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Invited review paper

Controlled synthesis of porous particles via aerosol processing and their applications

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ABSTRACT

Aerosol processes such as spray drying and/or spray pyrolysis for the controlled synthesis of porous particles were introduced in this review. Typical experimental setup, general experimental procedure for the preparation of porous particles, as well as key factors affecting the properties of final porous particles, was described. We then discussed the various routes for the controlled synthesis of porous particles: (1) the preparation of self-assembled porous particles with ordered pores by using organic template particles; (2) the preparation of pore size- and porosity-controlled particles from aggregated nanoparticles; (3) the preparation of nanoparticle-laden encapsulated porous particles from graphene nano-sheets and nanoparticles. Finally, we introduced interesting applications of the porous particles such as photocatalysts, drug delivery carriers, and biosensors.

Contents

1. Introduction

Porous particles have received substantial attention due to their enhanced physicochemical properties [1,2] and wide potential applications including photocatalysis [3–5], drug delivery [6,7], photonic materials [8], batteries [9,10], absorbents [11], and fuel cells [12,13].

In order to prepare spherical-shaped porous particles, aerosol processing such as a spray drying and/or pyrolysis method provides excellent controllability of pore size, porosity, particles size, and composition. Furthermore, the aerosol spray method is relatively simple and operates very fast. Thus, it is easy to scale up and the mass production of porous particles can be achieved simply [14].

The characteristics of porous particles are mainly determined in the preparation step of the colloidal precursor. Important factors affecting the properties of the final porous particles are size, shape, and aggregation of nanoparticles composing the colloidal suspension. The size and aggregation of colloidal nanoparticles determine the inter-particle pore size. In the case of nanoparticle shape, encapsulated porous particles can be produced when sheet

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particles, e.g., graphene, are used as starting colloidal particles. Additional important factors are the size and concentration of the organic templates such as polystyrene latex (PSL), polymethyl methacrylate (PMMA), and polyethylene glycol (PEG). Pore size and porosity can be tuned by manipulating the size and concentration, respectively, of the organic templates. In addition, a precursor solution with an organic template, e.g., titanium tetraisopropoxide (TTIP) with PSL, can produce porous particles with smooth surfaces after removal of the organic template [15]. Furthermore, a colloidal mixture of nanoparticles and nano-sheets as starting materials can generate porous particles encapsulated by nano-sheets.

In the atomization step, the size of the droplets generated by the atomizer is a key factor in determining the final particle size. Small particles can be fabricated from small droplets [16,17]. Typical atomizers for the preparation of porous particles are an ultrasonic nebulizer and a two-fluid nozzle, which produce droplets with a size of 1–10 μm and 10–1000 μm, respectively [18]. In addition, the physical properties of the colloidal precursor, e.g., the surface tension, viscosity, and density, can also influence the droplet size [17,19–21].

Sequentially, the atomized droplets are carried into a furnace of which the temperature is set to above the evaporation temperature of the solvent and the decomposition temperature of the organic templates; droplets are converted to porous particles. During the droplet-to-particle conversion, the droplet acts as a micro-reactor, in which evaporation of solvent, self-assembly of nanoparticles and nano-sheets, and decomposition of precursor and organic template occur to form the porous particles. For the collection of the as-prepared porous particles, several collectors are available, such as a filter, a cyclone, an electrostatic precipitator, or a combination of these collectors.

An excellent and comprehensive review of the production of controlled morphology particles via spray-drying was reported by Nandiyanto and Okuyama [14]. In addition, aerosol routes to functional nanostructured porous materials were also reviewed by Boissiere et al. [22]. Here, we focus only on the preparation and application of porous particles prepared using aerosol methods. This review is mainly organized into two sections. First, we introduce typical experimental setups as well as general experimental procedures for the preparation of porous particles and discuss the various routes for the controlled synthesis of porous particles, including self-assembled porous particles made using organic templating, pore size- and porosity-controlled particles from aggregated nanoparticles, and encapsulated porous particles from graphene nano-sheets. Finally, we introduce current applications of porous particles such as photocatalysts, drug delivery carriers, and biosensors.

2. Controlled synthesis of porous particles via aerosol processing

Typical schematic diagrams of the experimental apparatus for the preparation of porous particles are shown in Fig. 1. The system consists of an atomizer such as an ultrasonic nebulizer or a two-fluid nozzle for the spraying of the colloidal precursor, an electric tubular furnace for the drying and/or pyrolysis of the colloidal precursor, a particle collector such as an electrostatic precipitator, a cyclone, and a filter. The general experimental procedure for the preparation of porous particles is as follows: 1. Preparation of the colloidal precursor. 2. Spraying of the colloidal precursor into droplets. 3. Droplet-to-particle conversion by evaporation of the solvent and/or pyrolysis of the precursor in the furnace. 4. Removal of organic templates in the furnace. 5. Collection of porous particles.

2.1. Preparation of self-assembled porous particles by organic templating method

The aerosol organic templating method is an excellent and versatile technique to control pore size and porosity. In addition, self-assembling of the organic templates within the micro-reactor, i.e., colloidal droplets, enables the production of porous particles with hexagonally ordered pores [23,24].

Fig. 2(a) shows a schematic diagram for the preparation of porous particles with ordered pores using organic template particles [3,4,15,25–27]. A colloidal suspension containing a mixture of nanoparticles and organic templates, e.g., SiO_2 nanoparticles and PSL particles, was prepared for this technique. Colloidal droplets were sprayed using an ultrasonic nebulizer and were introduced by a carrier gas into an electric tubular furnace having two heating zones. In the low temperature zone, the solvent in colloidal droplets was evaporated, thus resulting in composite particles of nanoparticles and organic templates. During the solvent evaporation of colloidal droplets, the organic templates were self-assembled to form hexagonally close-packed structure within the droplets. As the composite particles were carried into the high temperature zone, of which temperature was set high enough to decompose the organic templates, the organic templates in the composites particles were completely decomposed. The decomposition of the

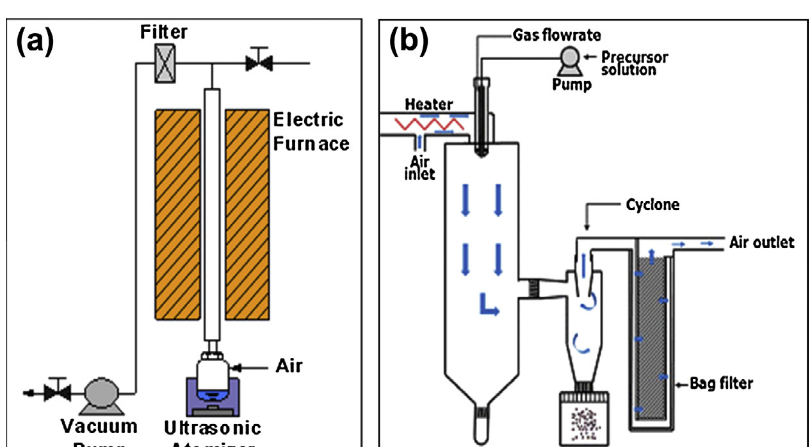

Fig. 1. Typical schematic diagrams of the experimental apparatus for the preparation of pore- and composition-controlled porous particles. Reprinted with permission from Ref. [6].