Porous Hybrid Materials with POSS

Sasikumar Ramachandran and Alagar Muthukaruppan

Abstract Massive applications and advantages of porous hybrid materials based on polyhedral oligomeric silsesquioxane (POSS) have generated enormous research interest in the development of porous POSS hybrid materials in both the industries and the academics. POSS, a well-known nanoporous inorganic building block materials with the formula $(RSiO_{1.5})_n$, $(n \geq 6)$ including definite cage-shaped three-dimensional structures is surrounded by organic functional groups, which were utilized to produce porous hybrid materials with organic molecules via copolymerization, grafting, and blending and also with metals by coordination. This chapter reviews the properties and importance of porosity of POSS and POSS hybrid materials.

Keywords POSS · Porosity · Polymer · Hybrid material · Low-k dielectric
Catalyst

1 Introduction

The combination of organic and inorganic materials in a single chemical entity was prepared few decades ago to achieve improved properties for high-performance industrial and engineering applications. For example, in an old house construction, they have used combination of straw materials of an organic fiber and inorganic clay as a thermal insulator. We would not really call this material a hybrid material in a scientific context, more likely it would count to the composite materials. But the

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other case, a mixture of a clay mineral and the organic dye indigo called Maya blue dye shows significantly high stability than that of the indigo alone; this material is often mentioned as hybrid material. Recently, the development of porous materials is considered as an important part of the present research for various applications in the area of energy and medicine. The homogeneous porous materials can be prepared through solgel method by self-assembling of surfactant molecules as templates. Usually, amphiphilic surfactants are used as a template in this procedure, in which the templates are removed by thermal process after the network formed. The resulting mesoporous materials possess pores with diameters between 2 and 10 nm which depends on the templates. The porous system consisted only of a purely inorganic silica network when it was discovered. The reactive organic functionalization of mesoporous materials made it possible to extend their potential applications. The following methods can be used to prepare organic–inorganic hybrid mesoporous materials: (i) the cocondensation of trialkoxysilanes in specific conditions and (ii) the surface functionalization of purely inorganic porous materials using monofunctional silane coupling agents [1].

The development of porous hybrid materials by hybridization of polymers with porous inorganic materials such as silsesquioxanes/POSS, MCM-41, SBA-15, and Zeolite, via grafting, blending, and copolymerization methods and hybrid POSS–metal coordination polymers has potential features [2–4]. Porous hybrid materials having POSS moieties are an emerging class of new materials that hold significant promise applications in catalysis, gas storage, separation, energy, and electronics. POSS/silsesquioxanes, a class of unique porous inorganic materials with the generic formulas $(RSiO_{1.5})_n$, where R is hydrogen or any alkyl, alkenyl, and aryl groups. These groups are extremely useful as platforms for assembling organic/inorganic hybrid materials via covalent bonds and are directly attached to silicon in the silane and typically do not react during the process of hydrolysis and condensation of trialkoxysilanes [5]. POSS/silsesquioxanes can be synthesized from chlorosilanes, silanols, silanolates, tetraalkoxysilanes, and organotrialkoxysilanes by hydrolysis/condensation process [6].

The term silsesquioxanes refers each silicon (sil) atom is bound to an average of one and a half (sesqui) oxygen (oxane) atom and to one hydrocarbon group/hydrogen atom (ane) which indicates that 1:1:1.5 ratio of hydrocarbon:silicon:oxygen atoms [7]. The silsesquioxane building blocks can be classified as non-caged and caged structure; the non-caged molecular structure can be further classified into partial cage structure (a), ladder structure (b), and random structure (c) (Fig. 1a), and the cage-like silsesquioxanes are usually called as polyhedral oligomeric silsesquioxanes (POSS) which are also denoted by the letters T_6, T_8, T_{10}, and T_{12} (Fig. 1b) based on the siloxane unit [8].

The IUPAC name of silsesquioxanes is complicated, and so the compounds are more conveniently named using the number of silsesquioxane linkages present in a molecule and substituents attached to the silicon atom. For example, $(HSiO_{1.5})_8$ is named as octa(hydridosilsesquioxane) or octasilsesquioxane. Further, these names are more simplified by letters using the siloxane chemistry, one to four oxygen bonds attached to silicon atoms referred as D, M, T, and Q, respectively, and the numerical

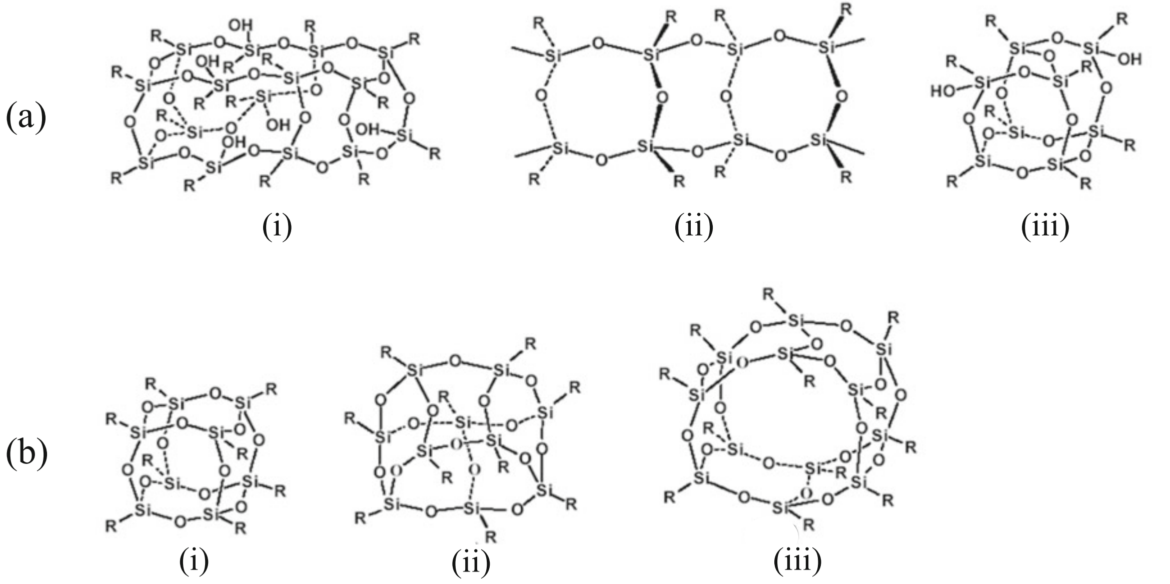


Fig. 1 Chemical structures of silsesquioxanes. **a** Non-caged silsesquioxanes: (i) random, (ii) ladder, (iii) partial caged structures, and **b** caged silsesquioxanes: (i) T_8, (ii) T_{10}, (iii) T_{12} structures. Reprinted from [8], © 2016 with permission from Royal Society of Chemistry

subscript states that the number of silicon atoms in the molecule and the superscripts denoting the number of oxygen atoms further attached to the other silicon atoms. Accordingly, $(HSiO_{1.5})_8$ is named as $(HT^3)_8$ or H_8T_8 or simply T_8 where an octameric cage structure was constructed by connecting each silicon atom to three oxygen atoms and hydrogen atom [9]. Among the polyhedral silsesquioxanes, octahedral cages (T_8) have been widely studied, and they are constructed with the rigid silica core (0.53 nm diagonal) and eight organic groups tethered to the silicon atoms which forms unique sphere like molecules with volumes less than 2 nm^3 and 1–3 nm in diameter [10]. The defined chemical structure and pore size of the octahedral/polyhedral cages offer a wide range of porous POSS hybrid materials.

Porous structured cross-linked polymers possess intrinsic physicochemical properties and have potential applications with the limited thermomechanical properties since that have attracted research interest in recent years by the scientific researchers in the development of porous structured covalently bonded organic–inorganic hybrid polymer nanocomposites [11]. The organics tethered inorganic POSS materials can be well dispersed in hybrid polymers through covalent bonds which can provide well-defined porous structure including excellent thermal and mechanical properties. Also POSS is a non-volatile, lightweight, odorless, nanoporous, and environmentally friendly material. The homogeneous arrangement of POSS units in the hybrid polymer nanocomposite materials can be stabilized by different polymerization techniques. The reinforcement of POSS nanoparticles into a polymer matrix increases the porosity, strength, modulus, and rigidity and reduces the flammability, heat discharge, and viscosity of the polymer. Despite the properties of polymer nanocomposites depend on the method of incorporation of POSS particles. There are two methodologies adopted for the dispersion of POSS into a polymer; (i) physical blending and (ii) chemical cross-linking. In the first approach, POSS nanoparticles are physically blended with polymer by melt mixing or solvent casting methods whereas in the second approach, POSS nanoparticles are bonded covalently with polymer. Various ranges of porous hybrid materials can be prepared from POSS and polymer materials by chemical cross-linking methods using different organic groups anchoring on POSS. Further, POSS can be divided into monofunctional POSS, multifunctional POSS, and molecular silica which refers the presence of only one of the reactive organic groups, more than one reactive organic groups, and non-reactive organic groups, respectively.

POSS molecules have been used to develop well-defined POSS–polymer hybrid porous structured films. These films can be prepared by directly blending/chemical cross-linking of POSS molecules and polymers. For example, octa(3-aminopropyl)-POSS was used to construct multilayered thin films via self-assembly approach with polyanion, which can be potentially applied in designing porous ceramic membranes. Further, the POSS-containing block copolymers could be self-assembled into thin films with a well-ordered structure by varying the parameters of the annealing process such as solvents and temperature [12]. By varying the functionalities of POSS building blocks, reaction conditions and cross-linkers could build porous structured hybrid networks. This chapter mainly devoted to discuss the construction of different sizes of porous hybrid materials with POSS and concurrently examine the properties and applications of the porosity of POSS hybrids.

2 POSS Materials

POSS is one of the familiar 3D building blocks which are used to construct new porous materials to alternate porous activated carbon, zeolites, metal–organic frameworks, porous organic polymers, etc. Their unique star-shaped nanostructures , physical and chemical properties, such as facile chemical modification, good pH tolerance, high temperature and oxidation resistance properties, specific reactivity, unique morphology and diverse porosity, make POSS an excellent building block for constructing multi-functional materials. In 1946, Scott discovered the first oligomeric organosilsesquioxanes, $(CH_3SiO_{1.5})_n$, by the cocondensation of methyltrichlorosilane and dimethylchlorosilane in specific reaction conditions. In 1995, Baney et al. reviewed the preparation, properties, structures, and applications of silsesquioxanes, especially those of ladder-like polysilsesquioxanes. However, in the past few years, much more attention has been paid to the silsesquioxanes with specific cage structures. However, the POSS is one of the well-known cage-structured porous molecules which can be embedded with mono-, di-, and multi-functional reactive sites that are naturally compatible with organic hosts and can be utilized to incorporate POSS into the polymeric materials through polymerization or grafting. In this manner, a large variety of POSS–polymer nanocomposites have been prepared as high-performance materials. Porous hybrid materials based on POSS precursors have been developed by various chemical methods including copper-mediated coupling, Friedel–Crafts reaction, Yamamoto reaction, Sonogashira cross-coupling, Suzuki coupling, hydrosilylation, solgel chemistry, thermolysis, self-assembly, Schiff base chemistry, radical polymerization, and electro-spinning. The formation of porous hybrid materials is subjected to the precursor of monomer and functional groups of POSS.

2.1 Organic Functional POSS Cages

In principle, the selected organic functional cubic POSS could offer access to the polymerization of organic–inorganic hybrids with controlled porosity, surface area and functionality via non-aqueous methods. It follows that the main aspects of POSS-nanobuilding blocks porosity characteristics include control over the porosity, pore size, and pore template. Design of the materials with the appropriate functional groups is important goal in the development of hybrid materials with high surface areas and controlled pore size. The ability to bridging the non-porous POSS building blocks might be useful for fabricating dense membranes, chemical barriers, and optical coatings. For example, POSS with non-reactive groups (Fig. 2a) has been used in polymer host in a molecular-level dispersion via physical blending and are studied as

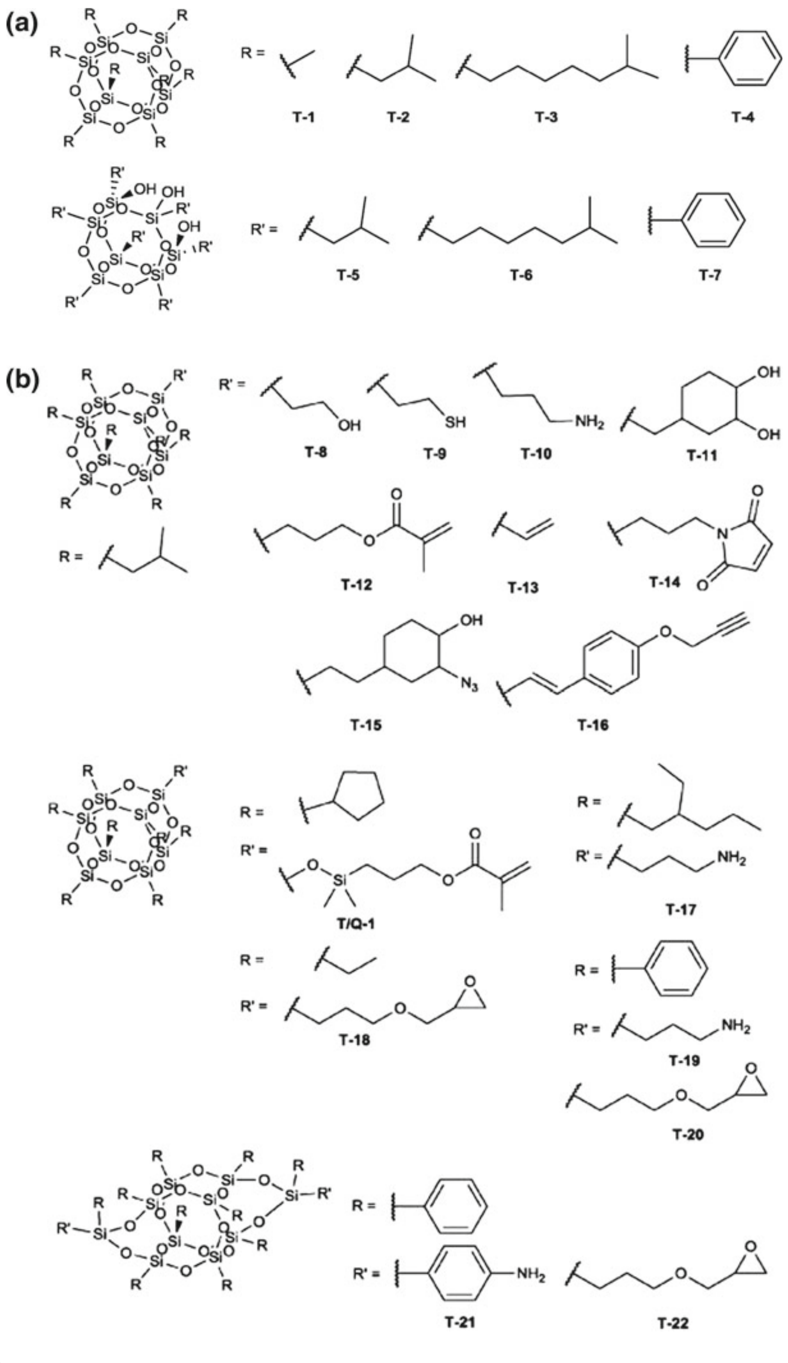


Fig. 2 Non-reactive organofunctional POSS (**a**), Mono- and di-functional POSS (**b**), Octa-functional POSS (**c**). Reprinted from [8], © 2016 with permission from Royal Society of Chemistry

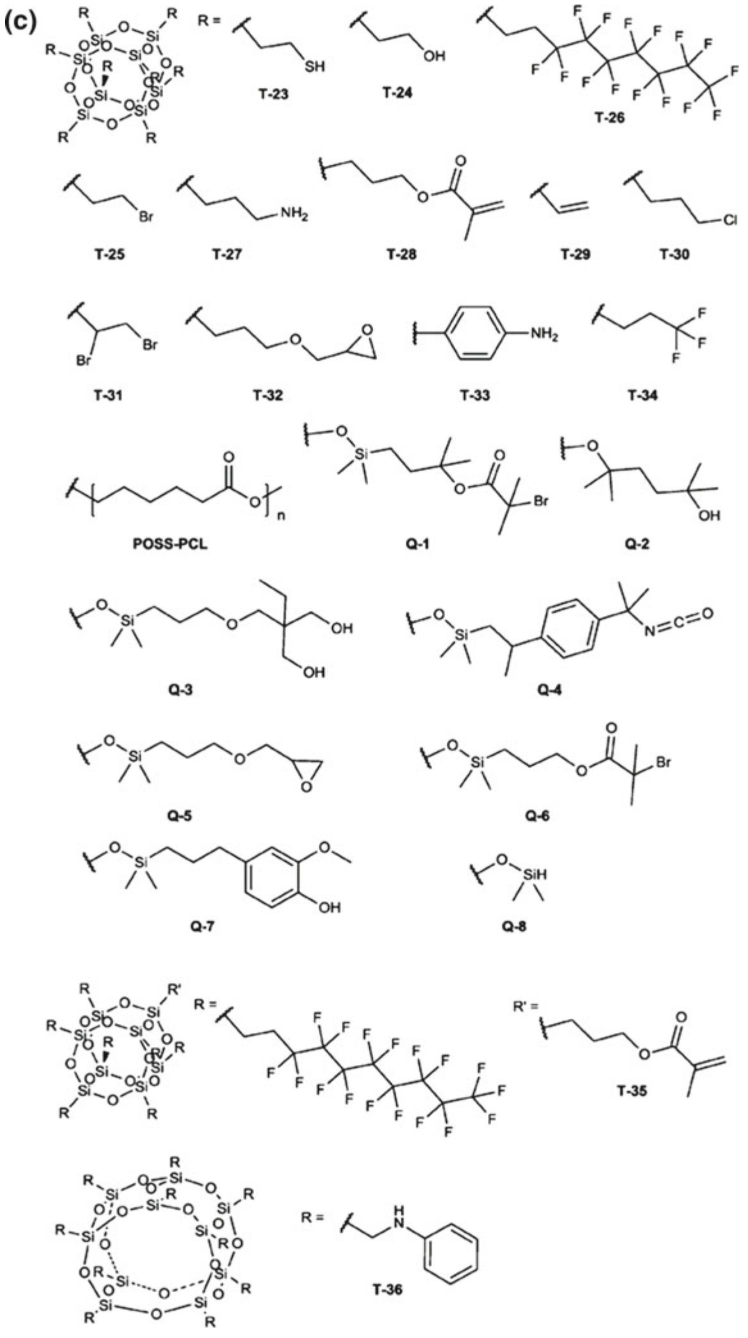
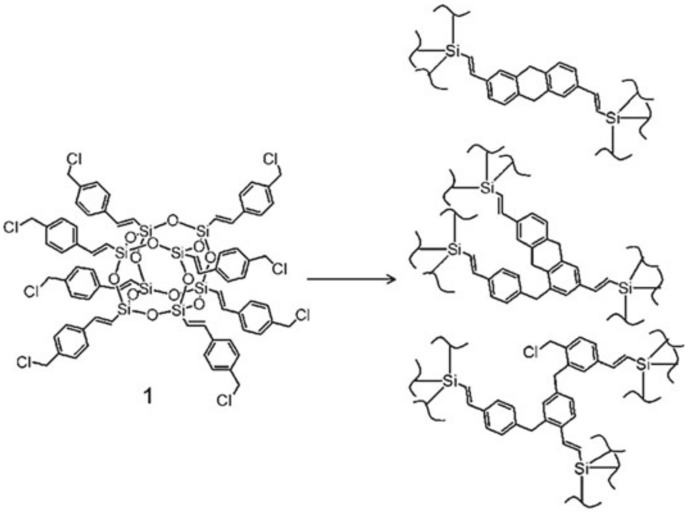


Fig. 2 (continued)

nanoscopic fillers. Further, mono- and di-functional reactive vertex groups of POSS (Fig. 2b) are used to cross-link covalently with the polymer matrix by polymerization or grafting. Most significantly, octa-functional reactive tether groups of POSS (Fig. 2c) were utilized to prepare different pore size of porous POSS hybrid materials, which would be homo-/copolymerization of POSS cages or POSS–polymer hybridization. The selectivity of incorporation of POSS functional reactive groups is associated with the polymer precursors that must be able to react with the polymer precursor otherwise it would be present as a blend; these reactive abilities of the organics can be by thermal, light, and catalyst. Multi-functional POSS gives a star-like macromolecule by initiating polymerization from the surface of the POSS, while the multi-reactive groups anchored POSS produce a heavily cross-linked polymer network. The well-ordered POSS–polymer hybrid matrix can be more precisely prepared via controlled polymerization, such as ATRP and RAFT. A large variety of POSS–polymer porous hybrids are possible to build up with these advanced polymerization strategies.

3 Porous Hybrid Materials with POSS

Organic–inorganic hybrid materials have long been known to play a major role in developing high-performance materials. Those hybrid materials are expected to exhibit new characteristics and both the advantages of organic and inorganic materials. In addition, hybrid materials have unique features which are not shown in the independent organic and inorganic materials. Thus, the hybrid materials have great interest to exploit their potential applications in the fields of mechanics, sensors, catalyst, medical, optical and electronic devices. Inorganic POSS is one of the versatile starting platforms which have one or more reactive sites, such as epoxy, thiol, amine, methacrylate, acrylate, styrene, norbornene, alcohol, and phenol, that provide ease compatibility of POSS with polymeric materials through the formation of strong covalent bonds. In this manner, a large diversity of POSS–polymer nanocomposites has been designed; they have many advantages in industrial appliances. Recently, benzoxazine-functionalized POSS has great attention in the development of hybrid polybenzoxazine thermosetting resins for high-performance and electrical applications. Lee et al. [13] reported the synthesis of a monofunctional POSS-benzoxazine which was used to incorporate into the polybenzoxazine system. Also, Zhang et al. [14] and Ariraman et al. [15] have been reported octahedral benzoxazine-functionalized POSS which was copolymerized with conventional benzoxazine results in the formation of porous structured POSS–polybenzoxazine matrix. They have been used as an interlayer low-*k* dielectric in microelectronics devices with good thermomechanical properties. Also the construction of porous POSS-based hybrids with those properties could be used to fabricate advanced devices. The rigid and cubic POSS with different functional groups has been well explored to construct three-dimensional porous hybrid polymer materials. Functional



1

PSN-5

Fig. 3 Synthesis of PSN-5 by Friedel-Crafts Self-Condensation of 1. Reprinted from [16], © 2011 with permission from American Chemical Society

porous materials have diverse applications, such as gas storage, dielectric, sensor, gas separation, and heterogeneous catalysis.

Chaikittisilp et al. [16] offered porous hybrid polymers via Friedel–Crafts alkylation polymerization of a benzyl chloride-terminated POSS monomer (Fig. 3) which shows Brunauer–Emmett–Teller (BET)-specific surface area of 2509 + 59 m^2 g^{-1} and a large total pore volume of 3.28 + 0.10 cm^3 g^{-1}. Further, acrylo-isobutyl-POSS and tetraphenylethene-containing acrylate-based copolymer (thickness of 560 nm) with uniform porous fiber-structured (~300 nm diameters) films have been developed by electro-spinning as an aggregation-induced emission (AIE)-active material, which shows significantly enhanced sensitivity to explosive vapors than the more thickness films, where the POSS cages are assisting in the formation of porous structures and subsequently increasing response to explosive vapors. The surface area of electro-spun thin film (S_{BET} 170 m^2 g^{-1}) is higher than that of the drop-cast thin films (S_{BET} 4 m^2 g^{-1}) [17]. Similarly, octa-tetraphenylethene-POSS-based microporous hydrogen-bonded organic framework (HOF) was developed via amide linkages [18], which shows a porosity of 101.9 m^2/g S_{BET}. The HOF exhibits a high fluorescence quenching effect with copper ion, and also the fluorescence of HOF has been recovered by cyanide. Also, a hybrid porous material was obtained via AIBN radical polymerization of octavinylsilsesquioxane (OVPOSS) with high S_{BET} of 1080 m^2 g^{-1} and 2 wt% hydrogen uptake [19].

Zhang et al. [20] offered a new approach to synthesis of mesoporous POSS hybrid materials with ordered structure, co-assembly of octa-ethyltriethoxysilyl-POSS around the P123 micelles and following condensation of triethoxysilyl and extraction of the obstructed P123 was generated mesoporous POSS network with uniform pore size, which exhibits a S_{BET} of 960 m^2 g^{-1} with a total pore volume of 0.91 cm^3 g^{-1}. Likewise, Li et al. [21] fabricated a series of ordered mesoporous silica and organosilicates using Pluronic F127 as a template via evaporation-induced self-assembly method. The weight ratios of tetraethyl orthosilicate (TEOS) and octa-ethyltriethoxysilyl-POSS precursors determined the mesophases, where the TEOS alone exhibits an ordered body-centered cubic (bcc) structure and was changed to ordered face-centered cubic (fcc) structure for 10 and 20 wt% of POSS and above 30 wt% of POSS showed disordered spherical pores. The porosity of the resulting hybrids was decreased from 831 to 537 m^2 g^{-1} while increasing the POSS content from 0–50 wt%, respectively.

Alves et al. [22] developed hybrid porous materials from OVPOSS via radical polymerization and thiol-ene click reaction using porogenic diluents such as tetrahydrofuran and polyethylene glycols. Highly porous monolithic building blocks with S_{BET} 700 m^2 g^{-1} or more and mesopore volumes of up to 2 cm^3 g^{-1} were prepared by choosing proper porogenic solvents and initiator. This approach explores a new route to derive porous hybrid adsorbents for a wide variety of applications.

Flexibility and length of the linking moieties and polycondensation reaction efficiency were determined the degree of porosity. Pawlak et al. [23] offered the hybrid porous structured frameworks, which were synthesized via hydrosilylation reactions of flexible linear siloxane spacers of 1,1,3,3-tetramethyldisiloxane (S-1) and 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (S-2) with octa(vinyl)-POSS using Pt(dvs) catalysts. The pore sizes of these two hybrid polymers were measured by positron annihilation lifetime spectroscopy. The S-1 exhibits a shorter linker with the free volume diameters of 5.32 ± 0.06 Å (POSS cages), 8.28 ± 0.05 Å, and 10.42 ± 0.05 Å (linker spacing), whereas S-2 has a longer linker with the diameters of 4.96 ± 0.04 Å (POSS cages) and 7.96 ± 0.06 Å (linker spacing). Further, based on the cross-linkers' length, the pores' shapes have shown as an ellipsoidal shape, and the S-1 and S-2 have similar pore sizes of 8–12 Å and 8–15 Å, respectively (Fig. 4). These pore sizes were related to the lengths of the cross-linkers.

Moreover, the PALS measurements revealed that the larger pore sizes of the polymers are not depending on the longer spacers. The S-1 shows a significant disorder and scatter in pore size, whereas the S-2 exhibits well-ordered POSS cages which were connected by the longer space linkers. Studies on the host–guest interactions of the complexes suggested that the presence of organic solvents strongly influenced on the molecular motion of the POSS units of S-2, whereas the S-1 remains rigid. This type of porous materials can be used for gas carriers and as containers for small organic compounds.

3.1 POSS–Polymer Hybrids

Polymers have widely been used as an adhesive in the preparation of composite films through covalent bonding and/or physical blending with inorganic species, includ-

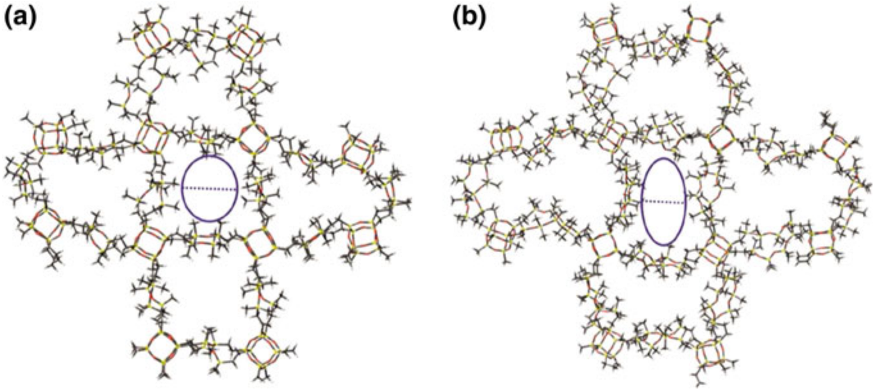


Fig. 4 Theoretical model of 1 (**a**) and 2 (**b**) with a pore size of 8–12 Å and 8–15 Å, respectively. Reprinted from [23], © 2015 with permission from American Chemical Society

ing silica. The incorporation of nanoparticles into the polymer thin films is useful to control porosity and permeability. The construction of thin films using large silica compounds has some limitations such as porosity, thickness, and strength of the film which are mainly defined by the size and stability of the silica species. Further, the liquid crystals or micelles are used as a template to attain nanometer-sized mesoporous silica films from a soluble silica source (e.g., TEOS) under hydrothermal or acidic conditions, despite problems arise from the limited stability of silica sols with <5 nm particles size. To overcome these limitations, the silica species are stabilized with organic molecules, for example, nanoporous POSS materials could be used as a nanosized building block with enhanced physical and chemical properties. The layer-by-layer self-assembly of octa(aminophenyl)silsesquioxane (OAPS) and poly-(styrene-4-sulfonate) (PSS) on the planar substrates and polystyrene particles formed as a multilayer thin film. The OAPS has adsorbed on PSS by promoting acid–base interactions between amine groups of OAPS and sulfonate groups of the PSS. Similarly, thin films have been constructed with alkylamines/amine-bearing organometallics and Bronsted acids, R-M(IV)(HPO_4)$_2$, H_2O (M = Zr, Ti, Sn, etc.), $HTiNbO_5$, and $HTaWO_6$, nH_2O [24]. OAPS is a prominent building block in the construction of ceramic membranes and different size and shape of siliceous capsular colloids and hybrid porous films on planar and spherical supports (Fig. 5).

Ye et al. [25] recently demonstrated POSS cross-linked polyimide (PI) aerogels, and OAPS was used to cross-link oligomers made from 3,3′,4,4′-biphenyltetracarboxylic dianhydride and bisaniline-p-xylidene; the resulting hybrids exhibit high thermal stability with 2% wt loss at 400 °C and low thermal conductivity of 14 mW(mK)$^{-1}$ at 760 Torr. SEM images of aerogels showed the porous morphology in which polymer fibers with diameters in the range of 15–50 nm tangled together and the S_{BET} of the aerogel was 240–260 m^2 g^{-1}. Furthermore, the reinforcement method of POSS cages into the polymer matrix is an important in the hybridization, because the physical properties of the hybrid materials were attributed

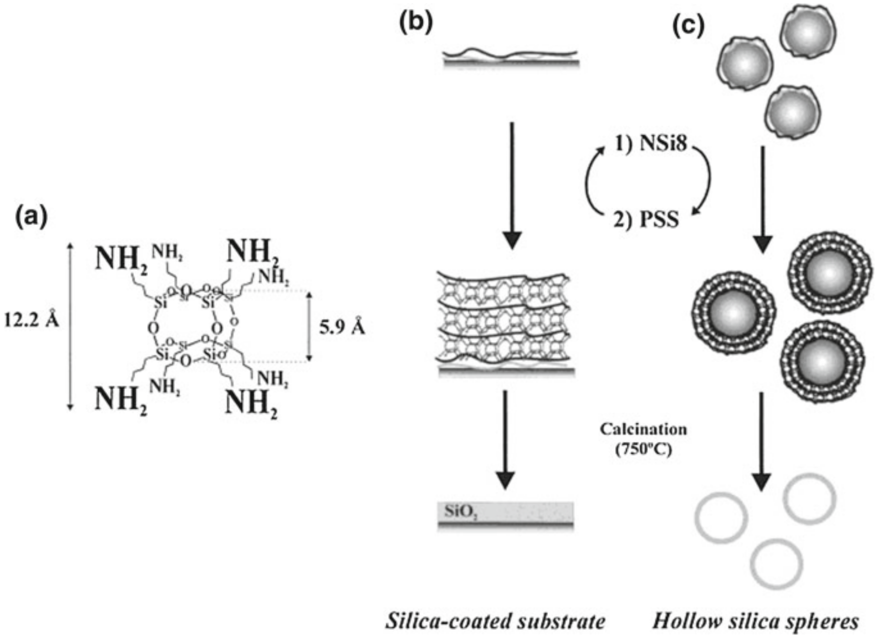


Fig. 5 Schematic diagrams of the LbL assembly of NSi8 molecules (**a**), with PSS on planar substrates (**b**), and on PS particles (**c**). Subsequent calcination results in supported thin silica films (**b**) or hollow silica spheres (**c**). Reprinted from [24], © 2002 with permission from American Chemical Society

to the homogeneous dispersion of POSS cages. Cozza et al. [26] demonstrated the homogeneous dispersion of POSS at a nanometric level into a polymer matrix by electro-spinning approach. Cellulose acetate was dissolved in the mixture of acetone/DMAc solvents with different weight percentages of epoxycyclohexylisobutyl-POSS and was used for the electro-spun and cast film preparation. This approach obliges in the molecular-level/nanosized clusters dispersion of POSS to develop alternative approaches capable to promote POSS distribution in the film. In addition, the hybrid micelles are derived from the combination of the hydrophobic segment of 3-iodopropyl-hepta(cyclopentyl)-POSS and hydrophilic part of polyoxazolines (POZO), where the micelle formation relies on the concentration of POSS incorporated into the POZO [27]. Consequently, the octa(isobutyl)-POSS is a non-amphiphilic and forms aggregates at all surface concentrations at the air/water interface; subsequently, the aggregation was dramatically decreased by blending with polydimethylsiloxane (PDMS) used as an amphiphilic (>10 wt% PDMS) which were studied by Brewster angle microscopy (BAM) [28]. Also, elastomers were developed from PDMS and POSS cages, the resulting POSS–PDMS nanocomposite elastomers show an improved thermal and mechanical properties, due to increase in the free volume of the final matrix [29].

Xiu Qiang et al. [30] demonstrated a series of star-shaped POSS-fluorinated acrylate copolymers, which are used to produce hydrophobic honeycomb-patterned micro-/nanoscale porous films via breath figure (BF) method, which depends on the influences of fluorine-based polymers and POSS cages, solvents utilized, and solution concentrations. These kinds of porous films could be retained after longtime preservation in an acid–base condition and show a great potential in cell culture, filtration, and tissue engineering applications. Likely, Hong et al. [31] reported POSS-fluorinated polyacrylates, which were synthesized by atom transfer radical polymerization. The hybrid porous films were optimized by varying the solution concentrations and solvents, and then the surface morphology of the porous films was evaluated which revealed that the amphiphilic-structured block copolymers are capable of forming well-organized porous films in a wide range of concentration, while star-shaped polymer without amphiphilic structure could only form regular porous array in some specific conditions. The ratios of pore diameter (D) and rim width (W), D/W, for the porous films were determined from SEM images and defined as fa. The influence of chemical composition and morphology on the surface hydrophobicity can be separated by the investigation of the correlation between fa and surface water CAs for the polymer films. The advantages of amphiphilic-structured block copolymers for porous films preparation are the ability to form hydrophobicity surface with much higher fa than those from hydrophobic polymer. The BF film with superhydrophobic surface was obtained by stripping the surface of the porous films, and the resulted films with pincushion-like structure show a high fa value.

A series of amphiphilic poly(vinyl alcohol)-POSS (PVA-POSS) hybrids have been synthesized via urethane linkage formation between the hydroxyl groups of PVA and the mono-isocyanate group of POSS macromers [32]. The electro-spun PVA-POSS fibers with highly porous crystalline structure show enhanced/controlled water resistance without the covalent cross-linking. The incorporation of POSS dramatically altered the solubility of the PVA-POSS hybrids, and hydrophobicity of PVA-POSS could be varied by controlling the concentration of POSS cages. Also, hybrid three-dimensional thermosetting resin of resol-type POSS–polymer ablative heat shielding material was produced from resorcinol formaldehyde (RF) and octa(phenyl)-POSS (OP-POSS) via facile in situ polymerization technique for thermal protection system (TPS) [33]. Further, POSS and 2-oxazoline-benzoxazine-based hybrids were prepared in one-pot reaction by the functionalization of OAPS via the formation of benzamidine structure by ring-opening and addition reactions between oxazoline and amino phenyl group at room temperature and subsequently the polymerization of benzoxazine at higher temperature [34]. However, higher content of OAPS may reduce the thermal properties of the nanocomposites. It is wondered that the introduced OAPS decreased the packing density and increased rigidity of the polymer matrix. OAPS may increase free volume by its nanoporous structure, and the Si–O core in OAPS leads to a plasticization of polymers, which decreases the Tg of the polymers. At high POSS content, the polymer matrix aggregation of POSS usually occurs, which is not advantageous for the thermal properties of the polymer. Therefore, particular concentration of POSS only can be utilized to enhance the thermal properties of the nanocomposites.

Hybrid mesoporous materials are synthesized from OAP-POSS and di-aldehyde through Schiff base chemistry; these hybrid materials show uniform mesoporous size and high specific surface areas. The molar ratio of POSS and aldehyde affects the porosity of the resultant POSS hybrid materials, where 1:0.7, 1:1, and 1:1.2 ratios show the S_{BET} of 637, 617, and 1103 m^2 g^{-1}, respectively, and beyond this ratio of 1:1.5 shows reduced S_{BET} [35]. Further, the condensation of OAPS and glutaraldehyde provides hybrid mesoporous networks via the formation of Schiff base. The material shows uniform mesoporous size and have S_{BET} of 641–1103 m^2 g^{-1} and pore volumes of 0.47–0.53 mL g^{-1} [35]. In addition, Liu et al. [36] fabricated the similar amine-terminated OAPS-glutaraldehyde hybrid networks with a specific surface area of 42.8 m^2 g^{-1} via modified reaction conditions, for the removal of acidic dye from wastewater. As a novel solid-phase adsorbent, these POSS nanohybrids possess selective adsorption properties for acidic dyes (e.g., methyl orange (MO). The strong electrostatic interactions between MO species and the amine groups of the nanohybrid are the main driving forces for MO adsorption, and the hybrid shows a maximum adsorption capacity of 237.5 mg g^{-1}. The adsorbed MO species could be effectively recovered by using the mixture of methanol/NaOH (9/1, v/v, 0.1 mol L^{-1} NaOH) as eluent. The cross-linked POSS nanohybrid appears to be a promising material in dye removal field which can be potentially applied for textile wastewater treatment.

Flexible polyurethane foams (PUFs) were largely used in mattresses, upholstered furniture, seats, etc., and needed to improve the quality of polyurethane foam which has been increased by adding POSS materials into the polyurethane foam via cross-linking. Recently, high compressive strength, thermally stable, and less water-absorbing polyurethane foams were constructed with defined cell structure and density by using 0–15 wt% of 1,2-propanediolisobutyl POSS (PHI-POSS) as a pendant group and octa (3-hydroxy-3-methylbutyldimethylsiloxy) POSS (OCTA-POSS) as a chemical cross-linker in the polyurethane polymer matrix. The addition of PHI-POSS into PUF significantly increased the number of foam cells with reduced average area of cells, whereas the OCTA-POSS decreased the number of foam cells and increased the average area of cells. Moreover, POSS cages form different sizes of lamellae-shaped crystals, distributed homogeneously in the bulk (PHI-POSS) or close to the self surfaces (OCTA-POSS). POSS-reinforced PUF hybrid foams possess greater compressive strength than the reference foam in the direction parallel and perpendicular to the direction of foam rise. The largest increase in compressive strength is observed for the 5 wt% OCTA-POSS/PUF hybrid, and it is about 192 kPa in a perpendicular direction and 189 kPa in the parallel direction, but further loading reverses the phenomenon. This is due to the crystalline nature of OCTA-POSS retained up to a particular concentration beyond that the PU closed cell structure was damaged. But, the compressive strength increases steadily with increasing PHI-POSS content in the PUF matrix, in all three directions is observed as compared with the reference foam. Also, due to increasing foam density, the PUF/POSS hybrids absorb less water than the pristine foam [37].

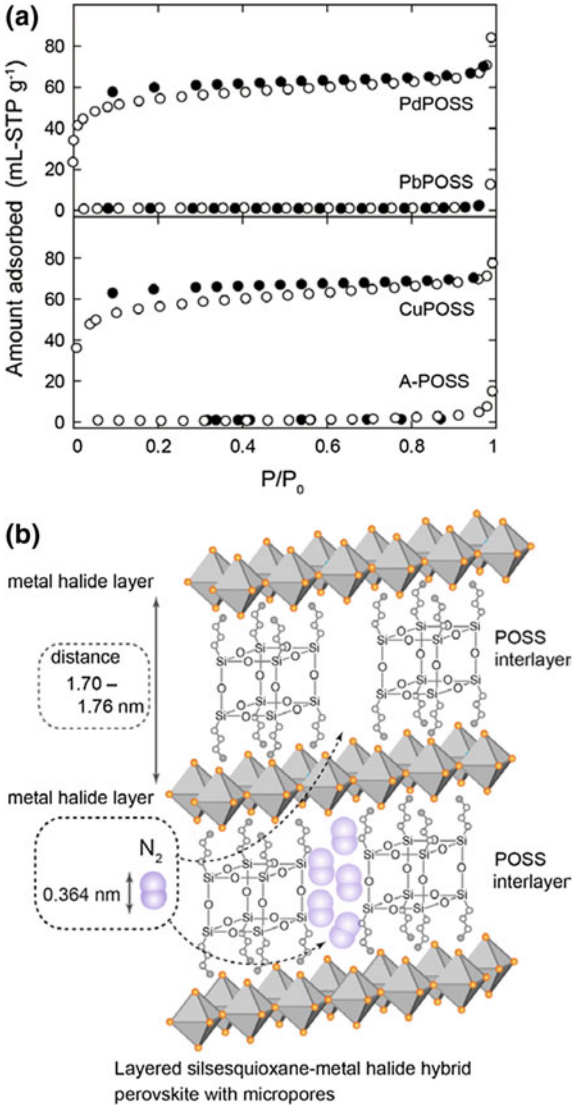
A sorbitol-based polyether polyol, polymeric 4,4′-diphenylmethane diisocyanate and dimethyl propane phosphonate (DMPP), PHI-POSS, and OCTA-POSS were used to prepare hybrid foam materials as a flame retardant. The incorporation of the POSS cages influences the cellular structure of PU as evidenced by a change in anisotropy index of the cross section parallel to the growth direction. The flammability results and thermogravimetric data suggest that the formation of char as a layer at the surface acts as an insulating barrier limiting heat and mass transfer with flame retardant and thus leading to decreased heat release rate, especially for systems containing OCTA-POSS. This is due to the formation of denser network by cross-linking of OCTA-POSS, whereas the pendant PHI-POSS cage does not impose such a prominent effect owing to its more loose arrangement in the PU matrix [38].

A high internal phase emulsion (HIPE) has been defined as an emulsion in which the internal phase occupies more than 74% of the volume. The porous structured polyHIPE nanocomposite with densities of around 1.5×10^2 kg/m^3 has been synthesized by cross-linking of 2-ethylhexyl acrylate (EHA) with vinyl silsesquioxane (VSQ) reinforcement. PolyEHA has a glass-transition temperature (T_g) of -50 °C and is flexible, and so EHA is often used as a cross-linked and reinforced elastomer. With increasing VSQ content, tan δ peak temperature, tan δ full width at half-maximum, room-temperature modulus, and stress at 40% strain all increased in a linear fashion, reflecting the increase in cross-linking through reaction with the reinforcing Si-O network. The VSQ-containing polyHIPE was compared to polyHIPE based on EHA cross-linked with divinylbenzene (DVB) and reinforced by reaction with a one vinyl tethered POSS, the tan δ peak temperature and modulus increased with increasing DVB content, reflecting the increase in cross-link density and in backbone rigidity [39]. In addition, polyHIPE nanocomposite with about 0.13 g/cm^3 densities was synthesized from EHA, DVB, organic cross-linker, and either methylsilsesquioxane (MSQ) or vinylsilsesquioxane (VSQ, SSQ cross-linker) [40]. The POSS-containing polyHIPE had significantly higher tan δ peak temperatures and moduli for similar Si contents. These properties were significantly larger for VSQ-based polyHIPE than for MSQ-based polyHIPE. Porous inorganic monoliths were produced on pyrolysis of these VSQ-containing polyHIPE. The most thermally stable polyHIPE nanocomposites were produced by the formation of SSQ-organic interconnected networks through VSQ and DVB cross-linking.

3.2 POSS–Metal Hybrids

POSS derivatives have been introduced into inorganic minerals to tune their physical properties. Kataoka et al. developed layered organic–inorganic hybrid perovskites with high crystallinity by self-assembling of metal halides ($CuCl_2$, $PdCl_2$, $PbCl_2$, and $MnCl_2$) and octa(Propylammonium)-POSS [41]. The presence of POSS as an interlayer between the metal halide perovskite layers producing the micropores enhances the low-dimensional properties of the materials. Also it has some magnetic ordering (CuPOSS and MnPOSS) and excitonic absorption/emission (PbPOSS) properties. The producing micropores in the perovskite materials by inserting POSS cages rendered a new approach the physical properties of the perovskite materials (Fig. 6).

Fig. 6 **a** N_2 sorption isotherms of silsesquioxane−metal halide complexes at 77 K (open circles, adsorption; filled circles, desorption). **b** Schematic diagram of layered POSS−inorganic hybrid perovskites with N_2 adsorbed between layers. Reprinted from [41], © 2015 with permission from American Chemical Society



Another approach has been made for the construction of dumbbell-shaped hybrid organic–inorganic molecules based on polyoxometalates (POM) and POSS with hierarchical supramolecular nanostructures [42]. A highly ordered lamellar morphology of POM-organic-POSS cocluster represents a strong thermodynamic force driving a nanoscale phase separation of the POM and POSS blocks. Further, coordination polymer networks have developed with ordered porous structure from eight carboxylic terminated POSS (S-POSS) and copper ions. The S-POSS was prepared by the treatment of octa(aminopropyl)-POSS with succinic anhydride; subsequently, the S-POSS was used as a ligand for making a network with metal centers [43].

Similarly, Hay et al. [44] reported linear titanium(IV)-POSS coordination polymer. Also, Sanil et al. [45] demonstrated a new method for the adsorption and separation of gases in the presence of relatively large amounts of moisture by enhancing the stability of $Cu_3(BTC)_2$ against moisture. To this, a metal–organic framework (MOF) was constructed by the functionalization of octa(aminopropyl)-POSS (O-POSS) with copper trimesate ($Cu_3(BTC)_2$) with enhanced hydrophobicity and stability against humidity. POSS modification was also successfully applied to other MOFs such as MOF-74 and MIL-100. $Cu_3(BTC)_2$ and O-POSS@$Cu_3(BTC)_2$ showed a S_{BET} of 1661 and 1514 m^2 g^{-1}, respectively. After the modification of $Cu_3(BTC)_2$ with O-POSS, there was no considerable decrease in the surface area. Due to the smaller window size of $Cu_3(BTC)_2$ (ca. 0.9 nm), it prevents the penetration of the larger size of O-POSS through the micropores of $Cu_3(BTC)_2$. After exposure to 90% relative humidity (RH), the S_{BET} of $Cu_3(BTC)_2$ drastically decreased from 1661 to 81 m^2 g^{-1}, whereas the S_{BET} of O-POSS@$Cu_3(BTC)_2$ slightly decreased from 1514 to 1476 m^2 g^{-1}. Also the SEM image of O-POSS@$Cu_3(BTC)_2$ showed there was no change in the morphology, but the morphology of $Cu_3(BTC)_2$ changed from cubic particles to agglomerated particles having an undefined shape. These results suggest that the surface modification of $Cu_3(BTC)_2$ with O-POSS dramatically enhances the stability of $Cu_3(BTC)_2$ against humidity.

Significant ion-exchanging capacity of the ionic-based porous materials shows important applications in various fields. Ionic liquids (ILs) often obtained from quaternization of N-heterocyclic compounds and alkyl halides, and also the POSS-based ILs were prepared by using the functional POSS moieties as cations or anions. However, Chen et al. [46] demonstrated the POSS-based porous cationic frameworks (PCIF-n), synthesized from octakis(chloromethyl)silsesquioxane (ClMePOSS) and N-heterocyclic cross-linkers [4,4′-bipyridine (4,4′-bpy), 1,2-bis(4-pyridyl)ethylene (bpe), N,N,N′,N′-tetramethylethylenediamine (tmeda), 1,3-bis(4-pyridyl) propane (bppa), 1,2-bis(4-pyridyl)ethane (bpea), bis(1-imidazolyl)methane (bim), and 1,4-diazabicyclo[2.2.2]octane (dabco)] as shown in Fig. 7. Hydrophobicity, mesoporosities with enhanced poly(ionic liquid)-like cationic structures, high surface areas (1025 cm^3 g^{-1}), and larger pore volumes (0.90 cm^3 g^{-1}) are the main advantages of the PCIF-n. Moreover, the most rigid molecule 4,4′-bpy shows the highest surface area of 1025 m^2 g^{-1}, whereas the less rigid bpe possesses lowered surface area of 396 m^2 g^{-1} and contrarily the flexible molecules bppa and bpea exhibit very low surface area ($\leq$40 m^2 g^{-1}), while the rigid cross-linkers of non-pyridine-based N-bearing organic molecules (bim, dabco, and tmeda) showed considerably high surface areas (183 ~ 729 m^2 g^{-1}) and also attained micro-/mesoporous frameworks. The resulting data revealed that the rigid structures of both POSS and N-bearing organic cross-linkers are the important prerequisites in the development of POSS-based porous cationic polymeric frameworks. Also, the PCIF-n materials were used as the supports for loading guest species ($PMo_{10}V_2O_{40}{}^{5-}$) to obtain the porous POSS–metal hybrid material denoted as PMoV@PCIF-1 as a potent heterogeneous catalyst for oxidation of cyclohexane and benzene.

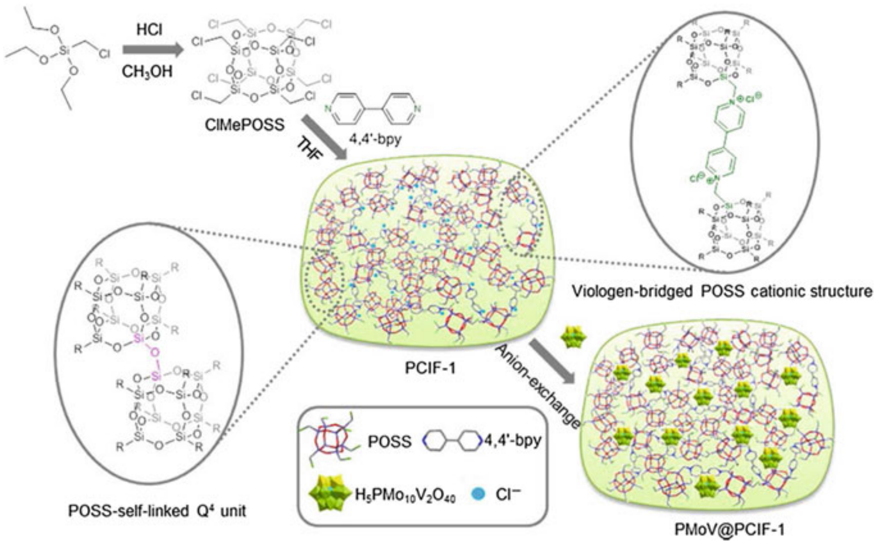


Fig. 7 Synthetic procedure of POSS-based porous cationic framework PCIF-1. From original synthesis of a new octakis(chloromethyl)silsesquioxane (ClMePOSS) monomer to the successive quaternization reaction of ClMePOSS with 4,4′-bipyridine (4,4′-bpy) to form PCIF-1. Then, bulky $PMo_{10}V_2O_{40}^{5-}$ (PMoV) anions are loaded into PCIF-1 to obtain the PMoV@PCIF-1 catalyst via anion-exchange process. Reprinted from [46], © 2015 with permission from Springer Nature

4 Properties of POSS Hybrid Porous Materials

Porous hybrids with pore properties such as pore size, pore volume, surface area, and pore geometry as well as shapes of materials (monoliths, films, and particles) including thermal and mechanical properties are technologically important materials especially in the field of adsorption, catalysis, and separation [47]. Well-defined POSS-based hybrid polymers with a variety of architectures have been developed including telechelic polymer, block copolymer, and star-shaped polymer hybrids by using variety of POSS precursors and unique living polymerization techniques, such as ring-opening/addition polymerization, free radical polymerization, coupling reactions, such as click chemistry and hydrosilylation reactions. Also, POSS nanoparticles have been self-assembled into aggregates in a selective solvents and form nanostructures in bulk [12]. The high compatibility of trisilanolphenyl-POSS/polycarbonate composites possesses significant transparency and crystallinity along with enhanced thermal and mechanical properties [48]. Also, Crowley et al. [49] reported POSS–poly(carbonate-urea)urethane (POSS-PCU) nanocomposites as a bio-scaffold for tissue engineering, which was optimized by dispersion of porogens (sodium chloride, sodium bicarbonate, and sucrose) onto the material surface to increase the surface porosity, thus providing additional opportunities for improved cellular and vascular ingrowth. The surface porosity of the composites relies on the size of porogens and larger porogens provided improved porosity. The larger pore sizes of these scaffolds favor for cellular integration and vascular ingrowth.

Brigo et al. [50] offered porous inorganic thin films from phenyl-bridged-POSS via sol-gel process. The structural and optical properties of the films were assessed and the formation of the porous system was investigated, after deposition and thermal treatments at increasing temperatures in the range of 60–800 °C. The spectral data indicate that the completely inorganic silica-based network at curing temperatures is higher than 500 °C, at which temperature the organic components of the hybrid film were eliminated and an elevated residual porosity was observed with a pore volume fraction of 35%. The films cured at 700 °C exhibited very low refractive index of 1.244 at 600 nm. Those micro- and mesoporous POSS hybrid thin films differentiate in pore dimension, dispersion, and connectivity from wide-spread developed mesoporous thin films for which large pores are produced by the removal of self-assembled polymeric units at higher temperature. The well-constructed porous structured hybrid POSS materials have shown significant properties, which lead to unlimited potentials for promising applications, such as biomedicine, electronic, sensors, optical, magnetic nanodevices, gas storage, and stimulated catalysts.

4.1 Porosity/Surface Area

More recently, porous materials with controlled porosity have been developed by the connection of inorganic building blocks themselves or with organics through the bridging groups, where the size of pores is controlled through the choice of the organic bridging groups that are capable of selective adsorption or catalysis. Copolymerization of hydride-terminated silyl POSS and alkene functionalized POSS through hydrosilylation process using Karstedt's catalyst offered porous materials [2]. The homogeneous porous materials have been developed by template synthesis method; organic templates are used during polymerization or cocondensation process which will be self-assembled uniformly, after that the templates are removed by the process of calcination, chemical oxidation or hydrolysis, whose pores size are roughly resembles to the size of the template. Accordingly, the acetylene-bridged POSS materials are allowed to the thermolysis process to burn away the acetylene template for obtaining the porous silica material. Also an alternative approach used low-temperature, inductively coupled plasma to eliminate organic bridging groups in cross-linked POSS xerogels and resulted in porous silica gels which pores size is larger than that of xerogels. The mesoporous silica gels can be obtained by treating non-porous alkylene-bridged POSS xerogels. The size of the pores can be increased by increasing the length of the bridging group.

The solgel process for the preparation of porous hybrid materials is sensitivity to the factors such as pH, aging time, catalyst, temperature, and solvent which are significantly controlled to permit the structure–property effects of the bridging group to be determined reproducibly. Many kinds of porous materials with different pore size have been prepared by changing the organic bridging groups. For example, arylene- and ethenylene-bridged POSS give rise to microporous materials with high surface areas of 1800 m^2/g including the mean pore diameters of <2 nm, whereas the alkylene-bridged POSS–polymer matrix with the bridging groups up to 10 carbons in length possess mesoporous xerogels. Despite, some of the literature suggested that the materials only with five- or six-atom bridges would be porous, while shorter or longer than that bridges led to be non-porous materials. But, another prepared porous hybrids exhibited high specific surface areas even with bridge lengths of two to four atoms. However, it has been suggested that the length of the organic bridges between the POSS cages is a critical factor in determining porosity. The length of the bridging groups is roughly proportional to the mean pore diameter of the hybrid material. Presence of unsaturated functional groups like aromatic and olefinic in the organic bridges could increase the rigidity and prevent the collapse of the formed pores during thermal process.

The condensation of metal alkoxides or alkoxysilanes has been mostly explored via solgel approach. The synthesis conditions such as concentrations of catalyst, type of catalyst, choosing solvent, temperature of the medium and also the drying circumstances of the materials are playing vital role in the formation of porous materials. Controlled processes of silane condensation under acidic or basic conditions offer gels which can be air-dried to get xerogels or supercritically dried to produce aerogels. For instance, POSS aerogels have been prepared as micro-/mesoporous materials based on organics-bridged bis(trialkoxy)silanes with surface areas up to 1000 m^2/g, pore volumes up to 0.6 mL/g. The further investigations on the synthesis of porous POSS–polymer hybrids offered types of pores generated during the condensation and cross-linking process with controlled surface area, porosity, and functionality. The positron annihilation lifetime spectroscopy (PALS) permitted to identify pores size of the cubic rigid POSS core (~0.3 nm) and in between of the POSS cubes (1–1.1 nm), while S_{BET} provided a view of the pore sizes in the range of 1–50 nm, whereas SAXS gives the overlapping confirmation of the two methods. The irreversible adsorption phenomena was happening at particular experimental conditions due to the presence of flexible linkages and micropores as well as mesopores in the hybrid polymers, which might be related to the swelling of a non-rigid porous structure.

4.2 *Morphology*

Liu et al. [51] reported the organic–inorganic mesoporous hybrid; the hybrid was prepared by two steps from octa-anionic-POSS and cationic surfactant: (i) lamellar precursor made of POSS and surfactant was prepared by template-directed synthesis; (ii) mesoporous structure was obtained via the reformation of lamellar precursor to hexagonal mesophase under hydrothermal treatment. The transformation can be illustrated by four stages, as (Fig. 8): (1) original lamellar structure, (2) corrugation of the lamellar sheets, (3) primary mesoporous structure, and (4) ordered mesoporous structure.

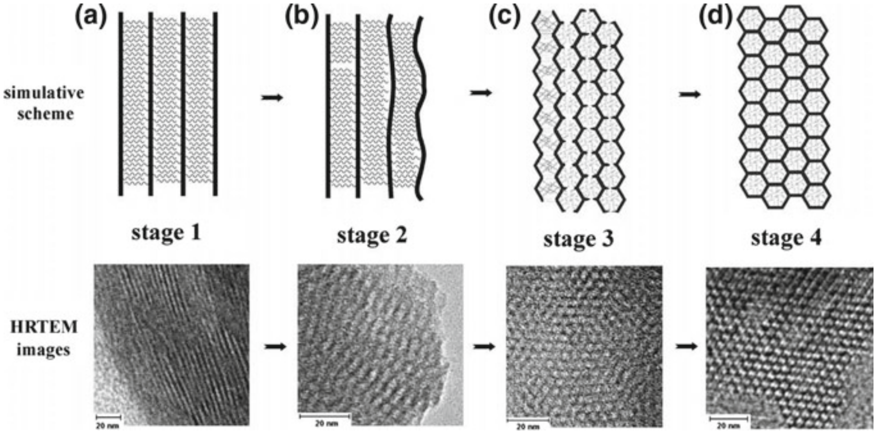


Fig. 8 Lamellar-to-hexagonal transformation process and corresponding HR-TEM images. **a** Original lamellar structure; **b** corrugation of the lamellar sheets; **c** primary mesoporous structure; **d** ordered mesoporous structure. Reprinted from [51]], © 2010 with permission from Elsevier

4.3 Thermal Properties

Incorporation of POSS molecules into the polymer system by blending/chemical cross-linking significantly enhances the thermal stability and porosity of the resulting POSS–polymer hybrid network. Alagar and coworkers [52] demonstrated the different functionalities of POSS reinforcement into the different kind of polymer materials and the thermal properties of resulting hybrid polymer materials with POSS. For example, a series of four different linear aliphatic ether-linked aromatic bismaleimides (AEBMIs) were synthesized, and then different ratios of POSS-AEBMI nanocomposites were prepared by Michael addition reaction. Data from thermal studies revealed that the particular ratios of POSS-AEBMI nanocomposites exhibit higher glass-transition temperature (T_g), thermal stability, limiting oxygen index, and lower dielectric constant when compared to that of neat AEBMI. Similarly, octa(maleimide)-POSS (OMPS), bisphenol-A-based cyanate ester (CE) and diaminodiphenylmethane (DDM) acting as a coupling agent were used to prepare CE-POSS hybrid network via in situ polymerization method by thermal curing [53], where the 5 wt% OMPS-incorporated nanocomposite shows higher glass-transition temperature than those of nanocomposites filled with a lower percentages of OMPS and neat amine-CE system. Also, Octakis(dimethylsiloxypropylglycidylether)silsesquioxane (OG-POSS)-reinforced polybenzoxazine nanocomposites exhibit significantly improved thermal stability and reduced dielectric constant [54]. Moreover, OAPS-incorporated epoxy-amine nanocomposites based on diglycidyl ether of bisphenol-A (DGEBA) and tetraglycidyl diamino diphenyl methane (TGDDM) were prepared and studied using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), indicate that the glass-transition temperatures of POSS (63 wt%) containing nanocomposites are higher than that of the corresponding neat epoxy systems [55]. Besides, the thermogravimetric analysis (TGA) shows that the POSS–epoxy nanocomposites exhibit high ceramic yields, suggesting that the improved flame retardant property. Similarly, the various compositions of OAPS-PI hybrids were prepared and thermal and dielectric properties of the nanocomposites were studied, higher content of POSS (15 wt%) in the nanocomposites substantially enhanced the glass-transition temperature (T_g), and thermal stability and char yield decreased the value of dielectric constant when compared to neat PI matrix [56].

4.4 Mechanical Properties

The nanoporous POSS cages' reinforcement into the polymer matrix by chemical cross-linking considerably increased the mechanical properties of the polymer hybrid system. In the glass state (−75 to −25°C), POSS–polymer hybrids exhibit higher value of dynamic storage moduli than that of the polymers. For example, 2 wt% of POSS cages introduced polyurethane (PU) polymer hybrids possessing significantly increased dynamic storage modulus [57]. However, the higher concentration of POSS-containing hybrids was showing less storage modulus than that of the PU. Due to the decreasing cross-linking densities of the hybrids with increasing concentration of POSS, the decreased densities could be attributed to an increase in the porosity of the POSS hybrids. The porosity of the matrix will rise by insertion of POSS cages which arises from the external porosity via increasing free volume of the nanocomposites and the nanoporosity of the POSS core with diameter of 0.54 nm. OAPS-incorporated epoxy-amine nanocomposites shows improved tensile, impact and flexural strength including thermal stability than that of the neat epoxy-amine system [58]. The OG-POSS and OAPS were used as a building block in the cyanate ester–epoxy nanocomposites; thermal, mechanical, and dielectric studies indicate the influences of POSS macromer existing in the nanocomposites, where the thermal stability and mechanical properties were enhanced significantly with increasing POSS content but decreased the value of dielectric constant and dielectric loss of the hybrid polymer system [59]. DDM and structurally modified diamines, namely bisphenol-A-based ether diamine, octane-diol-based ether diamine, and capron-based diamine, were used to cure DGEBA epoxy resin and were reinforced with different weight percentages of OAPS to obtain OAPS-epoxy-amine nanocomposites, where the epoxy-capron-based diamine cured matrix shows better improvement in tensile strength and impact strength of 39.8 and 137.0%, respectively, than those of epoxy-DDM system [60]. Additionally, the OAPS incorporation further improved the mechanical and thermal properties and also lowers the value of dielectric constant.

4.5 Catalytic Properties

Well-designed porous structured hybrid materials with POSS showed an excellent catalytic properties, Leng et al. [61] have been constructed porous amphiphilic polyoxometalate-paired ionic hybrids POSS–DIM_x–CIM_y–PW via free radical polymerization and ion exchange reaction using octavinyl-POSS and ionic liquids as building blocks. The POSS-free polymeric hybrid DIM_3–CIM_5–PW is a non-porous material with a surface area of only 6.2 cm^2 g^{-1}. POSS-containing polymer hybrid shows optimum specific surface area of 24.2 cm^2 g^{-1} and pore volume of 0.175 cm^3 g^{-1} and are found to be highly efficient catalysts for epoxidation of alkenes with H_2O_2 as oxidant. POSS–polymer hybrids show increasing relative pressure of $0.8 < P/P0 < 1$, indicating the presence of porous structures. This proves that the POSS plays an important role in the pore formation. Further, Scholder and Nischang [62] demonstrated the preparation of highly efficient and robust capillary flow reactors based on large surface area, hierarchically structured porous hybrid material constructed in situ from vinyl POSS. Functional variants of vinyl POSS show an excellent catalytic performance in Suzuki and carbon–carbon cross-coupling reactions. Also, Sangtrirutnugul et al. [63] reported POSS-based materials, poly-POSS-Tn ($n = 8$, 10, 12, and mix), were prepared in high yields via free radical polymerization of corresponding pure forms of methacrylate functionalized POSS monomers, MMA-POSS-Tn ($n = 8, 10, 12$), and the mixture form, MMA-POSS-Tmix (Fig. 9). The S_{BET} of the POSS hybrids decreased from 839 to 683 m^2 g^{-1} in the following trend: poly-POSS-T12 > poly-POSS-T10 > poly-POSS-Tmix > poly-POSS-T8. Also, the Barrett–Joyner–Halenda (BJH) analysis represents highest mesopores of poly-POSS-T12. The Pd nanoparticles immobilized on poly-POSS-Tn ($n = 8$, 10, 12, and mix) are well dispersed with 4–6 wt% Pd content and similar average particle sizes of 6.2–6.5 nm with the S_{BET} ranges of 521–850 m^2 g^{-1}. The stabilized POSS-based Pd nanoparticles catalyzed aerobic oxidation of benzyl alcohol to benzaldehyde in the reaction conditions of 90 °C, 6 h and a mixture of a H_2O/Pluronic (P123) solution, 72–100% yield. The PdNp@poly-POSS-T8 catalyst indicated the lowest catalytic activity, as a result of its lowest surface areas, total pore volumes, and amounts of mesopores. However, the PdNp@poly-POSS-Tmix catalyst showed an excellent catalytic activity in the conversion of various benzyl alcohol derivatives to the corresponding aldehydes in good to excellent yields.

4.6 Dielectric Properties

Dielectric properties of the materials can be improved by the incorporation of nano-sized filler-like POSS into polymeric matrices. The porous structured materials produced by POSS template or nanoporous POSS can generate air/vacuum in the hybrid materials which would help in the reduction of dielectric constant (κ) value of that materials [64]. Lee et al. [65] explained the reduction of κ value of PI/POSS hybrids

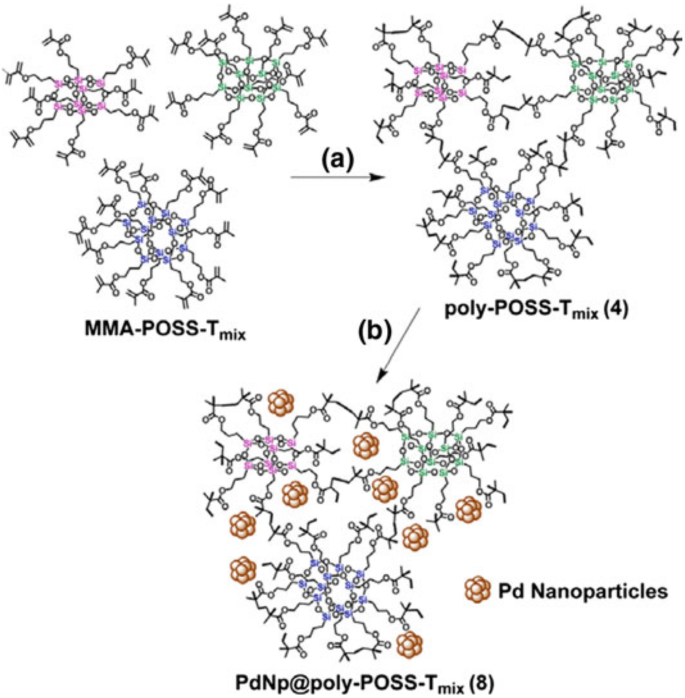


Fig. 9 A Representative Example for the Synthesis of Poly-POSS-Tmix and PdNp@poly-POSS-Tmix [**a** AIBN, PEG-200:THF (1:3 w/w), 60 °C, 24 h; **b** Pd(OAc)$_2$, NaBH4, CH3 OH, rt, 24 h]. Reprinted from [63]], © 2017 with permission from American Chemical Society

in terms of creating the porous silsesquioxane nanocores of the POSS and the free volume increase by the presence of the rigid and large POSS structure resulting in a loose polyimide (PI) network. The porosity of these nanocomposites is difficult to measure, and so they have adopted to measure the density to compare the relative porosity of these films. The density of pure PI and POSS are 1.38 and 1.10 g/cm^3, respectively. The measured dielectric constant of the PI is 3.22, whereas the PI/10 wt% epoxy—POSS is 2.65. However, OAPS/PI hybrid nanocomposites possess the lower value of κ (2.35) than that of PI ($\kappa = 4.45$) which inferred that the introduction of free volume into the hybrid matrix via restricted rotation of POSS by multiple point attachment to the PI backbone [66]. Accordingly, the proper insertion of POSS into a PI backbone can give rise to a reduction in the material's dielectric constant along with improved thermal and mechanical properties.

Leu et al. [67] reported porous POSS/PI nanocomposites as a low-κ dielectrics; nanoporous POSS-containing monoreactive amine group materials were reacted with poly(amic acid) having anhydride end groups. Polyimide chain-end tethered POSS can self-assemble into zigzag-shaped cylinders or lamellae by van der Waals force, 60–70 nm long and 5 nm wide. The resultant dielectric constant of the PI nanocomposite was reduced from 3.40 for the pure PI to 3.09 by incorporating 2.5 mol% of

POSS molecules. The PI/OAPS-POSS nanocomposites also exhibit a tunable dielectric constant with the change of content of OAPS-POSS, and the lowest value of 2.29 was observed 24.8 wt% of OAPS-POSS content. The reduction of dielectric constant was attributed to the POSS-induced external porosity and nanoporosity of POSS [68]. The low-κ nanoporous POSS-PI hybrid films could be developed by the incorporation of monoreactive functional group tethered octasilsesquioxanes into polymers via covalent bond [69]. Kuo and Chang [70] reported the grafting of a POSS derivative to POSS-PI hybrids having well-defined architectures. The presence of POSS molecules in a polymer matrix resulted in a nanoporous crystalline structure has both lower and tunable dielectric constants and controllable mechanical properties. Based on this approach, by controlling the amount of added POSS can be altered the dielectric constant of the film. Similarly, POSS-PI nanocomposites prepared by a graft polymerization of methacrylcyclopentyl-POSS (MA-POSS) with ozone-pretreated poly[N,N-(1,4-phenylene)-3,3,4,4-benzophenonetetra-carboxylic amic acid] (PAA), followed by thermal imidization which shows lower value of κ (2.2) than that of neat PI ($\kappa = 3.0$). The insertion of POSS cages into the side chain of PI films retained the nanoporous crystalline structure of the resulting matrix [71].

With minimal mole (2%) percentage of POSS-incorporated PI nanocomposites shows reduced κ value from 3.4 to 3.09 with retaining their tensile strength. The hybrid system self-assembled as lamellae or zigzag-shaped cylinders with 60–70 mm long and 5 mm wide, due to the formation of polar interactions between imide and van der Waal's forces between POSS cages [72]. Similarly, incorporation of 24.8 wt% OAPS into PI containing fluorine yielded 23% reduction in κ value, whereas 15 wt% Octakis(dimethylsiloxyhexafluoropropylglycidyl ether)silsesquioxane (OFG-POSS) in PI exhibits a 28% decrease in κ [73]. Moreover, the system retains high cross-link density, Young's modulus, porosity, and hydrophobicity but low polarizability. It is demonstrated that OFG-POSS efficiently reduces κ of PIs compared to other POSS derivatives.

Also, a nanoporous additive of fluorine-rich POSS cages (OF) were used to blend with UV-cured epoxy resin to decrease the κ value of the system by reducing polarizability, 10 wt% of OF reduces the κ value from 3.71 (plain epoxy) to 2.65 [74]. A poly(acetoxystyrene-co-octavinyl-POSS) (PAS–POSS) was developed as a low-κ organic–inorganic hybrid nanocomposites. The dielectric constant of PAS–POSS ($\kappa = 2.48$) is lowered than that of neat PAS ($\kappa = 2.81$), due to the increased relative porosity of the nanocomposite which arises from the intrinsic nanoporosity of POSS cages and the external porosity caused by the diluent effect of POSS [75].

Periodic mesoporous organosilica (PMO) is a distinct class of hybrid materials; POMs have shown diverse applications such as interconnect dielectrics for enabling smaller, faster, more powerful computer chips. Hybrid POSS-PMO thin film has been prepared using octa(triethoxysilylethyl)POSS by a template-directed, evaporation-induced, self-assembly (EISA) spin coating procedure, and the POSS-PMO thin film shrinks during those process. However, the POSS cage structure within the pore walls is retained and the mesoporous structure of the resulting POSS-PMO composites with ~1.5 nm pore size is maintained. Around 40% porosity of the hybrid POSS-PMO network was increased when compared to a reference POSS film, providing a reduced κ value from 2.03 (POSS-PMO) to 1.73 (POSS film) [76]. Joseph et al. [77] demonstrated the homogeneously dispersed hybrid syndiotactic polystyrene-POSS composites which exhibit low-κ value of 1.95 and loss of 10^{-4} at 5 GHz, with high thermal and mechanical properties. Moreover, POSS-based polybenzoxazine nanocomposites were prepared by the copolymerization of furan-containing benzoxazine compounds and methylmethacrylate-POSS (MMA-POSS). The dielectric constants of the nanocomposites reduced to 2.3 up to 0–70 wt% of POSS. Also the POSS orientation into lamellar structures in nanometer sizes further reduced the κ value of the nanocomposites to about 1.9 [78]. Thus, the structural arrangements are also significantly involved in the reduction of κ value of the nanocomposites.

Similarly, Alagar and coworkers [15] demonstrated a new class of lamellar structured POSS/bisphenol Z (POSS/BPZ) polybenzoxazine (PBz) nanocomposites with low-κ dielectrics. The BPZ-PBz and POSS-PBz layers were self-assembled by intermolecular hydrogen bonding in such a way as to form the lamellar structure during ring-opening polymerization. An advantage of this lamellar structure is that 30% POSS/BPZ polybenzoxazine nanocomposite exhibits an ultralow-κ value of 1.7 at 1 MHz as well as high thermal stability. Further, the combination of octa(glycidylether)-POSS, benzoxazine, and DGEBA-based low-κ materials developed with enhanced porosity or free volume; higher content of POSS (5.0 wt%) in PBZ/EP nanocomposites showed the lower values of κ (2.54) when compared to that of neat PBZ/EP ($k = 4.72$) [79]. However, POSS-reinforced polyurethane (PU)-based polybenzoxazine (PBz) nanocomposites demonstrated as an interlayer low-κ dielectric material based on the concept of polarization and porosity of the composite. Different weight ratios of hydroxyl terminated nanoporous POSS (OH—POSS) material and hydroxyl terminated benzoxazine (OH–Bz) materials containing a less polar long aliphatic chain were copolymerized with hexamethylenediisocyante (HMDI) to obtain POSS–Bz–PU nanocomposites. The κ value of the nanocomposites decreased with increasing aliphatic chain length and concentrations of POSS, but it is limited up to 30 wt% POSS–PU–PBz ($k = 1.94$), and beyond this concentration the reverse trend was observed which might be due to increasing density of the resulting nanocomposites by agglomeration of POSS nanoparticles [80]. The SEM images of 40% POSS–PU–PBz composites evidently support that the agglomerate formation of POSS particles. Also, two types of polybenzoxazine (PBZ) nanocomposites were prepared from benzoxazine monomer (BZ-Cy-OH) and organomodified MMT clay (OMMT) and OG-POSS (up to 7.5 wt%). The dielectric studies of these polybenzoxazine nanocomposites reveal that the POSS-reinforced nanocomposites have lower value of κ, whereas the OMMT clay possesses high-κ. This is due to changing the polarization of the resulting polymer nanocomposite matrix [81]. The biomaterial euginol-based POSS-OCN was hybridized in different ratios with bisphenol-A cyanate ester (BACY) to obtain porous structured BACY/POSS-OCN nanocomposites. The reinforcement of POSS-OCN significantly reduced the value of dielectric constant and dielectric loss as well; 30 wt% POSS-OCN/BACY nanocomposite possesses the lowest value of dielectric constant of 1.81 at 1 MHz [82]. Then different composition of OG-POSS and a flexible linear aliphatic alkoxy core-bridged bisphenol cyanate ester (AECE) nanocomposites demonstrated for low-

κ dielectrics; 10 wt% POSS-AECE$_4$ exhibits higher thermal stability and lower κ value of 2.4 when compared to that of neat AECE (κ =4.2) [83]. The increasing contact angle value and lowering surface free energy with POSS content inferred that the increasing hydrophobicity also contributes to the reduction of κ value.

A new approach has developed based on POSS-dendrimer hybrids to ultralow dielectric thin films for advanced microelectronics. This would be of particular interest to obtain nanoporous materials because they may avoid the porogen agglomeration and porogen matrix phase separation problems encountered with the so-called templating technique, where the thermally volatile dendrimer core is first added to the matrix and then removed from a two-component system by controlled temperature to produce well-defined voids in the remaining matrix. For example, hybrid materials having POSS cages and polyamidoamine dendrimer core were prepared and then allowed for the thermal treatment to create 3D nanodomained films or coatings as a low-κ material by removing thermally volatile dendrimer cores [84]. For example, a hybrid PEO-POSS template was used to prepare porous polyimide films, and thermally labile PEO-POSS nanoparticles would undergo oxidative thermolysis after blending with PI and to release small molecules as byproducts that diffuse out of the matrix to leave voids with the pore sizes of 10–40 nm into the polymer matrix which would efficiently reduce the value of κ (from 3.25 to 2.25) of the hybrid materials [85].

5 Applications of Porous POSS Hybrid Materials

POSS-based hybrid polymers have shown high glass-transition temperature, high decomposition temperature, and excellent oxygen permeability and also possess atomic oxygen resistance properties; they form a SiO$_2$ passivation layer during the thermal/UV treatment that prevents further decay of the underlying polymer [86]. Also those hybrids exhibit excellent flame-retardant properties and are used as a film coating for cabin items during space missions.

POSS-based epoxy resins can be used as an insulating glue to hold several metal layers of substrate in the printed circuit boards, which minimize shear stress with coefficients of thermal expansion between the circuit board and the Si chip [87].

The well-known binding properties of proteins to the silicone surfaces create more attention in the development of the biomedical devices. In addition, deposition of protein on silicone-based contact lenses is known to reduce both their medical performance and comfort. To overcome these drawbacks, POSS/silicone–protein interactions were studied which offered potential applications in biomedical fields [88].

Significant thermal and mechanical properties of POSS bring forward to the industries to solve the problem of higher temperature and oxidation resistance materials. POSS cages offer a simple alternative to rigid and high-resistant hybrid materials. POSS monomers can be easily soluble in most the organic solvents and are thermally stable which offered easy to blend or react with the organic molecules resulting hybrid polymers via radical, condensation, ring-opening polymerizations.

Highly porous three-dimensional array of cubes could offer excellent catalytic activities. POSS-based metal–organic frameworks are being explored as a catalyst for their ability to participate in chemical reactions [89].

Additionally, POSS-based metal–organic frameworks offered extensive applications in gas sorption, gas storage, and separation [90, 91]. The hybrid POSS-MOFs based materials sorption rate may be promising, but their structural, mechanical, and thermal stability needs to be improved.

Due to the presence of high porosity and stability of the Si-O cages in the hybrid matrix, coordination and hydrogen-bonded POSS–polymeric materials [92] might produce high-efficient gas storage materials.

POSS-based porous hybrid polymers and frameworks could be potentially applied for the fabrication of membranes, interlayer dielectrics, capacitors, insulators, monolithic columns, and medical devices.

Hybrid porous POSS–polymers can be applied as a promising material for H_2 and CO_2 storage; also those kinds of hybrids show selective CO_2 adsorbents rather than CH_4. These polymers are also show luminescent properties (maximum emission at ca. 420 nm), and they could be potentially applied as a blue light-emitting material [93].

5.1 Monolithic Columns

The monolithic column is being considered as a new-generation column for the chromatographic separation techniques; a novel organic–inorganic hybrid monolithic column was obtained by the cross-linking of inorganic octa-methacryl-POSS and organic long-chain quaternary ammonium methacrylate of *N*-(2-(methacryloyloxy)ethyl)-dimethyloctadecylammonium bromide via thermal initiated free radical copolymerization. Moreover, the permeability and porosity of the hybrid materials could be altered by varying the polymerization reagent composition. The incorporation of nanosized rigid POSS cages would be the responsible for thermal and mechanical properties of the POSS-based monolithic columns [94]. This work is enthused to develop various organic–inorganic hybrid monoliths through the copolymerization between organics and various POSS reagents for different applications. Later, organic–inorganic hybrid monolithic materials have been reported based on OVPOSS and appropriate multi-functional thiols as a linker [95]. Lin et al. [96] developed a series of epoxy–POSS and amine-based hybrid polymer monoliths with well-defined 3D skeletal and high-ordered microstructure (Fig. 10). These kinds of monoliths based on column chromatography exhibit high efficiency for the separation of small molecules, and this approach is versatility for the preparation of series of ordered porous hybrid monoliths with high surface area. Similarly, they were prepared by hybrid monoliths via thiol-methacrylate click polymerization reaction from methacrylate-POSS and multi-thiol cross-linkers such

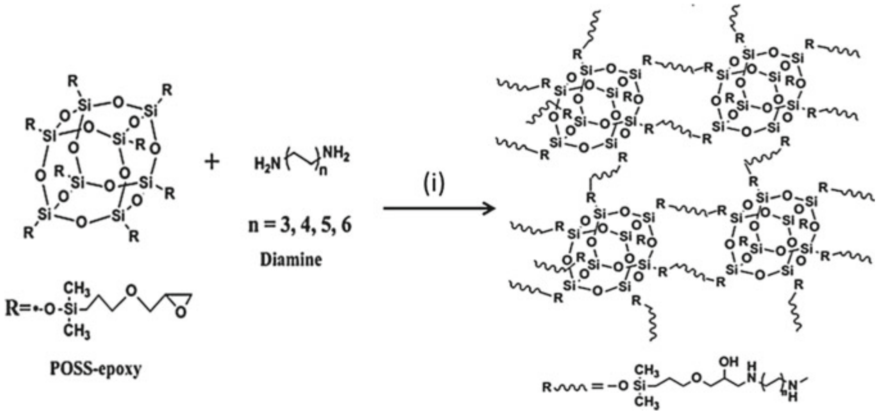


Fig. 10 Preparation of the hybrid monoliths via ring-opening polymerization of POSS–epoxy with different diamines. (i) PEG 10 000, propanol, 1,4-butanediol, 50 °C, 24 h. Reprinted from [96], © 2012 with permission from Royal Society of Chemistry

as trimethylolpropane tris(3-mercaptopropionate), 1,6-hexanedithiol, and pentaerythritol tetrakis(3-mercaptopropionate). These kinds of hybrid monoliths show high efficiency, and it can be used for the separations of polycyclic aromatic hydrocarbons, phenols, anilines, etc. [97].

Nischang and coauthors [98] reported two new hybrid monolithic columns based on OVPOSS, which were prepared by the copolymerization of vinylPOSS with pentaerythritol tetra (3-mercaptopropionate) or 2,20-(ethylenedioxy) diethanethiol via one-pot thiol-ene click reaction (Fig. 11), which monoliths show nanoscale network structures in an appropriate reaction conditions, and they were potentially used for the separation of uracil, benzyl alcohol, benzene, and alkylbenzenes.

Zhang et al. [99] reported new type of POSS-based hybrid monolithic column which prepared by thiol-acrylate click reaction using acryl-POSS as the cross-linker and sodium 3-mercapto-1-propanesulfonate as the monomer. The acryl-POSS cages were first constructed by self-polymerization and are polymerized with thiol monomer in one-pot and two-step approaches (Fig. 12). The one-pot approach has several potential applications in the separation of compounds, such as alkylbenzenes, basic compounds, phenolic compounds, a-casein or model proteins, and myoglobin. The efficiency of columns could be 60,000–73,500 plates/m for alkylbenzenes.

OG-POSS and polyethyleneimine (PEI)-based hybrid monolithic column was prepared by ring-opening polymerization; excess of unreacted amino groups on monolithic columns were treated chemically with g-gluconolactone or 1,2- epoxyoctadecane and physically coated with cellulose tris(3,5-dimethylphenyl-carbamate) (CDMPC) to obtain two different monolithic columns as shown in Fig. 13. High efficiencies (110,000 plates/m) of POSS-PEI hybrid monolithic column prepared for alkylbenzenes separation. The efficiency of g-gluconolactone-modified hybrid monolithic column could reach 60,000–80,000 plates/m for phenols, and also this

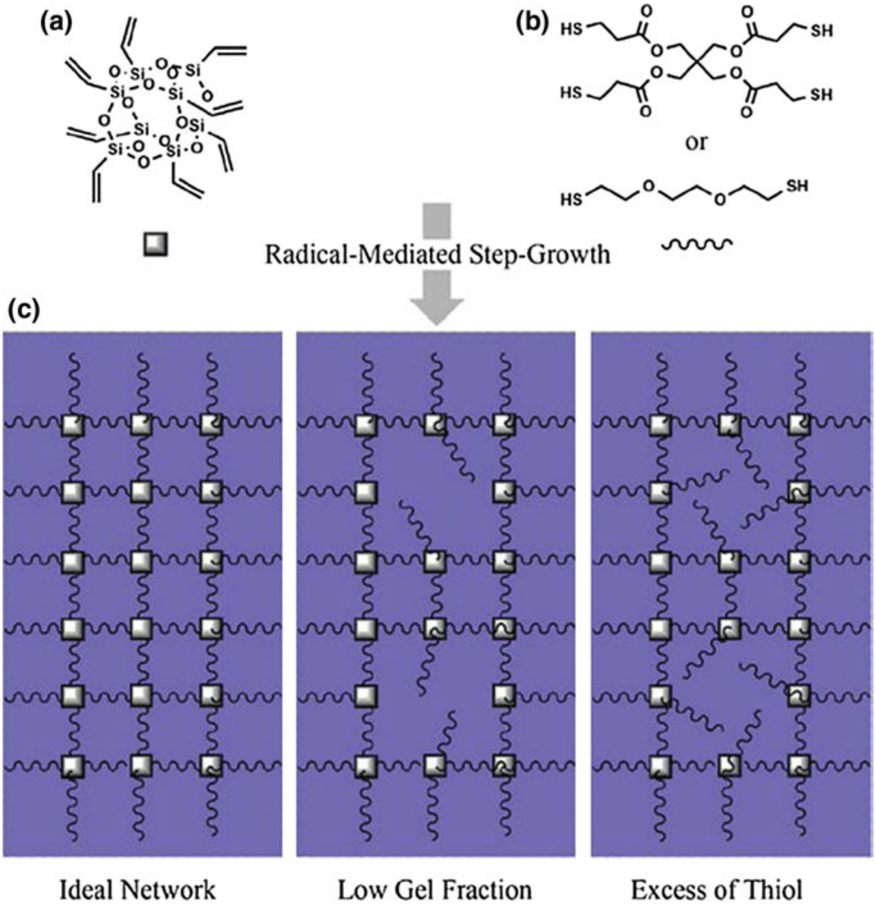


Fig. 11 Schematic diagram for the fabrication of POSS-PETMP and POSS-EDDT hybrid monolithic columns through the thiol-ene click reaction. Reprinted from [98], © 2015 with permission from Elsevier

column has high hydrophilicity which can potentially applied for the hydrophilic interaction liquid chromatography separation of phenols, small peptides, pyrimidines, purines, and nucleosides, with excellent peak shapes. Similarly, the CDMPC-modified column was used for the separation of basic racemates [100].

5.2 Biological Uses

The surface roughness and porosity have significant effect on hemocompatibility of blood-contacting biomaterials; porosity of POSS-PCU compromises its hemo-

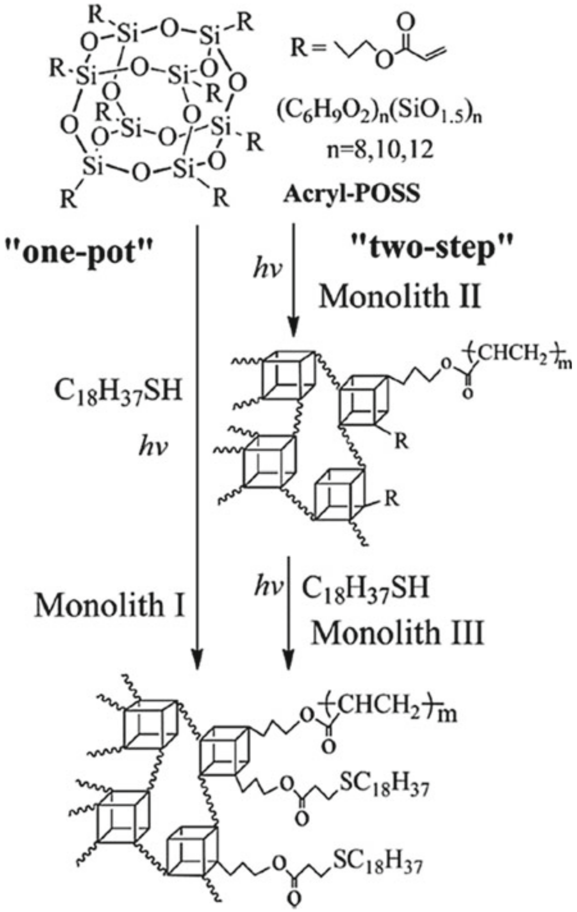


Fig. 12 "One-pot" and "two-step" methods for the preparation of C18-functionalized POSS-based hybrid monolithic columns through the thiol-acrylate click reaction. Reprinted from [99], © 2015 with permission from American Chemical Society

compatibility. The hemocompatibility of these materials was studied with different pore size of POSS-PCU films with PTFE as a control. Both tensile stress and strain decreased as the pores size of POSS-PCU increased, whereas the water contact angle (WCA) increased with the pore size of the film. However, when compared to PTFE, POSS-PCU showed both higher tensile stress and strain. Further, in whole-blood reactions, around 2–5 um pores size of POSS-PCU showed superior whole-blood compatibility index (BCI) than plain films and those with pores size around 35–45 um. Compared to porous PTFE, POSS-PCU showed lower thrombogenicity and higher hemocompatibility on the aspects of platelet activation, adhesion, and whole-blood reaction [101].

Teng et al. [102] reported highly porous star-shaped POSS–polycaprolactone-polyurethane (POSS-PCL-PU) films with improved mechanical and biological properties for tissue engineering. The high porosity, excellent biocompatibility, cell-substrate affinity, and unique surface nanotopography of the star-shaped POSS-PCL-

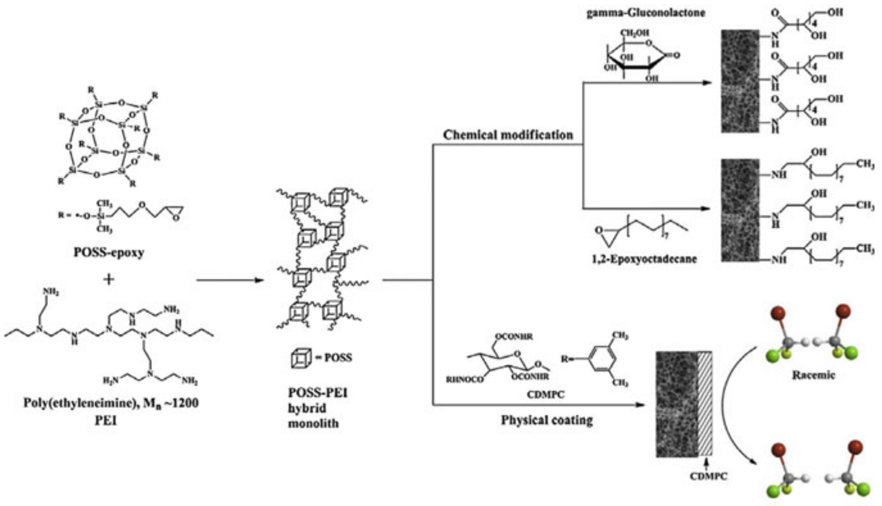


Fig. 13 Schematic diagram for the fabrication and post-modification of POSS-PEI hybrid monolithic column. Reprinted from [100], © 2013 with permission from Elsevier

PU film make it a great candidate as a tissue engineering scaffold biomaterial. The POSS-PCL-PU films have a high porosity of>75% and intrinsic nanoscale features that enhance cell attachment and growth. Compared to the porosity of the linear PCL-PU films of 43.1 ± 4.4%, star-shaped POSS-PCL-PU films exhibit a higher porosity of 75.7 ± 7.4%. The higher porosity with greater interconnectivity of pores enables more efficient transport of nutrients in the scaffolds without compromising the mechanical stability.

Janeta et al. [103] developed a macroporous scaffold through the reaction of 3-(trimethoxysilyl)propyl methacrylate-POSS (pTMSPMA–POSS) (Fig. 14) and the trifluoromethanesulfonate-POSS salt for sophisticated bone replacement, avoiding a long-lasting and complex methodology. The chemical composition, structural dimensions, topography, and microstructural properties of the hybrid macroporous scaffold fulfill the potential requirements for hard-tissue engineering.

He et al. [104] reported molecularly imprinted hybrid porous nanomagnetic-POSS-based materials for the determination of antibiotic residues in milk samples, which were constructed from nanomagnetic-OVPOSS (Fe_3O_4@POSS), methacrylic acid, and enrofloxacin via copolymerization. Compared to non-imprinted POSS nanoparticles (Fe_3O_4@NI-POSS), molecularly imprinted nanoparticles (Fe_3O_4@MI-POSS) showed higher adsorption and selectivity toward enrofloxacin template. The larger surface area and pore volume of MI-material would be responsible for its larger adsorption capacity than that of NI-material, S_{BET} of Fe_3O_4@POSS, Fe_3O_4@MI-POSS, and Fe_3O_4@NI-POSS are 625.96, 357.06, and 294.75 m^2 g^{-1}, respectively. Three fluoroquinolones (FQs) such as ofloxacin, enrofloxacin, and danofloxacin were selectively extracted from the milk simples

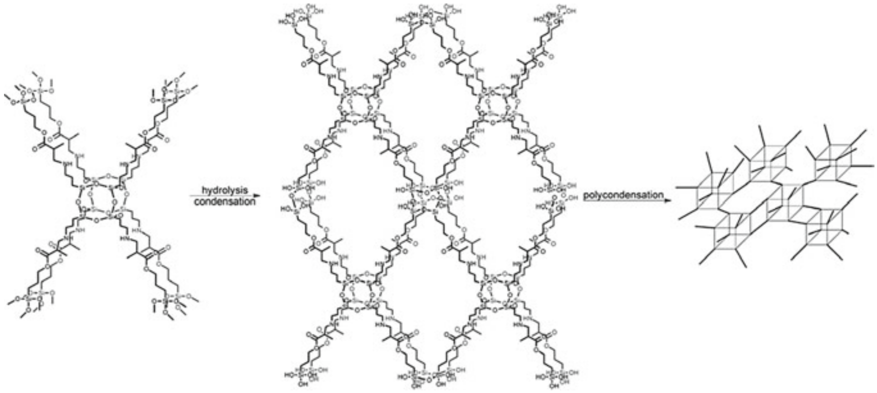


Fig. 14 General idea of the formation of the pTMSPMA–POSS network. Reprinted from [103], © 2016 with permission from Royal Society of Chemistry

through the Fe_3O_4@MI-POSS material which was combined with HPLC-UV detection. This technique would support to develop POSS-based molecularly imprinted porous hybrid materials with high efficiency for the analysis of complicated biological samples.

5.3 Gas Storage/CO_2 Adsorption

Wang et al. [105] have been prepared hybrid porous polymers via Heck reaction using octavinylsilsesquioxane and different tetrahedral silicon-centered precursors containing di-, tri-, or tetrabromophenyl groups. Their porosities have been tuned in the range of almost no porosity and to high porosity by altering the number of the connecting sites of silicon-centered units; POSS-silicon-centered tetrabromophenyl (HPP-5) hybrids possess high porosities with a maximum S_{BET} of 875 $m^2\ g^{-1}$ and total pore volume of 0.56 $cm^3\ g^{-1}$. For gas storage applications, HPP-5 exhibits the following properties: a high H_2 uptake of 7.76 mmol g^1 (1.56 wt%) at 77 K and 1.01 bar; a moderate CO_2 uptake of 1.04 mmol g^1 (4.58 wt%) at 298 K and 1.04 bar; and a low CH_4 uptake of 0.28 mmol g^1 (0.45 wt%) at 298 K and 1 bar. Similarly, cubic octavinylsilsesquioxane with planar tri-halogenated benzene shows tunable porosities with S_{BET} ranging from 479 to 805 $m^2\ g^{-1}$ and with the total pore volume ranging from 0.33 to 0.59 $cm^3\ g^{-1}$ [106].

Petit et al. [107] described the ionic grafting of polymer chains onto POSS cages to obtain liquid-like nanoparticles organic hybrid materials relevant to CO_2 capture. Increasing POSS units significantly enhance the thermal stability and porosity of the hybrid materials and CO_2 capture as well. Also, a series of POSS-based luminescent hybrid porous polymers were synthesized by Heck coupling reaction from octa(vinyl)-POSS and halogenated triphenylamine (TPA), porous and luminescent properties of those POSS hybrids were tuned by altering TPA species and reaction condition. The optimized tris(4- bromophenyl)amine-based POSS–polymer hybrid exhibits high porosity with a S_{BET} of 680 m^2 g^{-1} and pore volume of 0.41 cm^3 g^{-1} and also possesses reasonable CO_2 uptake of 1.44 mmol g^{-1} at 273 K and 0.77 mmol g^{-1} at 298 K at 1.01 bar and emits high yellow luminescence [108]. In addition, luminescence of these hybrids could be quenched by nitroaromatic explosives; thus, it can be used as chemical sensors for explosives detection. Excellent luminescent performance was obtained for the highest porous POSS–polymer hybrid which infers that the increased porosity can enhance the luminescence due to the interwoven porous network.

Similarly, Wang et al. [109] reported the octa(vinyl)-POSS and 2,7-dibromo-9-fluorenone-based hybrid porous polymer (HPP-1) as an eminent material for post-functionalization of amine by conversion of ketone moieties into amine functionalities. The HPP-1-amine shows enhanced CO_2 uptake than that of HPP-1, from 0.63 mmol g^{-1} (HPP-1) to 1.01 mmol g^{-1} (HPP-1-EDA, EDA = ethylenediamine) and 0.72 mmol g^{-1} (HPP-1- HDA, HDA = hexamethylenediamine) at 298 K and 1 bar. Further, the porosity of HPP-1-amine is not compromised, but the S_{BET} increased from 529 m^2 g^{-1} (HPP-1) to 651 m^2 g^{-1} (HPP-1-EDA) and 615 m^2 g^{-1} (HPP-1-HDA). Also by altering the monomer species and reaction conditions can increase the porosity of the HPP-1 containing POSS units and CO_2 uptake as well. Furthermore, the hybrid porous materials were synthesized using octa(phenyl)-POSS and formaldehyde dimethyl acetal via Friedel–Crafts (POPS-1) and Scholl coupling (POPS-2) reactions to obtain two different porous POSS hybrid materials. These materials are predominantly microporous and mesoporous with S_{BET} of 795 and 472 m^2 g^{-1} for POPS-1 and POPS-2, respectively. Moreover, POPS-1 can reversibly adsorb 9.73 wt% CO_2 (1 bar and 273 K) and 0.89 wt% H2 (1.13 bar and 77 K), and POPS-2 shows moderate gas uptake with 8.12 wt% CO_2 (1 bar and 273 K) and 0.64 wt% H_2 (1.13 bar and 77 K) [110].

5.4 Energy Storage

Tang et al. [111] demonstrated the nitrogen-doped carbon materials with well-defined nanoporous structure (Fig. 15) for the electrochemical energy conversion and storage devices. Different weight ratios of OAPS/resol were mixed and cured at 100 °C for 24 h, and then it was crushed and allowed to pyrolysis at 900 °C under nitrogen atmosphere for 3 h; the resulting powder was washed with 10 wt% of HF solution to remove silica moieties and was dried at 120 °C, and the obtained powder was denoted as *N*-doped nanoporous carbon (NNC). The NNC from OAPS to resol ratio of 95:5 showed adjustable nitrogen content (3.63–5.37%), large surface area (1942 m^2 g^{-1}), uniform and well-defined nanopores (0.85–1 nm), high nanopore volume (0.53–0.88 cm^3 g^{-1}) and also have high specific capacitance of 230 Fg^{-1} at 1 Ag^{-1}.

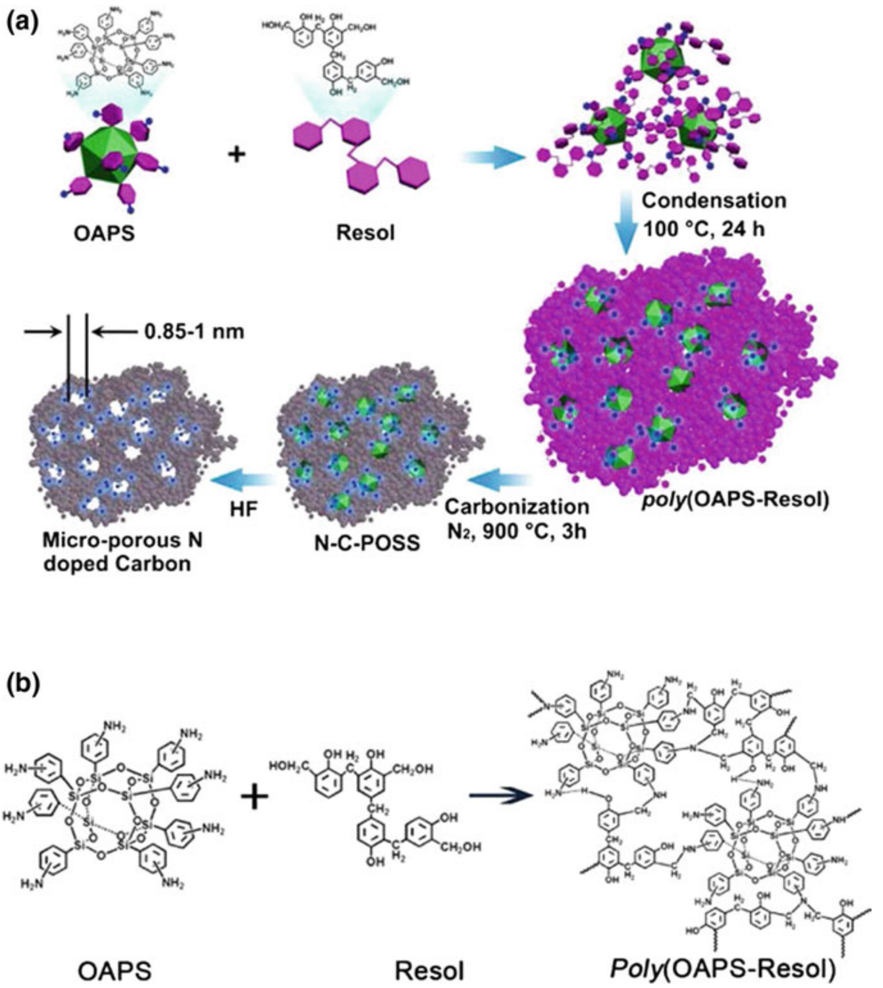


Fig. 15 **a** Schematic illustration of synthesis of OAPS-derived nitrogen-doped nanoporous carbon materials and **b** formation of poly(OAPS-resol) between OAPS and resol cross-linker via hydrogen bonding. Reprinted from [111], © 2016 with permission from Elsevier

Liu et al. [112] fabricated hierarchically porous structured carbon materials on the basis of self-assembly of POSS and amphiphilic triblock copolymers (PEO-PPO-PEO), where the POSS acts both as the carbon source and the self-template for producing uniform micropores while the block copolymers act as the soft templates for producing ordered mesopores. The obtained carbon materials with high specific surface area of over 2000 $m^2 g^{-1}$ and large pore volume of over 1.19 $cm^3 g^{-1}$ possess both quite uniform micropores with the size of 1 nm and highly ordered mesopores with the size of 4 nm, owing to the molecular-scale templating effect of POSS siloxane cages as well as the good assembly compatibility between the block copolymers and the aminophenyl-POSS. Galvanostatic charge/discharge test results show that their maximum specific capacitance can reach 163 Fg^{-1} in ionic liquid electrolyte and 216 Fg^{-1} in aqueous H_2SO_4 electrolyte, when measured in a symmetrical two-electrode cell. The advantage of the hierarchical micro-/mesoporous carbons over the strictly microporous carbons lies in their outstanding rate performance, due to dramatically reduced charge transfer resistance. The sample with the highest mesoporosity demonstrates a best rate capability with 94 and 97% of capacitance retention when the current density is increased from 0.25 to 10 A g^{-1} in ionic liquid and 1 M H_2SO_4, respectively.

5.5 Membranes

Only limited articles reported on porous POSS–polymer membranes; Dasgupta et al. [113] reported that the POSS–polyimide membranes for gas (H_2, N_2, CH_4, O_2, and CO_2) separation. Masakoto et al. reported the synthesis of inter- and intra-cubic porous structured homogeneous POSS-derived silica membranes and their single gas permeation characteristics. The amorphous silica structured membranes have a negligible number of pores larger than 0.35 nm and are appropriate to separate organic gas mixtures [73]. The controlled pore size of the silica networks was prepared by organic-template method, organotrialkoxysilanes are copolymerized with tetralkoxysilane, and the organic portion will burn out after pyrolysis and leave pores homogeneously where the size and shape of the organic groups determine the size and shape of the pores.

The homogeneous (HOMO)-POSS-derived silica membranes were prepared by the solgel method, and their single gas permeation characteristics were studied in the temperature range of 100–500 °C. Normalized Knudsen-based permeance (NKP) was applied for quantitative evaluation of membrane pore sizes less than 1 nm. By changing the calcination temperatures, pore size of the HOMO-POSS membranes was successfully tuned and the membrane shows loose amorphous silica structures compared to TEOS membranes, due to the difference in the minimum unit of silica networks. Compared to tetraethoxysilane (TEOS)-derived silica membranes HOMO-POSS membranes showed superior CO_2/CH_4 separation performance with a CO_2 permeance of 1.1×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with a CO_2/CH_4 permeance ratio of 131 at 100 °C. Membranes fired at 300 °C showed high hydrogen permeance of 2.0×10^{-6} mol m^{-2} s^{-1} Pa^{-1} with a high H_2/SF_6 permeance ratio of 1200 and a low H_2/N_2 permeance ratio (20) at 200 °C. HOMO-POSS-derived membranes fired at 550 °C showed uniform pore size of 0.42 nm with much higher activation energy and larger He/H_2 permeance ratios [114]. Also, a series of aminoethylaminopropylisobutyl functionalized POSS-based POSS–polyimide (POSS-PI) nanocomposite membranes shows unique gas transport properties; these POSS–polyimide membranes have a significant increase in permeability of gas compared to the pure polyimide membranes. The permeability order of membranes for four gas is as $P(CO_2) > P(O_2) > P(N_2) > P(CH_4)$. The PI-POSS-II has max CO_2 permeability (128%), whereas the PI-POSS-III shows high O_2 permeability (143%) [113]. The diverse characteristics of permeability coefficients of the different membranes can be explained by the variation of free volume, caused by the bulky nanoporous POSS cages exhibited within the polymer network.

6 Conclusion

Different approaches were demonstrated for diversity of porous structured POSS-based hybrid materials; the nanoporous POSS tethered with different organic functional groups were applied. In this chapter, the importance of porosity and the method of pores construction by using the combination of POSS and organics/metal ions were provided with their dielectric, catalytic, adsorption, thermal, and mechanical properties. The alignment of POSS by self-polymerization or copolymerization with organic polymers determined the formation of pores in the resulting hybrid POSS–polymer networks, where the arrangement varies with varying POSS functional groups. The largest porous POSS hybrid polymers with BET surface area of $2509 + 59\ m^2\ g^{-1}$ and a large total pore volume of $3.28 + 0.10\ cm^3\ g^{-1}$ were synthesized via Lewis acid-assisted Friedel–Crafts alkylation polymerization of benzyl chloride-terminated POSS. POSS-based catalysts have potential applications for epoxidation of alkenes, Suzuki and carbon–carbon cross-couplings, and aerobic oxidation of benzyl alcohol to benzaldehyde. Moreover, POSS-based organic–inorganic hybrid porous materials could be applied for a wide variety of gas storage, membranes, foams, chromatogram, biomedical, energy storage, and engineering applications.

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References

1. Kickelbick G (2014) Hybrid materials–past, present and future. Hybrid Mater 1
2. Pielichowski K, Njuguna J, Janowski B, Pielichowski J (2006) Polyhedral oligomeric silsesquioxanes (POSS)-containing nanohybrid polymers. In: supramolecular polymers polymeric betains oligomers. Springer Berlin Heidelberg, Berlin, Heidelberg, pp 225–296. https://doi.org/10.1007/12_077
3. Seçkin T, Köytepe S, Adıgüzel Hİ (2008) Molecular design of POSS core star polyimides as a route to low-κ dielectric materials. Mater Chem Phys 112:1040–1046
4. Zhang C, Babonneau F, Bonhomme C, Laine RM, Soles CL, Hristov HA, Yee AF (1998) Highly porous polyhedral silsesquioxane polymers. Synth charact J Am Chem Soc 120:8380–8391
5. Bassindale AR, Gentle TE (1993) Siloxane and hydrocarbon octopus molecules with silsesquioxane cores. J Mater Chem 3:1319–1325

6. Feher FJ, Budzichowski TA, Blanski RL, Weller KJ, Ziller JW (1991) Facile syntheses of new incompletely condensed polyhedral oligosilsesquioxanes:[(c-C5H9) 7Si7O9 (OH) 3],[(c-C7H13) 7Si7O9 (OH) 3], and [(c-C7H13) 6Si6O7 (OH) 4]. Organometallics 10:2526–2528
7. Ro HW, Soles CL (2011) Silsesquioxanes in nanoscale patterning applications. Mater Today 14:20–33
8. Zhou H, Ye Q, Xu J (2017) Polyhedral oligomeric silsesquioxane-based hybrid materials and their applications. Mater Chem Front 1:212–230
9. Hurd CB (1946) Studies on siloxanes. I. the specific volume and viscosity in relation to temperature and constitution. J Am Chem Soc 68:364–370
10. Wu J, Mather PT (2009) POSS polymers: physical properties and biomaterials applications
11. Wang F, Lu X, He C (2011) Some recent developments of polyhedral oligomeric silsesquioxane (POSS)-based polymeric materials. J Mater Chem 21:2775–2782
12. Zhang W, Müller AH (2013) Architecture, self-assembly and properties of well-defined hybrid polymers based on polyhedral oligomeric silsequioxane (POSS). Prog Polym Sci 38:1121–1162
13. Lee J, Cho H-J, Jung B-J, Cho NS, Shim H-K (2004) Stabilized blue luminescent polyfluorenes: introducing polyhedral oligomeric silsesquioxane. Macromolecules 37:8523–8529
14. Zhang K, Zhuang Q, Liu X, Yang G, Cai R, Han Z (2013) A new benzoxazine containing benzoxazole-functionalized polyhedral oligomeric silsesquioxane and the corresponding polybenzoxazine nanocomposites. Macromolecules 46:2696–2704
15. Ariraman M, Alagar M (2014) Design of lamellar structured POSS/BPZ polybenzoxazine nanocomposites as a novel class of ultra low-k dielectric materials. Rsc Adv 4:19127–19136
16. Chaikittisilp W, Kubo M, Moteki T, Sugawara-Narutaki A, Shimojima A, Okubo T (2011) Porous siloxane–organic hybrid with ultrahigh surface area through simultaneous polymerization–destruction of functionalized cubic siloxane cages. J Am Chem Soc 133:13832–13835
17. Zhou H et al (2014) Electrospun aggregation-induced emission active POSS-based porous copolymer films for detection of explosives. Chem Commun 50:13785–13788
18. Zhou H et al (2015) A thermally stable and reversible microporous hydrogen-bonded organic framework: aggregation induced emission and metal ion-sensing properties. J Mater Chem C 3:11874–11880
19. Wei Z, Luo X, Zhang L, Luo M (2014) POSS-based hybrid porous materials with exceptional hydrogen uptake at low pressure. Microporous Mesoporous Mater 193:35–39
20. Zhang L et al (2007) Mesoporous organic–inorganic hybrid materials built using polyhedral oligomeric silsesquioxane blocks. Angew Chem 119:5091–5094
21. Li J-G, Chu W-C, Kuo S-W (2015) Hybrid mesoporous silicas and microporous POSS-based frameworks incorporating evaporation-induced self-assembly. Nanomaterials 5:1087–1101
22. Alves F, Scholder P, Nischang I (2013) Conceptual design of large surface area porous polymeric hybrid media based on polyhedral oligomeric silsesquioxane precursors: preparation, tailoring of porous properties, and internal surface functionalization. ACS Appl Mater Interfaces 5:2517–2526
23. Pawlak T, Kowalewska A, Be Zgardzińska, Potrzebowski MJ (2015) Structure, dynamics, and host-guest interactions in POSS functionalized cross-linked nanoporous hybrid organic-inorganic polymers. J Phys Chem C 119:26575–26587
24. Cassagneau T, Caruso F (2002) Oligosilsesquioxanes as versatile building blocks for the preparation of self-assembled thin films. J Am Chem Soc 124:8172–8180
25. Ye Q, Zhou H, Xu J (2016) Cubic polyhedral oligomeric silsesquioxane based functional materials: synthesis, assembly, and applications. Chem–An Asian J 11:1322–1337
26. Cozza ES, Monticelli O, Marsano E (2010) Electrospinning: a novel method to incorporate POSS into a polymer matrix. Macromol Mater Eng 295:791–795
27. Kim K-M, Keum D-K, Chujo Y (2003) Organic−inorganic polymer hybrids using polyoxazoline initiated by functionalized silsesquioxane. Macromolecules 36:867–875
28. Hottle JR, Deng J, Kim H-J, Farmer-Creely CE, Viers BD, Esker AR (2005) Blends of amphiphilic poly (dimethylsiloxane) and nonamphiphilic octaisobutyl-POSS at the air/water interface. Langmuir 21:2250–2259

29. Baumann TF, Jones TV, Wilson T, Saab AP, Maxwell RS (2009) Synthesis and characterization of novel PDMS nanocomposites using POSS derivatives as cross-linking filler. J Polym Sci, Part A: Polym Chem 47:2589–2596
30. Qiang X, Ma X, Li Z, Hou X (2014) Synthesis of star-shaped polyhedral oligomeric silsesquioxane (POSS) fluorinated acrylates for hydrophobic honeycomb porous film application. Colloid Polym Sci 292:1531–1544
31. Hong Q, Ma X, Li Z, Chen F, Zhang Q (2016) Tuning the surface hydrophobicity of honeycomb porous films fabricated by star-shaped POSS-fluorinated acrylates polymer via breath-figure-templated self-assembly. Mater Des 96:1–9
32. Kim C-K, Kim B-S, Sheikh FA, Lee U-S, Khil M-S, Kim H-Y (2007) Amphiphilic poly (vinyl alcohol) hybrids and electrospun nanofibers incorporating polyhedral oligosilsesquioxane. Macromolecules 40:4823–4828
33. Gupta R, Kandasubramanian B (2015) Hybrid caged nanostructure ablative composites of octaphenyl-POSS/RF as heat shields. RSC Adv 5:8757–8769
34. Cao H, Yan D, Sun X, Xu R, Yu D (2009) Synthesis and characterization of a novel 2-oxazoline-benzoxazine compound with incorporated polyhedral oligomeric silsesquioxane. Des Monomers Polym 12:565–578
35. Qin Y, Ren H, Zhu F, Zhang L, Shang C, Wei Z, Luo M (2011) Preparation of POSS-based organic–inorganic hybrid mesoporous materials networks through Schiff base chemistry. Eur Polym J 47:853–860
36. Liu J, Yu H, Liang Q, Liu Y, Shen J, Bai Q (2017) Preparation of polyhedral oligomeric silsesquioxane based cross-linked inorganic-organic nanohybrid as adsorbent for selective removal of acidic dyes from aqueous solution. J Colloid Interface Sci 497:402–412
37. Hebda E, Ozimek J, Raftopoulos KN, Michałowski S, Pielichowski J, Jancia M, Pielichowski K (2015) Synthesis and morphology of rigid polyurethane foams with POSS as pendant groups or chemical crosslinks. Polym Adv Technol 26:932–940. https://doi.org/10.1002/pat.3504
38. Michałowski S, Hebda E, Pielichowski K (2017) Thermal stability and flammability of polyurethane foams chemically reinforced with POSS. J Therm Anal Calorim 130:155–163. https://doi.org/10.1007/s10973-017-6391-4
39. Normatov J, Silverstein MS (2007) Silsesquioxane-cross-linked porous nanocomposites synthesized within high internal phase emulsions. Macromolecules 40:8329–8335
40. Normatov J, Silverstein MS (2008) Interconnected silsesquioxane—organic networks in porous nanocomposites synthesized within high internal phase emulsions. Chem Mater 20:1571–1577
41. Kataoka S et al (2015) Layered hybrid perovskites with micropores created by alkylammonium functional silsesquioxane interlayers. J Am Chem Soc 137:4158–4163
42. Hu M-B et al (2013) POM–organic–POSS cocluster: creating a dumbbell-shaped hybrid molecule for programming hierarchical supramolecular nanostructures. Langmuir 29:5714–5722
43. Banerjee S, Kataoka S, Takahashi T, Kamimura Y, Suzuki K, Sato K, Endo A (2016) Controlled formation of ordered coordination polymeric networks using silsesquioxane building blocks. Dalton Trans 45:17082–17086
44. Hay MT, Seurer B, Holmes D, Lee A (2010) A Novel Linear Titanium (IV)-POSS Coordination Polymer. Macromolecules 43:2108–2110
45. Sanil E et al (2015) A polyhedral oligomeric silsesquioxane functionalized copper trimesate. Chem Commun 51:8418–8420
46. Chen G et al (2015) Construction of porous cationic frameworks by crosslinking polyhedral oligomeric silsesquioxane units with N-heterocyclic linkers. Sci Rep 5:11236
47. Kanamori K, Nakanishi K (2011) Controlled pore formation in organotrialkoxysilane-derived hybrids: from aerogels to hierarchically porous monoliths. Chem Soc Rev 40:754–770
48. Zhao Y, Schiraldi DA (2005) Thermal and mechanical properties of polyhedral oligomeric silsesquioxane (POSS)/polycarbonate composites. Polymer 46:11640–11647
49. Crowley C et al (2016) Surface modification of a POSS-nanocomposite material to enhance cellular integration of a synthetic bioscaffold. Biomaterials 83:283–293

50. Brigo L, Faustini M, Pistore A, Kang HK, Ferraris C, Schutzmann S, Brusatin G (2016) Porous inorganic thin films from bridged silsesquioxane sol–gel precursors. J Non-Cryst Solids 432:399–405
51. Liu L, Hu Y, Song L, Gu X, Chen Y, Ni Z (2010) Mesoporous hybrid from anionic polyhedral oligomeric silsesquioxanes (POSS) and cationic surfactant by hydrothermal approach. Microporous Mesoporous Mater 132:567–571
52. Devaraju S, Vengatesan M, Selvi M, Alagar M (2014) Thermal and dielectric properties of newly developed linear aliphatic-ether linked bismaleimide-polyhedral oligomeric silsesquioxane (POSS-AEBMI) nanocomposites. J Therm Anal Calorim 117:1047–1063
53. Jothibasu S, Devaraju S, Venkatesan MR, Chandramohan A, Kumar AA, Alagar M (2012) Thermal, thermoechanical and morphological behavior of Octa (maleimido phenyl) silsesquioxane (OMPS)-cyanate ester nanocomposites. High Perform Polym 24:379–388
54. Chandramohan A, Devaraju S, Vengatesan M, Alagar M (2012) Octakis (dimethylsiloxypropylglycidylether) silsesquioxane (OG-POSS) reinforced 1, 1-bis (3-methyl-4-hydroxymethyl) cyclohexane based polybenzoxazine nanocomposites. J Polym Res 19:9903
55. Nagendiran S, Alagar M, Hamerton I (2010) Octasilsesquioxane-reinforced DGEBA and TGDDM epoxy nanocomposites: characterization of thermal, dielectric and morphological properties. Acta Mater 58:3345–3356
56. Devaraju S, Vengatesan M, Alagar M (2011) Studies on thermal and dielectric properties of ether linked cyclohexyl diamine (ELCD)-based polyimide POSS nanocomposites (POSS-PI). High Perform Polym 23:99–111
57. Liu H, Zheng S (2005) Polyurethane networks nanoreinforced by polyhedral oligomeric silsesquioxane. Macromol Rapid Commun 26:196–200
58. Chandramohan A, Alagar M (2013) Preparation and characterization of cyclohexyl moiety toughened POSS-reinforced epoxy nanocomposites. Int J Polym Anal Charact 18:73–81
59. Chandramohan A, Dinkaran K, Kumar AA, Alagar M (2012) Synthesis and characterization of epoxy modified cyanate ester POSS nanocomposites. High Perform Polym 24:405–417
60. Sethuraman K, Prabunathan P, Alagar M (2014) Thermo-mechanical and surface properties of POSS reinforced structurally different diamine cured epoxy nanocomposites. RSC Adv 4:45433–45441
61. Leng Y, Zhao J, Jiang P, Wang J (2015) Amphiphilic porous polyhedral oligomeric silsesquioxanes (POSS) incorporated polyoxometalate-paired polymeric hybrids: Interfacial catalysts for epoxidation reactions. RSC Adv 5:17709–17715
62. Scholder P, Nischang I (2015) Miniaturized catalysis: monolithic, highly porous, large surface area capillary flow reactors constructed in situ from polyhedral oligomeric silsesquioxanes (POSS). Catal Sci Technol 5:3917–3921
63. Sangtrirutnugul P et al (2017) Tunable porosity of cross-linked-polyhedral oligomeric silsesquioxane supports for palladium-catalyzed aerobic alcohol oxidation in water. ACS Appl Mater Interfaces 9:12812–12822
64. Ayandele E, Sarkar B, Alexandridis P (2012) Polyhedral oligomeric silsesquioxane (POSS)-containing polymer nanocomposites. Nanomaterials 2:445–475
65. Lee Y-J, Huang J-M, Kuo S-W, Lu J-S, Chang F-C (2005) Polyimide and polyhedral oligomeric silsesquioxane nanocomposites for low-dielectric applications. Polymer 46:173–181
66. Song L, He Q, Hu Y, Chen H, Liu L (2008) Study on thermal degradation and combustion behaviors of PC/POSS hybrids. Polym Degrad Stab 93:627–639
67. Leu C-M, Reddy GM, Wei K-H, Shu C-F (2003) Synthesis and dielectric properties of polyimide-chain-end tethered polyhedral oligomeric silsesquioxane nanocomposites. Chem Mater 15:2261–2265
68. Huang J, Lim PC, Shen L, Pallathadka PK, Zeng K, He C (2005) Cubic silsesquioxane–polyimide nanocomposites with improved thermomechanical and dielectric properties. Acta Mater 53:2395–2404
69. Leu C-M, Chang Y-T, Wei K-H (2003) Polyimide-side-chain tethered polyhedral oligomeric silsesquioxane nanocomposites for low-dielectric film applications. Chem Mater 15:3721–3727

70. Kuo S-W, Chang F-C (2011) POSS related polymer nanocomposites. Prog Polym Sci 36:1649–1696
71. Chen Y, Chen L, Nie H, Kang E (2006) Low-κ nanocomposite films based on polyimides with grafted polyhedral oligomeric silsesquioxane. J Appl Polym Sci 99:2226–2232
72. Joshi M, Butola BS (2004) Polymeric nanocomposites—Polyhedral oligomeric silsesquioxanes (POSS) as hybrid nanofiller. J Macromol Sci Part C: Polym Rev 44:389–410
73. Zhao J, Fu Y, Liu S (2008) Polyhedral oligomeric silsesquioxane (POSS)-modified thermoplastic and thermosetting nanocomposites: a review. Polym Polym Compos 16:483
74. Wang YZ, Chen WY, Yang CC, Lin CL, Chang FC (2007) Novel epoxy nanocomposite of low Dk introduced fluorine-containing POSS structure. J Polym Sci, Part B: Polym Phys 45:502–510
75. Zhang C, Xu HY, Zhao X (2010) Structure and properties of low-dielectric-constant poly (acetoxystyrene-co-octavinyl-polyhedral oligomeric silsesquioxane) hybrid nanocomposite. Chin Chem Lett 21:488–491
76. Seino M, Wang W, Lofgreen JE, Puzzo DP, Manabe T, Ozin GA (2011) Low-k periodic mesoporous organosilica with air walls: POSS-PMO. J Am Chem Soc 133:18082–18085
77. Joseph AM, Nagendra B, Surendran K, Bhoje Gowd E (2015) Syndiotactic polystyrene/hybrid silica spheres of POSS siloxane composites exhibiting ultralow dielectric constant. ACS Appl Mater Interfaces 7:19474–19483
78. Tseng M-C, Liu Y-L (2010) Preparation, morphology, and ultra-low dielectric constants of benzoxazine-based polymers/polyhedral oligomeric silsesquioxane (POSS) nanocomposites. Polymer 51:5567–5575
79. Selvi M, Devaraju S, Vengatesan M, Go J, Kumar M, Alagar M (2014) The effect of UV radiation on polybenzoxazine/epoxy/OG-POSS nanocomposites. RSC Adv 4:8238–8244
80. Alagar M (2015) Dielectric and thermal behaviors of POSS reinforced polyurethane based polybenzoxazine nanocomposites. RSC Adv 5:33008–33015
81. Vengatesan M, Devaraju S, Dinakaran K, Alagar M (2011) Studies on thermal and dielectric properties of organo clay and octakis (dimethylsiloxypropylglycidylether) silsesquioxane filled polybenzoxazine hybrid nanocomposites. Polym Compos 32:1701–1711
82. Ariraman M, Sasikumar R, Alagar M (2016) Cyanate ester tethered POSS/BACY nanocomposites for low-k dielectrics. Polym Adv Technol 27:597–605
83. Alagar M, Devaraju S, Prabunathan P, Selvi M (2013) Low dielectric and low surface free energy flexible linear aliphatic alkoxy core bridged bisphenol cyanate ester based POSS nanocomposites. Front Chem 1:19
84. Dvornic PR, Hartmann-Thompson C, Keinath SE, Hill EJ (2004) Organic−inorganic polyamidoamine (PAMAM) dendrimer−polyhedral oligosilsesquioxane (POSS) nanohybrids. Macromolecules 37:7818–7831
85. Lee Y-J, Huang J-M, Kuo S-W, Chang F-C (2005) Low-dielectric, nanoporous polyimide films prepared from PEO–POSS nanoparticles. Polymer 46:10056–10065
86. Schwab JJ, Lichtenhan JD (1998) Polyhedral oligomeric silsesquioxane (POSS)-based polymers. Appl Organometal Chem 12:707–713
87. Gong D, Long J, Jiang D, Fan P, Zhang H, Li L, Zhong M (2016) Robust and stable transparent superhydrophobic polydimethylsiloxane films by duplicating via a femtosecond laser-ablated template. ACS Appl Mater Interfaces 8:17511–17518
88. Bassindale AR, Codina-Barrios A, Frascione N, Taylor PG (2008) The use of silsesquioxane cages and phage display technology to probe silicone–protein interactions. New J Chem 32:240–246
89. Qiu LG, Xie AJ, Zhang LD (2005) Encapsulation of catalysts in supramolecular porous frameworks: size-and shape-selective catalytic oxidation of phenols. Adv Mater 17:689–692
90. Bordiga S et al. (2004) Electronic and vibrational properties of a MOF-5 metal–organic framework: ZnO quantum dot behaviour. Chem Commun 2300–2301
91. Collins DJ, Zhou H-C (2007) Hydrogen storage in metal–organic frameworks. J Mater Chem 17:3154–3160

92. Sun D et al (2003) Novel silver-containing supramolecular frameworks constructed by combination of coordination bonds and supramolecular interactions. Inorg Chem 42:7512–7518
93. Ahmad N, Noh AM, Leo C, Ahmad A (2017) CO_2 removal using membrane gas absorption with PVDF membrane incorporated with POSS and SAPO-34 zeolite. Chem Eng Res Des 118:238–247
94. Wu M, Ra Wu, Li R, Qin H, Dong J, Zhang Z, Zou H (2010) Polyhedral oligomeric silsesquioxane as a cross-linker for preparation of inorganic−organic hybrid monolithic columns. Anal Chem 82:5447–5454
95. Alves F, Nischang I (2013) Tailor-made hybrid organic-inorganic porous materials based on polyhedral oligomeric silsesquioxanes (POSS) by the step-growth mechanism of thiol-ene “click” chemistry. Chem-A Eur J 19:17310–17313
96. Lin H, Ou J, Zhang Z, Dong J, Zou H (2013) Ring-opening polymerization reaction of polyhedral oligomeric silsesquioxanes (POSSs) for preparation of well-controlled 3D skeletal hybrid monoliths. Chem Commun 49:231–233
97. Lin H, Ou J, Liu Z, Wang H, Dong J, Zou H (2015) Facile construction of macroporous hybrid monoliths via thiol-methacrylate Michael addition click reaction for capillary liquid chromatography. J Chromatogr A 1379:34–42
98. Alves F, Nischang I (2015) Radical-mediated step-growth: preparation of hybrid polymer monolithic columns with fine control of nanostructural and chromatographic characteristics. J Chromatogr A 1412:112–125
99. Zhang H, Ou J, Liu Z, Wang H, Wei Y, Zou H (2015) Preparation of hybrid monolithic columns via “one-pot” photoinitiated thiol-acrylate polymerization for retention-independent performance in capillary liquid chromatography. Anal Chem 87:8789–8797. https://doi.org/10.1021/acs.analchem.5b01707
100. Lin H, Ou J, Tang S, Zhang Z, Dong J, Liu Z, Zou H (2013) Facile preparation of a stable and functionalizable hybrid monolith via ring-opening polymerization for capillary liquid chromatography. J Chromatogr A 1301:131–138
101. Zhao J, Farhatnia Y, Kalaskar DM, Zhang Y, Bulter PE, Seifalian AM (2015) The influence of porosity on the hemocompatibility of polyhedral oligomeric silsesquioxane poly (caprolactone-urea) urethane. Int J Biochem cell Biol 68:176–186
102. Teng CP, Mya KY, Win KY, Yeo CC, Low M, He C, Han M-Y (2014) Star-shaped polyhedral oligomeric silsesquioxane-polycaprolactone-polyurethane as biomaterials for tissue engineering application. NPG Asia Mater 6:e142
103. Janeta M, Rajczakowska M, Ejfler J, Łydżba D, Szafert S (2016) Synthesis and microstructural properties of the scaffold based on a 3-(trimethoxysilyl) propyl methacrylate–POSS hybrid towards potential tissue engineering applications. RSC Adv 6:66037–66047
104. He H-B et al. (2014) Fabrication of enrofloxacin imprinted organic–inorganic hybrid mesoporous sorbent from nanomagnetic polyhedral oligomeric silsesquioxanes for the selective extraction of fluoroquinolones in milk samples. J Chromatogr A 1361:23–33
105. Wang D, Yang W, Li L, Zhao X, Feng S, Liu H (2013) Hybrid networks constructed from tetrahedral silicon-centered precursors and cubic POSS-based building blocks via Heck reaction: porosity, gas sorption, and luminescence. J Mater Chem A 1:13549–13558
106. Wang D, Yang W, Feng S, Liu H (2014) Constructing hybrid porous polymers from cubic octavinylsilsequioxane and planar halogenated benzene. Polym Chem 5:3634–3642
107. Petit C, Lin K-YA, Park A-HA (2013) Design and characterization of liquidlike POSS-based hybrid nanomaterials synthesized via ionic bonding and their interactions with CO_2. Langmuir 29:12234–12242
108. Wang D, Li L, Yang W, Zuo Y, Feng S, Liu H (2014) POSS-based luminescent porous polymers for carbon dioxide sorption and nitroaromatic explosives detection. RSC Adv 4:59877–59884
109. Wang D, Yang W, Feng S, Liu H (2016) Amine post-functionalized POSS-based porous polymers exhibiting simultaneously enhanced porosity and carbon dioxide adsorption properties. RSC Adv 6:13749–13756
110. Wang S, Tan L, Zhang C, Hussain I, Tan B (2015) Novel POSS-based organic–inorganic hybrid porous materials by low cost strategies. J Mater Chem A 3:6542–6548

111. Tang H et al (2016) Octa (aminophenyl) silsesquioxane derived nitrogen-doped well-defined nanoporous carbon materials: synthesis and application for supercapacitors. Electrochim Acta 194:143–150
112. Liu D et al (2016) Self-assembly of polyhedral oligosilsesquioxane (POSS) into hierarchically ordered mesoporous carbons with uniform microporosity and nitrogen-doping for high performance supercapacitors. Nano Energy 22:255–268
113. Dasgupta B, Sen SK, Banerjee S (2010) Aminoethylaminopropylisobutyl POSS—Polyimide nanocomposite membranes and their gas transport properties. Mater Sci Eng: B 168:30–35
114. Kanezashi M, Shioda T, Gunji T, Tsuru T (2012) Gas permeation properties of silica membranes with uniform pore sizes derived from polyhedral oligomeric silsesquioxane. AIChE J 58:1733–1743