Materials and Design 111 (2016) 206–212

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Facile synthesis of asymmetrical flower-like silica

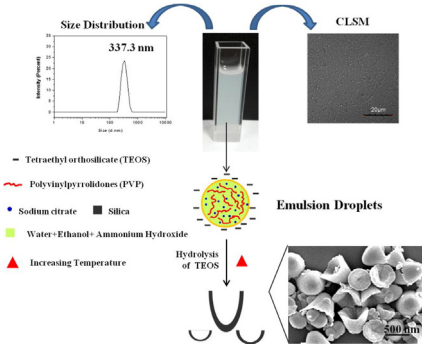
Jing Wang, Yan Lu *

Key Laboratory of Display Materials & Photoelectric Devices, Ministry of Education, Tianjin Key Laboratory for Photoelectric Materials and Devices, School of Materials Science & Engineering, Tianjin University of Technology, Tianjin 300384, PR China

HIGHLIGHTS

- Asymmetrical flower-like silica is synthesized by biosilicification.
- The morphology was determined by the reaction temperature.
- The growth mechanism is proposed based on scanning electron microscopy images.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 May 2016
Received in revised form 30 August 2016
Accepted 31 August 2016
Available online 01 September 2016

Keywords:
Silica
Asymmetrical particles
Flower-like
PVP

ABSTRACT

Synthesis of non-spherical silica micro-/nano-particles is an essential and interesting research topic for their unique property and potential application in biomedicine. Herein, an new asymmetrical flower-like silica with size ranging from about 200 nm to 600 nm was prepared by simply changing the reaction temperature in the water/polyvinylpyrrolidone (PVP)/*n*-pentanol system. Further, the effect of reaction conditions including temperature, concentration of sodium citrate and average molecular-weight of PVP on the morphology of the resultant silica was studied in detail. The growth mechanism of flower-like silica is proposed based on SEM images with different reaction times. This work provides a facile method to fabricate anisotropic silica which may find its application in drug delivery.

1. Introduction

Non-spherical micro-/nano-particles have attracted great attention due to unique property and potential application in drug delivery [1–3]. A lot of reports have shown that the micro-/nano-particle shape is an important factor for delivery efficiency [4–10]. For example, mesoporous silica nanoparticles (MSNP) with an aspect ratio of 2.1–2.5 can be taken up in larger quantities by HeLa cells in vitro compared to the shorter or longer silica nanorods [5]. The long MSNP can be used as ideal antioxidant carriers to protect cells from oxidative injury [8]. Gold nanorods exhibit longer circulation time in the blood, and higher accumulation in the tumors compared with their corresponding spherical counterparts [9]. Comparing with sphere micelles, rod-shaped micelles also show the enhanced therapeutic efficacy with the elimination half-life of ≈18-fold longer than that of free drugs, which results in a higher rate of accumulation in tumor tissues [10]. The stiff polystyrene micro-particles with different shape were phagocytized by alveolar macrophages depended on the contact angle with cells [11]. Cylindrical polymer particles with dimensions of 450 nm × 150 nm

* Corresponding author.
E-mail address: luyan@tjut.edu.cn (Y. Lu).

http://dx.doi.org/10.1016/j.matdes.2016.08.093
0264-1275/

(aspect ratio = 3) were internalized by HeLa cells at a rate 4 times faster than those with dimensions of 200 nm × 200 nm (aspect ratio = 1) [12]. To date, various non-spherical micro-/nano-particles such as mesoporous silica nanoparticles, Au nanoparticles, polymer particles, cylindrical polymer brushes, polymer micelles have been prepared for optimizing drug delivery efficiency. Among them, silica material received extensive attention because of its ease of synthesis, non-toxic, good biocompatibility. Various silica micro-/nano-particles with different morphologies including sphere [13–15], cube [16], tubes [17–19], rods [20–23], hollow sphere [2,24–27], and core–shell complex [28–30] etc. have been successfully fabricated through Stöber process, template methods or biosilicification. But, the development of new method to achieve non-spherical silica particles with novel shapes is still desired for efficient delivery platform.

Bioinspired silicification is one of the most promising ways to achieve some unique silica structures such as tubes [31], plates [32], helical ribbons [33], doughnuts [34], chiral structure [3,35]. In this method, different additives such as polypeptides, polysaccharide, proteins, peptides, enzymes, synthetic polymers, even small molecules, may facilitate the formation of various silica nanostructures by catalyzing, promoting aggregation, providing scaffoldings or a combination of these mechanisms [36,37]. Recently, Yang et al. designed a one step method to form a protective silica shell on yeast cells using a short peptide adsorbed on the surface of cell to catalyze the silicification of tetraethyl orthosilicate (TEOS) on the cell surface [38]. Li et al. prepared Janus silica hollow spheres via interfacial biosilicification using the oil-in-water (O/W) emulsion formed by poly(ethylene glycol)-*b*-poly(L-lysine)-*b*-poly-(styrene) as template [26]. As well all known, polyvinylpyrrolidone (PVP) has been widely used as a stabilizer and structure-directing agent to synthesize ZnO [39] and Au [40–42] nanoparticles with different morphology. Zhang et al. had successfully prepared a series of nanoparticles of ZnO and SiO_2 with different morphologies in water/PVP/*n*-pentanol (WPN) system. In the procedure, Au nanoparticles stabilized by the sodium citrate, coordinated with PVP–water molecules to form aggregations, were used as soft template to control the morphologies of the resulting nanoparticles [43]. Similarly, Anke et al. synthesized the rodlike silica colloids with diameter of 200–300 nm and a length varying from 300 nm to 3 μm by only adding a certain amount of sodium citrate instead of Au nanoparticles stabilized by sodium citrate [22]. In addition, silica Janus particles [44] and hollow silica nanomaterials with different morphologies [2] have also been obtained by adding other precursors with different functional groups or changing the solvents. Recently, Yang et al. also fabricated bent rigid silica rods using WPN system [23].

Inspired by these pioneering works, we synthesized an asymmetrical flower-like silica by changing the reaction temperature in the WPN system in the presence of sodium citrate. The effect of the concentration of sodium citrate and the average molecular weight of PVP on the formation of silica were also carefully investigated. Further, the growth mechanism of flower-like silica was proposed based on SEM images with different reaction times.

2. Experiment

2.1. Materials

Polyvinylpyrrolidones with various average number-molecular weight were purchased from Aladdin (M_n = 8000), Sigma-Aldrich (M_n = 40,000) , Alfa (M_n = 58,000) and Beijing Chemical Reagent Company (M_n = 30,000) , respectively. *n*-pentanol (99%) was provided by Sigma-Aldich. Tetraethyl orthosilicate (TEOS), ammonium hydroxide (28–30 wt%), sodium citrate tribasic dihydrate and anhydrous ethanol were analytical grade and were obtained commercially and used as received unless otherwise mentioned.

2.2. Instruments

Scanning electron microscopy (SEM) was carried out on a JEOL 6700 instrument at 5 kV and 10 mA. The dispersed sample was dropped onto a silicon substrate and dried at room temperature. Platinum ultrathin film was coated on the surface of sample before SEM observation. Laser scanning confocal microscopy (LSCM) images were taken with an Olympus FV1000-IX81 confocal system. The dispersed sample was dropped between two slides and sealed with nail polish before observation.

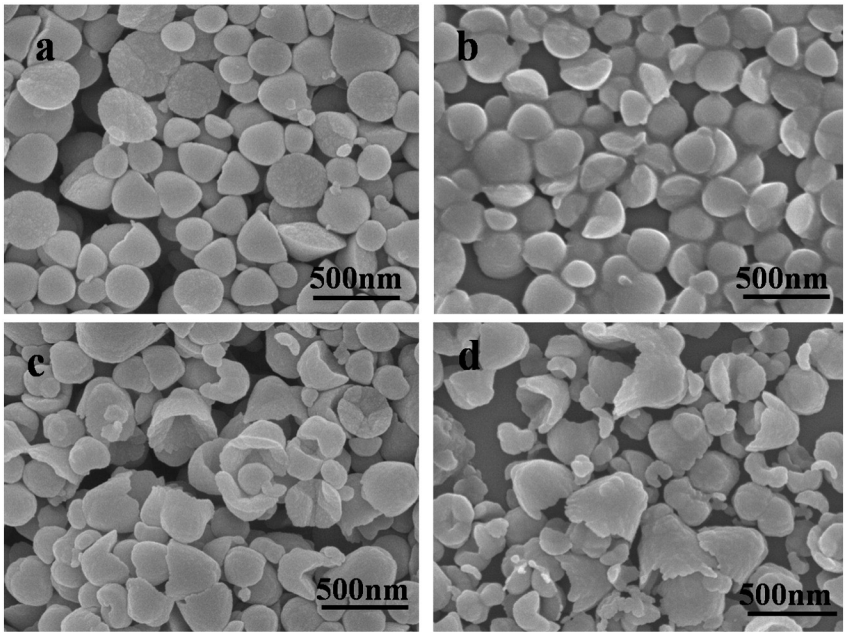


Fig. 1. SEM images of asymmetric silica synthesized under different temperature: a, 28 °C; b, 40 °C; c, 50 °C; d, 80 °C; PVP (M_n = 40,000, 0.6 g). The concentration of sodium citrate was of 0.34 M.