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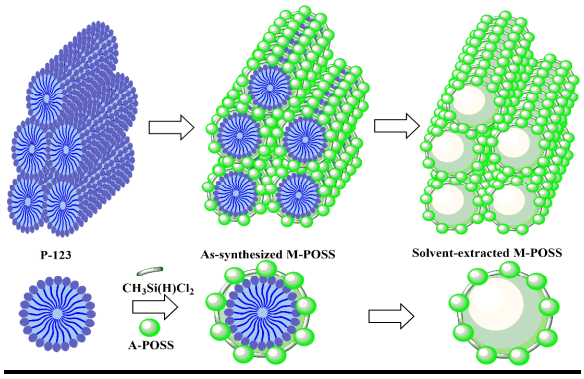
Graphical abstract

A novel mesoporous silica with high surface area and ordered porosity has been developed using N-methylamino POSS and dichloro methylsilane.



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LETTER

Synthesis of novel hierarchical mesoporous organic–inorganic nanohybrid using polyhedral oligomericsilsesquioxane bricks

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A successful method has been demonstrated for the synthesis of mesoporous organic-inorganic nanohybrid using amine functionalized polyhedral oligomericsilsesquioxane (POSS) and pluronic polymer as silica precursor and structure directing agent, respectively. The results confirmed the presence of porous structure, along with the high surface area and uniform pore size distribution which can be utilized for various applications namely catalysis, drug-delivery etc.

Porous materials with well-ordered porous structure receives a lot of attention in these days owing to their unique properties such as high surface area, ordered pores, highly active terminal functional groups, and high hydrothermal stability.[1] These excellent physical properties help us to tap the potential of these materials for various applications including catalysis, desalination, sensor, adsorption, drug delivery, hyperthermia, theranostics, etc.[2] Therefore, several techniques have been adopted to develop novel synthetic protocols for the fabrication of well-ordered mesoporous materials and this process resulted in the discovery of series of novel class of porous materials. A number of efforts are also directed towards the control of the structure and properties of these exciting materials as they mainly determine the application possibility of the materials. As a result, various strategies have been developed and implemented to modify structural and textural properties of mesoporous silica via different silica precursors, structure directing agents and co-solvents[3] along with the different synthesis conditions including ageing time, solution pH, synthesis and calcination temperatures, etc.[4] The choice of silica precursor plays a major role in determining the structure and texture of mesoporous materials because the chemistry of silica offers a flexible state which paves the way for a better control of mesostructuration. Many sources of silica precursors have been utilized by the researchers like tetraalkylortho silicates, aromatic fluorinated organosilane, sodium silicate, aminopropyltrialkoxysilanes, etc.[5]

Polyhedral oligomericsilsesquioxane (POSS) belongs to the class of interesting material which consists of –Si–O– inorganic inner framework that is surrounded by organic moieties. This material possesses interesting features like smaller size (1-3 nm),[6] zero-dimensionality, high mechanical strength, rigidity etc., which permits the expansion of the horizon for the application of this material to a variety of fields including mechanical, chemical, optical and biomedical.[7] Recent studies revealed the synthesis of hybrid POSS matrices utilizing different polymers or by using different cross linkers such as R_2SiCl_2, $Me_2Si–O–SiMe_2$, etc.,[8] The suitability of a material for a particular application is highly dependent on the functionality and also on the associated properties like high surface area, ordered porous structure, etc., and hence, the usage of potential monomers for constructing the desired silica frame work becomes highly significant. Few reports by various researchers, relies on the use of POSS which are terminated with vinyl & aminophenyl groups by utilizing triethoxysilane& 1,4-bis(triethoxysilyl) benzene as cross-linkers. A detailed literature survey revealed that, only a few works of this kind are available and it is also noteworthy that this is the first of its kind to use $–NMe_4$ terminated POSS & CH_3SiHCl_2 as silica source for making mesoporous framework.[9] This hybrid mesoporous POSSmaterial is highly biocompatible and non-toxic, and hence it can be imbibed for various bio-medical applications like drug-delivery, theranostics, etc.,

As for our knowledge, this current work on the synthesis of M-POSS using amine terminated POSS (A-POSS) as a silica source and pluronic P-123 as a structure directing agent is the first of its kind. Here, Dicholoromethylsilane (CH_3SiHCl_2) has been used as a cross linker for the integration of POSS moiety and the structure directing agent (P-123). The synthesized mesoporous organic-inorganic nanohybrid has been characterized using Fourier-transform infra-red spectroscopy (FT-IR) and silicon magic angle spinning nuclear magnetic resonance spectroscopy (^{29}Si-MAS-NMR) to elucidate the nature and coordination of the framework structures while the textural properties have been obtained by using N_2physisorption analysis and field emission transmission electron microscopy (FE-TEM).

FE-TEM images of both the as-synthesized M-POSS and the solvent extracted M-POSS are shown in Fig. 1a & 2b, respectively. The micrographs showed the formation of flake like morphology in both as-synthesized and solvent extracted samples, revealing that the process of solvent extraction does not play any significant role in controlling the morphology of the samples. However, the pores are more clearly discernible in the sample extracted with the solvent compared to the as-synthesized M-POSS, and this may be attributed to the removal of pluronics, which is the structure directing agentin the solvent extraction step

and therefore the empty pores. The solvent extracted sample shows uniform pores which are almost similar to that of the samples prepared using the pluronic P-123 surfactant and other silica sources such as tetraethylorthosilicate. The pore size was calculated from the FE-TEM image and was found to be around 2–4 nm, approximately.

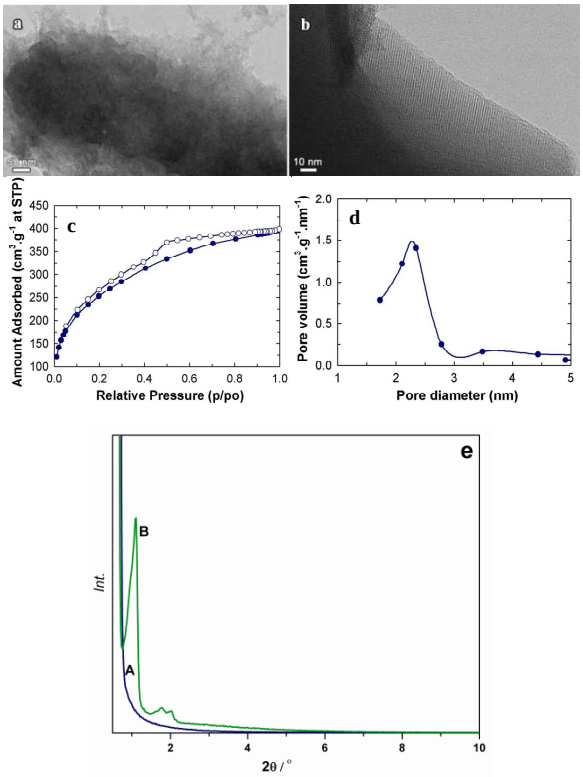

Fig. 1 Transmission electron micrographs of as-synthesized (a)& solvent extracted (b) M-POSS, nitrogen physisorption (c) & BJH isotherms (d) of solvent extracted M-POSSand powder XRD patterns of as-synthesized (A) & solvent extracted (B) M-POSS.

Nitrogen adsorption-desorption measurement was used for the determination of textural parameters of the samples namely specific surface area, specific pore volume and the pore size distribution. Fig. 1c & 2d shows the nitrogen adsorption–desorption isotherm and BJH isotherm of solvent extracted M-POSS, respectively. The sample displays type IV isotherm with a sharp capillary condensation step at a higher relative pressure, which indicates the presence of mesoporosity in the sample. A hysteresis loop (H_4) at a relative pressure P/P_0 of 0.4 to 0.6 was also seen which may be ascribed to the presence of microporosity in the mesoporous structure along with the distribution of uniform pores resulted by the agglomerated plate–like particles. The BET surface area derived from the isotherm of solvent extracted material is found to be 750 m^2/g. The pore size was calculated from BJH was found to be 2.25 nm, which is in consistent with the pore diameter obtained from the FE-TEM analysis (Fig. 1b). Moreover, a sharp diffraction peak was observed at (2θ=) 1.1°, 1.9° & 2.0° in the powder XRD patterns(Fig. 1e), which reveals the presence of ordered mesoporosity in the M-POSS. But, the as-synthesized material doesn't show any peak and this may be attributed to the presence of structure directing agent (P-123). This confirms that even though the POSS compound is one of the largest source of silica(1-2 nm), it could be easily modified as the frame of meso-channels.

Fig. 2 shows the FT–IR spectrum of as-synthesized (a) and solvent extracted (b) M–POSS. The presence of absorption bands at 1300, 875 and 760 cm^{-1} confirms the Si–CH_3 stretching while an intense broad band arises at 1100 cm^{-1} is attributed to the Si–O–Si stretching in both the samples. The solvent extracted sample shows a sharp band at 2200 cm^{-1} which corresponds to the Si–H stretch whereas a weak band is observed at the same wavenumber in the case of as-synthesized sample. The as-synthesized sample shows alkyl band stretching in between 2800–3000 cm^{-1} which is due to the presence of structure directing agent whereas, the solvent extracted sample shows only –CH_3 umbrella stretching and that may be assigned to the –CH_3 connecting moiety (–O–Si(CH_3)(H)–O–) in POSS.

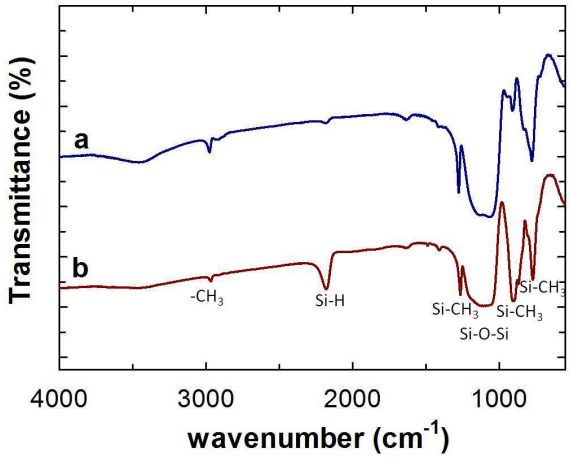

Fig. 2 FT-IR spectra of as-synthesized (a) and solvent extracted (b) M-POSS.

The nature and coordination of the organic-inorganic framework in the wall structure of the M-POSS were analysed by the CP MAS ^{13}C and ^{29}Si NMR spectroscopy and the results are shown in Fig. 3. In ^{13}C–NMR spectrum (Fig. 3A), a signal is clearly observed at 0 ppm which corresponds to the –CH_3 that is present in the connecting moiety of POSS in M-POSS (–O–Si(*CH_3)(H)–O–). This was also further confirmed by the FT-IR spectroscopy. On the other hand, the ^{29}Si–NMR spectrum shows the chemical shifts at –34.2, –65.0, –100.0, and –109.2 ppm (Fig. 3B). The signals obtained at –34.2 & –65.0 ppm are due to the silica species connected with alkyl group. The peak at –65.0 ppm may be attributed to –O–Si*H(CH_3) –O– in the M-POSS whereas the peak at –34.2 ppm may be due to the presence of free –Si*–O–N(Me)$_4$ in the M-POSS moiety. The chemical shift for –Si– present in the POSS moiety of M-POSS was received at –100.0 and –109.2 ppm and this can be very well assigned to the –Si*(–OSi)$_4$ and –Si*(–OSi)$_3$–O–SiH(CH_3) – , respectively.

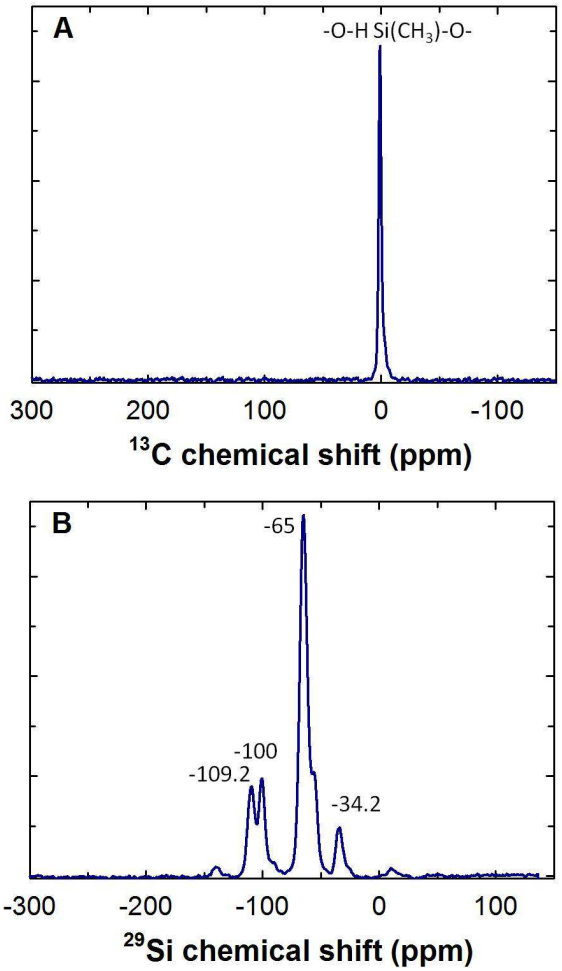

Fig. 3 CP MAS ^{13}C and ^{29}Si–NMR of solvent extracted M-POSS.

Finally, the drug loading ability of M-POSS was evaluated using hydrophobic Ibuprofen as a model drug and is shown in Fig. 4. The loading of model drug Ibuprofen in M-POSS shows a time-dependant increase up to 6 h and then it gets saturated further. The maximum percentage loading of Ibuprofen in M-POSS was found to be 95% within 6 h due to the presence of associated special features in M-POSS such as high surface area and ordered porosity along with hydrophobicity.

In conclusive, we demonstrated a successful synthesis of a novel mesoporous organic-inorganic nanohybrid using a new POSS based silica precursor through the self-assembly of organic structure directing agent pluronic P-123 and coupling agent $Cl_2SiH(CH_3)$. This hybrid material possesses a high surface area along with uniform pore size distribution. FE-TEM and nitrogen physisorption revealed that the pores are highly ordered and the pore diameter of the material is in the range of 2 to 4 nm. It also showed an efficient 95% of drug loading ability within 6h. Moreover, the presence of active N-methyl functionalities makes it suitable for replacing with any organic moieties. These features create an excellent platform for designing a series of novel organic-inorganic hybrid nanostructures and that will have a major contribution for a wide variety of applications such as in chiral separation, filtration, catalysis, drug-delivery etc.,

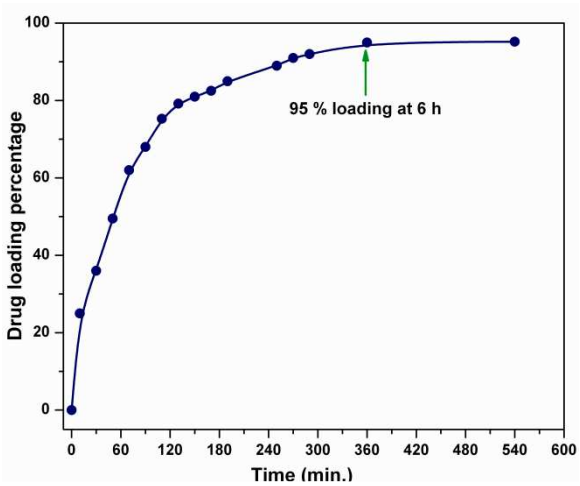

Fig. 4 Determination of drug loading efficiency of M-POSS using the model drug, Ibuprofen.

Experimental

Preparation of mesoporous POSS

A-POSS was synthesized in accord to the procedure reported previously.[10] Initially, tetramethylammonium hydroxide, methanol, and deionized water were mixed together followed by dropwise addition of tetraethoxysilane under nitrogen atmosphere. The product obtained was separated through filtration. Mesoporous POSS was synthesized as shown in Fig. 5. Briefly, 4 g of P-123 was dissolved in 40 g of deionized water and 40 g of 2N HCl. The reaction mixture was stirred for 4 h at 40 °C in order to get a clear solution. 4 g of silica precursor (A-POSS) along with the equal molar ratio of cross–linker (CH_3SiHCl_2) was added to the reaction mixture. The ageing process was carried out in an autoclave at 80 °C. The final as-synthesized product was filtered and then washed to remove P-123 and dried at 80 °C. The structure directing polymer was removed by solvent extraction method which was carried out at 100°C in ethanol and concentrated HCl medium. The final product was separated out through filtration and washed sequentially with ethanol and water and represented as M-POSS. Finally, the sample was dried and characterized.

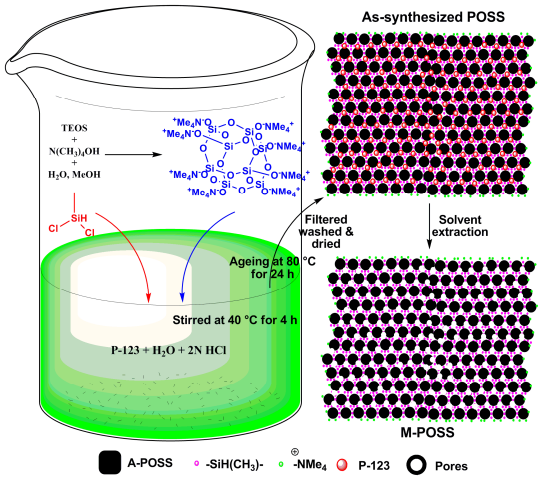

Fig. 5 Schematic representation depicting the synthesis of M-POSS.

Characterization

The internal morphology was imaged using FE–TEM, JEM 2100F, JEOL, Japan. All the samples were prepared by dispersing in ethanol and coated on carbon coated copper grid. It was then allowed to dry and analysed under FE-TEM. The structural properties were studied using FT–IR and ^{13}C &^{29}Si CP/MAS nuclear magnetic resonance spectroscopy (Solid-state NMR, 400 MHz Avance II, Bruker, Germany). FT-IR spectra were recorded on a Jasco–6300, USA between 400 and 4500 cm^{-1} by averaging 10 scans with a resolution of 10 cm^{-1}. Nitrogen adsorption–desorption isothermal analysis was conducted at -196 °C on anAutosorb–1, Quantachromeanalyzer. All the samples were outgassed at 150 °C for 6 h prior to the nitrogen adsorption measurements. The specific surface area was calculated by the BET method. Pore size distribution was obtained from desorption branch of the nitrogen isotherms by the Barrett-Joyner-Halenda method (BJH). The ^{29}Si-NMR spectra were recorded at a frequency and spinning rate of 79.49 MHz & 6 KHz, respectively while the ^{13}C-NMR spectra was performed at a frequency of 100.62 MHz and spinning rate of 10 KHz. X-ray powder diffraction (XRD) patterns were recorded on a PANalytical XERT-MPD diffractometer system by using $Cu_{K\alpha}$ radiation with a wavelength of 0.154 nm. The scan was performed between ($2\theta =$) 0.5° and 10° with the scan speed of 0.02°/3s. For the determination of drug loading efficiency, a model drug Ibuprofen was used in M-POSS. Briefly, 100 ppm of chloroformic Ibuprofen solution was added to 20 mg of M-POSS. The supernatant liquid was separated from the above solution at a constant time interval and the intensity was recorded at an excitation wavelength of 253 nm using UV-visible spectrophotometer. Then the percentage of drug loading was calculated using the following formula

$$DLP = (TC - CT)/TC \times 100\,\% \qquad \text{Equation 1}$$

Where DLP, TC & CT represents drug loading percentage, total concentration of drug and concentration of drug at time t (min.), respectively.

Acknowledgement

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Notes and references

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