



Colloidal liquid aphrons directed growth of sol–gel silica exhibiting bimodal porosities



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ARTICLE INFO

Article history:

Received 1 November 2012

Received in revised form

19 May 2014

Accepted 7 April 2015

Available online 17 April 2015

Keywords:

Colloidal liquid aphrons (CLAs)

Porous silica

Interfacial confined hydrolysis

–condensation

ABSTRACT

We report a new method to prepare bimodally porous, macroporous–mesoporous silica materials utilizing TEOS co-constructed template with colloidal liquid aphrons (CLAs). The macroporous and mesoporous texture of obtained silica is characterized using a combination of fluorescence microscopy, SEM, TEM, and nitrogen volumetric adsorption analysis. The appearance of macropores is attributed to the interfacial confined hydrolysis–condensation of silica source where as the mesopore formation is consistent with the pores resulting from the compact packing of nanometer silica particles under weak base-catalysed reaction condition. This bimodally porous silica materials can be prepared either as monoliths or as isolated spherical particles by adjusting the TEOS concentration in the oil phase.

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1. Introduction

Multiply porous materials combining the benefits of each pore size regime—larger pores allow for better molecular accessibility and convective mass transfer while the smaller pores provide high surface areas and large pore volumes [1–3]. The shape of those materials included monolith, xerogel, membrane and sphere. Therefore, such materials have attracted much attention owing to their potential applications in large molecule catalysis [4,5], bimolecular separations [6], and chromatographic supports [7]. The template method along with a mild sol–gel process is the main approach for the preparation of hierarchical porous silica [8], and those templates could be hard, soft and dual ones. For instance, water-insoluble polystyrene (PS) microsphere as a hard macropore template and amphiphilic surfactant as a soft mesostructural template has been used to prepare macroporous/mesoporous silica materials [9]. Microgel as soft template was developed and hierarchical porous materials of the composite microspheres of PAM/TiO₂, and poly (NIPAM-co-AA)/SiO₂ were successfully obtained [10,11] in our group. Foams such as commercial polyurethane (PU) were also used as a macrostructure scaffold and trilock copolymer Pluronic P123 as a mesostructure template to prepare hierarchically porous silica materials via economical pathway [3].

Emulsion as simple and feasible templates including the use of oil/water (O/W), water/oil, solid silica sphere stabilized, w/o/w and high internal phase emulsions (HIPREs) to design macroporous–mesoporous silica have been reported [2,12–14].

In this present paper, we demonstrate the use of colloidal liquid aphrons (CLAs) to direct the growth of silica. The structure of CLA was first proposed by Sebba [15], who suggested that polyaphron phases (the aggregate of CLAs) resemble a biliquid foam while the individual CLA, stabilized by a mixture of non-ionic and ionic surfactants, dispersed in a continuous aqueous phase, consists of spherical, micron-sized oil droplets surrounded by a thin aqueous “soapy-shell”, as shown in Fig. 1. Based on the CLA structure, the macroporous materials should be achieved after sol–gel silica “transcription” by such emulsions, and in this paper we provide proof-of-principle demonstrations for the above research design. The principle about this approach was shown in Scheme 1.

Previously, the use of colloidal aphrons to produce macroporous silica has been reported [16,17]. In those studies, the aphrons were prepared by entraining air in the surfactant solution producing foam template [16,17]. Such research results provide possibility for the construction of macroporous silica using “colloidal liquid aphrons (CLAs)” as template, such as explored herein. A significant advantage of CLA as template is that it allows the introduction of TEOS into oil phase when template was prepared and it also enable silica to deposit from inside to outside. In such way the morphology of CLA can be maintained to the maximum. Fortunately, such macroporous silica materials were prepared in

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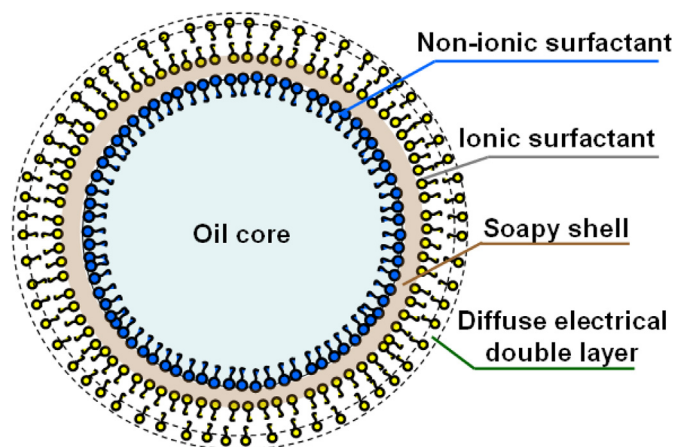


Fig. 1. Structure of colloidal liquid aphrons (CLAs) proposed by Sebba.

this paper. Moreover, uniform mesopores were found in this research under mild base-catalyzed sol–gel process. The formation of those mesopores in the macroporous walls is attributed to the compact packing of nanoscale silica spheres, which also designed synthesized in our previous work when microgel was used as soft template to develop hierarchical porous materials of the composite microspheres of PAM/TiO₂, and poly (NIPAM-co-AA)/SiO₂ [10,11].

To explain the formation of macro–mesoporous silica materials based on the experimental results provided by fluorescent microscope, SEM, TEM, and nitrogen volumetric adsorption analyzer, we proposed a mechanism of *interfacial confined hydrolysis–condensation of TEOS*. This method described here offers a new and feasible strategy for the creation of a widely applicable, general class of hierarchically porous materials.

2. Experimental

2.1. Materials

n-decane (C.P.) as an oil phase was purchased from Beijing Chemical Reagent Corporation. Sodium dodecyl sulphate (SDS, C.P.) as anionic surfactant, anhydrous ethanol (95%, A.R.) as a washing reagent, ammonium hydroxide (25%, AR) as catalyst, tetraethoxysilane as a silica source TEOS (98%) were purchased from Xi'an Chemical Reagent Corporation. Triethylene glycol monododecyl ether, C₁₂E₃, as non-ionic surfactant was obtained from Xingtai Lanxing Auxiliary Factory. The water used in this study was deionized and doubly distilled.

2.2. Preparation of colloidal liquid aphrons (CLAs) emulsion

The recipe of CLA synthesis was made referring to the method described by Matsushita et al. [18]. In the first stage, an aqueous phase was prepared by dissolving SDS in water (0.5% g/mL) at the ambient temperature and kept stirring at 800 rpm in order to generate rich bubbles. Then, an oil phase *n*-decane containing C₁₂E₃ (1% V/V C₁₂E₃ in *n*-decane) was added in the above water phase under vigorous stirring, until the volume ratio of the oil phase to water phase defined as PVR in the emulsion is 2.5.

2.3. Synthesis of CLA-derived silica

In order to introduce the silica source, TEOS was added with ratio of $V_{n\text{-decane}}/V_{\text{TEOS}} = 7:3$ into the oil phase as described above mentioned. Then the aqueous phase prepared was added to the prepared oil phase under vigorous stirring as step 2.2 stated, as a result, the CLA emulsions containing TEOS as part of oil phase were obtained. The silica deposition was initiated when ammonium hydroxide or acetic acid (as a contrast experiment) as the catalyst was added by a stepwise method to the emulsion. The resultant emulsions were “aged” for 4 days at room temperature with continuously stirring to guarantee the full hydrolysis and condensation of TEOS. Then the aimed hierarchically porous silica materials could be prepared by ethanol extraction for several times and drying in an incubator at room temperature.

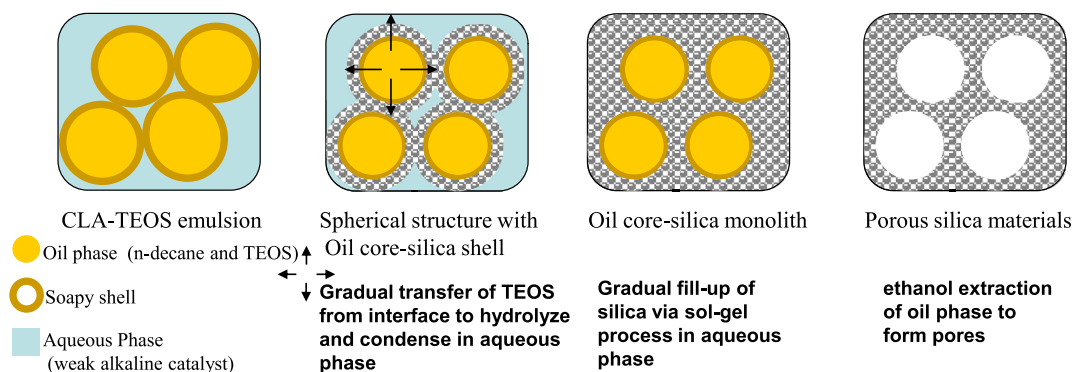
2.4. Characterizations

The droplet size and morphology of CLAs and TEOS-CLAs under optical and fluorescent emitted conditions were observed using a Leica AF6000LX Inverted fluorescence microscope. The morphology of ethanol-extracted dehydrated silica was investigated by a Philips XL-20 scanning electron microscopy (SEM), using an accelerating voltage of 30 kV. To analyze the structure of the silica wall, samples were dispersed in ethanol and observed under a Hitachi H-600 transmission electron microscope (TEM) at an acceleration voltage of 10 kV. Nitrogen adsorption isotherms were obtained at –196 °C using a volumetric adsorption analyzer ASAP2020 manufactured by Micromeritics.

3. Results and discussion

3.1. Observation of colloidal liquid aphrons (CLAs) emulsion

The light micrographs of CLAs emulsions were shown in Fig. 2A. The droplets can be forced into contact with each other when the internal phase volume is greater than 75% v/v. The overall



Scheme 1. Artistic illustration of CLAs directed silica cellular construct via interfacial confined hydrolysis–condensation of TEOS.

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