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Hollow Nano Silica: Synthesis, Characterization and Applications

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1. Introduction

Since the discovery of mesoporous silica molecular sieves by Beck et al. (Beck et al., 1992; Kresge et al., 1992), mesoporous materials have opened many new possibilities for application in the fields of catalysis (Tanev et al., 1994), separation, and nanoscience (Wu & Bein, 1994; Agger et al., 1998; Li et al., 2003; Yu et al., 2005]. In recent years, fabrication of silica materials with designed structure (e.g. thin films, monoliths, hexagonal prisms, toroids, discoids, spirals, dodecahedron and hollow sphere shapes) is an important research in modern materials chemistry. Among them the fabrication of monodispersed hollow spheres with control size and shape is fastest developing area (Schacht et al., 1996; Bruinsma et al., 1997; Fowler et al., 2001). It is generally accepted that hollow sphere with mesopores will exhibit more advantages in mass diffusion and transportation as compared with conventional hollow spheres with solid shell. They can serve as a small container for application in catalysis and control release studies (Mathlowitz et al., 1997; Huang & Remsen, 1999). The methods currently used to fabricate a wide range of stable hollow spheres include nozzle reactor processes, emulsion/phase separation, sol-gel processing, and sacrificial core techniques. The fabrication of hollow spheres has been greatly impacted by the layer-by-layer (LbL) self-assembly technique (Decher, 1997). This method allows the construction of composite multilayer assemblies based on the electrostatic attraction between nanoparticles and oppositely charged polyions. By varying the synthetic methodology and reactants, it is highly probable to achieve the materials with interesting morphology and properties.

The presence of pores of uniform size lined with silanol groups confers these mesoporous materials as a potential candidate for hosting a variety of guest chemical species, such as organic molecules, semiconductor clusters, and polymers (Moller & Bein, 1998). For example, MCM-41 was reported as a drug delivery system (Vallet-Regi et al., 2001). Ibuprofen has been shown to readily adsorb from an *n*-hexane solution into the porous matrix of MCM-41, and to slowly release into a solution simulating physiological fluid. Furthermore, it has been found that in this host/guest system there is a strong interaction between the silanol groups and the carboxylic acid of the ibuprofen molecule. Having proven the feasibility of this system for drug retention and delivery, further effort should be made in gaining control of the amount of drug delivered, and its release rate. It can be thought that this delivery rate could be modulated by modifying the interaction between the

confined molecule and the mesoporous matrix with different morphology. Here, one of the advantages of nanocuboids compared to conventional mesoporous materials is reflected in their much higher storage capacity. Ibuprofen with the molecules size of 1.0 x 0.6 nm was used to examine the storage capacity.

Nanomaterials are the talk of today's Materials researchers. Mesoporous hollow silica spheres were recently invented. It is important due to the drug storage property. Synthesis of mesoporous silica nano hollow cuboids is the very recent advancement (Venkatathri et al., 2008) in this category. In the present invention, the physicochemical property of mesoporous silica's, Nanocrystalline MCM-41 and Nanohollow cuboids were compared. It is found that Nanohollow cuboids store much more drug molecules say Ibuprofen.

2. Experimental

Silica Nanohollow cuboids are synthesized as follows. 3.57 ml of triethanolamine (TEtA, 98%, Aldrich, USA) was added to a solution containing 74 ml of ethanol (99%, Aldrich, USA) and 10 ml of deionized water. 6 ml of tetraethoxyorthosilicates (TEOS, 98%, Aldrich, USA) was added to the above prepared mixture at 298 K with vigorous stirring. The reaction mixture was stirred for another 1 h. A solution containing 5 ml of TEOS and 2 ml of octadecyltrimethoxy silane (C18TMS, 90 %, Aldrich, USA) was added to the above solution (11.4 SiO_2: 6 TEtA: 1 C18TMS: 149 H_2O: 297.5 EtOH) and further reacted for 24 h. The resulting octadecyl group incorporated silica nanocomposite was retrieved by centrifugation. The sample was washed several times with distilled water, dried and calcined at 823 K for 8 h in air to obtain hollow cuboids silica material.

Nanocrystalline Silica MCM-41 is synthesized as follows. Cetyltrimethylammonium bromide was dissolved in 120 g of deionized water to yield a 0.055 mol l^{-1} solution, and 9.5 g of aqueous ammonia (25 wt%, 0.14 mol) was added to the solution. While stirring, 10 g of tetraethoxy silane (0.05 mol) was added slowly to the surfactant solution over a period of 15 min resulting in a gel with the following molar composition: 1 TEOS: 0.152 cetyltrimethylammonium bromide; 2.8 NH_3: 141.2 H_2O. The mixture was stirred for one hour then the white precipitate was filtered and washed with 100 ml of deionized water. After drying at 363 K for 12 h, the sample was heated to 823 K (rate 1 K min^{-1}) in air and kept at this temperature for 5 h to remove the template.

X-ray diffractograms (XRD) were recorded on Rigaku Multiplex diffractometer using Cu Kα radiation and a proportional counter as detector. A divergence slit of 1/328 on the primary optics and an anti-scatter slit of 1/168 on the secondary optics were employed to measure data in the low angle region. The particle size and shape were analyzed by a Scanning electron microscope (SEM), Topcon, SM-300. Transmission electron micrographs (TEM) of the samples were scanned on a on a JEOL JSM-2000 EX electron microscope operated at 200 kV. The samples for TEM were dispersed in isopropyl alcohol, deposited on a Cu-grid and dried. Thermogravimetry (TG) analysis of the crystalline phase was performed on an automatic derivatograph (Setaram TG 92). The specific surface area (BET) of the samples was determined using a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before N_2 adsorption samples was evacuated in vacuum at 573 K. The data points of p/p$_0$ in the range of about 0.05–0.3 were used in the calculations. The

Fourier transform Infrared (FT-IR) spectra in the framework region were recorded in the diffuse reflectance mode (Nicolet 60SXB) using 1:300 ratio of sample with KBr, pellet. Ultraviolet – visible (UV-Vis.) spectroscopic analysis were carried out using Shimadzu, UV-2450 spectrometer.

Ibuprofen (IBU) drug (Ranbaxy Chem. LTD., 99%) was dissolved in hexane solution at a concentration of 30 mg/ml. 1.0 g nanocuboids or MCM-41 was added into 50 ml IBU hexane solution at room temperature. Sealing the vials to prevent the evaporation of hexane, then the mixture was stirred for 24 h. The nanocuboids or MCM-41 adsorbed with IBU was separated from this solution by centrifugation and dried under vacuum at 60 ^{0}C. Filtrates (1.0 ml) was extracted from the vial and diluted to 10 ml, and then was analyzed by UV/vis spectroscopy at a wavelength of 235-320 nm.

3. Results and discussion

The X-ray diffraction pattern calcined MCM-41 and hollow cuboids are given in Fig. 1a,b. The pattern shows their identity. The pattern from as-synthesized sample did not change much on calcinations. Both the as-synthesized and calcined patterns of hollow cuboid shows three Bragg diffraction peaks, which can be assigned to the (1 0 0), (1 1 0) and (2 0 0) reflections of a hexagonal symmetry structure (*P6mm*) typical for MCM-41. *d* spacing and unit cell parameter (a$_0$) calculated from the XRD data are 12.6 nm and 14.54 nm respectively (Grun et al., 1999).
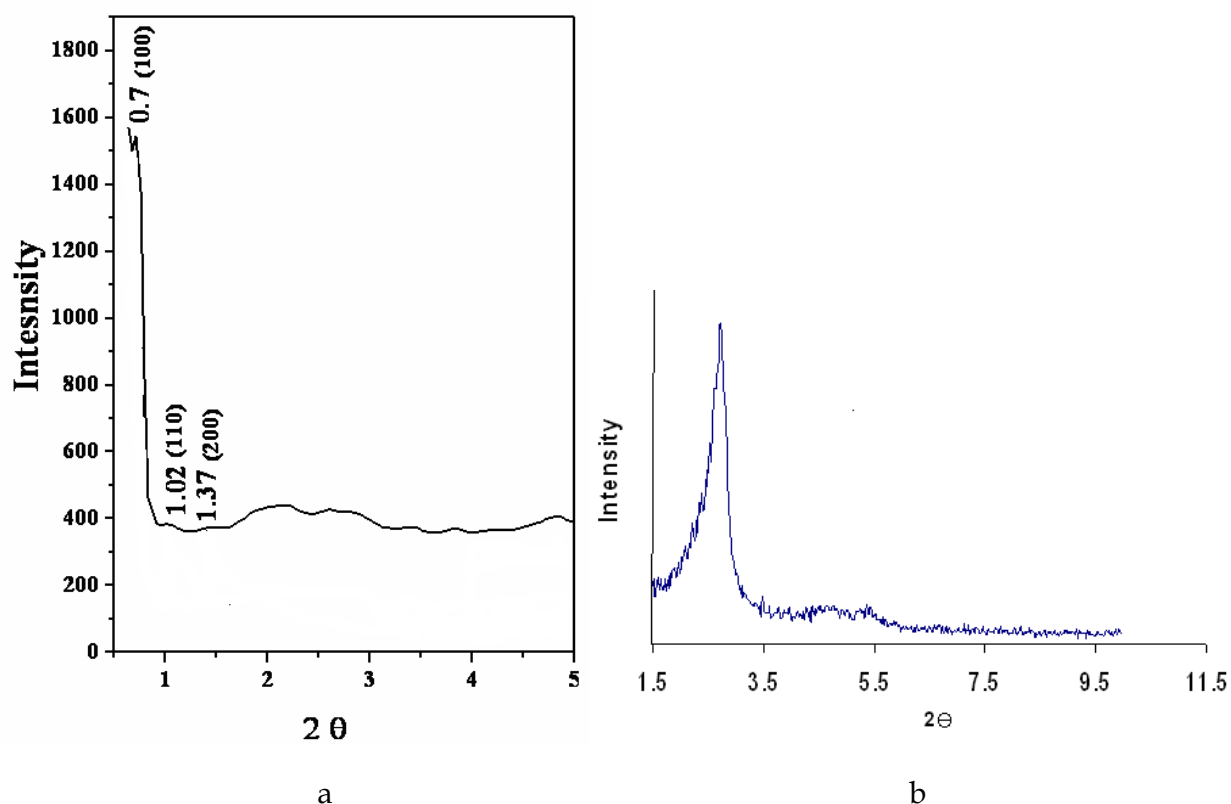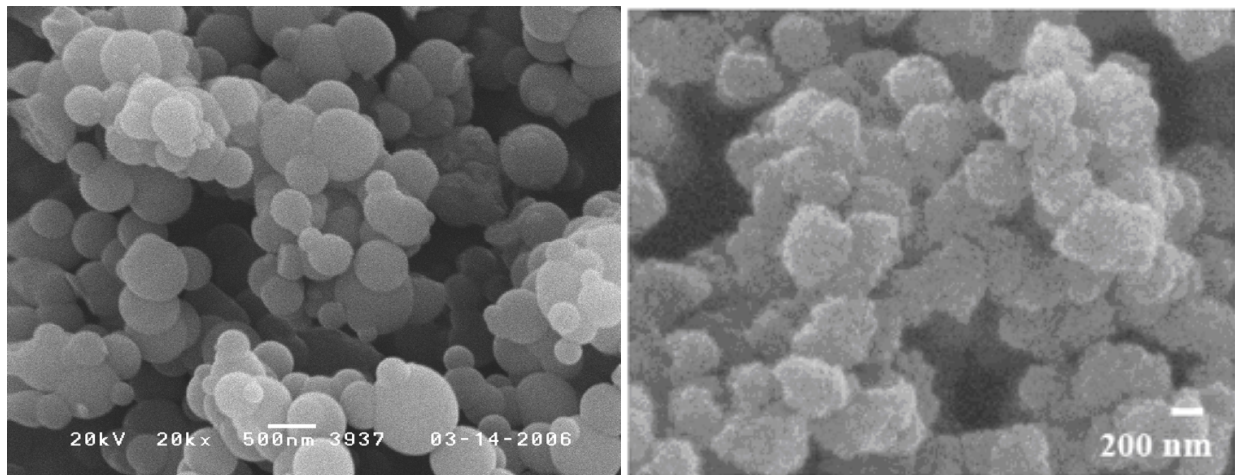

Fig. 1. X-ray diffraction pattern of calcined mesoporous silicas a) Nanohollow cuboids and b) Nanocrystalline MCM-41

Fig.2a,b shows the scanning electron micrograph of MCM-41 and hollow cuboids. MCM-41 particle size is 200 – 500 nm with spherical shape. Hollow cuboids are aggregate of cuboids with 500 nm particle size.
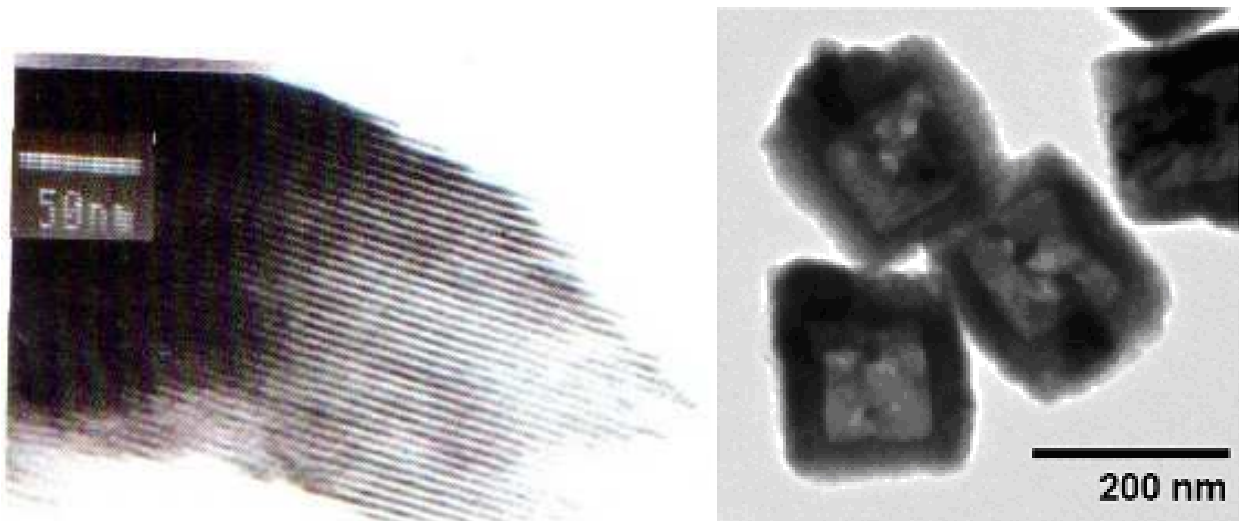

a   b

Fig. 2. Scanning electron micrograph of calcined mesoporous silicas
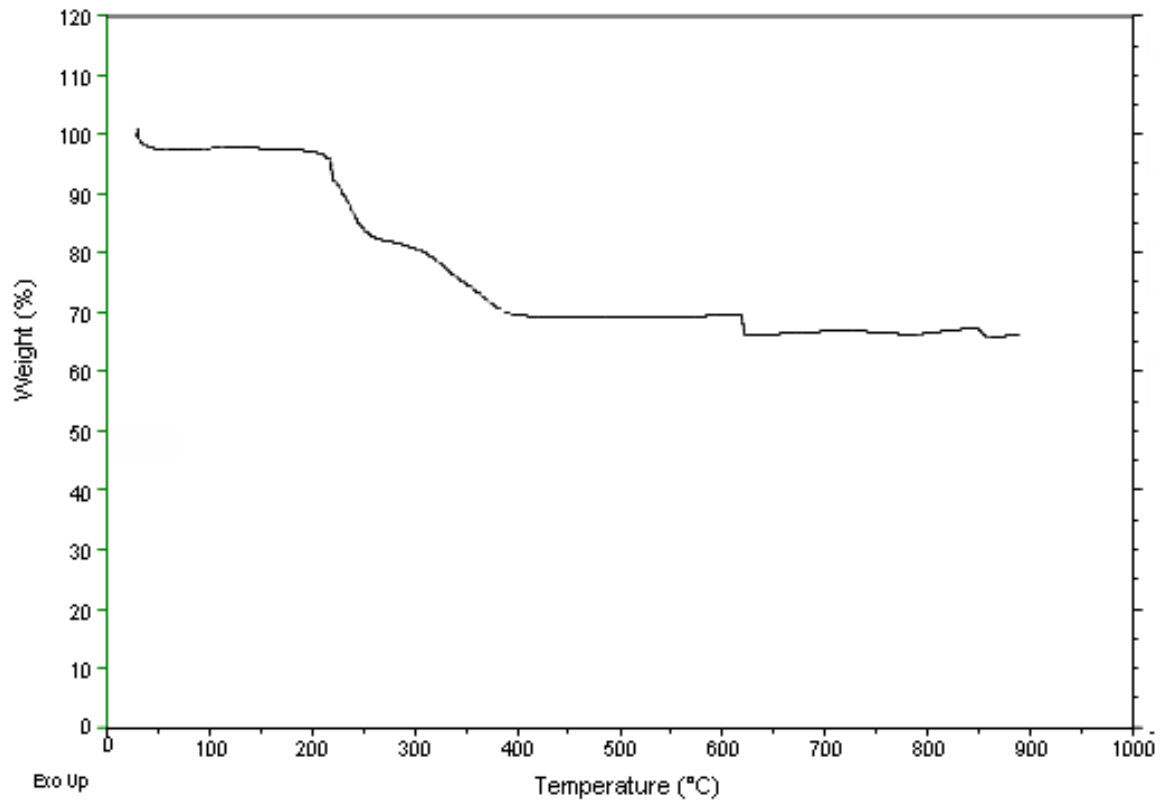a) NanocrystallineMCM-41 and b) Nanohollow cuboids

Transmission electron micrograph of MCM-41 and hollow cuboids are given in Fig. 3a,b. MCM-41 shows hexagonal array of channels characteristic of Mesoporous structure. By Fast Fourier Transform (FFT) of the TEM images, we estimate a unit cell dimension of 3.3 nm. TEM of cuboids shows core and shell structure. It can be seen from the images that the average inner diameter of the cuboids are nearly 100 nm, with outer shell thickness 50 nm. The particle sizes are uniform similar to SEM results. This distinguished pore channel arrangement with most of them running through the shell, are favorable for the access of guest molecules.
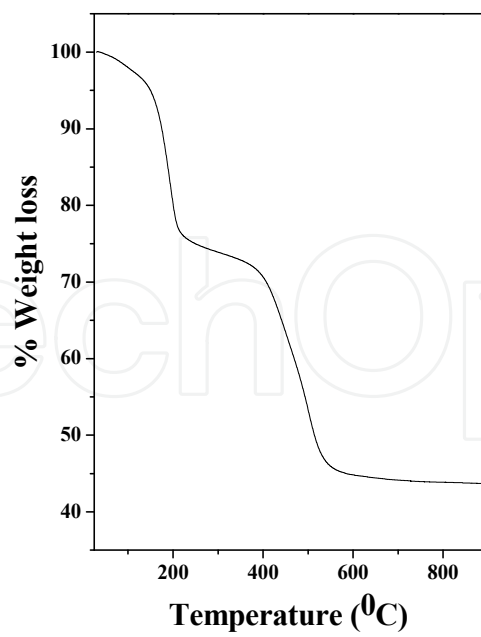

a   b

Fig. 3. Transmission electron micrograph of calcined mesoporous silicas
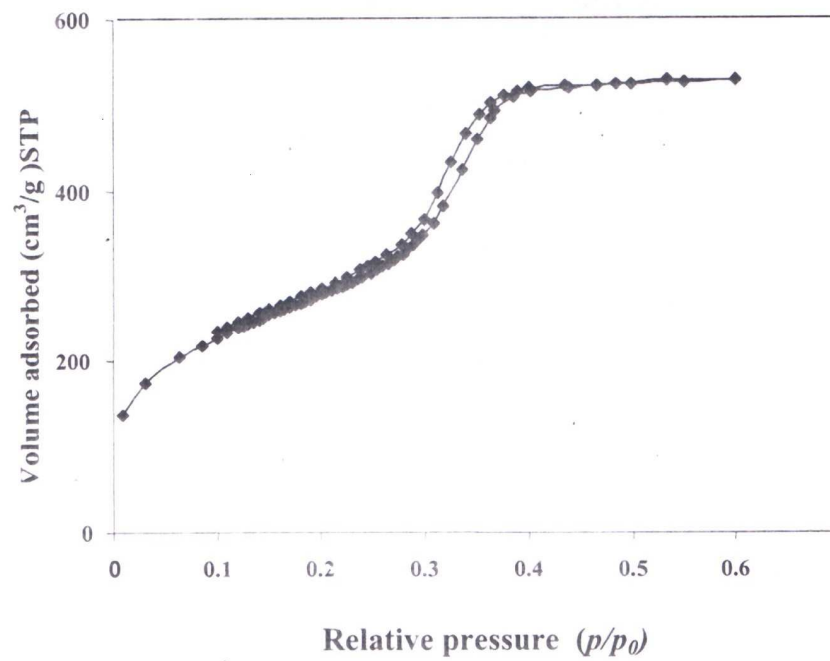a) NanocrystallineMCM-41 and b) Nanohollow cuboids

a

b

Fig. 4. Thermogravimetric profile of as-synthesized mesoporous silicas,
a) Nanocrystalline MCM-41 and b) Nanohollow cuboids.

The Thermogravimetry of MCM-41 and hollow cuboids were given in Fig. 3a,b. MCM-41 shows the 30 % loss at 25 - 625 °C due to the loss of template. The initial endothermic loss is due to loss of physisorbed water. Later the exothermic loss is due to oxidative decomposition of template. According to the curve the cuboids began to lose its weight at the beginning of heating, likely because of desorption of the physisorbed water and ethanol. It eliminates almost 25 % of its weight in the temperature range 25-200°C and losses almost 30 % weight in the temperature range of 200-500 °C. The later weight loss is due to the oxidative decomposition of the template.

Typical nitrogen sorption isotherms for MCM-41 and hollow cuboids are shown in Fig. 5a,b. In case of MCM-41, the nitrogen isotherms indicate a linear increase of the amount of adsorbed nitrogen at low pressures (P/Po = 0.35). The resulting isotherm can be classified as a type IV isotherm with a type H2 hysteresis, according to the IUPAC nomenclature (Fujiwara et al., 2004; Brunauer et al., 1940; de Boer, 1958; IUPAC, 1957). The steep increase in nitrogen uptake at relative pressures in the range between P/Po = 0.40 and 0.60 is reflected in a narrow pore size distribution. Thus, the variation of the catalyst in the solution during the growth process enables one to adjust and to control pore structural parameters such as the specific surface area (900 m²/g), the specific pore volume (1.29 cm³/g), and the average pore diameter (239 A°) and medium pore width (302 A°). The nitrogen adsorption/desorption isotherms of nanocuboid is of type IV nature (Fig. 5b) and exhibited a H1 hysteresis loop, which is typical of mesoporous solids (Wu et al., 2002). Furthermore, the adsorption branch of the isotherm showed a sharp inflection at a relative pressure value of about 0.68. This is characteristic of capillary condensation within uniform pores. The position of the inflection point indicates mesoporous structure, and the sharpness of these steps indicates the uniformity of the mesoporous size distribution. Correspondingly, the pore size distribution of the calcined sample shows a narrow pore distribution with a mean value of 1.90 nm. The sample with a specific surface area of 792 m²/g and pore volume of 0.51 cm³/g was obtained using the Brunauer–Emmett–Teller (BET) and Barrett– Joyner– Halenda (BJH) methods, respectively.

The Fourier transform Infrared spectra of as-synthesized MCM-41 and hollow cuboids are shown in Fig. 6a,b. Peaks around 1700 and 3430 cm⁻¹ corresponding to the carboxyl and hydroxyl groups (Li et al., 2002) respectively. The adsorption peak belonging to the Si-O stretching vibration of Si-OH bond appears at 960 cm⁻¹(Shan et al., 2004). The weak peaks at 2855 and 2920 cm⁻¹ belong to the stretching vibrations of C-H bonds, which show a few organic groups are adsorbed on the spheres. The peaks for carboxyl, hydroxyl and C-H vibrations are weak in MCM-41, shows the lesser organics, resulting of organic template. The strong peaks near 1100, 802 and 467 cm⁻¹ agree to the Si-O-Si bond which implies the condensation of silicon source (Agger et al., 1998).

Fig. 7 shows the UV ray absorbance spectra of 30 mg/ml ibuprofen hexane solutions (Zhu et al., 2005) before (a) and after (b) the interaction with nanocuboid and (c) MCM-41. The drug put in contact with nanocuboid and MCM-41 does not show any sign of degradation, since the positions of the absorbance maxima remain unchanged after the interaction and no new bands appear. The Ultraviolet ray absorbance intensity of filtrate decreases after Ibuprofen solution interaction with nanocuboids and MCM-41. This shows the remaining Ibuprofen is adsorbed over the molecular sieves. It was calculated that 561.8 mg and 270.5 mg ibuprofen
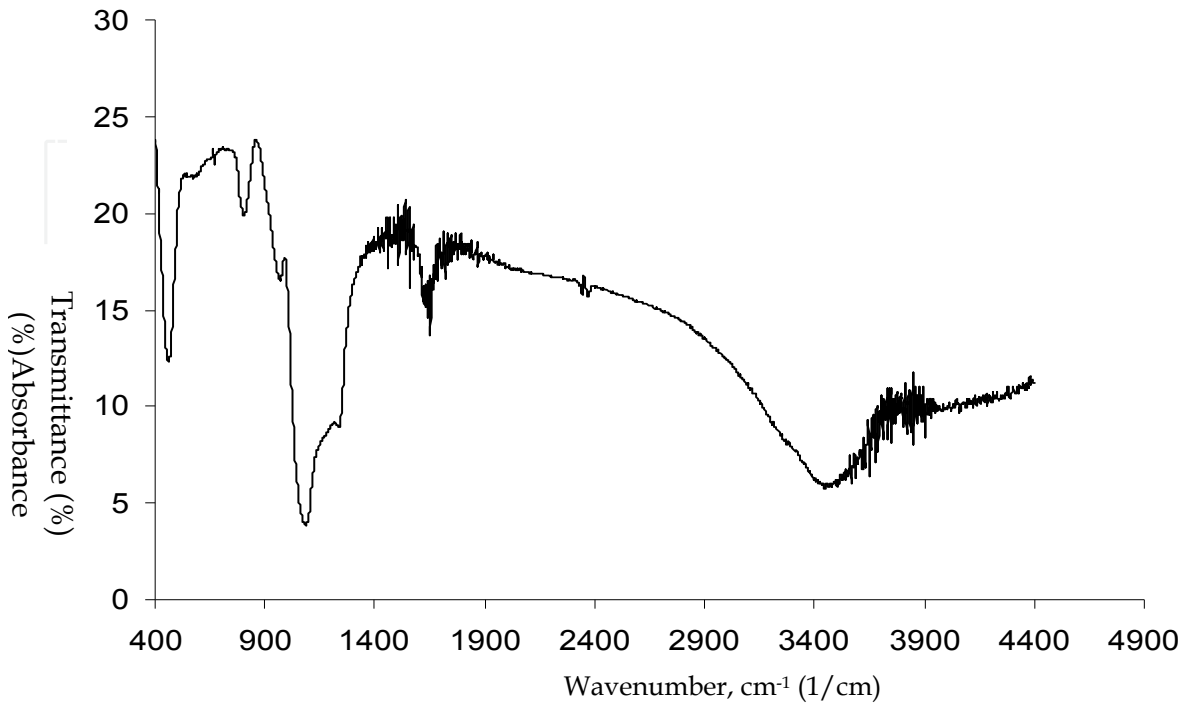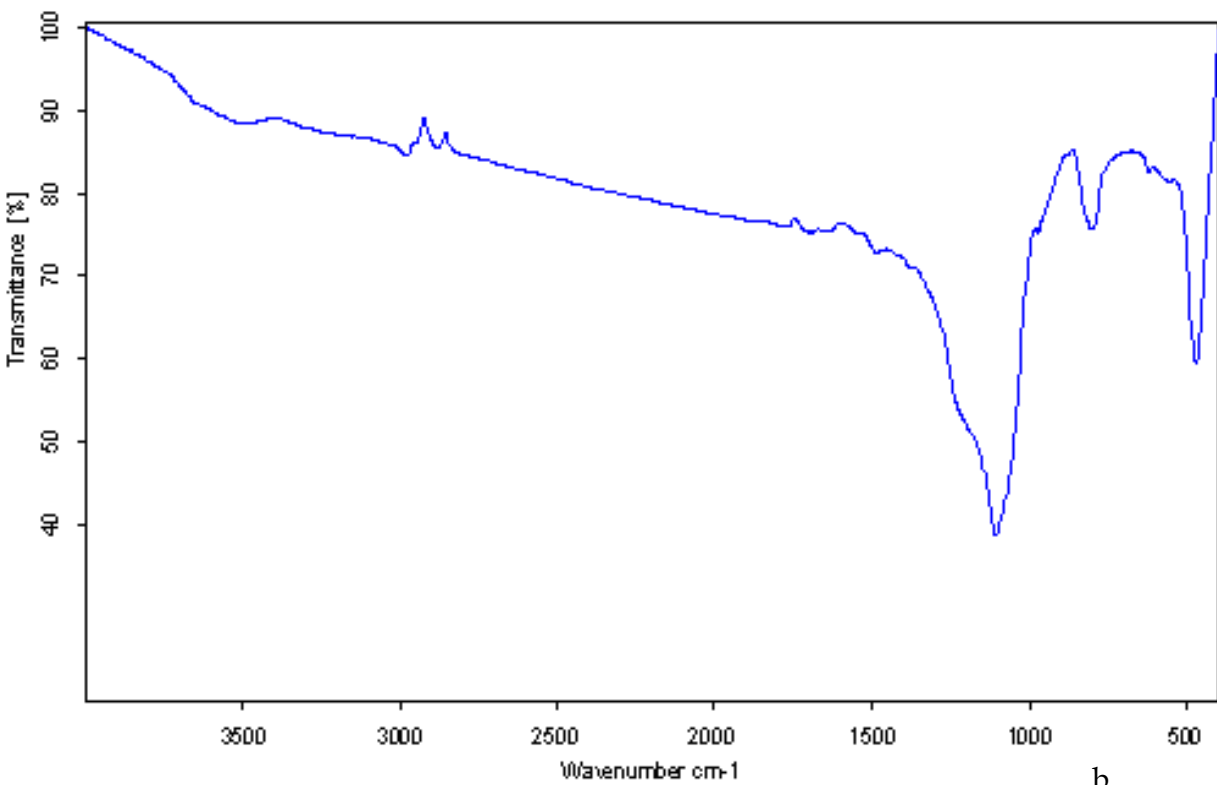
a
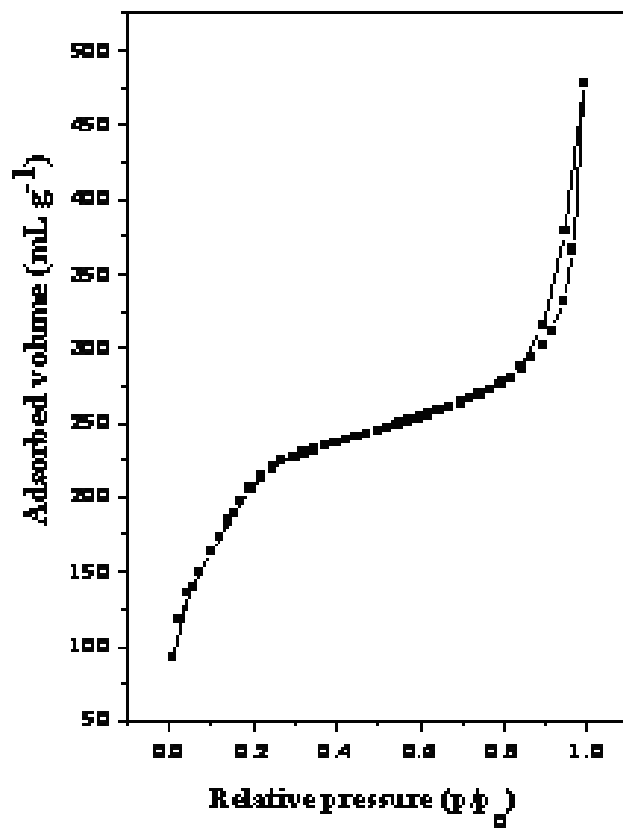
b

Fig. 5. Nitrogen adsorption/desorption isotherms of calcined mesoporous silicas, a) Nanocrystalline MCM-41 and b) Nanohollow cuboids.

Fig. 6. Fourier transform Infrared spectroscopic analysis of as-synthesized mesoporous silicas, a) Nanohollow cuboids and b) a) Nanocrystalline MCM-41.
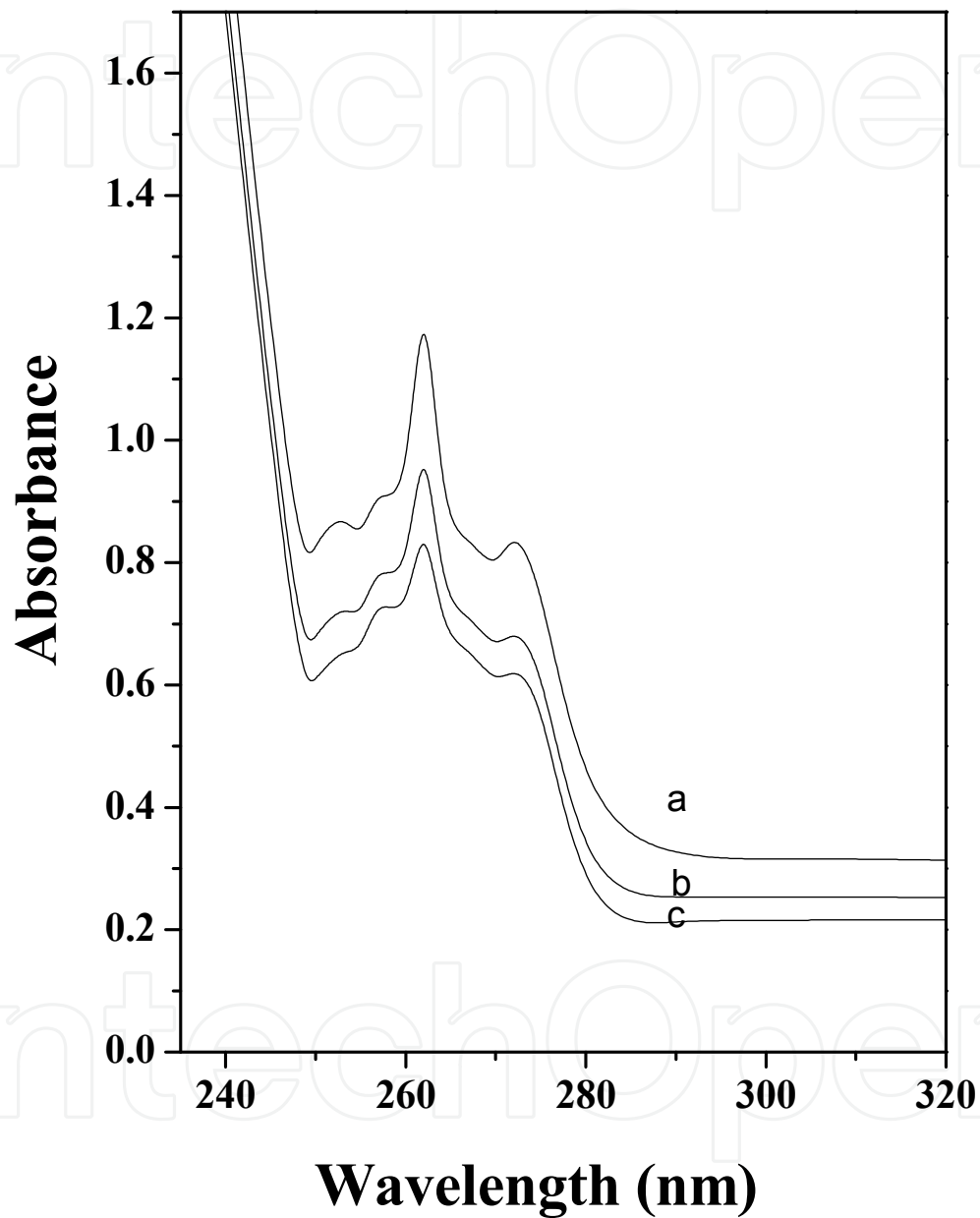
Fig. 7. The Ultraviolet – visible absorbance spectra of 30 mg/ml ibuprofen hexane solutions before (a) and after (b) the interaction with calcined mesoporous silica Nanohollow cuboids and (c) mesoporous Silica Nanocrystalline MCM-41.

molecules can be stored in per gram nanocuboid and MCM-41, respectively from Ultraviolet ray absorbance according to Beer–Lambert Law (Jeffery et al., 1997). The surface area and pore volume of MCM-41 and nanocuboid are very close to each other, but much more ibuprofen molecules can be stored into nanocuboid than into MCM-41. This illustrates that the hollow cores could hold more than half drug molecules of total storage amount.

Tetraethylorthosilicate (TEOS) was hydrolyzed in the presence of basic triethanolamine. However the hydrolysis rate of TEOS using triethanolamine is very slow as compared to hydrolysis with NH_3. For example, using the molar ratio described above, TEOS can be hydrolyzed in 2h using NH_3 whereas triethanolamine took 24 h to hydrolyze the TEOS. In the present synthetic recipe, triethanolamine not only act as a catalyst for the hydrolysis but also it acts as a reactant. The hydrolyzed silica monomers react with triethanolamine to give respective oxide. Such silicate-triethanolamine adduct are held together with hydrogen bonding. The triethanolamine sandwiched silica layer condensed and form nanocuboids. MCM-41 is reported to crystallize by self assembly of surfactant/template (Grun et al., 1999) in similar to nanocuboids.

4. Conclusion

A novel procedure was invented to synthesize mesoporous Silica Nano hollow cuboids with uniform size and morphology. It is characterized by various physicochemical techniques. The results are compared with Nanocrystalline silica MCM-41. Transmission electron micrographs shows, 150 nm hollow diameter and 50 nm shell thickness in hollow cuboids. Further, the mesoporous silica Nanohollow cuboids were found to store much more guest molecules than conventional mesoporous silica Nanocrystalline MCM-41.

5. Acknowledgement

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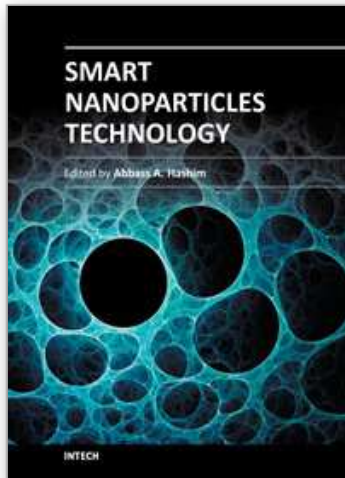
In the last few years, Nanoparticles and their applications dramatically diverted science in the direction of brand new philosophy. The properties of many conventional materials changed when formed from nanoparticles. Nanoparticles have a greater surface area per weight than larger particles which causes them to be more reactive and effective than other molecules. In this book, we (InTech publisher, editor and authors) have invested a lot of effort to include 25 most advanced technology chapters. The book is organised into three well-heeled parts. We would like to invite all Nanotechnology scientists to read and share the knowledge and contents of this book.

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