Colloids and Surfaces A 529 (2017) 696–704

Contents lists available at ScienceDirect

Colloids and Surfaces A

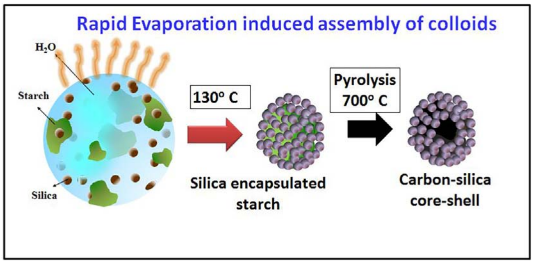
journal homepage: www.elsevier.com/locate/colsurfa

Spray-dried encapsulated starch and subsequent synthesis of carbon-silica core-shell micro-granules

Debashish Sarkar[a], D. Sen[b,d,*], B.K. Nayak[a,d], S. Mazumder[a,d], A. Ghosh[c]

[a] Nuclear Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[b] Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[c] Glass and Advanced Materials Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[d] Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400 094, India

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Encapsulation
Starch
Silica
Core shell
Microgranules

ABSTRACT

Encapsulation is a widely used method to preserve core material from environmental influences and for controlled release of the core material. Here, we demonstrate a fast and facile method to prepare such core-shell microgranules by encapsulating starch with nanometric silica particles using spray drying. The virgin spray dried powder contained silica at shell and starch at the core. The powder granules were pyrolyzed to convert the virgin encapsulated starch granules into carbon-silica core-shell microgranules. The mesoscopic structure of the synthesized microgranules was probed by electron microscopy, scattering techniques and infrared spectroscopy.

1. Introduction

Encapsulation of active ingredients, such as oils [1,2] fatty acids, drugs, food items [3], is a common practice to preserve the core material from unwanted exposure to the environment leading to oxidation, photo-degradation, enzyme degradation etc. Encapsulation of drugs and active ingredients have been implemented for controlled release [4], better thermal stability, improved flowability and to retain nutritional values of the core materials.

Various methods are employed for this purpose [5–7]. Physical processes, such as air suspension coating, centrifugal extrusion, pan coating etc., suffer from various drawbacks which include bigger particles, broad size-distribution and adverse heating effects. Chemical processes like coacervation, lyophilization suffers from drawbacks, such as selective applicability and difficulty in mass production.

Spray drying, a well-established industrial technique, has been used to produce powder granules for food, pharmaceutical and chemical industries. This process is preferred for encapsulation over other techniques as it is faster, more economical and efficient [8–10]. During spray drying process, feed solution containing core and wall material in a solvent, is fed into a hot chamber in the form of atomized droplets. The droplets are then subjected to pass through a hot chamber so that the liquid part of the droplets evaporates rapidly, producing powder granules. The morphology of the spray-dried granules could be

---

[*] Corresponding author at: Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India.
E-mail address: debasis@barc.gov.in (D. Sen).

http://dx.doi.org/10.1016/j.colsurfa.2017.06.054
Received 4 April 2017; Received in revised form 19 June 2017; Accepted 20 June 2017

controlled by controlling various spray drying parameters [11–14]. When the feed solution contains colloidal particles, evaporation induced self-assembly of these particles takes place by the action of the dominating capillary forces over electrostatic repulsion [15]. This phenomenon could be utilized to produce porous shell on the encapsulated core material.

For encapsulation, the choice of wall material is crucial and depends on the particular application. Usually an amphipathic carrier is chosen as wall material for encapsulation. As the droplets start to dry, the hydrophobic part of the amphipathic carrier attaches itself to the surface of the active ingredient. Subsequent drying increases the concentration of the wall material on the surface of the core material and forms a shell, thus achieving encapsulation [16]. Most amphipathic carriers suffer from lack of thermal stability at high temperature [17–19].

In the present work, we propose encapsulation by spray drying using difference in diffusion coefficient due to particle size differences. According to Stokes-Einstein relation, the diffusion of particles in a colloidal solution is related to particle size via the relation $D = \frac{k_B T}{6\pi\eta r}$ where D is the diffusion coefficient of the particle with radius r, η is the viscosity of the solvent, T is absolute temperature and k_B is Boltzmann constant. We propose encapsulation of sub-micron sized starch fragments with nanometric silica by spray drying using the difference in their diffusion due to size difference. Silica nanoparticles are chosen as wall material due to their high biocompatibility [20,21] thermal stability and high surface-functionality because of the presence of ample hydroxyl groups on its surface.

At this juncture, it is worth mentioning that core-shell micro and nanoparticles have been getting much attention lately due to their applicability as catalysts, controlled drug delivery system, efficient energy storage device etc. [22]. Further, core material could be used as a template to produce hollow micro and nanoparticles [23,24]. Noble metal doped silica-carbon core-shell has been used as catalyst [25,26]. Sulfonated silica-carbon core-shell has been used as a catalyst to reduce cellulose to glucose [27]. Surfactant mediated sol-gel method has been used to prepare silica-carbon core-shell [28]. Das et al. have used the hydrophobic nature of carbon black to prepare silica-carbon core-shell microgranules [29].

Here we demonstrate: I) encapsulation of starch by silica nanoparticles in the form of microgranules by spray drying, II) transformation of the encapsulated microgranules into carbon-silica core-shell micro granules by pyrolysis of the virgin encapsulated starch powder in inert gas atmosphere. Mesoscopic structure of these granules has been characterized by electron microscopy and scattering techniques.

2. Method

2.1. Sample preparation

Edible corn-starch was obtained from Agro culture India Private Limited, Gwallor, India. A colloidal suspension of silica nanoparticles (LUDOX TM-40) was obtained from Sigma-Aldrich®. 1 wt% starch and 2 wt.% colloidal silica solution were mixed in distilled water. The solution was heated at 75 °C for 30 min under magnetic stirring. The solution was kept under continuous magnetic stirring during spray drying. A laboratory spray dryer (LU 228, Labultima, Mumbai) was used for this purpose. A compressed air spray-nozzle had been used to produce 10–20 micrometer sized droplets. The inlet temperature was kept at 130 °C with aspiration flow rate 45 m^3/hr. The atomization pressure was kept at 2.5 kg/cm^2 and feed pump flow rate was maintained at 2 ml/min. The spray dried powder was collected in glass cyclone separator. The spray-dried powder was found to be free-flowing and white in color. The virgin powder was pyrolyzed at 700 °C in nitrogen gas atmosphere for three hours. The color of the powder sample turned gray after pyrolization. The pyrolyzed sample was etched using NaOH solution by keeping the powder granules in NaOH solution (5 mol/l) for 24 h under magnetic stirring. After etching, the powder was separated from solution using centrifugation and washed several times with distilled water and ethanol followed by drying in a convection oven.

2.2. Sample characterization

The structural features of the virgin and pyrolyzed powder were probed by small-angle neutron and x-ray scattering (SANS and SAXS) techniques. The scattering profiles were recorded as a function of scattering wave vector transfer which is defined as q = 4πsin(θ)/λ where 2θ and λ are scattering angle and wavelength of either neutron or x-rays, respectively. The overall size of the granules was probed in the low-q region (0.003–0.1 nm^{-1}) using medium-resolution small-angle neutron scattering facility (MSANS) at Guide Tube Laboratory, Dhruva reactor, Mumbai, India [30]. Two silicon (111) single crystals were used as monochromator and analyzer, respectively. The monochromator selects neutrons of wavelength 0.312 nm. The higher q region (0.1–2.0 nm^{-1}) is probed using a laboratory based SAXS instrument having Cu-kα X-ray source (wavelength 1.54 Å). The sample to detector distance was ~1 m. The raw scattering data were corrected for background, transmission, instrumental resolution effects before further analysis.

The morphology of the spray dried granules was examined using Field Emission Scanning Electron Microscope. Direct imaging of the granules were done using Carl Zeiss Auriga FE-SEM model. The electron acceleration potential was kept at 2 KeV.

The DLS measurement had been performed to find out the sizes of starch fragments and silica nanoparticles using Horiba Scientific sz-100. The detector was kept at 173° scattering angle and a solid state laser of wavelength 532 nm was used. The nanoparticles and starch slurry were put in a quartz cuvette for the measurement.

The FTIR spectrum for the samples was collected using Bruker IFS 125HR instrument using Globar source, KBr beam splitter and LN_2 cooled MCT detector. The samples were uniformly mixed (1:20 ratio) with KBr and made into pellets of diameter 13 mm. The radiation was incident normally on the sample. The spectra were taken in transmittance mode. The resolution was 4 cm^{-1}.

The Raman spectra were recorded on a triple stage Raman spectrograph (JobinYvon T64000) equipped with LN_2 cooled CCD detector. A 532 nm laser was used. Raman shift from 15 cm^{-1} to 3200 cm^{-1}had been recorded.

3. Results & discussion

After spray drying, the virgin powder sample was white in color and was free flowing. After calcination at 700 °C in inert nitrogen gas atmosphere, the sample turned gray. When put in water and stirred, the solution looked completely black. As the refractive index of water and silica are close (1.33 for water and 1.47 for silica), silica looked almost transparent and the color of carbon trapped inside silica became predominant.

In Dynamic Light Scattering experiment, light scattered by particles, dispersed in a solvent and going through Brownian motion, is recorded over time. Intensity recorded at a certain time and after some delay time is compared. As bigger particles diffuse slowly the scattered light intensity pattern recorded at two different times would look similar whereas intensity pattern due to smaller particles would vary rapidly due to smaller particle's rapid Brownian motion. If I(t) and I(t + τ) denote scattered intensity at a time t and after certain delay time τ, then intensity autocorrelation function is defined as [31].

$$g_2(q, \tau) = \left\langle \frac{I(t)I(t+\tau)}{I^2(t)} \right\rangle$$