Materials Letters 206 (2017) 150–153

Contents lists available at ScienceDirect

Materials Letters

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

Self-templated route to synthesis bowl-like and deflated balloon-like hollow silica spheres

Yubing Dong [a,*], Enliang Wang [a], Lujun Yu [a], Rui Wang [a], Yaofeng Zhu [a], Yaqin Fu [a,*], QingQing Ni [a,b]

[a] Key Laboratory of Advanced Textile Materials and Manufacturing Technology Ministry of Education, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, China
[b] Department of Functional Machinery and Mechanics, Shinshu University, 3-15-1 Tokida, Ueda 386-8576, Japan

ARTICLE INFO

Article history:
Received 5 April 2017
Received in revised form 13 June 2017
Accepted 2 July 2017
Available online 3 July 2017

Keywords:
Hollow silica sphere
Freeze-drying
Particles
Powder technology

ABSTRACT

Hollow silica spheres (HSS) have attracted considerable attention in recent years because of their unique physical and chemical properties, as well as can be used for wide range potential applications. In this study, a novel HSS was successfully synthesized via silica sol self-templated route and vacuum freeze-drying assistant method. The experimental results revealed that the HSS exhibited bowl-like and deflated balloon-like morphology structure and thin sphere shell was approximately 30 nm. The particle size of the HSS was almost between 0.20 and 2.50 μm. The possible mechanism for the formation of the HHS was discussed and proposed.

1. Introduction

Hollow silica spheres (HSS) have been attracting a great deal of attention for potential application in catalysis loading, drug delivery, energy storage, pigments, electronics, and environmental remediation [1–6], because of their biocompatibility, chemical inertia, low density, high specific surface area, excellent thermal insulation and mechanical stability, easy functionality, and optical scattering properties.

The development of synthetic methodologies of the HSS has been studied in great detail. Various methods, including the self-assembly method [7,8], emulsion technology [9,10], and template-based technique [6,11], have been reported in the literatures. Template-based method is the most commonly used method, which includes hard template and soft template. However, hard template (such as, inorganic spheres and metallic components) requires a long preparation time and complex. Alternatively, soft template (such as, surfactant micelles and emulsion droplets) requires surfactant [6]. Therefore, developing a simple and auxiliary-free (no surfactant, organic or inorganic components) method for synthesis of HSS is desired.

In this paper, we reported a novel auxiliary-free synthesis method of HSS via silica sol self-templated route and vacuum freeze-drying assistant technology. The morphology, chemical structure and particle size distribution of the as-synthesized HSS were investigated by SEM, TEM, FTIR, Coulter DELSA Nano, XRD, XPS, and EDS, respectively, and a possible formation mechanism of the HSS was discussed and presented.

2. Experimental section

Preparation of HSS: A three-step procedure was conducted to prepare HSS, as shown in Fig. 1. Firstly, tetraethoxysilane (TEOS, 2.000 g), absolute ethanol (10.000 g), and *p*-toluene sulfonic acid (PTSA, 0.020 g, as catalyst) were added into a three necked-flask and stirred under a nitrogen atmosphere at room temperature for 30 min. Secondly, the silica sol was pour into a mesh nebulizer carefully. And the silica sol droplets were produced by the mesh nebulizer near the top of a stainless steel cup filled with liquid nitrogen stirred at a high speed. Then, enough deionized (DI) water was poured into the stainless steel cup. Once the mixture frozen, the stainless steel cup was placed into a freeze-dryer (Labconco Freezone freeze-dryer system, Labconco 7400030, USA) immediately and the frozen solution was freeze-dried under 0.1 mbar at −55 °C for 7 days. Finally, the resulting HSS powder was obtained.

Characterization: The morphology and elements of the HSS were conducted under a field emission scanning electron microscope (FESEM, Ultra 55, Zeiss, Germany) equipped with an energy-dispersive X-ray spectrometer (EDS, Oxford, United Kingdom) and operated at voltage of 3 kV and 10 kV, respectively. The inner microstructure of the HSS were examined under a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) operated at

* Corresponding authors.
E-mail addresses: dyb19831120@zstu.edu.cn (Y. Dong), fyq01@zstu.edu.cn (Y. Fu).

http://dx.doi.org/10.1016/j.matlet.2017.07.016
0167-577X/

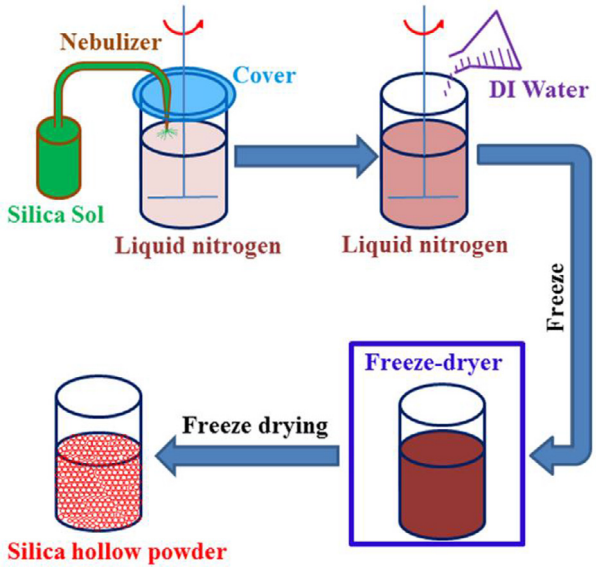

Fig. 1. Schematic for preparation of HSS.

200 kV. Fourier transform infrared (FTIR) spectra (resolution 4 cm^{-1}) were recorded after the samples were obtained as KBr pellets, with a KBr beam-splitter and KBr windows on a Thermo Nicolet 5700 spectrometer (Thermo Electron Corp., USA) at room temperature. The sample dried at 105 °C and cooled to room temperature under vacuum and then mixed with KBr to form a pellet. The particle size distribution of the HSS was determined using a dynamic light scattering system (Coulter DELSA Nano, Beckman-Coulter Co., Ltd., USA). A drop of the HSS suspension sample (about 5 μL) was diluted with 5 mL of DI water. The diluted HSS suspension was further dispersed by water bath ultrasonic machine for 15 min, and placed it immediately inside the sample holder of Coulter DELSA Nano. The phase structure of the sample was characterized by X-ray diffraction (XRD, Bruker AXS D8, Germany) using Cu Ka (k = 1.5406 Å) radiation at 40 kV. The X-ray photoelectron spectroscopy (XPS) spectra of the sample were measured on a Kratos AXIS Ultra DLD XPS (Kratos, UK) using aluminum Kα (1486.6 eV) as the X-ray source operated at 15 kV.

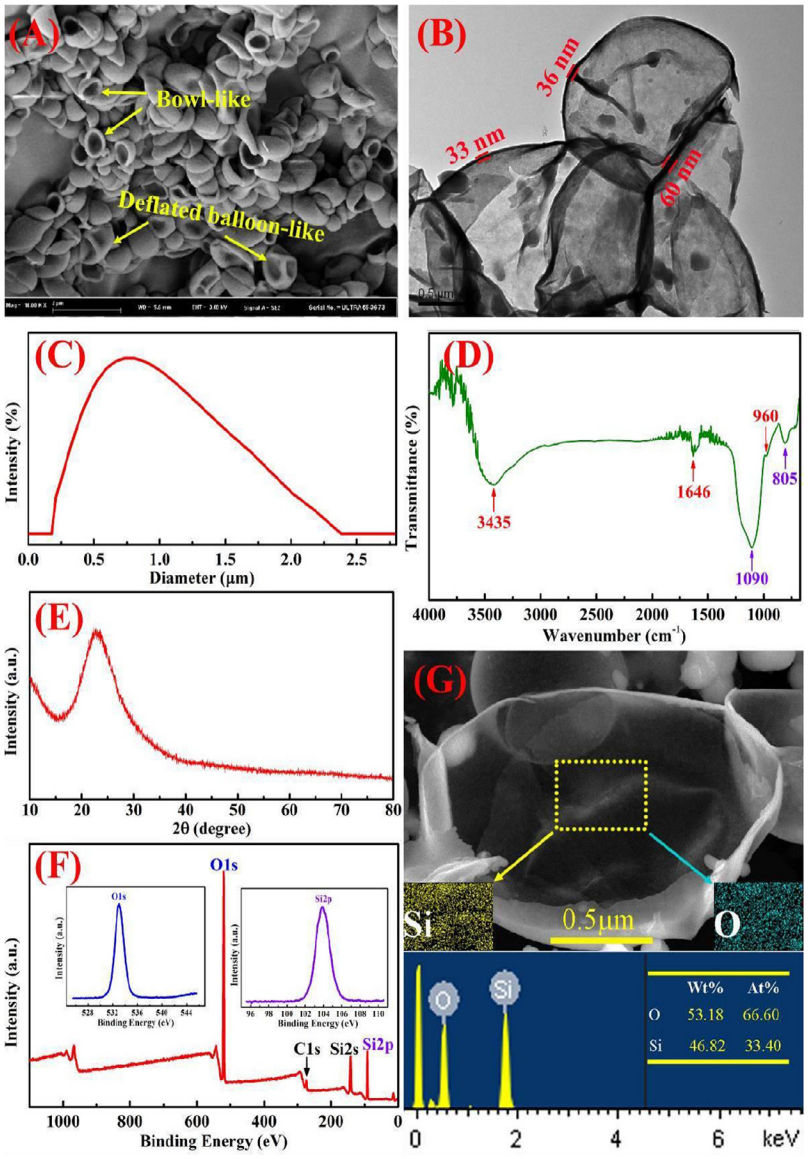

Fig. 2. (A) FESEM image; (B) TEM image; (C) particle size distribution; (D) FTIR spectra; (E) XRD spectra; (F) XPS spectra; and (G) EDS spectra of as-synthesized HSS.