Fabrication of cellulose based superhydrophobic microspheres for the production of magnetically actutable smart liquid marbles

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ABSTRACT

Cellulose microspheres were fabricated on the basis of sol-gel transition using NaOH/urea/H₂O as the solvent system. These microspheres had an average diameter of about 30 µm. Upon modification with Fe₃O₄ and poly (DOPAm-co-PFOEA), superhydrophobic magnetic cellulose microspheres were generated, which were analyzed by FTIR, TG, XRD, XPS and water contact angle tests. Magnetic cellulose microspheres contained approximately 15 wt% of Fe₃O₄. Poly(DOPAm-co-PFOEA)/Fe₃O₄/cellulose microspheres and had a low surface energy and a high water-repellency. These superhydrophobic microspheres were also converted into liquid marbles via an easily scalable process.

Keywords: Superhydrophobic microspheres; Magnetically actutable; Smart liquid marble; Cellulose microsphere

1. INTRODUCTION

The development of superhydrophobic materials with an extremely high water-repellency has gained great attention due to their interesting potential applications in terms of self-cleaning, anti-corrosion, fuel transport, and low dragging coatings.¹² These materials are essentially fabricated by combining material surface roughness with low surface energy material.

Cellulose, a natural biopolymer, has been widely used in various sectors (e.g., paper, food, textiles, cosmetics, and pharmaceuticals).³⁴ Compared with synthetic polymers, cellulose has a number of advantages: biocompatibility, renewability, biogradability, thermal and chemical stability, among others. Cellulose has a huge potential in the design of specialty materials with well-defined properties. Due to its abundant hydroxyl groups, the modification of cellulose has attracted increasing attention. As a result of physical or chemical modification, functional moieties can be incorporated into cellulose.

Magnetic cellulose microspheres can be fabricated on the basis of in-situ synthesis, and these materials have excellent adsorption capacity and controlled delivery on bovine serum albumin.⁵ The filter paper coated by chitosan and beeswax has strong resistance to water vapor and grease.¹¹ Cellulose acetate can be generated by reacting cellulose with acetic anhydride, and its hydrophobicity can be improved by increasing the degree of substitution (DS); this cellulose derivative can also be formed into liquid marbles once water droplets are embedded into its matrix.¹⁵

Interestingly, in one study, the grafting of methyl acrylate onto cellulose fibers via atom transfer radical polymerization (ATRP) was reported.⁷ In this process, the hydrophobicity of cellulose fibers was significantly improved. For the grafted fibers with a degree of polymerization of 300, water contact angle was increased to 133°. Upon modification with SiO₂ nanoparticles and octyltrimethoxysilane, surface energy of the filter paper was further reduced, resulting in the generation of superhydrophobicity and superoleophilicity.¹⁰

In our previous study,⁵ we reported the concept of using superhydrophobic magnetic cellulose microspheres as building blocks for the fabrication liquid marbles, which had a remarkable stability in terms of liquid droplet transportation and manipulation. As a continuation of this study, the process for the fabrication of superhydrophobic magnetic cellulose microspheres and their morphological characteristics were investigated.

2. EXPERIMENTAL

2.1 Materials

The raw cellulose was bamboo dissolving pulp, which was obtained from Sichuan Tianzhu Bamboo Resources Development Co. Ltd. (Sichuan, China). The gel permeation chromatographic (GPC) ( Waters 1515) measurements showed that cellulose had a Mn of 141 k and a Mw of 56 k. Analytical-grade ethanol, ammonia, sodium hydroxide (NaOH), urea, ferric chloride, ferrous chloride, and other reagents were purchased from Aladdin Reagent (Shanghai) Co. Ltd. and used without further purification.
2.2 Fabrication of cellulose microspheres (CM)

11 g of cellulose was added to 200 mL of NaOH/urea/H₂O (7:12:81 by weight) solution at -13 °C with stirring for 10 min to generate a homogenous cellulose solution. 100 mL of cellulose solution was added into 600 mL of the solution of Span-80 in paraffin oil (5 wt%) and stirred at 800 rpm for 5 h. The cellulose droplets were converted into solids, and CM was regenerated when the suspension was heated to 45 °C followed by sufficient washing with distilled water and ethanol.

2.3 Fabrication of magnetic cellulose microspheres (MCM)

0.15 g of FeCl₃ and 0.4 g of FeCl₄ (mole ratio FeCl₃: FeCl₄ = 2:1) were dissolved in deionized water, and 1 g of CM was added to the solution by stirring under vacuum. 0.86 mL of ammonia (25 %) was added and stirred to allow for complete reaction. The MCM was obtained by washing the mixtures with water to remove excess ammonia, NH₄Cl and impurities.

2.4 Fabrication of superhydrophobic magnetic poly(DOPAm-co-PFOEA)/Fe₃O₄/cellulose microspheres (PMCM)

Poly(DOPAm-co-PFOEA) (derived from N-(3,4-dihydroxyphenethyl) acrylamide (DOPAm) and 2-perfluorooctyl)ethyl acrylate (PFOEA)) was synthesized according to the following procedure: (1) DOPAm (1.9 g, 9.0 mmol), 2-(perfluorooctyl)ethyl acrylate (PFOEA, 4.7 g, 9.0 mmol), and AIBN (24.6 mg, 0.15 mmol) were added into 3 mL of DMF, and nitrogen was bubbled into the mixture to remove oxygen; (2) the resultant mixture was then stirred for 18 h at 70 °C.

0.1 g of poly(DOPAm-co-PFOEA) was dissolved in 50 mL of 1,1,1,3,3,3-hexafluoro-2-propanol, and 1 g of MCM was added and stirred for 96 h at room temperature. The resultant mixture was centrifuged and washed with deionized water. Finally, the product was dried at 120 °C for 2 h under vacuum to generate the PMCM.

2.5 Fabrication of liquid marbles

Liquid marbles were prepared by shaking water droplets onto a layer of PMCM. 5 µL of water was rolled over the powders to form stable magnetic liquid marbles.

2.6 Characterizations

Water contact angle was tested with a contact angle instrument (DSA30, GER KRUSS) by placing water droplets on the surface of molded powders. Cellulose microspheres were observed with an optical microscope (XPL-60). Fourier transform infrared spectroscopic spectra of cellulose microspheres were recorded with a FTIR spectrometer (Bruker, VERTEX70) having a resolution of 4 cm⁻¹. Thermal gravimetric analysis of microspheres was conducted with a TG-DTA instrument (Netzsch STA 449F3). X-ray diffraction patterns were recorded with a MiniFlex-2 diffractometer. The data were collected by using the Cu-Kα radiation in the scanning range of 5° to 60° at a scanning speed of 5 °/min. Surface chemical composition of cellulose-based microspheres was tested by using an X-ray photoelectron spectrometer (XPS, ESCALAB 250 spectrometer) with Al Kα X-ray source. Magnetic properties of PMCM were tested with a PPMS-9 vibrating sample magnetometer (Quantum Design, USA) at 300 K.

Figure 1. Optical microscopic image of cellulose microspheres. Inset is the size distribution measured with a laser particle size analyzer.

3. RESULTS AND DISCUSSION

CM can be fabricated via a sol-gel transition process with NaOH/urea/H₂O as the solvent system. The generation of MCM can be achieved by CM modification with Fe₃O₄. In this study, MCM was modified with poly(DOPAm-co-PFOEA) for superhydrophobicity development. Figure 1 shows the optical microscopic image and size distribution of CM. CM exhibited a spherical shape, and its particle size distribution was tested with a laser particle size analyzer. CM had a diameter of 20-60 µm and an average particle diameter of 30 µm.

Cellulose, CM, MCM and PMCM were characterized by FTIR spectroscopy. As shown in Figure 2, the characteristic peaks of cellulose located at 1640 cm⁻¹ and 898 cm⁻¹ can be attributed to the stretching vibration of β-(1-4) glycosidic bond of gluconolactone. The absorption peak of CM at 3445 cm⁻¹ shifted to a higher wavenumber compared with that of cellulose, possibly indicating enhanced intermolecular hydrogen bonding as a result of cellulose regeneration. The characteristic absorption peak of the Fe-O bond of Fe₃O₄ located at 587 cm⁻¹ showed the presence of Fe₃O₄ in MCM. When compared to MCM,
new absorption peaks in PMCM appeared at 1739 cm$^{-1}$, 1576 cm$^{-1}$, 1203 cm$^{-1}$, which corresponds to stretching vibration of the C=O bonds, amide II and stretching vibration of the C-F bonds, respectively. These results indicated that poly(DOPAm-co-PFOEA) was chemically bound to MCM.

Figure 3 shows the TG curves of cellulose, CM, MCM, and PMCM. Weight losses (3 wt.%, 80 wt.%, and 13 wt.%) of cellulose during first, second and third stages can be attributed to water evaporation (30-120 °C), oxidative decomposition of cellulose (260-380 °C) and carbon oxidation based decomposition of cellulose (370-580 °C), respectively. The weight difference between CM and MCM showed that approximately 15 wt% of Fe$_3$O$_4$ existed in MCM.

Figure 4 shows the XRD patterns of cellulose. The diffraction peaks at 2θ = 15.2°, 16.3°, and 22.7° can be indexed as (110), (110) and (200) planes, which are characteristic of cellulose I crystal. In the case of CM, the peaks at 2θ = 12.1°, 20.3° and 22.7° are characteristic of (110), (110) and (200) planes of cellulose II crystal. These results indicated that the typical crystalline structure of cellulose I was converted into cellulose II in the sol-gel process. In the curves of MCM and PMCM, the peaks at 2θ = 12.1°, 20.3° and 22.7° can be observed, indicating that these samples maintained the typical crystal form of the cellulose II. More importantly, diffraction peaks at 30.7°, 35.5°, 43.3°, 57.2° and 62.7° can be indexed as the (111), (220), (400), (422) and (511) planes of Fe$_3$O$_4$, respectively, confirming the successful modification of cellulose microspheres with Fe$_3$O$_4$.

In order to verify the modification of CM with Fe$_3$O$_4$ and poly(DOPAm-co-PFOEA), XPS spectra of unmodified/modified microspheres were tested. Figure 5A shows the wide scan spectra of cellulose, CM, MCM and PMCM. The wide scan spectra of cellulose and CM showed two main signals corresponding to C1s and O1s. In the spectrum of MCM, the presence of a typical peak with binding energies of 710 eV corresponds to Fe1s. Furthermore, the presence of poly(DOPAm-co-PFOEA) on the PMCM surface can be evidenced from the new peak (689 eV) associated with the fluorine species of poly(DOPAm-co-PFOEA). As shown in Figure 5B, C1s core level spectra of cellulose, CM and MCM can be curve-fitted into three components, with binding energies of 284.6, 286.4 and 287.9 eV, corresponding to C-C, C-O and O-C=O, respectively. Compared with MCM, two new
peaks (291.3 eV for C-F$_2$ and 293.5 eV for C-F$_3$ the C1s core level spectra of PMCP) can be observed. These results indicated that the poly (DOPAm-co-PFOEA) was deposited onto MCM. The DOPAm$^{23}$ moieties in poly(DOPAm-co-PFOEA) anchored to the magnetic Fe$_3$O$_4$ nanoparticles$^{24,25}$ and PFOEA moieties covered the outmost surface of PMCM.$^5$

![Figure 5](image.png)

**Figure 5.** Wide scan spectra (A) and C1s core level spectra (B) of cellulose (a) CM (b), MCM (c) and PMCM (d)

To evaluate the magnetic properties of PMCM, PMCM were measured with a vibrating sample magnetometer. Figure 6 shows magnetization as a function of applied magnetic field. The saturation magnetization obtained from the hysteresis loop was 9.4 emu/g, showing that PMCM had good magnetic properties. The small hysteresis loop and low coercivity showed that the magnetization of PMCM had a superparamagnetic behavior.

![Figure 6](image.png)

**Figure 6.** Magnetic hysteresis loops of the cellulose-based microspheres at 300 K.

To evaluate the hydrophobicity of PMCM, water contact angles were tested by placing water droplets on molded powders. The contact angle of CM was less than 10$^\circ$ (Figure 7A), due to the hydrophilic nature of cellulose. Upon modification with poly(DOPAm-co-PFOEA), water contact angle of PMCM increased to 154.7$^\circ$ (Figure 7B). These results indicated PFOEA moieties containing fluorinated units imparted cellulose-based microspheres a low surface energy, leading to superhydrophobicity development.

![Figure 7](image.png)

**Figure 7.** Interaction of 5 µL of water droplets with CM (a) and PMCM (b)

Due to the low surface energy of PMCM, PMCM can encapsulate liquid droplets to form liquid marbles. Liquid marbles are droplets covered by hydrophobic micro- or nano-scaled particles.$^{26}$ Hydrophobic$^{5,27,33}$ or Janus$^{34,35}$ micro- or nano-particles were generally used to fabricate liquid marbles. As a result of surface encapsulation with hydrophobic materials, the apparent surface energy of liquid decreases. Liquid marbles have attracted significant attention in miniature reactors, microfluidics, drug transport, gas sensing and water pollution detection, etc.$^{36-43}$
Liquid marbles were fabricated by coating 5 µL of water with PMCM (Figure 8). The liquid marbles maintained the spherical shape and showed a non-wetting behavior in terms of solid surfaces. Owing to the presence of magnetic Fe₃O₄, the liquid marbles can be actuated by magnetic force.

4. CONCLUSION

The process for the fabrication of superhydrophobic magnetic cellulose-based microspheres and their morphological characteristics were investigated. On the surface of modified cellulose-based microspheres, DOPA moieties were anchored to magnetic Fe₃O₄, while PFOEA moieties were coated onto the surface to impart low surface energy and excellent liquid repellency. These cellulose microspheres encapsulated water droplets to form stable liquid marbles, which may find use in microreactors, micro-pumps, gas and water pollution sensors, biological engineering, and biomedical applications.

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