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A facile synthesis of monodispersed mesoporous silica nanospheres with *Pm*3*n* structure

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ABSTRACT

Mesoporous silica nanoparticles (MSNs) have attracted increasing attention for their potential biomedical and catalytic applications. This study reported a facile synthesis of monodispersed mesoporous silica nanospheres (<100 nm) with highly ordered 3D porous structure (*Pm*3*n* symmetry) at room temperature by using dodecyltrimethylammonium bromide (C_{12}TMAB) as template and carboxymethyl cellulose (CMC) as dispersing agent *via* a rapid two-step pH-modulated method. The silica nanospheres were characterized by XRD, SEM, TEM, dynamic light scattering (DLS), N_2 physisorption and ^{13}C MAS-NMR spectroscopy. The monodispersed mesoporous silica nanospheres possessed high specific surface area and large pore volume (>1 $cm^3\ g^{-1}$). The presence of CMC increased the solution viscosity and retarded the silica growth rate, thus led to small particle diameter and narrow particle size distribution.

1. Introduction

The synthesis of nano-sized mesoporous silicas, also called mesoporous silica nanoparticles (MSNs) has attracted increasing interest in terms of their potential use in catalytic and biomedical applications [1–12]. Especially, MSNs are being widely used as supports of chiral catalysts for epoxidation, hydrogenation, hydroformylation, Aldol and Diels–Alder reactions, and etc. [13,14]. Ordered MSNs have been also explored as effective drug delivery systems for therapeutic agents to fight against various kinds of diseases, such as bone/tendon tissue engineering [15–18], diabetes [19,20], inflammation [21], and cancer [22].

Aforementioned MSNs are mainly ordered or disordered MCM-41 type materials with one-dimensional channel system [23–32]. Compared with MCM-41, ordered silica nanoparticles with 3-dimensional (3D) pore structure are more favorable for diffusion and transport of guest molecules [33–36]. As an example, Popat et al. reported that MCM-48 type MSNs with a 3D open network structure and high surface area displayed the highest adsorption capacity and the rapidest adsorption rate compared to MCM-41, SBA-15 and IBN-1 types of silica nanoparticles [37]. Among all the MSNs with 3-D pore network, cubic *Pm*3*n* structured silica with cavities interconnected with small windows [38,39] is a promising material as a carrier for biologically active molecules [40,41].

It is well known that the efficacy of endocytosis, sensing, and drug loading and release of these materials are strongly related to the silica particle size, morphology, and dispersity [42]. Previous studies have shown that particles less than 100 nm have the advantages such as fast mass transport, effective adhesion to substrates and good dispersity in solutions [43–46]. Moreover, substantial size variation in nanoparticles results in large differences in their hydrodynamic properties and negatively affects the application of the nanoparticles in medical practice, thus it is essential to ensure the monodispersity of the silica nanoparticles [47]. However, reduce in particle size brings about defects and high-energy surfaces in the silica “crystal”, which leads to a less ordered structure and also high tendency to aggregate. The aggregated nanoparticles are apt to descent and accumulate from the solution. High dilution method is frequently applied to prepare a stable colloid solution of MSNs [48–51]. However, the collection of MSNs from a highly-diluted solution (the molar ratio of H_2O/Si as high as 5000) requires considerable time cost and energy input, which will inevitably limit the practical application of MSNs so obtained [52]. Much effort has been done to overcome these drawbacks and also to achieve the large scale synthesis of highly dispersed silica nanoparticles in high yield. A general strategy is the

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addition of dispersing agent. Suzuki et al. prepared well-ordered hexagonal *p*6*mm* mesostructured silica nanoparticles using a double surfactant system, where Pluronic F127 ($EO_{106}PO_{60}EO_{106}$) suppresses the grain growth and stabilizes the ordered mesostructure [24]. Moller et al. synthesized colloidal suspensions of nanometer-sized mesoporous silicas by using the base triethanolamine (TEA) instead of ammonia in the conventional synthesis of MSNs. TEA acts as complexing agent for silicate species and additionally as an encapsulator for mesoporous particles, thus protecting the small particles from growth and aggregation [29]. Yokoi et al. successfully synthesized uniform-sized silica nanospheres with a well-ordered cubic closed pack (ccp) lattice in the presence of basic amino acids [53]. Despite all these achievements, there is so far no report on high yield synthesis of MSNs with highly ordered cubic *Pm*3*n* structure yet. Apparently the synthesis of highly ordered, homogeneously dispersed small nanosized silicas with 3D porous properties still remains a great challenge.

*Pm*3*n* mesostructured silica is initially prepared in concentrated acid solution by using alkyltriethylammonium surfactant as template [38]. Afterwards, Che et al. have accomplished plenty of impressive works in synthesis and morphology control of *Pm*3*n* structured mesoporous silica [54–59]. The synthesis conditions such as acidity and temperature play a vital role in controlling the morphologies of the resulted materials [56,57]. Yamada et al. pointed out that the addition of polyols into the synthesis gel contributes to reducing silica particle diameter [60]. As a member of the polyol family, carboxymethyl cellulose (CMC) has been employed in the synthesis of MCM-41 nanoparticles [61]. Inspired by these works, herein we present a facile synthesis of monodispersed silica nanospheres with highly ordered cubic 3D *Pm*3*n* symmetry at room temperature for the first time. The synthesis was performed in a much more concentrated solution than those in many previous reports, therefore giving a significant higher yield of silica. The effect of CMC on the diameter and dispersity of mesoporous silica crystals is highlighted in the present study.

2. Experimental

2.1. Chemical reagents

All the chemical reagents (analytical grade) were purchased form Sinopharm Chemical Reagent Co., Ltd., China and used as received without further purification.

2.2. Materials synthesis

In a typical synthesis, 0.516 g of sodium carboxymethyl cellulose (CMC) was dissolved into 80 mL of deionized water followed by acidification by sulfuric acid to pH ≈ 2 (solution A). 0.8 g of surfactant dodecyltrimethylammonium bromide ($C_{12}TMAB$) was dissolved in 10 mL of deionized water (solution B). Then solution B was added to solution A dropwise. After being stirred for about 30 min, 2.08 g of tetraethyl orthosilicate (TEOS) was added into the solution and hydrolyzed for about 1 h at room temperature. Under stirring, 3.06 g of ammonia solution (25%) was then poured into the mixture. The resulting milky mixture was stirred for another 5 min and then kept at a static condition for 24 h. The molar ratio of the mixture was 1 TEOS: $0.25C_{12}TMAB$: $0.11–0.235H_2SO_4$: 0–0.25 CMC: 4.5 NH_3: $500H_2O$, assuming the molar weight of CMC equals to 258 g/mol. The white solid product was recovered by centrifuge, washed with water and dried at 373 K overnight. The template was removed by calcining the product in air at 823 K for 5 h. The resulting materials were denoted as S-*x*CMC, where *x* represented the molar ratio of CMC/TEOS varying from 0 to 0.25.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku-Ultima diffractometer, with Cu Kα radiation at 35 kV and 25 mA. Nitrogen sorption isotherms were measured on a Quantachrome Autosorb-3B volumetric adsorption analyzer. The samples were outgassed at 573 K for 6 h before measurement. The Brunauer- Emmett-Teller (BET) specific surface area was calculated using adsorption data acquired at a relative pressure (p/p_0) range of 0.01–0.1 and the total pore volume determined from the amount adsorbed at a relative pressure of about 0.99. The primary and secondary pore size diameters were calculated from the analysis of adsorption branch of the isotherm using non-local density functional theory (NLDFT) algorithm and Barret-Joyner-Halenda (BJH) algorithm, respectively. Scanning electron microscope (SEM) was performed on a Hitachi S-4800 field emission scanning electron microscope (FE-SEM, Hitachi, Japan) with an acceleration voltage of 3 kV. Transmission electron microscopy experiments were conducted on TECNAI G2 F30 operating at 300 kV. For the TEM image, the specimens were dispersed in ethanol and placed on holey copper grids. Dynamic light scattering (DLS) studies were carried out on a Malvern NanoZS zetasizer at 25 °C in ethanol solution. Thermogravimetric analysis (TG) was performed using a NET2SCH STA449F3 TGA analyzer with heating rate of 10 °C min^{-1} from 25 to 800 °C under an air flow. ^{13}C MAS NMR spectra were measured on a VARIAN VNMRS 400WB NMR spectrometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the template-free silica materials obtained at different amounts of CMC. For S-0CMC, three resolved peaks are observed in the 2θ range of 2–4°, which are indexed to the (200) (210) and (211) characteristic diffraction peaks of cubic *Pm*3*n* symmetry. Peaks corresponding to the high-index planes in the 2θ range of 4–6° could also be observed. The XRD pattern reveals that the silica sample exclusively possesses cubic *Pm*3*n* symmetry, which is consistent with our previous findings [62]. It should be noted that when *x* equals to 0.10–0.20, the diffraction peaks due to *Pm*3*n* symmetry becomes well resolved,

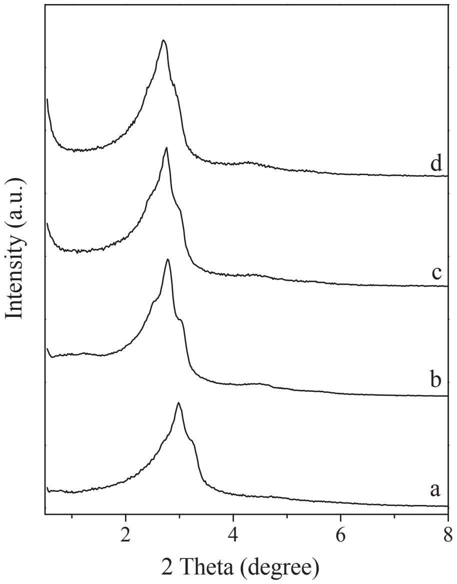

Fig. 1. XRD patterns of the S-*x*CMC samples with various *x*: (a) $x = 0$, (b) $x = 0.10$, (c) $x = 0.20$ and (d) $x = 0.25$.