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Protocols

Porous nano-structured micro-granules from silica-milk bi-colloidal suspension: Synthesis and characterization

Priyanka Biswas[a,e], D. Sen[a,e,*], S. Mazumder[a,e], J.S. Melo[b,e], C.B. Basak[c], Kinshuk Dasgupta[d]

[a] Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085, India
[b] Nuclear Agriculture & Biotechnology Division, Bhabha Atomic Research Centre, Mumbai, 400085, India
[c] Glass and Advanced Materials Division, Bhabha Atomic Research Centre, Mumbai, 400085, India
[d] Materials Group, Bhabha Atomic Research Centre, Mumbai, 400085, India
[e] Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094, India

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ABSTRACT

Synthesis and characterization of nano-structured porous granules, with fairly defined morphology and porosity, is crucial because such granules are widely utilized for various technological applications. However, an easy, one-step, economic synthesis protocol for large scale production is extremely desirable. In the present work, we have reported the synthesis and characterization of the nano-structured micro-granules using aerosol drying of bi-colloidal suspension of nano-silica and milk. Removal of soft organic component from the granules results in formation of meso and macro pores with moderate specific surface area. Granule morphology and porosity depends strongly on the concentration ratio of the individual components in the drying aerosol as well as the interaction between them.

1. Introduction

Over the years, porous materials [1] have found numerous applications in technology and in everyday life [2–9]. In this regard, synthesis of material with defined shape, pore size and specific surface area are indeed desirable, as these attributes determine their utility for specific application. The common synthesis protocols [10–17] of porous materials are often complex, utilize expensive chemicals and involve significant energy consumption. Many a times, the materials are obtained as monolith but not as defined shaped granules. Furthermore, even though many syntheses of nano-porous materials are quite successful at smaller scale in laboratory, they become extremely difficult to upscale. This necessitates a cost effective and fast synthesis process, preferably using inexpensive raw materials. The optimization of process-parameters, as well as the choice of material, is indeed crucial for improving their functional characteristics. Meso/macro porous silica micro-granules have been considered fascinating for various technological applications [18]. Such granules are used even in everyday commodities, such as abrasives in toothpaste [19], anti-caking agent in various powdered food items [20] or as fragrance and flavor carriers [21,22].

Spray drying [23,24], a well established method in food and pharmaceutical industries, have proved to be a reliable technique for synthesizing nano-structured micro-granules [25] in recent times. It is worth mentioning that this is a cost effective, one step and energy efficient protocol where atomized colloidal droplets are transformed almost instantaneously into desiccated powder granules. The associated assembly of the colloidal particles [26–30] in a drying aerosol droplet, as induced by solvent evaporation, results in formation of micro-meter sized powder granules constituting of inter-locked nanostructures [23–27]. Several physico-chemical properties [25,28,29], such as interaction among the colloidal particles [29], rapidness of drying [31], etc. govern the ultimate morphology of the formed granule and the correlation among the constituent nanostructures. Needless to say, such aerosol drying method can be implemented for bi-colloidal suspension (i.e., stable mixture of two colloids) to obtain composite nano-structured

* Corresponding author at: Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085, India.
E-mail addresses: debasis@barc.gov.in, debasis.sen@gmail.com (D. Sen).

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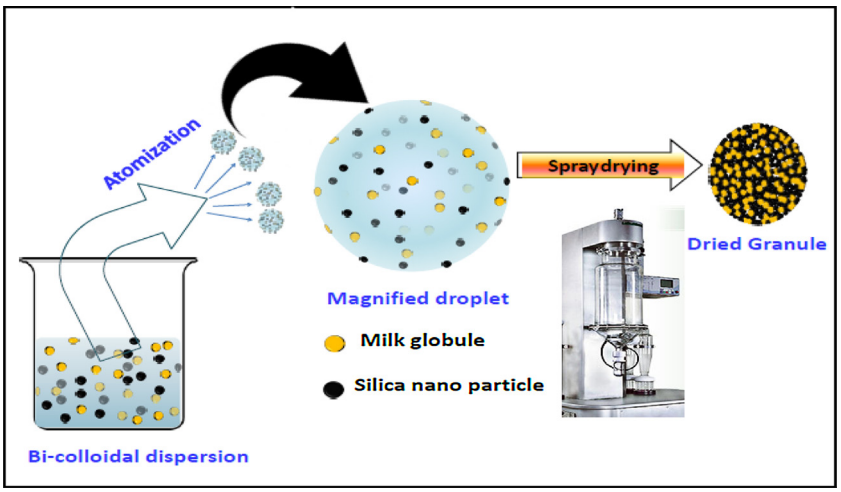

Fig. 1. Schematic diagram showing the synthesis method, spray drying.

granules [26]. Removal of one of the components from such two component system would ultimately form porous granule [32] having interlocked correlated nano-particles as the skeleton.

According to IUPAC convention [33], pores are classified in three categories, namely, micro (<2 nm), meso (2–50 nm), macro (>50 nm). In general, for preparation of meso-porous materials, micelles, polymer or liquid crystal etc. are used as templates [34–41] while for macro porous materials, use of bacterial templates [30] has also been reported. As the size of the formed pore is governed by the size of template [38,40,42], it is often difficult to incorporate hierarchical pore-systems (*i.e.*, combination of meso as well as macro pores in the same material) just by using single template. From the application point of view, as in case of catalysis, the active sites are often located in the micro-pores and meso-pores, while the macro-pores aid mass transfer. Thus, an economic and facile process, such as, aerosol drying proves advantageous to synthesize porous materials with hierarchical pore sizes using single template.

The use of nano-silica in industry is ubiquitous. Colloidal silica is widely used because of its thermal stability, ease of functionalization [43] and bio-compatibility. In our present work we have used nano-silica as the hard component and milk as the soft component of the bi-colloidal suspension. Thus, nano-silica constitutes the skeleton of the synthesized granules while milk acts as template. It should be noted that the choice of the soft component is indeed crucial when the objective is to incorporate hierarchical pore structure in the granules. Milk in its natural colloidal form has several soft constituents [44,45]. Essentially, it is a complex emulsion containing fat globules and casein micelles, which remain suspended in an aqueous phase. Shear during the atomization process during spray drying can partially break the relatively large sized globules as well as agglomerates into smaller forms. Moreover, the re-agglomeration of fraction of these broken units during sol to powder transition can lead to larger agglomerates as well. Thus, depending on the initial milk concentration in droplet, both meso and macro pores are templated in the porous granules.

2. Experimental

30% by weight of HS-40 silica nano suspension [LUDOX®, Sigma Aldrich, USA, ζ potential ∼ − 48 mV], and VISA silica nano suspension [M/S. VISA Chemicals, Mumbai, India with two types of silica: one with ζ∼ − 44 mV and other with ζ ∼ +53 mV] were diluted to 2% by weight dispersion by adding distilled water. Amulya brand of milk powder [Gujarat Co-operative Milk Marketing Federation Ltd., Anand, India] was mixed with distilled water to make 1, 2 and 3% by weight emulsions (ζ ∼ − 35 mV). The total fat-content of the milk powder was 20% (http://www.amul.com/products/amul-amulya-info.php). 2% by weight colloidal HS40 was mixed with the milk emulsions (1, 2 and 3%) separately to make three types of bi-colloidal dispersions. VISA silica with +ve ζ and −ve ζ (2% by weight) were also mixed to 2% by weight milk suspension individually to make another two separate bi-colloidal suspensions. For convenience, the bi-colloidal granules with HS40 will be referred to as S-H1, S-H2, and S-H3 for 1, 2, and 3% of milk in the granule respectively. Similarly, 2% by weight milk composite with VISA silica of +ve ζ and −ve ζ will be referred to as S-VP and S-VN, respectively. Each of these bi-colloidal solutions was prepared as 100 mL precursor solutions for aerosol drying. Spray dryer, LU-228 (LABULTIMA, India) was used for this purpose. The precursor solution was fed into an atomizer at a constant feed rate of 2 mL min^{-1}. The atomizer nebulizes the suspension into tiny aerosol droplets with an average diameter of 10 μm [31]. A constant aspirator rate and inlet temperature of 160 °C was maintained throughout the synthesis processes. The resulting powder granules were ultimately collected in a glass cyclone separator. For reference and comparison, pure silica dispersions (2% by weight) for HS-40, VISA (+ve ζ) and VISA (-ve ζ), were also subjected to aerosol drying under the identical drying conditions. The synthesis technique for composite granules is presented schematically in Fig. 1.

Removal of milk from the resulting composite granules after spray drying was attempted by two different processes: i) washing the freshly spray-dried granules (500 mg) with 50 mL of 10% (v/v) hydrogen peroxide solution where the aliquots were kept overnight under continuous stirring. The granules were recovered after disposing off the clear decants ii) the samples were calcined at 450 °C for about 7 h to remove the template component through thermal treatment. Field-Emission Scanning-Electron Microscopy (FESEM) experiments were performed on the porous granules using Carl Zeiss Auriga FESEM model. Micrographs were obtained for the granules before and after peroxide treatment as well as calcinations. Fourier Transform Infrared (FTIR) spectroscopic analysis was carried out for all the composite granules, as well as for pure silica granules.

Small-angle X-ray scattering (SAXS) measurements was carried out using a laboratory based facility with sample to detector distance of nearly ∼107 cm. Radial averaged scattering data was obtained (accessible wave vector transfer (q) range 0.1–2.0 nm^{-1}). Small-Angle Neutron Scattering (SANS) experiments were carried out using a double crystal based medium resolution small-angle