Advances in Colloid and Interface Science 214 (2014) 17–37

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

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

Sol-Gel processing of silica nanoparticles and their applications

Lok P. Singh *, Sriman K. Bhattacharyya, Rahul Kumar, Geetika Mishra, Usha Sharma, Garima Singh, Saurabh Ahalawat

CSIR-Central Building Research Institute, Roorkee, 247667, India

ARTICLE INFO

Available online 6 November 2014

Keywords:
Silica nanoparticles
Sol-gel method
Polymer
Drug delivery system
Nano-engineered concrete

ABSTRACT

Recently, silica nanoparticles (SNPs) have drawn widespread attention due to their applications in many emerging areas because of their tailorable morphology. During the last decade, remarkable efforts have been made on the investigations for novel processing methodologies to prepare SNPs, resulting in better control of the size, shape, porosity and significant improvements in the physio-chemical properties. A number of techniques available for preparing SNPs namely, flame spray pyrolysis, chemical vapour deposition, micro-emulsion, ball milling, sol-gel etc. have resulted, a number of publications. Among these, preparation by sol-gel has been the focus of research as the synthesis is straightforward, scalable and controllable. Therefore, this review focuses on the recent progress in the field of synthesis of SNPs exhibiting ordered mesoporous structure, their distribution pattern, morphological attributes and applications. The mesoporous silica nanoparticles (MSNPs) with good dispersion, varying morphology, narrow size distribution and homogeneous porous structure have been successfully prepared using organic and inorganic templates. The soft template assisted synthesis using surfactants for obtaining desirable shapes, pores, morphology and mechanisms proposed has been reviewed. Apart from single template, double and mixed surfactants, electrolytes, polymers etc. as templates have also been intensively discussed. The influence of reaction conditions such as temperature, pH, concentration of reagents, drying techniques, solvents, precursor, aging time etc. have also been deliberated. These MSNPs are suitable for a variety of applications viz., in the drug delivery systems, high performance liquid chromatography (HPLC), biosensors, cosmetics as well as construction materials. The applications of these SNPs have also been briefly summarized.

Contents

* Corresponding author. Fax: +91 1332 272272.
E-mail address: lpsingh@cbri.res.in (L.P. Singh).

http://dx.doi.org/10.1016/j.cis.2014.10.007

1. Introduction

In the last two decades, material science and engineering has come out with some excellent nanomaterials exhibiting novel features due to their unique physio-chemical properties [1–3]. The preparation of nanoparticles like silica, alumina, titania, zirconia, silicon nitride, silicon carbide with improved properties has been successful in several areas [4–10]. Recent advances in the preparation of SNPs (<100 nm) are focusing the morphological architecture such as spheres, hollow spheres, fibers, tubules, helical fibers etc. At the moment, it is generally accepted that the reduction in size to sub-atomic or nanolevel cannot be achieved with the conventional top-down methods, therefore, the bottom-up approach has been widely accepted as a promising route for preparing nanoparticles. This strategy is faster, precise, energy efficient and therefore, extensive research is going on towards the preparation of nanoparticles through this route. Several techniques are available to synthesize SNPs viz., flame spray pyrolysis, chemical vapour deposition, sol-gel process, micro-emulsion etc., however, among these sol-gel process remains the most popular one, due to its ability to control the size, distribution and morphology of the particles through systematic monitoring of the reaction parameters [11]. In 1864, the term 'sol-gel' was firstly introduced by Graham during his work on silica sols [12]. The sol-gel technique offers a low-temperature method for synthesizing materials that are either purely inorganic or both inorganic as well as organic. The process, based on the hydrolysis and condensation reaction of organometallic compounds in alcoholic solutions, offers many advantages for the synthesis of nanoparticles including excellent control of the reaction kinetics, ease of compositional modifications, customizable microstructure, introduction of various functional groups etc. [13–16]. In the sol-gel process, there are two distinct stages during the synthesis; the first stage is a colloidal suspension of particles in a liquid medium that is referred to as the sol. The particles react with each other forming a cross linked 3D polymeric chain which converts into gel in the second stage [17–19].

A number of modifications/developments in sol-gels process like the use of surfactants/polymers as a template, varieties in precursors, reaction conditions, drying techniques etc. have been reported in recent years [20]. Quaternary ammonium cationic surfactants such as cetyltrimethylammonium bromide (CTAB) were the first used as templates to prepare highly ordered MSNPs. Since the applications of cationic surfactants as template, this method has been widely used to prepare SNPs with high surface area, tunable pore sizes, large pore volume etc.

The MSNPs have a regular porous structure with uniform pore size, large surface area and superior thermal stability, therefore, they are suitable for a variety of applications in the diverse fields such as drug delivery, biosensors, molecular separations, catalysis, HPLC etc. [21–26]. In drug delivery systems, MSNPs have been used as carrier of drug, as guest molecules are simply adsorbed on the mesopore surface of the SNPs. As no functional group acts as a gate to control the release of the loaded substances, the release is controlled either by the size or the morphology of the pores. The MSNPs are the material of interest, as the stationary phases due to their high connectivity, accessibility, defined porous structure and large surface area for HPLC applications. In biosensors field, MSNPs improve the sensitivity and response time of sensors due to their high porosity that allows large amount of sensing molecules encapsulated on the surface for quick response time and low detection limit. Highly dispersed SNPs enhance the thermal, mechanical, optical, abrasion resistance and surface hardness properties of composite coatings. In the construction sector, SNPs are the innovative materials explored to enhance the strength and durability of cement based construction products. The use of SNPs in cement based products leads to three distinct advantages. The first one is the production of ultra high strength and more durable concrete for specific applications. The second, is the reduction of the amount of cement required in concrete of comparable strengths and thereby, decreasing the impact of construction materials on environment. The third advantage is the reduction of construction time as SNPs can produce high-strength concrete with less curing time.

To present an overview of recent research progress in the field of the preparation of SNPs using sol-gel method exhibiting featured morphologies, uniform pore system, high specific surface area etc., this review article is organized as follows:

The review outlines a general introduction of nanomaterials and classification of preparation methods namely instrumental, mechanical and chemical. Next, the influence of the reaction conditions like temperature, pH, concentration of reagents, drying techniques, solvents, precursors, aging time etc. has been discussed. Thereafter, in the next section, the control of morphology and size of the SNPs using soft templates viz., surfactants, electrolytes, polymers etc. has been extensively reviewed. Finally, the applications of SNPs have been briefly summarized.

2. Preparation of nanoparticles

The manufacturing of nanomaterials can be classified as bottom-up and top-down approaches (Fig. 1). The bottom-up approach involves building up from the atom or molecular constituents to meso-level and top-down approach involves making smaller sizes through etching or grinding from the bulk materials. There are varieties of techniques available for preparing nanostructured materials and these can be divided into three based categories:

2.1. Gaseous state preparation

The metallic, metal oxides and ceramic nanomaterials can be prepared by this method. This method involves:

2.1.1. Gas condensation

In this technique, a metallic or inorganic material is vaporized using thermal evaporation sources such as a Joule heated refractory crucibles or electron beam evaporation devices, in an atmosphere of 1–50 m bar. The ultrafine particles are formed by collision of evaporated atoms with residual gas molecules requiring a gaseous pressure of more than 3 MPa (10 torr). The vaporization sources may be resistive heating, high energy and low energy electron beam. The clusters form in the vicinity of the source by homogenous nucleation in the gas phase grew by incorporation of atoms in gas phase. It comprises of an ultra-high vacuum system fitted evaporation source, a cluster collection device of liquid nitrogen filled cold finger scrapper assembly and compaction device. During