Chemical Engineering Journal 292 (2016) 139–146

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Novel inkjet droplet method generating monodisperse hollow metal oxide micro-spheres

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HIGHLIGHTS

- Inkjet system was used to generate hollow metal oxide particles.
- PSL particles as template material were evaporated by heating.
- Hollow particles have 41–85 nm sized pores on the surface.
- Hollow particle size can be controlled by adjusting droplet size.
- Hollow TiO_2 was demonstrated as a photoelectrochemical cell.

ARTICLE INFO

Article history:
Received 17 September 2015
Received in revised form 1 February 2016
Accepted 6 February 2016
Available online 9 February 2016

Keywords:
Inkjet system
Drying module
PSL
Metal oxide nanoparticles
Hollow sphere

ABSTRACT

A novel method to synthesize monodisperse hollow TiO_2, SnO_2 and ZnO microspheres was developed. Water droplets generated from an inkjet nozzle contain clusters of polystyrene latex (PSL) particles covered with metal oxide nanoparticles were continuously dried up forming PSL clusters decorated with metal oxide nanoparticles. By heating the clusters up to 400 °C, the PSL particles are evaporated forming hollow spheres. Monodisperse hollow TiO_2, SnO_2 and ZnO spheres in the size range of 5.1–8.6 μm were consequently generated with a narrow particle size distribution. And the hollow TiO_2, SnO_2 and ZnO spheres have 41.0 nm, 30.0 nm, and 85.3 nm sized pores, respectively. The method enables us to have simpler and faster process to generate hollow TiO_2, SnO_2 and ZnO spheres and to control the diameter of hollow spheres easily by adjusting waveform applied to a nozzle compared to other processes. A potential applicability to photoelectrochemical cells was demonstrated for the prepared hollow TiO_2 grown a Si substrate.

1. Introduction

Hollow micro/nano structures are of great interest in many current and emerging areas of technology. The large fraction of void space in hollow structures has been successfully used to encapsulate and to control the release of sensitive materials such as drugs [1] and DNA [2]. Also, the void space in hollow particles has been used to modulate refractive index, to lower density, to increase active area for catalysis, and to improve the particle's ability to withstand cyclic changes in volume [3], and to expand the array of imaging markers suitable for early detection of cancer [1]. Especially, hollow TiO_2 and SnO_2 spheres provide high porosity [4] and photovoltaic [5], and hollow ZnO spheres provide photocatalytic properties [6]. Hollow TiO_2 and SnO_2 spheres were used for gene delivery [2], hydrogen production and storage [4], and rechargeable batteries [5]. Hollow ZnO spheres were used for catalysts, gas sensors, and photonic devices [6].

Synthetic strategies for hollow structures are broadly categorized into four methods, such as conventional hard templating method [7] and soft templating method [8], as well as newly emerging methods based on sacrificial templating method [9] and template-free method [10]. In hard templating method, monodisperse silica particles and polymer latex colloids are commonly employed as the hard template. These templates are advantageous for several reasons including narrow size distribution, and availability in a wide range of sizes from commercial sources. The hard templating method is advantageous due to its simple synthesis process but disadvantageous for requiring special care of the

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http://dx.doi.org/10.1016/j.cej.2016.02.021
1385-8947/

shells during template removal. In soft templating method, the liquid character and deformability of emulsion droplets provide important advantages for hollow particle synthesis. Compared with solid templates, the liquid cores can be easily removed by low-stress-generation process. However, the attachment of solid particles to soft template is a complex process. In sacrificial templating method, template itself involves as a reactant in the synthetic process. The process is efficient when the sacrificial template is completely consumed during the reaction. However, the disadvantage of sacrificial template is the high level of impurities. Template-free method is called self-assembly or self-aggregate approaches. In template-free method, hollow core/shell structures can be prepared by simply adjusting the synthetic conditions. But, it takes long time to produce hollow particles [1].

Especially, metal oxide hollow spheres were produced by various methods. Using hard template method, hollow TiO_2 [11], SnO_2 [12] and ZnO [13] spheres were produced with the diameters of 250–400 nm, 700 nm and 200 nm–1 μm, respectively. Hollow TiO_2 [14] and Cu_2O_8 spheres were produced by soft template method, and the outer diameters of the hollow spheres are 3–20 μm and 100–250 nm, respectively. Hollow Cu_2O and ZnO [15] spheres produced by sacrificial template method have the outer diameters of 1–5 μm. TiO_2 [16] and Cu_2O [17] produced by template-free method have the size range of 200–500 nm in outer diameter. The hollow particle size is affected by template size in hard template method, reaction time in sacrificial method and free-template method, and temperature in soft template method.

But, using the above mentioned hard templating methods are time consuming to generate hollow particles. In previous studies, a method of hard template to generate hollow TiO_2, SnO_2 and ZnO particle takes a long time to dry ethanol to make PS@TiO_2, PS@SnO_2, PS@ZnO powder. In the case of TiO_2, polystyrene-acrylic acid (PSA) and tetrabutyltitanate (TBOT) and hard template were washed three times with anhydrous ethanol and heated in vacuum oven at 90 °C for 12 h, and dried PSA and TBOT and hard template were calcinated in a furnace at 500 °C to generate hollow structure [18]. In the case of SnO_2, The tin oxide (SnO_2) coated polystyrene (PS@SnO_2) stock solution in ethanol was dried at 50 °C for 24 h. Then, the dried PS@SnO_2 powder was transferred to an air-flow electric oven at 450 °C for 1 h to remove the hard template [19]. Thus, in order to produce hollow TiO_2, SnO_2 and ZnO particles, it took approximately 16–25 h, including a heat treatment process and reaction time. Therefore, one needs a new method that can produce hollow particles rapidly and simply.

In this study, we utilized an inkjet nozzle and a drying module to produce micron sized TiO_2, SnO_2 and ZnO hollow spheres. The inkjet nozzle can control the diameter of a droplet in the range of sub micrometer to 100 micrometer without adversely affecting the chemical properties [20–22] by adjusting the various parameters of the waveform applied to the inkjet nozzle and eject a variety of solution materials. And drying module helps drying process shortly. It is possible to make the hollow particles in the early hours. It takes only 15 min to generate hollow particles. Metal oxides (TiO_2, ZnO and SnO_2) have widely been used as a photoelectrochemical catalyst [23–27]. To show a potential applicability of the prepared samples to a photoelectrochemical cell, an electrochemical work station was used.

2. Experimental methods

A solution (1.4 mL) containing PSL particles (ca. 1 μm) and 0.1 g of TiO_2, SnO_2 or ZnO nanoparticles (NPs) (<150 nm) were mixed in 40 mL of distilled water (2 MΩ cm). Before using the mixture for our experiments, it was treated with an ultrasonic bath for 1 h in 40 °C condition in order to make the mixture well dispersed. The details are described in the Section 3. Field emission scanning electron microscope (JEOL JSM-7000F and Hitachi S-4800) images were taken to examine the particle morphology such as the diameter and pore size of hollow TiO_2, SnO_2 and ZnO particles. SEM image analysis was conducted using Image J software. Information about the chemical composition and hollow structure of the particles can be obtained from EDS (Oxford Instruments INCA X-sight LN2 EDS) analysis with a probe current of 10–9 A, acceleration voltage of 15 kV, and working distance of 10.0 mm conditions. A process of evaporation of PSL particles was observed by using an in situ transmission electron microscope (TEM) (JEM-2011 HR, JEOL) with an accelerating voltage of 200 kV and the heating rate was 20 °C/min that temperature was increased up to 400 °C.

The photoelectrochemical properties were examined using a three electrode electrochemical setup in 0.1 M Na_2SO_4 electrolyte solution, where an Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively. The working TiO_2 electrode was electrically connected with a Cu wire, which was sealed with epoxy. A CH Instruments 660D electrochemical workstation was used under UV (365 nm) light illumination using a Prizmatix MIC-LED-365.

3. Results and discussion

Fig. 1 shows an overall schematic diagram of our experimental set-up. The set-up consists of inkjet droplet generator, heated gas supply and drying module. The inkjet droplet generator has an inkjet nozzle with the diameter of 50 μm (Microfab, MJ-AT 50 μm) and was inserted into the drying module. The inkjet nozzle consists of a glass capillary surrounded by piezoelectric material. When an electric voltage is applied to the piezoelectric material by the function generator, it expands the glass capillary, which results in an ejection of a droplet [28]. In our experiments, the

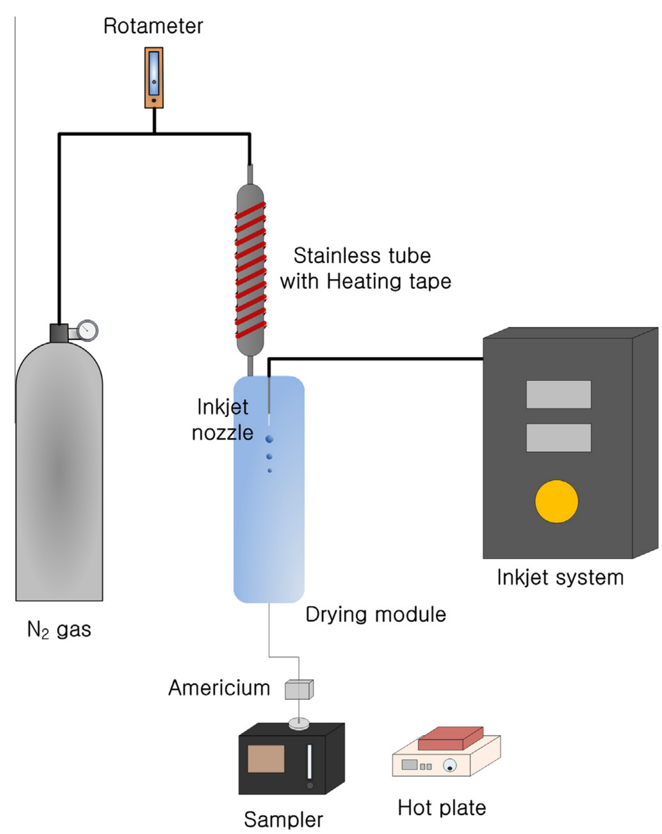

Fig. 1. Schematic of experimental set-up for the generation of hollow particles.