Controllable microemulsion method for the synthesis of Mg(OH)$_2$/PS core–shell structures

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Abstract
A core–shell structured Mg(OH)$_2$/PS with enhanced surface lipophilicity was successfully synthesized by a microemulsion template. The core magnesium hydroxide was prepared in a cetyltrimethyl ammonium bromide (CTAB)/isopropanol/cyclohexane/water microemulsion, and the shell polystyrene (PS) was formed in situ by adding styrene monomer into oil phase of the microemulsion. The Mg(OH)$_2$/PS core–shell nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), thermogravimetry/differential scanning calorimetry (TG/DSC) and Fourier transform infrared spectroscopy (FT-IR). The results indicated that the obtained nanoparticles is a core–shell structure and well-dispersed; the polystyrene shell thicknesses could be controlled in the range of 9.11 to 13.36 nm by simply changing the dosage of styrene monomer. Due to its polymer coating modification and integrated core–shell structure, the Mg(OH)$_2$/PS is with excellent surface lipophilicity and easy to mix with the organic phase. The results provide a facile method to produce the surface-modified inorganic material for functionality.

1 | INTRODUCTION

With the advancement of nanotechnology and the improvement of environmental awareness [1–3], magnesium hydroxide nanoparticles are being paid more and more attention as a kind of environment-friendly flame retardant [4, 5]. Due to their remarkable flame retardant property, non-toxicity and cost-effectiveness, many researchers were prompted to prepare magnesium hydroxide nanoparticles following a variety of methods [6–9]. However, as a kind of inorganic substance, magnesium hydroxide surface is hydrophilic, which results in bad dispersion and is difficult to mix with polymer matrix [10].

Surface modification, which comprises alteration of the nanoparticle surface from hydrophilic to lipophilic via organic or polymer coating, is one of the ways to obtain a high level of dispersion of inorganic nanoparticles in the polymer matrix [11, 12]. It has been reported that magnesium hydroxide can be successfully modified by hexylphosphoric acid, vinyltrichlorosilane and octadecyl dihydrogen phosphate [13–15]. However, these methods usually include two steps: the first is to prepare magnesium hydroxide nanoparticles by a precipitation reaction, and the second is to add a modification agent to achieve surface coating [16–17]. Due to the small nano-size, the magnesium hydroxide particles are prone to reunite and agglomerate before coating modification occurs, which results in incomplete modification and the process is cumbersome. Therefore, the surface modification and dispersion of magnesium hydroxide remain a significant challenge for researchers.

Coating polymer on the magnesium hydroxide surface to form a stable core–shell structure is an effective way to achieve modification purpose. At present, there are many reports on inorganic–inorganic core–shell materials, such as the synthesis of Pt-SiO$_2$, Fe$_2$O$_3$@TiO$_2$, CdS/TiO$_2$, Fe@SiO$_2$ [18–21], and microemulsion method plays a certain role in the construction of the core–shell material [18]. As to inorganic–polymer composite, Jassim prepared ZnO/polystyrene nanocomposite films via sol–gel process [22], Jang synthesized CdS/PMMA core/shell nanoparticles using dispersion-mediated interfacial polymerization [23], and Guo constructed MnO$_2$@PPy nanorods via an in situ self-polymerization process [24].

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are few studies on the construction of inorganic-polymer core–shell nanoparticles. This work reports the approach towards the preparation of Mg(OH)\(_2\)/PS nanoparticles in water-in-oil microemulsion and shows evidence that uniform controllable coating of polystyrene can be successfully performed on Mg(OH)\(_2\) and the shell thickness can be systematically tuned by varying the experimental parameters. Direct synthesis of Mg(OH)\(_2\)/PS core–shell nanoparticles have been carried out for the first time using microemulsion template and the synthesized material shows good lipophilicity, which is beneficial to disperse in polymer matrix.

2 | EXPERIMENT

Magnesium chloride hexahydrate, sodium hydrate, cyclohexane, isopropanol and ethyl alcohol were purchased from Tianjin Guangfu Technology Development Co. Ltd (Tianjin, China). Cetyltrimethyl ammonium bromide (CTAB, 99%) and azodiisobutyronitrile (AIBN, 98%) were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Styrene (98%) was purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). All chemicals were of analytical grade and used without further purification and/or treatment. Deionized water was used in all experiments.

In this experiment, 2 g CTAB, 5 mL cyclohexane and 5 mL magnesium chloride hexahydrate solution (1 mol/L) were mixed together, then 5 mL isopropanol was added drop-wise and a transparent microemulsion was observed. Then 10 mL sodium hydroxide (1 mol/L) was added and stirred for 30 min to obtain magnesium hydroxide dispersion (for comparison, the magnesium hydroxide was separated and dried for Mg(OH)\(_2\) nanoparticles). After that, a certain amount of styrene was slowly dropped into and 0.052 g AIBN was added for promoting polymerization. The Mg(OH)\(_2\)/PS was synthesized by stirring for 8 h at 80\( ^\circ\)C under nitrogen protection; at the same time, the condensation reflux was used to prevent cyclohexane volatilization. Finally, the Mg(OH)\(_2\)/PS was separated by centrifugation and washed with ethanol and deionized water, respectively, followed by drying for 12 h at 60\( ^\circ\)C. A series of Mg(OH)\(_2\)/PS nanoparticles were synthesized by changing the amount of styrene as in the above steps. The corresponding synthetic conditions are listed in Table 1.

The X-ray diffraction (XRD) patterns were recorded on a D/MAX-2500 diffractometer (Rigaku, Japan) operating at 100 mA and 40 kV using monochromated Cu K\(\alpha\) radiation (\(\lambda = 1.541\) Å). Scanning electron microscopy (SEM) images were collected on MERLIN Compact (ZEISS, German). X-ray photoelectron spectra (XPS) were recorded on an Axis Ultra DLD (Kratos Analytical Ltd., UK) equipped with an Al K\(\alpha\) radiation for exciting photoelectrons. The X-ray source was operated at 15 kV and 150 W and the energy calibration was achieved by setting the binding energy of carbon at 284.6 eV. Thermogravimetry/differential scanning calorimetry (TG/DSC) analysis was carried out on a STA449F3 thermoanalyzer (Netzsch, German), under N\(_2\) atmosphere, at a heating rate of 10\( ^\circ\)C/min. Fourier transform infrared (FT-IR) spectrum was recorded on a MAGNA-560 spectrometer (Nicolet, USA) with the KBr pellet method in the range of 400–4000 cm\(^{-1}\).

3 | RESULTS AND DISCUSSION

The typical powder XRD patterns of Mg(OH)\(_2\) and Mg(OH)\(_2\)/PS are given in Figure 1. The diffraction pattern has eight broad peaks at 18.46\(^\circ\), 32.78\(^\circ\), 37.92\(^\circ\), 50.78\(^\circ\), 58.62\(^\circ\), 62.06\(^\circ\), 68.24\(^\circ\) and 72.06\(^\circ\), corresponding to (001), (100), (101), (102), (110), (111), (103) and (201) of magnesium hydroxide (JCPDS 44-1482), respectively. The diffraction peaks of Mg(OH)\(_2\) are sharp and intense, indicating their highly crystalline nature. Comparing XRD patterns of Mg(OH)\(_2\) and Mg(OH)\(_2\)/PS, the peak positions of Mg(OH)\(_2\)/PS do not change, indicating that the coating does not affect the crystal structure of magnesium hydroxide. The peak intensity is weakened after adding styrene, indicating there is a coating material on the surface of magnesium hydroxide, which affects the strength of the peak. The small peaks appearing at 31.5\(^\circ\) and 45.2\(^\circ\) of the Mg(OH)\(_2\)/PS sample can be well indexed to magnesium chloride hydrate (JCPDS 2-136); this further illustrates the presence of the coating material in which the chloride ion impurities are coated.

![XRD patterns of samples: (a) Mg(OH)\(_2\); (b) Mg(OH)\(_2\)/PS](image-url)
and the washing process with ethanol and deionized water which does not remove chloride ion impurities completely.

Figure 2 shows scanning electron microscopy (SEM) images of Mg(OH)$_2$ and Mg(OH)$_2$/PS. The Mg(OH)$_2$, as shown in Figure 2a, is in uniform flake structure and the particles are well dispersed in nanoscale. The w/o microemulsion is chosen for this experiment, in which the aqueous phase is in the form of magnesium chloride solution, when the precipitant sodium hydroxide is added, the OH$^-$ pass through the interface membrane and react with Mg$^{2+}$ in the aqueous phase to form magnesium hydroxide crystallites. The product size is maintained in a certain range as all the stages of nucleation, growth, and crystallization of nanoparticles are confined to the aqueous phase of the droplets to avoid the continued growth of the particles so that the size distribution is narrowed and uniform. When the styrene monomer is added, the styrene monomer enters the oil phase and the polymerization reaction takes place under the action of an initiator. A granular coating layer is formed on the surface of the magnesium hydroxide particles to obtain Mg(OH)$_2$/PS particles, with a uniform morphology and clear boundary, as shown in Figure 2b–d.

The size of Mg(OH)$_2$/PS synthesized under different amounts of styrene added was analysed. As Figure 2b–d shows, with the increase in the amount of styrene, more polystyrene is formed on the surface of magnesium hydroxide, and the coating is gradually improved from the edge of the particles to a full package of particles. When the addition of styrene is 0.5 g, as shown in Figure 2b, only a small number of PS pellets are formed on the edge of magnesium hydroxide, with a coating thickness of 9.11 nm. When the addition amount of styrene is 2.6 g, as shown in Figure 2c, PS pellets are evenly distributed on the edge of the magnesium hydroxide and form an annular shape, and the coating thickness is 9.26 nm. When the addition amount of styrene is 4.2 g, as shown in Figure 2d, PS pellets are distributed on both the edge and the surface of the magnesium hydroxide sheet, with a coating thickness of 13.36 nm. It can be concluded that the coating thickness increases with the increase of styrene monomer dosage. The experiments show that the coating integrity and thickness can be controlled by adjusting the addition amount of styrene monomer. The coating thickness and styrene dosage of samples are listed in Table 2.

To further confirm the existence of PS coating on the surface of magnesium hydroxide particles, XPS analysis was carried out. Figure 3 shows the XPS survey spectrum of the PS/Mg(OH)$_2$ with 2.6 g styrene. It can be found that the sample contains Mg, O and C elements (the atomic ratios are presented in Table 3). The Mg 2s and Mg 2p peaks are observed at 88.6 and 49.6 eV, respectively; the O 1s peak is observed at 530.6 eV. The existence of PS was proven by the carbon signal with a peak at 284.6 eV, and the broad carbon peak at 285.5 eV identified additional carbon species, which was caused by the magnesium hydroxide environment, identified PS is combined with Mg(OH)$_2$. Compared with the sample before etching, the intensity of C 1s peak in the sample after etching was obviously weaker and the atomic ratio of C1s is decreased from 19.24% to 10.32%, which confirmed the existence of PS coating. The result was consistent with the structure model in SEM.

TG and DSC curves were determined to investigate the thermal stability of Mg(OH)$_2$/PS sample, as shown in Figure 4. TG curve displays a slow weight loss stage in the temperature range from 100$^\circ$C to 250$^\circ$C corresponding to the release of H$_2$O and the thermal decomposition of polystyrene. The obvious weight loss stage is ascribed to the decomposing of Mg(OH)$_2$ in the temperature range from 250$^\circ$C to 400$^\circ$C. Given the observed weight loss rate of about 27.4% in this temperature range, this weight loss is slightly less than the theoretical weight loss of magnesium hydroxide (30.89%) [25]. It can be ascribed to the polystyrene coated on the surface of Mg(OH)$_2$ that affects the decomposition of magnesium hydroxide. After 400$^\circ$C, the curve changes relatively gently, and it can be considered that the sample decomposition is complete, and the stable magnesium oxide is produced.

The DSC curve of the sample shows three apparent peaks, one curve is gradual and can be observed at 60–120$^\circ$C,

![FIGURE 2 SEM images of Mg(OH)$_2$ and Mg(OH)$_2$/PS synthesized at different styrene content: (a) Mg(OH)$_2$; (b) Mg(OH)$_2$/PS with 0.5 g styrene; (c) Mg(OH)$_2$/PS with 2.6 g styrene; (d) Mg(OH)$_2$/PS with 4.2 g styrene.](image)

| Number | Styrene, g | Coating thickness, nm |
|--------|-----------|-----------------------|
| b      | 0.5       | 9.11                  |
| c      | 2.6       | 9.26                  |
| D      | 4.2       | 13.36                 |

| Name    | Binding energy (eV) | At%  |
|---------|---------------------|------|
| O 1s    | 530.6               | 59.79|
| C 1s    | 284.6               | 19.24|
| Mg 2s   | 88.6                | 18.47|
| Mg 2p   | 49.6                | 2.49 |

The size and the coating process of Mg(OH)$_2$/PS synthesized under different amounts of styrene added was analysed. As Figure 2b–d shows, with the increase in the amount of styrene, more polystyrene is formed on the surface of magnesium hydroxide, and the coating is gradually improved from the edge of the particles to a full package of particles. When the addition of styrene is 0.5 g, as shown in Figure 2b, only a small number of PS pellets are formed on the edge of magnesium hydroxide, with a coating thickness of 9.11 nm. When the addition amount of styrene is 2.6 g, as shown in Figure 2c, PS pellets are evenly distributed on the edge of the magnesium hydroxide and form an annular shape, and the coating thickness is 9.26 nm. When the addition amount of styrene is 4.2 g, as shown in Figure 2d, PS pellets are distributed on both the edge and the surface of the magnesium hydroxide sheet, with a coating thickness of 13.36 nm. It can be concluded that the coating thickness increases with the increase of styrene monomer dosage. The experiments show that the
corresponding to the heat absorption peak of sample surface water and small molecular organic matter removal. The other curve is obvious at 250–400°C, and the maximum heat flow is observed around 349.15°C, which is lower than uncoated Mg(OH)₂ (357°C) [25, 26]. The third curve is a small heat absorption peak that can be obvious at 780°C, which corresponds to the melting of magnesium chloride, which is consistent with the XRD analysis results that there were chloride ion impurities coated in Mg(OH)₂/PS.

FT-IR analysis was further carried out to verify the structural composition of Mg(OH)₂/PS. As shown in Figure 5, the intensities of the FT-IR peaks corresponding to magnesium hydroxide, such as the O–H stretching vibration peak at 3702 cm⁻¹ and the Mg–O stretching vibration peak at 435 cm⁻¹, the broad peak at 3427 cm⁻¹ and 1630 cm⁻¹ belongs to the stretching vibration of the absorbed water [27]. Significantly, the new stretch at 2920 cm⁻¹ and 2851 cm⁻¹ can be assigned to asymmetric and symmetric vibration of the C–H, corresponding to polystyrene long chains (–CH₃ and –CH₂–) [22]. In addition, the overlaid peaks in the range of 1378–1497 cm⁻¹ are attributed to the -C=Å- flexural vibration of benzene [28], confirmed the existence of polystyrene coating. The coating of polystyrene changed the surface properties of magnesium hydroxide, which is helpful for the miscibility with polymers matrix when used as a flame retardant.
In order to further investigate the surface performance of Mg(OH)$_2$/PS, the water-oil two-phase dispersion experiment was studied. The Mg(OH)$_2$/PS was added into 1:1 water–toluene system, after being deposited for 24 h, the toluene phase appears in a cloudy condition and forms a homogeneous suspension, while the water phase is clear. It can be interpreted that the surface-modified Mg(OH)$_2$/PS was with better lipophilicity.

As discussed above, magnesium chloride hexahydrate was used as water phase in this work, cyclohexane was used as oil phase, the ionic surfactant, CTAB, and a cosurfactant, isopropanol, were used to form a water-in-oil microemulsion. As the Figure 6 shows, when sodium hydroxide was added, magnesium chloride and sodium hydroxide reacted first to form magnesium hydroxide crystal, and the surfactant CTAB in the system was adsorbed on the surface of magnesium hydroxide to form a stable CTAB micelle layer [29]. The thus treated magnesium hydroxide particles acted as nuclei and the surface changed into a certain degree of lipophilic. Then the styrene monomer was added, the styrene entered into the oil phase and polymerized itself under the action of an initiator and formed polystyrene particles. The organic group benzene in polystyrene and the long-chain alkyl group in CTAB were combined by Van der Waals force so that the polystyrene was adsorbed on the surface of the CTAB micelle layer to form a stable polystyrene coating layer, and the core–shell structure Mg(OH)$_2$/PS nanoparticles were obtained.

4 CONCLUSION

In the water-in-oil microemulsion system, magnesium hydroxide is formed in the water phase, and polymer monomer is introduced to the oil phase and polymerized on the magnesium hydroxide surface to form a coating layer under the connection of CTAB. The synthesized Mg(OH)$_2$/PS nanoparticles are with well dispersity and good surface morphology. The shell thickness can be well controlled by changing the dosage of styrene monomer and the shell can change the magnesium hydroxide surface performance from hydrophilic to lipophilic, making it easier to mix with polymer material, thereby overcoming the problem of poor compatibility between the conventional inorganic additives and the polymer matrix. This synthesis technology can produce the surface-modified inorganic material for functionality and the process can be easily reproduced and scaled up because no complicated synthesis and tedious steps are involved.

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FIGURE 6 Schematic diagram of Mg(OH)$_2$/PS core–shell nanoparticles growth

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