



Research Article

Synthesis and Characterization of Surfactant-Templated Mesoporous Silica Nanoparticles

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ABSTRACT

Silica particles as a nanoparticulate carrier material for pharmaceutical agents have received considerable attention the past few years, since the material holds great promise for biomedical applications. Silica nanoparticles (MSNs) with highly ordered mesoporous structures have been synthesized using Tween-80, a commercially available non-ionic surfactant in acidic media. The produced nanoparticles displayed large specific surface area ($\sim 1070 \text{ m}^2/\text{g}$) with an average particle size of 100 nm. Under acidic conditions at room temperature, the nonionic surfactant tween-80 frequently forms 2-d hexagonal mesoporous silica structures. The calcined ordered mesoporous silicas reported in this paper are thermally stable in boiling water for at least 48 h.

Key words: *Mesoporous silica, Nanoparticles, Tween 80*

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Article Info: Date received: 08 Jan. 2010

Date accepted : 10 March 2010

INTRODUCTION

Surfactants are widely used in emulsifying, defoaming/antifoaming, coating, thickening, solubilizing, cleaning, lubricating, wetting, pharmaceutical, coal and petrochemical industries, and household applications. Most surfactants are cytotoxic because they are able to damage biological membranes and induce the release of intracellular enzymes [1, 2]. Generally, the cytotoxicity of the different types of surfactants was in an order of cationic > anionic > nonionic.[3] Tween-80, a common non-ionic surfactant, display excellent interfacial stabilization properties and are

low cost, nontoxic, and biodegradable. Pinnavaia and co-workers used nonionic surfactants in aqueous solutions to synthesize wormlike disordered mesoporous silica and alumina in neutral media assembled by hydrogen bonding interactions [4]. Attard et al. [5] have synthesized hexagonal mesoporous silica phases using concentrated ($\sim 50 \text{ wt } \%$) C12EO8 solutions and suggested that the formation of mesoporous silica under these conditions occurs by a “real” liquid crystal template route. It should be noted, however, that the methanol produced by hydrolysis of tetramethyl orthosilicate (TMOS) initially

destroys the liquid crystalline order formed by the surfactant. This, along with the varying concentration of water during the hydrolysis of TMOS and condensation of silica species under acid synthesis conditions, make the preservation of the liquid crystalline order throughout the composite assembly process questionable. [6] It is well known that mesoporous silica nanoparticles (MSNs) possess some excellent properties such as facile multi functionalization, excellent biocompatibility and biodegradability, high specific surface area and pore volume, tunable pore structures and excellent physicochemical stability [7–10]. Recently, it was found that PEGylated MSNs had good blood compatibility as they demonstrated minimized nonspecific binding to human serum protein (HSA), the phagocytosis of THP-1 macrophages and the hemolysis of human red blood cells (HRBCs) [11]. It was also revealed that MSNs could be effectively endocytosed, which mainly depended on their particle sizes [12, 13]. Also, MSNs are universally addressed as a major candidate for use as carriers in controlled drug delivery systems (DDSs), and in these cases, drug molecules must be loaded into MSNs after the removal of the surfactant template from the pore channel systems [14–19]. Mesoporous silica materials organized with nonionic surfactant species that display periodic structural order and that are made under neutral or basic synthesis conditions have not yet been reported. Of considerable interest in this regard is the report by Voegtlin et al. [20] of the synthesis of ordered mesoporous silica that gives an improved X-ray diffraction pattern by using nonionic surfactants in the presence of fluoride anions under near-neutral

conditions. They postulate that the F^- ions are coordinated to silica intermediates, $S^0H^+(F^-)^0$, which apparently provide sufficient electrostatic shielding and effective hydrogen bonding to form mesoporous silica structures that yield relatively narrow (100) Bragg diffraction peaks (full width at half-maximum (fwhm) 0.15-0.5 with Cu KR radiation). Here we report new mesoporous silica structures that include two-dimensional hexagonal mesostructures synthesized by using nonionic tween-80 surfactants. Under these conditions, our results show that the structure of ordered mesoporous silica is controlled predominantly by the surfactant species selected. Under the reaction conditions used here, nonionic tween-80 surfactants often result in the formation of hexagonal mesostructures at room temperature. Importantly, after calcination the mesoporous products are thermally stable even in boiling water.

EXPERIMENTAL SECTION

Chemicals Tetraethylorthosilicate (TEOS) and non-ionic surfactant tween-80 were obtained from Sigma Aldrich. All the chemicals used in the experiments were obtained from commercial sources as analytical reagents without further purification. Distilled water was used throughout the study.

Synthesis of Surf@MSNs.

Mesoporous silica nanoparticles were synthesized at room temperature (RT) by using non-ionic surfactant tween-80 as structure directing agents. In a typical preparation, 1.8 g of Tween-80 was dissolved into 100 ml of 1 M HCl aqueous solution under vigorous stirring at room temperature.

Then 5.6 ml of TEOS as silicon resource was added dropwise within 20 min. The vigorous stirring was continued for 24 h, and then the milk-white as-synthesized materials were collected by centrifugation. In order to remove the surfactant adsorbed on the outside surface, the as-synthesized materials were washed for three times with ethanol. The final products were dried for 12 h at 100 °C in vacuum to obtain Tween@MSNs.

Characterization of Surf@MSNs.

Scanning Electron Microscopy:

Particle sizes were measured using scanning electron microscopy (SEM, JEOL, 5200). Clean glass capillaries were used to transfer a droplet of each sample of suspension to glass slide. The samples were allowed to dry and then micrographs were taken at a number of random locations on the slide. The size of the particles was calculated from the SEM pictures using an average of 100 to 200 particles in almost all cases.

BET analysis:

BET surface area, pore volume and pore diameter of Tween@MSNs was measured by using Micromeritics Gemini6 automated gas sorption system model. The determination of micropore volume, micropore surface area, and external surface area was estimated by using the standard t-plot calculations, while the pore size and distribution was estimated using Broekhoff and de Boer (BdB) reports.

Powder X-ray diffraction:

X-ray powder diffraction (XRD) patterns were taken on a Scintag PADX diffractometer

equipped with a liquid nitrogen cooled germanium solid-state detector using Cu KR radiation. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP 2000 system. The sample was pretreated at 200°C overnight in the vacuum line. The data were analyzed by the BJH (Barrett-Joyner-Halenda) method using the Halsey equation for multilayer thickness.

RESULTS AND DISCUSSION

The SEM image of Tween@MSNs was given in Fig.1. The shape of synthesized nanoparticles was hexagonal and particle size distribution is narrow, ranged from of 80- 120 nm in diameter. The average size of the particles is about 100nm. This result indicate that tween-80 molecules can fully cover the newly created surface of silica nanoparticles, preventing to further aggregation of silica particles during the reaction and drying process. The estimated BET specific surface area was 1070 m²/g, with a measured mesoporous volume of 0.68 cm³/g and an average pore size of 25 Å. In Fig. 2, the BET isotherm is depicted and also the pore size distribution in the inset figure obtained by the Broekhoff and de Boer (BdB) method. As it can be seen it is a characteristic type IV isotherm of mesoporous materials with a step in the range of P/P₀ = 0.2– 0.4 which is typical for the filling of standard mesoporous systems. The powder XRD pattern (Figure 3 (bottom)) of as-synthesized mesoporous silica prepared in the presence of nonionic surfactant tween-80 shows evidence of three well- defined peaks at 2θ values between 1 and 8° that can be indexed as (100), (110), and Bragg reflections. This material is thermally stable

after calcination at 500 °C, as evidenced by retention of a well-resolved hexagonal XRD pattern (Figure 3 (top)), which reflects a unit cell parameter of $a=72.5\text{\AA}$. After calcination, the intensities of the XRD peaks are substantially greater than those measured from the as-synthesized products, suggesting that Tween@MSNs is stable.

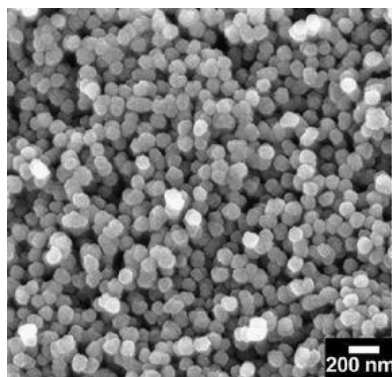


Fig.1. SEM image of Tween@MSNs.

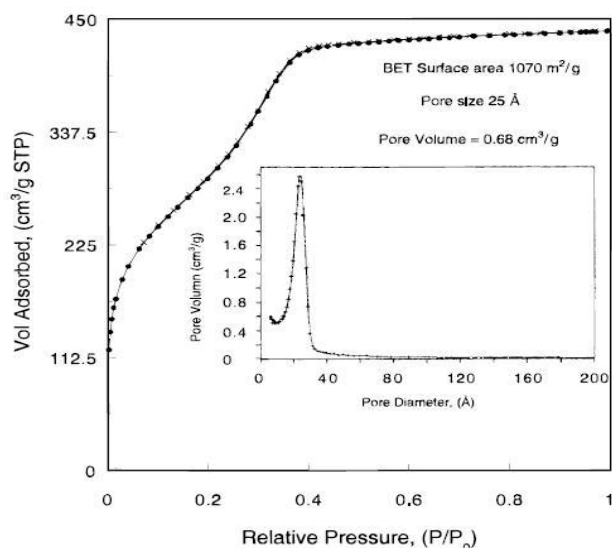


Fig. 2. Nitrogen adsorption isotherm for synthesized Tween@MSNs. The insert image shows the pore size distribution.

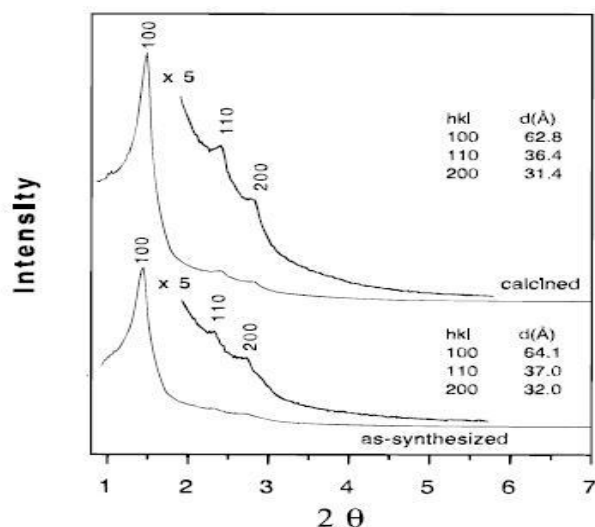


Fig.3. Powder X-ray diffraction patterns of the Tween@MSNs at room temperature.

CONCLUSION

The novel method for the synthesis of porous hollow silica nanoparticles by employing non-ionic surfactant tween-80 as template was developed. The Tween@MSNs had a hexagonal hollow structure with an average diameter of 100nm and with a measured mesoporous volume of 0.68 cm³/g, an average pore size of 25 Å, as well as a surface area of 1070 m²/g. Due to their superiorities such as mesoporous structure, smaller size and biocompatibility, these mesoporous silica nanoparticles are expected to be useful in applications involving bioscience, biomaterials, and drug delivery. Research is underway using these particles for the synthesis of prosthetic materials.

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