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# Morphology controlling of micrometer-sized mesoporous silica spheres assisted by polymers of polyethylene glycol and methyl cellulose

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**Abstract**

Based on the PEG (polyethylene glycol)'s function of bridging flocculation and the MC (methyl cellulose)'s function of formation of liquid crystal in aqueous solution, the morphology of micrometer-sized mesoporous silica spheres with good dispersivity were synthesized by adding the mixture of PEG and MC into the aqueous solution containing F127 and TEOS. It was found that only when PEG was added, the micrometer sized spheres could be synthesized, the spheres possess meso-pores from 2.5 nm to 3.0 nm, and the specific surface area was from 744 $m^2/g$ to 861 $m^2/g$ by changing the amount of PEG, but the dispersibility of microspheres needs to be improved. Only when MC was added, the dispersibility of resultant spheres was good, but the out surface of spheres was not smooth. Then, when suitable amount of PEG and MC were simultaneously added, the spheres with good dispersibility and smooth out surface were obtained.


*Keywords:* Mesoporous; Morphology control; Silica spheres; Water-soluble polymer; Assembly

## 1. Introduction

Since the synthesis of M41S materials in 1992 [1,2], the mesoporous silica with controlled nanostructures and macroscopic morphologies has attracted much attention because of their emerging applications in the areas of catalysis, adsorption, chromatography, and controlled release of drugs [3,4]. Especially, mesoporous silica spheres with diameter in the range of 3–10 μm are very promising chromatography supports in high-performance liquid chromatography (HPLC) to obtain high column efficiency [5].

Mesoporous silica spheres of several micrometers in size have been synthesized by various methods. The acid-prepared mesoporous spheres (APMS) have been synthesized using cationic surfactant under acidic conditions [6,7]. Various mesoporous silica spheres have also been synthesized using nonionic surfactant as templates under static and acid conditions, either by salt-assisted self-assembly [8,9] or by addition of CTAB as cosurfactant [10–13]. Two-step synthesis routes have also been developed to prepare mesoporous silica spheres either by pH adjustment [14–16] or by addition of small amounts of fluoride as catalysts [16–19]. The above silica spheres have been proposed as stationary phases for capillary size exclusion chromatography (SEC) [20], normal-phase HPLC [7,21], and RP-HPLC [7,12,22,23]. However, the methods for preparing mesoporous silica spheres with uniform particle size and good dispersibility are still required [24].

Some researchers found that in the sol–gel process, PEG can adsorb on silica sols in acidic aqueous solution [25] and cause a phase separation by bridging flocculation [26,27]. Therefore, PEG can accelerate the coagulation and precipitation of colloidal silica particles by temperature-induced bridging flocculation under hydrothermal conditions. In additional, the thermoseparation of MC has also been investigated extensively [28–31]. MC forms thermoreversible hydrogel in aqueous solution, which is three-dimensional networks of polymer chains cross-linked via either physical or chemical bonds and entraps a large volume of water. The characteristics of MC have been used to prepare

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size-controllable zeolite nanocrystals by controlling zeolite growth rate [32]. The recent research indicated that a liquid crystalline (LC) phase in dilute MC solutions was observed [33]. The nematic droplet with a diameter of 10–40 μm was formed in fibrillar- and branch-like LC phase.

Based on the special function of PEG and MC in the sol–gel process, by adding PEG, MC and the mixture of PEG and MC into the prehydrolysis solution of tetraethyl orthosilicate (TEOS) with F127 as the template, micrometer-sized silica spheres were synthesize and the morphology of mesoporous silica was controlled.

## 2. Experimental section

### 2.1. Material

The chemicals used for the synthesis: triblock copolymer F127 ($EO_{106}PO_{70}EO_{106}$) and P123 ($EO_{20}PO_{70}EO_{20}$) were purchased separately from Sigma and BASF. Methyl cellulose (MC, 12–18 cp) was purchased from Acros. Tetraethyl orthosilicate (TEOS) was purchased from Xilong Chemical Reagent. Other reagents were obtained from Beijing Chemical Reagent Corporation. All the chemicals were analytical reagents and they were used as received without further purification.

### 2.2. Preparation of mesoporous silica

Unless otherwise specified, mesoporous silica was prepared by two-step synthesis method with F127 as the template. In a typical synthesis: 0.4 g of F127 and 0.2 g of water-soluble polymer (WSP) were dissolved under stirring in 20 g of 0.1 M HCl aqueous solution (WSP content is about 1 wt%), and then 1.9 g of TEOS was added. The resultant mixture was stirred for 16 h at room temperature to obtain a clear solution. The solution was transferred into an autoclave and treated at 100 °C for 24 h. The resultant solid product was filtered, washed with deionized water and ethanol, air-dried at 80 °C overnight, and then calcined at 550 °C for 6 h.

For comparison, some samples were treated under hydrothermal conditions with an oxidant added to remove the organic templates instead of calcinations. In the above synthesis, the solid product after being washed was mixed with 12 g of 30% wt $H_2O_2$ solution, and treated in an autoclave at 100 °C for 24 h. Then the resultant solid product was filtered, washed with deionized water and ethanol, and air-dried at 80 °C overnight.

### 2.3. Characterization

Scanning electron microscopy (SEM) observations were performed on a Hitachi S-450 microscope operating at 20 kV and a JEOL JSM 7401F microscope operating at 1.0 kV. Light-scattering measurements were carried out on a DAWN-EOS light-scattering instrument (Wyatt, USA). X-ray powder diffraction (XRD) patterns were obtained with a Rigaku D/max-RB diffractometer in reflection mode using Cu Kα radiation with a voltage of 40 kV. Transmission electron microscopy (TEM) experiments were performed on a JEOL JEM2010 microscope operating at 200 kV. Nitrogen adsorption–desorption isotherms were measured at 77 K using a Quantachrome Autosorb-1-C Chemisorption–Physisorption Analyzer after the samples were outgassed for 30 min at 200 °C. The BET surface area was calculated from the adsorption branches in the relative pressure range of 0.05–0.25, and the total pore volume was evaluated at a relative pressure of about 0.99. The particle size distribution was measured using a Mastersizer 2000 and evaluated by a volume concentration.

## 3. Results and discussion

### 3.1. General synthesis of mesoporous silica

Compared with classical synthesis of SBA-16, 0.1 M (instead of 2 M) of hydrochloric acid was used with water-soluble polymer (e.g. PEG (poly(ethylene glycol), $M_{av} = 20{,}000$)) added in the two-step method, a proper pH (~1.0) must be required to control the rate of hydrolysis and condensation and consequently obtain a stable solution. Lower pH of the incipient solution leads to phase separation and the resultant formation of irregular particles during the hydrolysis process. Higher pH of the incipient solution cannot facilitate the hydrolysis of TEOS and the self-assembly between silica oligomers and organic templates. Appropriate amount of PEG can facilitate the formation of silica spheres through hydrogen-bonding assistant assembly. The synthesis conditions of the corresponding samples are listed in Table 1. It was found that

Table 1
Synthetic conditions and porous properties of representative samples

| Sample | Reactant composition | | | | | $S_{BET}$ ($m^2$/g) | $V_{total}$ (mL/g) | $D_A$ (nm) | $d$ Spacing (nm) |
|---|---|---|---|---|---|---|---|---|---|
| | F127 (g) | PEG (g) | HCl (mmol) | $H_2O$ (g) | TEOS (g) | | | | |
| S1 | 0.4 | 0 | 2.0 | 20 | 1.9 | 657 | 0.53 | 3.3 | 10.5 |
| S2 | 0.4 | 0.05 | 2.0 | 20 | 1.9 | 861 | 0.61 | 2.8 | – |
| S3 | 0.4 | 0.1 | 2.0 | 20 | 1.9 | 761 | 0.48 | 2.5 | 11.2 |
| S4 | 0.4 | 0.2 | 2.0 | 20 | 1.9 | 772 | 0.58 | 3.0 | 11.3 |
| S5 | 0.4 | 0.4 | 2.0 | 20 | 1.9 | 744 | 0.56 | 3.0 | – |
| S6 | 0.4 | 0.8 | 2.0 | 20 | 1.9 | 771 | 0.53 | 2.8 | 11.3 |