

Applications of mesoporous silica nanomaterial: an over view**P. Renuka Devi and K.G.Dhanalakshmi*****Biotechnology Centre, Anna University of Technology Coimbatore, Coimbatore – 641 047,
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2012; Accepted 27 July, 2012****Abstract**

Nanomaterials are physical substances with at least one characteristic dimension between 1-100nm. Porous inorganic material show good stability under extreme physical and chemical conditions. Interestingly, both of these characteristics are present in Mesoporous Silica Nano (MSN) materials. MSN materials have a highly regular porous structure with uniform pore size, vast surface areas and superior thermal stability. Hence MSN is suitable for a variety of applications in the field of drug delivery, biosensors, molecular separations, catalysis and separation efficient catalyst for the degradation of plastics. In this overview, we present various synthesis methods of MSN and recent research developments of a series of surface-functionalized mesoporous silica nano materials. We have also discussed about the applications of MSN in various fields.

Keywords: Mesoporous silica nanomaterial, Drug delivery, Biosensors, Catalyst.

Introduction

National Science Foundation (NSF) defines Nanotechnology, as research and technology development at the atomic, molecular, or macromolecular level, in the scale of approximately 1-100nm range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size (N.S.F, 2000)

According to Salamanca Buentello *et al.*, (2005), the term nanotechnology covers almost all fields of science and engineering. Nanomaterials have been widely used in biomedical and pharmaceutical fields like tissue engineering, gene therapy, chemotherapy,

peptide / protein delivery, molecular imaging, and high-through put screening or assay.

Mesoporous nano materials can be used for catalysis, separation technology and basic science etc., the interest on this material was created when it was known for plastic degradation. This overview mainly describes about the recent advances in synthesis, pore size adjustment and applications of mesoporous silica material not only as plastic cracking material but also as biologically useful material.

Synthesis of Mesoporous silica nanomaterial (MSN)**Different types of Synthesis of Mesoporous Silica**

The synthesis of MCM - 41 (Mobil Composition of Matter) is the initial name given for a series of mesoporous materials that were first synthesized by

Mobil's researchers in 1992. MCM - 41 (Mobil Composition of Matter No. 41 or Mobile Crystalline Material) is reminiscent of the synthesis of zeolites with a self-assembled surfactant molecular array forming the template. These surfactants are burned off at a later stage of preparation in order to yield the mesoporous MCM-41. Liquid extraction is another method to recover the surfactant from the as-synthesized MCM-41, and it allows the surfactant to be recovered for reuse. Depending on extraction conditions, MCM-41 materials after Kawi and Lai (2002) claims that Supercritical Fluid Extraction (SFE) can retain their uniform pore-size distribution and high surface areas and have a larger pore size than the calcined MCM-41. The extracted template is also unmodified and may be reused in future synthesis. SFE also allows much faster extraction as compared to conventional liquid extraction.

Samata *et al.* (2003) synthesized iron-rich highly ordered mesoporous Fe-MCM - 41. Ziolek *et al.* (2004) synthesized templates for MCM-41 mesoporous molecular sieves using transition metals like copper, iron, niobium, vanadium and molybdenum. Yaofeng shao *et al.* (2005) synthesized hydrothermally stable and long range ordered Ce-MCM-48 and Fe-MCM-48 materials. Ying Li *et al.* (2005) performed direct synthesis of highly ordered iron-substituted SBA-15 (Fe-SBA-15) material under weak acidic conditions.

The concept on microwave heating was introduced by Zaki Seddegi *et al.* (2002). MCM-41 samples with smaller pore diameters and thinner walls were achieved by microwave heating than the materials synthesized using conventional heating. They have also showed that MCM-41 with all-silica composition catalyzes the cracking of high-density polyethylene. The cracking activity of the catalyst increases with its crystallinity. MCM-41 with small pore diameter gave higher activity than that with large pore diameter.

There are two major pathways by which these ordered mesoporous materials are synthesized. (i) a hydrothermal synthesis in which the products precipitate from inorganic surfactant aqueous solutions under alkaline or acidic conditions at temperatures as high as 373 K and (ii) a solvent evaporation method in which the source solution is concentrated with the evaporation of the solvent to form an ordered inorganic surfactant mesostructure. Using these methods small scale production only can be done.

Whereas Akira Endo *et al.* (2006), found a method for large scale and continuous formation of mesoporous silica. There are two rate processes in their synthesis method (i) the rate of solvent evaporation includes the self-assembly of the surfactant micelles and (ii) the rate of polycondensation of the silica species. It is considered that the well ordered mesostructures can be obtained only when these two rate processes are well balanced. To produce the large amount of the products within a short time, it is necessary to evaporate the solvent rapidly without changing the "balance" of these two methods.

Yeping Xu *et al.* (2008) have suggested a novel, fast and environmentally benign synthetic pathway for the synthesis of pure and functionalized mesoporous silica. This pathway employs hyper branched polyglycerol (PG) with average molecular weights of 5000 and 6000 g mol⁻¹ as templating agents. This low cost template is innocuous, biocompatible, and works without requiring organic solvents. The templating mechanism was based on the size of hyper branched PGs revealed from small-angle neutron scattering (SANS) measurements. They have shown that single-particle PG dendrimers that can be adjusted from 2 to 5 nm, which corresponds to molecular weights of 2,000 to 10,000 g mol⁻¹. The expected template size of PG with an average molecular weight of 6,000 g mol⁻¹ is around 4 nm based on SANS

measurements. As a template, hyper branched PG differs greatly from the surfactants described above. Owing to its almost spherical structure, it cannot form micelles or large-scale clusters. As a result of the good water solubility of PG, the template can be removed by water extraction without the need for organic solvents.

Different Pore Shapes can be achieved

The presence of organic functional groups in mesoporous frameworks can modify the hydrophilicity / hydrophobicity of pore surface as well as the surface reactivity of Periodic Mesoporous Organosilicas (PMOs), which provide the opportunity to tune mechanical, electronic, and optical properties of hybrid materials with a wide range of applications. Helical and concentric circular (CC) mesostructured materials with pure silica composition have been successfully synthesized through acid or basic-catalyzed sol-gel processes by using chiral or achiral surfactants as templates and tetraethyl orthosilicate (TEOS) or sodium silicate as silica sources. This discovery is helpful in understanding the supramolecular cooperative assembly of hybrid materials and their structural and morphological evolution, which are important in the future applications of PMO materials (Pei Yuan, 2009). Ordered mesoporous silicates are synthesized from various sources like layered silicates and they are used in drug delivery formulations (Kresge *et al.*, 1992; Kimura and Kuroda, 2009; Linnell *et al.*, 2011; Arruebo, 2012 and Kruk, 2012).

Cost effective method of MSN synthesis

Beck *et al.* (1992) and Qian Zhao *et al.* (2011) described a cost effective synthesis method that 28.4 g of sodium silicate was dispersed into 50 ml distilled water, and 9.11 g of CTAB was dissolved in 50 ml of distilled water while stirring and warming. A transparent gelatinous solution was obtained. After that heating was stopped. Then sodium silicate solution was

slowly added into the gelatinous solution under vigorous stirring for 10 min and the pH value of the mixed solution was adjusted to 11 by drop wise addition of sulfuric acid (5 Vol %). After stirring for 1 h again, the resulting suspension was transferred into a 100 ml Teflon-lined stainless steel autoclave and was crystallized at 140°C for 48 h in an oven. Then the autoclave was cooled down to room temperature, the crystalline material was separated by filtration. The obtained sample was washed with distilled water and dried at 120°C for 24 h. The dried sample, denoted as s-MCM-41, was heated to 550°C at a heating rate of 2°C/min and calcined at 550°C in air for 10 h to remove template (CTAB), the calcined sample was designated as MCM-41.

Applications

Biological Applications of MSN

MSN were well tolerated by serological, hematological, and histopathological examinations of blood samples and mouse tissues after intravenous injection (50 mg/kg) (Lu *et al.*, 2010).

Drug Delivery

The primordial systems employing MSNs for drug delivery took advantage of the high surface areas and pore volumes of these silica materials. Guest molecules are simply adsorbed on the mesopore surface. No functional group acts as a gate to control the release of the loaded substances. The release was controlled either by the size or the morphology of the pores. Results showed that the MCM - 41 type mesoporous structure with channel-like pores packed in a hexagonal fashion was able to load large quantities of drug molecules and release them over a relatively long period of time. No significant difference was observed between the release profiles of materials with different pore sizes (Igor Slowing *et al.*, 2007; Yan *et al.*, 2012, Tang *et al.*, 2012 and Linnell *et al.*, 2011).

MSN based double drug delivery system

Yannan Zhao *et al.* (2009) have demonstrated that phenyl boric acid-functionalized MSN can serve as an efficient co-delivery system for saccharide-responsive controlled release of insulin and cAMP. The good biocompatibility, cellular uptake properties, and efficient intracellular release of cAMP set up the basis for future *in vivo* controlled-release biomedical applications (Vallet Regi, 2010). MSN based drug delivery systems are practiced in delivering anticancer drugs, siRNA and DNA constructs, membrane impermeable proteins etc. (Lu *et al.*, 2007; Xia *et al.*, 2009 and Slowing *et al.*, 2007)

Intracellular Delivery of Fluorescent dye

Huichen Guo *et al.*, (2011) have made a research on Hollow Mesoporous Silica Nanoparticles (HMSNs) for intracellular delivery of fluorescent dye. They have successfully identified that these HMSNs, with large pores and high efficacy to adsorb chemicals such as the fluorescent dye Fluorescein isothiocyanate (FITC), could serve as a delivery vehicle for controlled release of chemicals administered into live cells, opening potential to a diverse range of applications including drug storage and release as well as metabolic manipulation of cells.

Biosensors

According to Igor Slowing *et al.* (2007) micro and mesoporous silica provide two important unique advantages (1) *High porosity*. The large surface areas and pore volumes allow the encapsulation / immobilization of large amounts of sensing molecules per particle for fast response times and low detection limits (2) *Optical transparency*. This unique feature permits optical detection through layers of the material itself. Because of these advantages, different types of porous-silica based materials have been employed for building biosensors.

Immobilization of Bioactive Molecules

The immobilization process is very efficient if the support exhibits high surface area and the size of the pores is similar or slightly higher than the diameter of the biomolecule. The pore entrapment can improve the enzyme activity, because the protein maintains its native structural integrity. The mesopore size of materials MCM-41, SBA-15, SBA-16, MSU-X, synthesized with the common ionic and non ionic surfactants, does not go beyond 10 nm. This forbids their use as supports for immobilization of molecules when their minimum dimension is higher than that size. (Giraldo *et al.*, 2008).

Stationary Phase – High performance liquid chromatography (HPLC)

Mesoporous silicas are interesting materials as stationary phases for HPLC due to their high surface area and their organized porous structure. Moreover their content of silanol groups as well as their chemical and mechanical stability under the chromatographic operation conditions is similar to those of the precipitated silica. Mesoporous silica constituted by loose particles agglomerates selected by sedimentation was the first material used in HPLC. The chemical nature of the surface and the morphologic and porous properties determine the efficiency of a given separation. In order to avoid pressure drop and facilitate the flow of the mobile phase through the column, the particle size of the stationary phase must be between 3 - 10 mm (Giraldo *et al.*, 2008).

Non Biological Applications of MSN

In addition to biological applications, MSN play a major role in catalysis, separation, refineries and polymer degradation.

Mesoporous silica in catalysis

The mesoporous materials are ones of the most promissory catalysts due to their high surface area and

pore volume, besides of the possibility of surface modification and pore distribution control. The adequate diffusion of molecules through the catalyst pores allows the direct interaction with the acidic sites on the wall surface, promoting the conversions. Although it is possible to use the mesoporous silica in basic catalysis, most of the applications found in literature involve acidic catalysis, which is carried out by incorporation of moderate or strong acidic sites in the silica framework. In the last decade an important application corresponds to the use of mesoporous silica as catalytic support or template for the synthesis of carbon nanotubes (Davis, 1998; Martinez-Triguero *et al.*, 1999 and Giraldo *et al.*, 2008).

Metal Nanoparticles Confined in Mesoporous materials as Catalysts

Jumming Sun and Xinhe Bao (2008) declare that supramolecular self-assembled porous materials have opened a new way to get nanoparticles hosted in the channels of such materials. Due to the confinement of uniform pore structures, most of the trapped metal nanoparticles could keep their uniformity even after a relatively high-temperature process (e.g., high temperature activation, pre-treatment, etc.). It definitely provided the prerequisite for keeping them highly dispersed and thus maintaining activity during catalysis.

Molecular Sieves

Mesoporous silica serves as molecular sieves in industries like petroleum refineries, air separation and nuclear waste management. Michale Tsapatsis claims that fundamental advances in understanding and controlling growth and predicting their properties may enable the incorporation of these materials in thermo electric devices, micro reactors, and as corrosion resistant coatings. Mesoporous silica and other molecular sieves are made in bulk quantities, and issues

of structural perfection (defect density), particle size and shape uniformity, external surface perfection, and purity are compromised.

Refining Industries

According to Bapan *et al.*, (2003), mesoporous silica with large pore size will facilitate the flow of reactant and product molecules in and out of the pore system. Large pore systems are required for shape selective conversions of bulky molecules in the refining industry for the upgrading of heavy fractions, oxidation of heavy organics from industrial waste waters, and in the fine chemicals and pharmaceutical manufacturing.

Polymer Degradation

Plastics and polythene are unavoidable material in day to day life. Though the usage of plastics as packaging, storage, protection materials, it is very essential to note that accumulation of such materials on the earth crust causes various problems like infertility of the soil, destruction of marine organisms etc due to their very slow biodegradation. The cracking of HDPE had been demonstrated on all-silica MCM- 41 materials by Zaki Seddegi *et al.* (2002) A fast reaction rate and a light product composition of mesoporous silica indicate a high catalyst activity for cracking. The product compositions were different in both catalyst mediated and without catalyst reactions. The activity of mesoporous silica for HDPE cracking has been already published by many researchers. However Zaki Seddegi *et al.* (2002) described carbenium ion-mediated mechanism for the cracking reaction. It has been claimed that the cracking of HDPE over all-silica MCM-41 occurs via free radical mechanism and that the pore structure acts as a reaction vessel stabilizing the free radicals in comparison with thermal cracking in the absence of a catalyst. Apart from this many other polymers can be degraded using MSN (Garforth Arthur *et al.*, 1999).

Conclusion

In a nutshell, MSN has been noticed in nanoscience and biomedical science for its versatile usage. The biocompatibility nature of MSN draws a special attention in drug delivery. The porous nature of the material helps to create biosensors, to immobilize enzymes and to create stationary phase in HPLC. Also porous nature makes MSN as molecular sieves. Apart from this, thermal stability with vast surface area of MSN allows it to be a very good catalyst for cracking of polymer. Different synthesis methods including, cost effective methods and methods for achieving different pore shapes have been discussed in this over view. Finally, MSN is a multiple ability material which can be used in many branches of science.

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