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Mesoporous silica nanoparticles with controllable morphology prepared from oil-in-water emulsions

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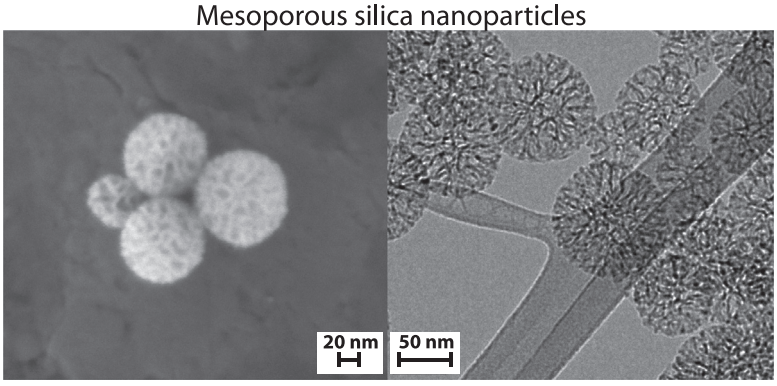
HIGHLIGHTS

- A simple synthesis of 40–50 nm large mesoporous silica particles is presented.
- The particle and the pore sizes are controlled by the type of surfactant used.
- A mechanism for the formation is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous silica nanoparticles are an important class of materials with a wide range of applications. This paper presents a simple protocol for synthesis of particles as small as 40 nm and with a pore size that can be as large as 9 nm. Reaction conditions including type of surfactant, type of catalyst and presence of organic polymer were investigated in order to optimize the synthesis. An important aim of the work was to understand the mechanism behind the formation of these unusual structures and an explanation based on silica condensation in the small aqueous microemulsion droplets that are present inside the drops of an oil-in-water emulsion is put forward.

1. Introduction

Mesoporous silica is of interest in many applications such as catalysis, drug delivery, separation technology, chemical sensors, nanoreactors, and photonics [1–8] because it has a large surface area and it is chemically inert, thermally stable, biocompatible and inexpensive. The mesoporous silica is most commonly prepared in the form of particles, typically ranging from a few hundred nm to a few μm. The pore diameter of mesoporous materials is by definition within the range of 2–50 nm [9,10] but the mesoporous silica particles that are attracting most interest have pore sizes in the lower range of this interval, typically below 15 nm.

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There is currently considerable interest in loading the pores of mesoporous material with active agents such as synthetic homogeneous catalysts, enzymes, drugs, and pesticides [11–14]. Mesoporous silica particles are well suited for this purpose because the pore dimension can be tailor-made to fit a specific molecule and altering the pH of the surrounding medium can vary the surface charge of the pore walls. The charge of the walls may influence the rate of immobilization of the guest molecule, as well as the activity of this molecule once entrapped in the pore [15,16]. In order to further optimize the environment for immobilized molecules, the silica pore walls can be easily functionalized with silanes terminated with various functional groups (e.g. thiol, carboxyl, amine, methyl) [17].

If the guest molecule is a catalyst, such as an enzyme [18–20] or a metal–organic compound [21–24], it will only exert its action when situated close to the pore openings where it can meet the substrate in the surrounding medium. A catalyst buried in the inner part of the pore will be less exposed to the substrate and will thus be less active. For such applications it is therefore advantageous to use as small particles as possible, with more shallow pores, but still with a pore diameter in the 2–15 nm range. However, the established methods of preparing ordered mesoporous silica particles do not give very small particles. It turns out to be difficult to prepare such particles with large pores and a spherical shape below 100 nm in diameter.

In 2009 Nandiyanto et al. [25] presented a one-pot method to synthesize a new class of nano-sized mesoporous silica particles. The synthesis route was the following. First an oil-in-water emulsion was formed with the silica precursor tetraethylorthosilicate (TEOS), styrene and octane as oil component. A cationic surfactant was used as emulsifier, a basic amino acid was added as a catalyst for TEOS hydrolysis, which leads to formation of the silica polymer, and a free radical initiator was added to initiate the polymerization of styrene. The two polymerization processes were believed to occur simultaneously within the oil droplets. After completed polymerization, octane, which only served as a solvent for the polymerizing species, was removed to give a composite sphere consisting of interdigitated polystyrene and silica domains. Removal of the polystyrene by calcination gave the porous silica particles. By varying either the octane or styrene concentration Nandiyanto et al. indicates a particle size range of 20–80 nm and a pore size range of 4–15 nm. Such spherical silica particles are referred to as dendritic silica particles and typically have pores in the meso range; however, they are not ordered like the well-known materials in the SBA and MCM series [26,27].

We have synthesized and utilized mesoporous silica particles as hosts for enzymes for several years [12,16,18,19] and we have recently become interested in these very small silica nanoparticles with pores in the meso range. The reason for this interest is that small particles possess shallower pores compared to the larger SBA and MCM particles and could therefore result in more efficiently loaded pores and enzymes more accessible to the surrounding environment, thus increasing the efficiency in terms of enzymatic activity per gram of mesoporous silica. We have therefore looked into the synthesis of such particles in detail with the aim to understand the mechanism behind the formation of these unusual structures. Emphasis has also been put on simplifying the previously developed synthesis protocol. The mechanistic view that has emerged differs considerably from that published by Nandiyanto et al. [25]. In this paper we present studies from a series of reactions, using different protocols and different kinds of surfactants as structure directing agent, and the collected results constitute the basis for a completely new mechanism for formation of silica particles with a diameter of 40–90 nm and with pore diameters of 3–9 nm.

2. Materials and methods

2.1. Chemicals

Cetyltrimethylammonium bromide (CTAB, ⩾99%), tetraethylorthosilicate (TEOS, ⩾99%), L-lysine (⩾98%), 2,2′-azobis(2-methyl propionamidine) dihydrochloride (AIBA, 97%), ethanolamine (⩾98%), styrene (99%) and n-octane (98%) were all purchased from Sigma–Aldrich. Ethylan 1008 (octa(ethylene glycol)monodecyl ether, $C_{10}E_8$) was received as a gift from AkzoNobel Surface Chemistry (Stenungsund, Sweden). The cationic gemini surfactants N,N′-didodecyl-N,N,N′,N′-tetramethyl-N,N′-ethanediyl-di-ammonium dibromide (12-2-12) and N,N′-didodecyl-N,N,N′,N′-tetramethyl-N,N′-hexanediyl-di-ammonium dibromide (12-6-12) were synthesized as described in the literature [28].

2.2. Particle synthesis

The reference material was synthesized using a protocol adapted from Nandiyanto et al. [25], where CTAB is used as the structure directing agent, TEOS as silica source, octane and styrene as hydrophobic components and lysine as a catalyst. In the synthesis an oil-in-water emulsion was first formed by vigorously stirring 200 mg CTAB, 62 g Milli-Q water, 19.9 g n-octane and 45 mg L-lysine for 1 h at 70 °C in a three-necked reactor. Thereafter 2.77 g styrene, 2.0 g TEOS and 77.6 mg AIBA (used as polymerization initiator) were added and the mixture was stirred and kept under N_2 atmosphere at 70 °C for 20 h. Prior to use the styrene was prewashed with 2.5 M NaOH in order to remove the stabilizer. The suspension was decanted into a funnel and cooled to room temperature. The mesoporous particles where collected and freeze dried. Finally the residual organic material was removed through calcination, by increasing the temperature from room temperature to 650 °C during 8 h and holding for 6 h at 650 °C.

2.3. Variations of the synthesis conditions

In order to study the formation process of the particles several different synthesis experiments were performed. Except for the particular component to be varied all other parameters were kept the same to avoid artifacts from compositional or conditional variations. The following components were varied:

MPS-1: Styrene and AIBA were removed from the synthesis in absence of N_2 gas flow.
MPS-2: The same conditions as for MPS-1 were used and the catalyst L-lysine was replaced with an equal molar amount of ethanolamine.
MPS-3: The same conditions as for MPS-2 were used and CTAB was replaced with an equal molar amount of a cationic gemini surfactant with two C_{12} chains and with a C_6 linker (N,N′-didodecyl-N,N,N′,N′-tetramethyl-N,N′-hexanediyl-di-ammonium dibromide).
MPS-4: The same conditions as for MPS-2 were used and CTAB was replaced with an equal molar amount of a cationic gemini surfactant with two C_{12} chains and with a C_2 linker (N,N′-didodecyl-N,N,N′,N′-tetramethyl-N,N′-ethanediyl-di-ammonium dibromide).
MPS-5: The same conditions as for MPS-2 were used and CTAB was replaced with an equal molar amount of the nonionic surfactant Ethylan 1008 ($C_{10}E_8$).

The chemical structures of the four surfactants are shown in Fig. 1.