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Magnetic polymer enhanced hybrid capsules prepared from a novel Pickering emulsion polymerization and their application in controlled drug release

K. Zhang [a], W. Wu [a,*], K. Guo [b], J.-F. Chen [a,b], P.-Y. Zhang [b,*]

[a] Key Laboratory for Nanomaterials, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029,China
[b] Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029,China

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ABSTRACT

Magnetic polymer enhanced hybrid capsules (MPEHCs) were successfully prepared from a novel Pickering emulsion polymerization. The resultant products were characterized by Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Fourier transform infrared spectrum (FTIR), Thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and Vibration sample magnetometer (VSM). It was proved that the MPEHCs consist of SiO_2 outer shell and magnetic polymer inner shell with particle sizes from 0.8 μm to 2 μm and thickness about 140 nm. The MPEHCs were applied as a drug carrier to study their controlled release behaviors and ibuprofen was used as a model drug. The curve of release behaviors of ibuprofen exhibited a typical sustained release pattern, indicating that the MPEHCs could be applied as a promising drug vehicle for controlled release systems.

1. Introduction

Hollow microspheres with well-defined structure have attracted more and more interest because they have many potential applications such as delivery systems (for drugs, cosmetics, dyes, inks, etc.), encapsulation, confined-space catalysis and separation [1–4]. A variety of chemical and physicochemical methods have been reported for the preparation of hollow materials [5–7]. A common approach for the preparation of hollow inorganic sphere is to coat a template core in solution by either controlled surface precipitation of precursor or direct surface reaction utilizing specific functional group on the core to induce the coating, followed by removal of the template core by calcination or solvent etching [8–15]. Disadvantages are that these methods are time-consuming and step-complicated. Recently, Pickering emulsion is of particular appeal as a simple method to prepare hollow capsules and core-shell structured composite spheres [16–20]. Our group prepared magnetic hollow SiO_2 microspheres via a Pickering emulsion route, however, the hollow microspheres were too fragile to be used as drug carriers. The mechanical robustness became the most important challenge to restrict the application of our synthesized capsules. As we known, the strength of the capsules can be enhanced by linking the individual building blocks together. Bon et al. prepared polymer network reinforced capsules via Pickering emulsion polymerization and the capsules are double-shelled [20]. Advantage of this method is that the formed inner polymer shell can interlock the outer building blocks, enhancing the capsule rigidity. In addition, the polymer shell is permeable, which can control the release of small molecules. Recently, multilayer hollow capsules have received a great deal of attention as smart drug delivery carriers [21,22]. The multilayer capsules provide opportunities to create advanced materials with higher complexity because the capsule walls can be fabricated from a variety of compounds. In this paper, we use a modified Pickering emulsion approach to prepare magnetic double-shelled capsules and study their controlled release behavior for model drug ibuprofen. This preparation process entails the entrapment of magnetic particles in the inner polymer shell and formation of the outer SiO_2 shell, exploiting a polymer network reinforced magnetic hollow capsules, which are more suitable to be used as drug carriers due to their magnetism, enhanced mechanical strength and biocompatibility.

2. Experimental

2.1. Materials

All reagents are of analytical grade. Styrene was bought from Tianjin Chemical Reagent Corporation (China). SiO_2 nanoparticles were supplied by Beijing Spaceflight Saide Corporation (China). Methacryloxypropyltrimethoxysilane (MPTMS), 4-vinylpyridine, oleic acid, ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) and azo-bis-isobutryonitrile (AIBN)

* Corresponding author. Tel.: +86 1064443134; fax: +86 1064434784.
E-mail addresses: wuwei@mail.buct.edu.cn (W. Wu), zhangpy@mail.buct.edu.cn (P.-Y. Zhang).

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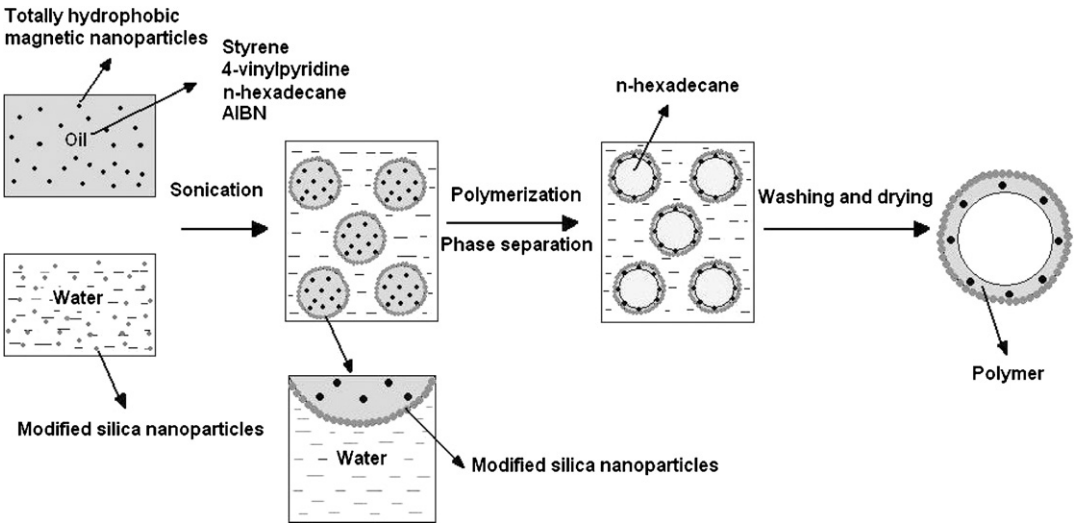

Scheme 1. Schematic illustration of the fabrication of MPEHCs.

were provided by Beijing Chemical Reagent Corporation (China). Styrene was distilled twice under reduced pressure before use, and the other reagents were used without further purification. Deionized water (resistivity > 10 MΩ cm^{-1}) was used throughout the study.

2.2. Modification of SiO_2 nanoparticles

5 g of SiO_2 nanoparticles were added to 130 mL of ethanol/water mixture (v/v, 12/1) under agitation. A definite amount of MPTMS was dropped to the SiO_2 dispersion and reacted at 65 °C for 24 h. After reaction, the mixture was centrifuged. The modified SiO_2 nanoparticles (MSNs) were washed with water and ethanol, respectively, and subsequently dried under vacuum at 60 °C for 10 h.

2.3. Preparation of hydrophobic Fe_3O_4 nanoparticles (HFNs)

1.35 g of $FeCl_3{\cdot}6H_2O$ and 0.6 g of $FeCl_2{\cdot}4H_2O$ were dissolved in 50 mL of distilled water at 30 °C. Then 50 mL of 0.5 M NaOH was added rapidly into this solution while stirring vigorously under inert gas of N_2. After precipitating, the Fe_3O_4 particles were collected by a permanent magnet and then dispersed into 40 mL of oleic acid/ethanol (v/v, 1/3) solution with stirring at 50 °C for a period of 6 h. The black powder was rinsed by ethanol for several times to remove excess modifiers and ions.

2.4. Preparation of magnetic polymer enhanced hybrid capsules (MPEHCs)

The synthesis strategy is presented in Scheme 1. A representative preparation procedure is as follows: 0.9 g of MSNs were ultrasonically dispersed into water for 15 min, and then pH value of the MSNs dispersion was adjusted to 3 by using 1 M HCl. 0.1 g of HFNs were dispersed in oil phase consisting of 0.9 g of styrene, 0.5 g of 4-vinylpyridine and 1.1 g of n-hexadecane, in which 0.04 g of AIBN had been dissolved, and this dispersion was subsequently mixed with the MSNs dispersion. A stable Pickering emulsion was generated via digital sonifier for 14 min at 60% amplitude with 40 s pause every minute sonication. The resulted Pickering emulsion was poured into a 100 mL three-neck flask equipped with a nitrogen inlet and a reflux condenser. The emulsion was agitated mildly (50 r/min) and polymerized at 78 °C for 24 h. The precipitates after filtration were washed with water and ethanol for three times, respectively, and dried at 60 °C under vacuum for 12 h.

2.5. Controlled drug release from MPEHCs

Ibuprofen was entrapped into MPEHCs by dissolving into n-hexadecane at 38 °C beforehand, and the other steps were the same as the process presented in the synthesis of MPEHCs. After being washed with deionized water to get rid of the unentrapped drug, the powders were dried in a vacuum oven at 65 °C for 5 h. The ibuprofen release profiles of ibuprofen-MPEHCs were determined as follows: a certain amount of ibuprofen-MPEHCs was precisely weighed and mixed with 800 mL of phosphate buffer solution with a pH value of 7.4 at 37 °C. After each predetermined time interval, 3 mL solution was acquired from the release medium and the concentration of ibuprofen released was measured using a UV spectrophotometer (ShimadzuUV2501-PC, Japan). The sampling solution was then collected back into the release medium.

2.6. Characterization

The morphology and size of the as-synthesized product were observed by TEM (TEM, JEM-3010) equipped with energy dispersive spectroscopy (EDS) and SEM with EDX spectroscopy (SEM, S-4700). The contact angle measurement was performed on a contact angle goniometer (K100). FTIR were obtained by a Nicolet Avatar 360 FTIR spectrometer in the range 4000–0 cm^{-1} with 32 scans. TGA was performed with a STA-449C apparatus under nitrogen gas at a flow rate of 25 cm^3/min. XPS analysis was conducted on an ESCALAB250 spectrometer and all the binding energy values were referenced to the adventitious C 1s position at 284.6 eV. Vibration sample magnetometer (VSM, Lake shore-7410) was used to measure the hysteresis loops of MPEHCs.

3. Results and discussion

3.1. Features of MSNs and HFNs

MSNs and HFNs were used as building blocks to prepare MPEHCs, so their size and shape influenced the morphology and structure of the resulted MPEHCs. The TEM images of MSNs and HFNs are shown in Fig. 1a and b, respectively. It can be seen that the MSNs have an anomalous shape and their average size is about 20 nm, and the HFNs are sphere-like and have an average size of 12 nm as estimated from TEM.

FTIR spectra were further used to characterize the surface of MSNs and HFNs, respectively. The FTIR spectra of MSNs and HFNs