) modified attapulgite needle (org-ATP) as seeds. The different morphologies of ATP, ATP@PMMA particles, and ATP@DP particles were characterized by transmission electron microscopy, and the encapsulation mechanism was also discussed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2082–2088, 2008

Key words: attapulgite; encapsulation; soapless seeded emulsion polymerization; core-shell particles; double-layer polymer shell

INTRODUCTION

Encapsulation of inorganic particles by polymers has long been an interesting research subject. Polymers encapsulating inorganic nanoparticles show improved thermal, mechanical, optical, and other properties because of the combined properties of inorganic nanoparticles and organic polymers, and they can be widely used in plastics, rubbers, cosmetics, inks, coatings, etc.

Extensive research has been reported involving silica,[1–6] titania,[7,8] magnetic particles,[9,10] zinc oxide,[11,12] calcium carbonate,[13,14] metal,[15–17] and CdS[18] particles with either micrometer or nanometer sizes.

The cores used were usually spherical or quasi-spherical inorganic particles. The encapsulation of the inorganic particles with other than spherical shape such as nanoneedles[19,20] and layered silicate,[21–24] is rarely reported. It seems that spheres are easier to be encapsulated than needles because of easier stabilization by the reaction medium.

Most recently, the double-layer polymer shells were fabricated from the nanoparticle surfaces to improve their chemical and/or physical properties. Yu et al. prepared the titanium dioxide inorganic core and polymer shell poly(styrene-*co*-divinylbenzene)-methacrylic acid (P[(St-*co*-DVB)-MAA])[25] and poly(methyl methacrylate-*co*-ethylene glycol dimethacrylate)-methacrylic acid (P[(MMA-*co*-EGDMA)-MAA])[26] composite particles by two-step dispersion polymerization. Wang et al. reported the preparation of the novel core (PBA/OMMT)–shell (PS) structured complex by γ-ray radiation emulsion polymerization of styrene with poly (butyl acrylate) (PBA) and the intercalated or exfoliated organophilic montmorillonite (OMMT) as seeds.[27]

Attapulgite particle is a kind of needle-shaped silicate. The particles are ∼ 20 nm in diameter and the length is from several hundreds nanometers to several micrometers. The ATP needles are different in length. ATP is a hydrated magnesium aluminum silicate containing ribbons of a 2 : 1 phyllosilicate structure.[28] In the present work, we encapsulate ATP needle-shaped particles with poly(methyl methacrylate) (PMMA) and polystyrene (PS) through two-stage seeded emulsion polymerization. The PMMA encapsulated attapulgite (ATP@PMMA) was used as the seeds in the second time soapless emulsion polymerization of styrene. The morphology of the resulting attapulgite needle encapsulated with double-layer polymer shell (ATP@DP) composite particles was investigated by transmission electron microscopy (TEM) and the mechanism will be discussed.

EXPERIMENTAL

Materials

Attapulgite nano-fibrillar clay (ATP) with the average diameter of 325 mesh, was provided by Jingyuan, Gansu, China. Cetyltrimethylammonium bromide
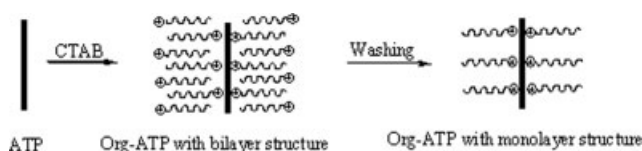
Scheme 1 The org-ATP with bilayer or monolayer structure.

(CTAB) was an analytical grade reagent received from Tianjin Chemical, Tianjin, China, and used without further purification. The monomers, styrene (St) and methyl methacrylate (MMA) (analytical reagents, Tianjin Chemical Tianjin, China) were dried over CaH_2 and distilled under reduced pressure. The initiator, potassium persulphate (KPS, Tianjin Chemicals, Tianjin, China) was recrystallized from ethanol before use. All other reagents used were analytical reagents. Distilled water was used throughout.

Org-ATP

ATP was purified by the procedure reported previously[29] and then pretreated with the surfactant CTAB in ultrasonic bath as follows: 5.0 g attapulgite, 2.0 g CTAB, 400 mL water were mixed into a beaker. The mixture was sonicated in an ultrasound bath for 8 h, the sediments were discarded, and the stable supernatant suspension was used for further experiments. We call org-ATP the resulting particles.

Org-ATP suspension for emulsion polymerization

Hundred milliliter of org-ATP suspension was centrifuged at 3000 rpm for 2 min at first. The sediment at the bottom was thrown away. And the org-ATP was separated by centrifugation at 13,000 rpm for 15 min from the stable suspension.

Two-stage soapless emulsion polymerization

After the wet org-ATP was dispersed into 50 mL H_2O with ultrasonic agitation for 30 min, 0.1 mL MMA was added into the flask. The mixture was irradiated in ultrasonic bath for 1 h, and 0.003 g KPS initiator was added. The flask was then subjected to electromagnetic stirring at 70°C for 1 h and then cooled to room temperature. The prepared ATP@ PMMA composite particles were used as a seed for the second stage of the seeded emulsion polymerization.

St (0.5 mL) was added to the flask. Then the solution was maintained at room temperature for 24 h under ultrasonic agitation, allowing the monomers to swell the seeds. After that, the reactor was heated to 70°C under nitrogen with a stirring speed of 300 rpm. KPS initiator (0.015 g) was then added to the solution and reacted at 70°C for 6 h. The composite particles were separated by centrifugation at 13,000 rpm for 15 min for the Fourier transform infrared spectroscopy (FTIR) and Thermogravimetric analysis (TGA) analyses.

Analysis and characterizations

Elemental analysis (EA) of C, H, and N was performed on Elementar vario EL instrument. Bruker IFS 66v/s infrared spectrometer was used for the FTIR spectroscopy analysis. TGA was performed with a Perkin-Elmer TGA-7 system (Perkin-Elmer Corporation, USA) at a scan rate of 10°C/min to 800°C in N_2. The morphologies of the ATP@DP composite particles were characterized with a JEM-1200 EX/s TEM.

RESULTS AND DISCUSSION

Org-ATP

The general purpose of the pretreatment with CTAB is to introduce the organic chains to the ATP needles'
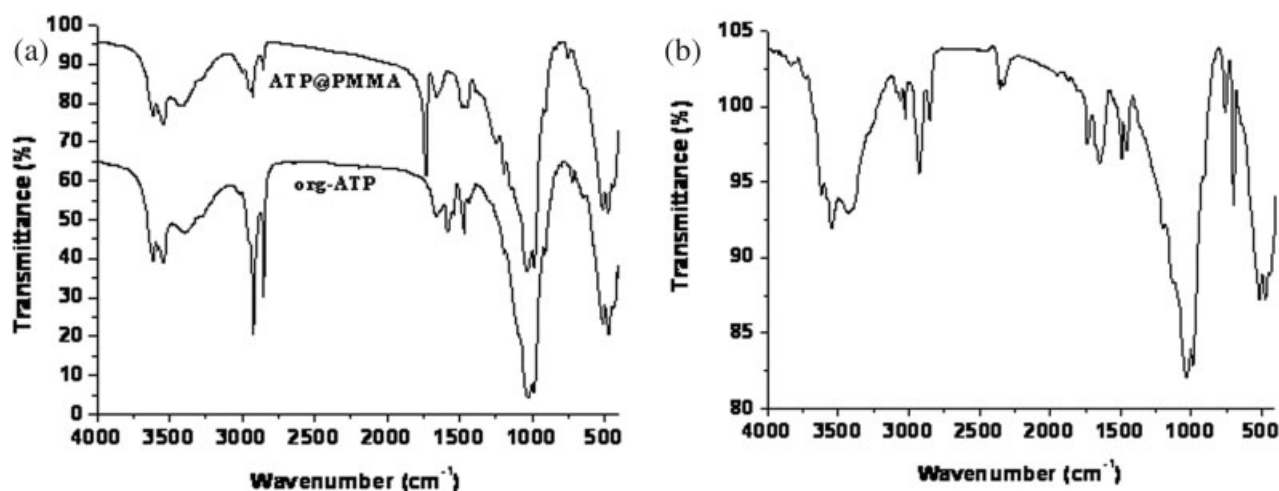

Figure 1 FTIR spectra. (a) FTIR spectra of the org-ATP and ATP@PMMA, (b) FTIR spectrum of the ATP@DP.
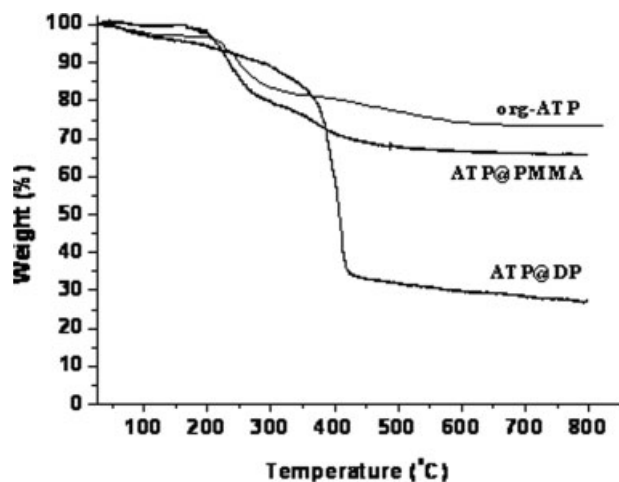
Figure 2 TGA curves of the org-ATP, ATP@PMMA, and ATP@DP.

surface and the ATP needles' surfaces became more hydrophobic so that thay have more affinity for the monomers, facilitating encapsulation. The cationic surfactant CTAB was used for that purpose in the present work, because of the existence of negative charge centers on attapulgite.

If the CTAB is enough and not excessive, the organic chains of CTAB can form monolayer and bilayer structures on the ATP needles' surfaces (Scheme 1). The org-ATP dispersion was used as seed in the soapless emulsion polymerization of styrene. So the superfluous CTAB molecules in the org-ATP dispersion were washed off. If the CTAB adsorbed attapulgite clays were washed with water for two times, the products could not dispersed in water and dispersed in organic solvents such as toluene. It demonstrated that the bilayer structure was formed on the ATP surface. And the outer layer might be washed off to form the monolayer structure after being washed with more than one time with water. So the organo-ATP dispersion for the further soapless emulsion polymerization was washed with water for only one time.

It was found that about 0.445 mmol CTAB/g org-ATP, calculated from the N EA results. The absorbance bands at 2926 cm^{-1} and 2855 cm^{-1} ascribed to C—H of the CTAB was found in the FTIR spectrum of the org-ATP [Fig. 1(a)]. It indicated that the CTAB was assembled onto the surfaces of attapulgite. As shown in the TGA analysis (Fig. 2), the weight loss at $\sim$ 240°C was attributed to the CTAB molecules adsorbed and the maximum rate was at 311°C.

After being centrifugated, the org-ATP was dispersed into water again. The suspension has a good stability. There were few CTAB molecules in water. The suspension was used for further experiments.

ATP@PMMA

After the soapless emulsion polymerization of MMA in the org-ATP suspension, the characteristic absorbance bands at 1734 cm^{-1} ascribed to the characteristic absorptions of PMMA was found in the FTIR spectrum [Fig. 1(a)]. This indicated that PMMA chains were absorbed to the ATP-needles. The particles are also testified by the TGA analysis (Fig. 2). The maximum decomposition rate of the products was found at $\sim$ 203.2°C, attributed to the decomposition of surfactant. The maximum decomposition rate of the products was found at $\sim$ 344.5°C, attributed to the decomposition of PMMA absorbed. The percentage of encapsulating (PE) (polymer/attapulgite mass ratio)[12] was found to be 35.2%, calculated from the TGA analysis.

ATP@DP

The second monomer styrene was added and polymerized directly in the ATP@PMMA suspension. After the soapless seeded emulsion polymerization of St, the characteristic absorbance bands at 3026–3105, 758, and 697 cm^{-1} ascribed to the characteristic absorptions of PS were also found in the FTIR spectrum [Fig. 1(b)]. This indicated that PS chains had been adsorbed onto the ATP-PMMA particles. The PE was found to be 224%, calculated from the TGA analysis.

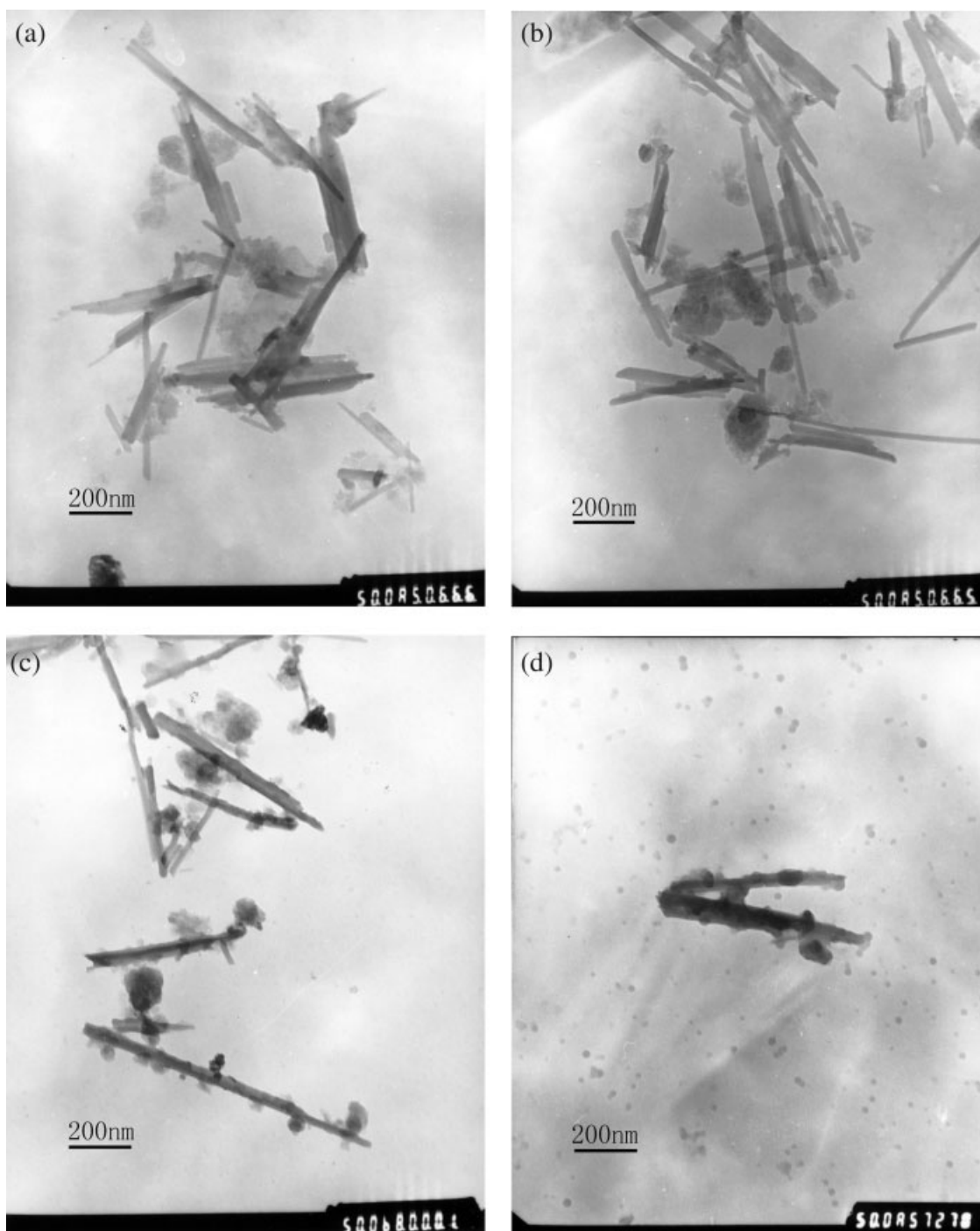**Figure 3** The TEM image of the bare ATP nanoneedles.

Figure 4 The TEM images of the ATP@PMMA composite particles.

Morphological analysis and encapsulation mechanism

The TEM images of the bare ATP nanoneedles, ATP@PMMA, and ATP@DP composite particles were given in Figures 3–5. Clearly, the width of the ATP nanoneedles after polymerization of MMA was about twice that before polymerization. The PMMA particles did not encapsulate the attapulgite very well. The ATP@PMMA composite particles showed string-bead shaped structure [Fig. 4(c)] or core-shell structure [Fig. 4(d)]. In the cases of encapsulation of ATP needles by the soapless polymerization, the general purpose of the pretreatment with CTAB is to introduce the organic chains and the ATP needles' surfaces became more hydrophobic so that they have more affinity for the monomers, facilitating encapsulation. After the ATP was organo-modified by CTAB, its surface was hydrophobic. So the mono-
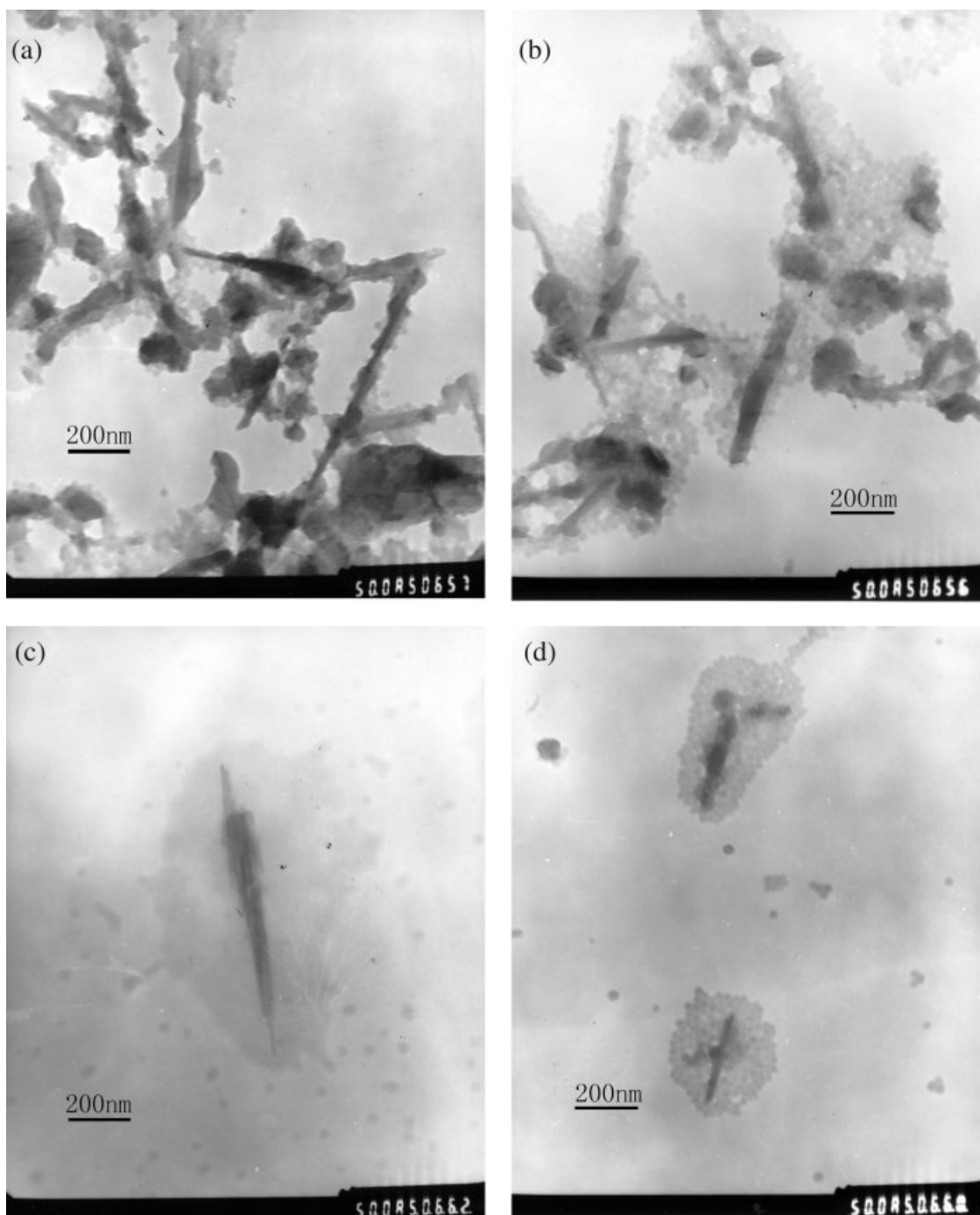
F3-F5

Figure 5 The TEM images of ATP@DP composite particles.

mer MMA was adsorbed onto the hydrophobic sur-face to form the oil phase in the latex (Scheme 2). However, the ATP has a long length/diameter ratio (LDR) so the monomer encapsulated ATP latex was not stable because of the big surface tension. It is inclined to form the string-bead shaped structure, and only the ATP fibrillar single crystal with a short length/diameter ratio could lead to the core-shell structure, as shown in Figure 4.

After the addition of the second monomer styrene, it adsorbed onto the surfaces of the PMMA shell of the ATP@PMMA composite particles. And the dou-ble-layer polymer shell formed after the second time seeded emulsion polymerization because of the poor compatibility between the two layers of PS and PMMA. Most of the emulsifier CTAB molecules were enwrapped in the PMMA layer and there was few free emulsifier CTAB molecules in aqueous solu-
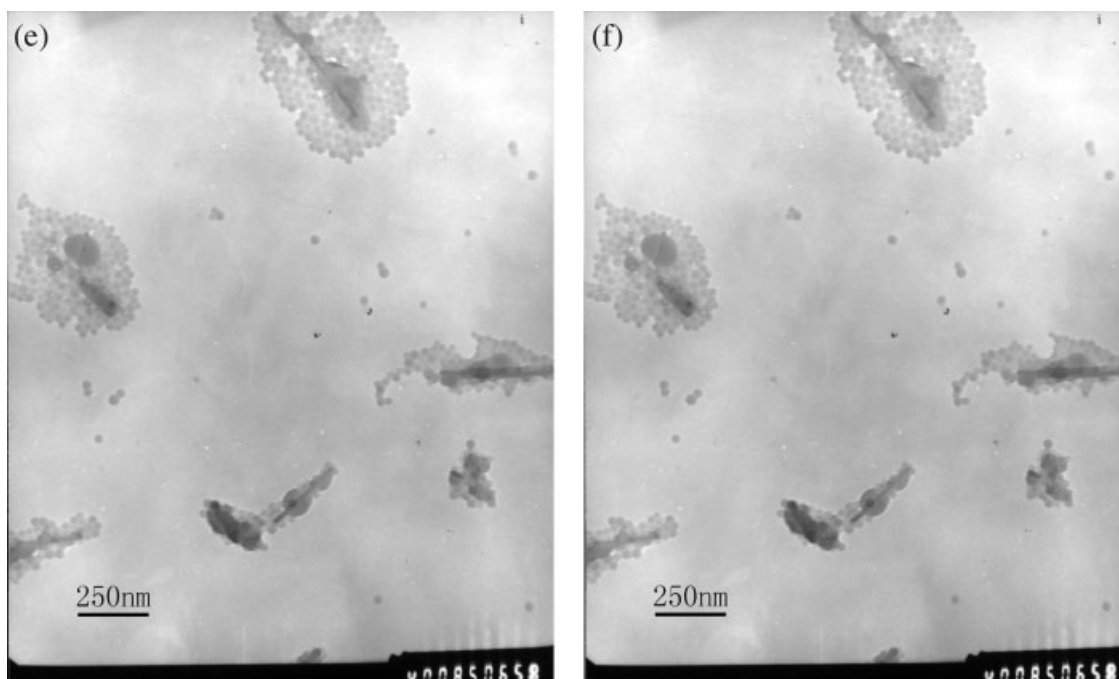
Figure 5 (*Continued from the previous page*)

tion when the second monomer styrene was polymerized. So the PS formed in the second time seeded emulsion polymerization was in the form of nanoparticles with diameter of about 20 nm and encapsulated the ATP@PMMA composite particles completely (Fig. 5). The two layers can be distinguished easily: the inner and the darker was the PMMA shell which encapsulates the needle and the PS nanoparticles wraps the ATP-PMMA as a whole.

The ATP needles which have short length/diameter ratios were encapsulated very well. The ATP needles can be encapsulated completely and the particles like the core of Chinese date or like olives [Fig. 5(c–f)]. As for the ATP needle with long length/diameter ratios, the composite particles with double-layer polymer shell like the bead-string shapes. The PS particles absorbed to the ATP@PMMA particles' surface and encapsulate them.
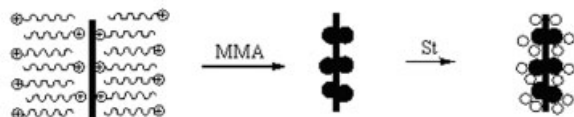
CONCLUSION

ATP@DP composite particles were prepared by two-stage seeded emulsion polymerization. The ATP needles with long length/diameter ratios were encapsulated by the two polymer shell to form the bead-string shape, whereas the attapulgite ATP needles with short length/diameter ratios were encapsulated by the two polymer shell very well and form the core-shell particles like the Chinese date or olives.

Scheme 2 The formation mechanisms of the different morphologies of the ATP@DP composite particles.

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