Silsesquioxane-Containing Hybrid Nanomaterials: Fascinating Platforms for Advanced Applications

Fuping Dong,* Liangyu Lu, and Chang-Sik Ha*

This article is dedicated to Prof. Hatsuo Ishida on the occasion of his 70th birthday

Silsesquioxanes (SSQs), with the general formula, $(RSiO_{1.5})_n$—where R stands for an organic group, such as alkyl, aryl, alkoxy, or H—are a type of molecular-level organic/inorganic hybrid silica-based material. These materials contain reactive or nonreactive organic moieties as well as inorganic Si–O–Si frameworks. In the past few years, extensive efforts have been made using SSQs to construct multifunctional nanocomposites with suitable properties for a range of applications. In this review, the recent various applications of SSQ-containing hybrid materials are discussed, in addition to updates of the nanocomposite applications. Various physical structures and chemical reactions in SSQ-based hybrid nanomaterials are emphasized with regard to applications in the field of polymer nanocomposites, catalysts, adsorption, sensors, and biomedicine. This review focuses on results reported in the recent five years (2013–2018).

1. Introduction

Hybrid nanomaterials are one of the important parts for functional nanocomposites.[1] Organic/inorganic hybrid nanomaterials have unique properties from their organic and inorganic components. Hybrid nanomaterials usually have a large surface-to-volume ratio allowing more reactions to occur on the surface. In addition, hybrid nanomaterials are easy to synthesize and modify chemically, which can provide versatile platforms for many applications.[2,3]

Silsesquioxanes (SSQs) are a family of organic–inorganic hybrid nanomaterials obtained from the hydrolysis and polycondensation of trialkoxysilane or trichlorosilane monomers containing organic groups.[4,5] SSQs can have a range of properties, such as high chemical and thermal resistance, biocompatibility, and luminescence, depending on the type of precursor used

Prof. F. Dong, L. Lu
Department of Polymer Materials and Engineering
College of Materials and Metallurgy
Guizhou University
Guiyang 550025, China
E-mail: fpdong@gzu.edu.cn
Prof. C.-S. Ha
Department of Polymer Science and Engineering
Pusan National University
Busan 46241, Republic of Korea
E-mail: csha@pnu.edu

for synthesis.[6–8] The main reason for the development of SSQ-containing hybrid nanomaterials lies in the combination of inorganic and organic moieties on the nanoscale or even molecular scale.

SSQ-containing hybrid nanomaterials have potential applications as nanofillers for polymer matrices, catalysts, adsorption, sensors, biomedicine, etc. In this critical review, emphasis has been placed on the applications of SSQ-based hybrid nanomaterials with superior properties owing to their inherent chemical and physical characteristics.

2. General Features of SSQs

SSQs refer to all compounds with the general composition, $R(SiO_{1.5})_n$, and are generally categorized depending on the different nanostructures, such as amorphous compounds, ladder-like structure, open cage, and polyhedral oligomeric silsesquioxane (POSS) molecules.[4] POSS, as a cage-like SSQ molecule, 1.5 nm in size, is comprised of an inorganic Si–O–Si framework covered externally by organic groups. The nanoscale size with tunable surface chemistry makes the compounds quite suitable as building blocks for hybrid nanocomposites. Kickelbick summarized the structure, synthetic approaches, properties, and potential applications of SSQ compounds.[9] Croissant et al. reviewed the synthesis and applications of nonporous SSQs and bridged SSQs with high organic contents.[1] Kuo and Chang reviewed the synthesis of POSS compounds; miscibility of POSS with polymers; thermal, mechanical, electrical properties; and the corresponding applications of POSS-related nanocomposites.[10] Recently, Yang et al. summarized POSS/polymer nanocomposites for fire retardance[11] and He et al. reviewed the POSS for optoelectronic materials.[12] In addition, some other review articles on SSQs-containing hybrid materials also have been reported, as shown in **Table 1**. These review articles summarized SSQ nanoparticles(NPs) or SSQ-containing nanocomposites for multifunctional applications, including reinforcement for polymers, organic semiconducting materials, or nanomedicine. Readers interested in related topics can refer to these review articles and the references cited therein. This review presents the state-of-the-art applications of SSQs-containing hybrid nanomaterials.

2.1. Chemical Structures

SSQs are interesting organic/inorganic hybrid nanomaterials with silicon atoms attached to one or more inert or active organic groups.[18] SSQs with two or more different organic groups in the structure can also be prepared for multifunctional applications.[16]

Compared to post-functionalized silica, SSQs show a uniform and high coverage of organic groups, which imparts unique functionality, which is quite suitable for a range of applications. SSQs with functional organic groups can be used to design and fabricate SSQ-containing hybrid nanomaterials by being grafted onto polymers or copolymerized with polymers.[19,20]

The performance of SSQs is determined not only by the initial monomer structure, but also the synthetic condition.[6] In a sol-gel process, SSQs are synthesized from the hydrolysis and polycondensation of trialkoxysilane or trichlorosilane. In the first step, silanols (Si–OH) are obtained after a hydrolytic reaction in the presence of an acidic or basic catalyst. The silanols obtained from the hydrolytic reaction is then connected covalently via Si–O–Si linkages to form the rigid $(SiO_{1.5})$ cores, surrounded by organic substituent groups on the surface. SSQs can be modified easily and work as building blocks for a range of organic/inorganic hybrid materials.[21] The organic repetitive units provide SSQs with tunable surface chemistry of the outside surface and inner wall.

The surface chemistry of SSQs makes their structures designable and compatible with polymeric or biological surfaces. SSQs with different functional groups on the surface have different properties and performance. For example, phenyl-functionalized SSQs are promising as gas separation membranes or surface coatings for electronic or optical devices owing to their excellent thermal stability and electrical insulation.[22,23] Vinyl-functionalized SSQs can be grafted or copolymerized with polymers because of the unsaturated groups on the surface.[24,25] Amino-functionalized SSQs hybrid composites show high reactivity and oxidation resistance.[26,27] Mercapto-functionalized SSQs can adsorb proteins or metal ions.[28,29]

2.2. Physical Structures

As one type of hybrid nanomaterial, SSQs are rigid nanomaterials with an inorganic core linked by a Si–O–Si network and organic moieties on the surrounding surface.[30] Inorganic components on SSQs make them applicable to an extreme environment with thermal or chemical degradation.

By controlling the reaction conditions of SSQ monomers, the hydrolysis and polycondensation process can result in a variety of different structures. The microstructure of SSQs includes a random cross-linked structure, ladder-type structure, and (partial) cage structure.[31] As a cage structure, polyhedral oligomeric silsesquioxanes (POSSs) are types of nanosized organic/inorganic SSQ materials with the formula, $(RSiO_{1.5})_n$. In the rigid 3D POSS structure, organic substituents are attached to the Si–O–Si framework, which is quite suitable for the construction of hybrid porous structured nanomaterials for versatile applications.

Fuping Dong has been an associate professor in the Department of Polymer Materials and Engineering, Guizhou University (GZU), China since 2016. He received his Ph.D. in polymer science and engineering from Pusan National University in 2012, under the supervision of Professor Chang-Sik Ha. Then, he worked for another year as a postdoctoral researcher at the same university. Before he joined GZU, he worked for three years as a post-doctoral researcher in Friedrich-Schiller-Universität Jena, Germany. His research interests include the fabrication of porous organic materials and polysilsesquioxane colloids for versatile applications.

Liangyu Lu is currently an M.Sc. student in the Department of Polymer Materials and Engineering at Guizhou University. She received her B.Sc. in the Department of Polymer Materials and Engineering in Huaqiao University in 2017. Her research interests focus on the development of organic/inorganic porous materials for CO_2 adsorption and drug delivery.

Chang-Sik Ha has been a professor at the Department of Polymer Science and Engineering, Pusan National University, Republic of Korea since 1982. He received his Ph.D. in chemical engineering from Korea Advanced Institute of Science and Technology, Seoul, Republic of Korea in 1987. He was appointed as a University Distinguished Professor in 2016. He served as a Vice President of PNU, Director of the Pioneer Research Center for Nanogrid Materials, and the Honorary Professor of University of Queensland, Australia. His research interests include organic–inorganic hybrid nanomaterials, periodic mesoporous organosilicas (PMO), and functional polymers like polysilsesquioxanes for various applications.

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Table 1. List of noteworthy review articles related to SSQs-containing hybrid materials.

Authors	Publication year	Main topic	Reference
Yang et al.	2017	Polymer/POSS nanocomposites for fire retardance	[11]
He et al.	2017	POSS for organic optoelectronic materials	[12]
Croissant et al.	2016	Syntheses and applications of SSQs with a high organic content	[1]
Mohamed and Kuo	2016	Polybenzoxazine(PBZ)/ POSS nanocomposites	[13]
Chrusciel and Lesniak	2015	Hybrid epoxy–silicon containing materials	[14]
Kickelbick	2014	SSQs	[9]
Kamino and Bender	2013	Silicone containing organic semi-conducting materials	[15]
Dong and Ha	2012	Multifunctional materials based on polysilsesquioxanes	[16]
Kuo and Chang	2011	POSS related polymer nanocomposites	[10]
Seifalian et al.	2011	**POSS nanocage for** Nanomedicine	[17]

2.3. Basic Properties

SSQ materials composed of robust silica cores and functional groups at the corners have unique chemical and physical properties. As organic/inorganic hybrid nanomaterials, SSQs exhibit chemical and thermal resistance as well as mechanical strength, which originates from the inorganic Si–O–Si framework.[32] SSQs also have flexibility and compatibility with polymers and biological systems, which are served by the organic component. In particular, the POSS nanoparticles possess high physical properties, such as high thermal stability, mechanical stability, and dielectric property.[33]

SSQs have become promising nanofillers for polymers based on their chemical structure and excellent physical properties.[34] The adsorption of gas molecules, metal ions, or drug molecules with an improved loading or adsorption efficiency can be ensured by the covalent conjugation of guest molecules or ions with a porous SSQ structure. Unlike conventional hybrid nanoparticles, SSQs with organic moieties on the surface are compatible with the system or surface of polymers and biology. The stability and biocompatibility of SSQ-based hybrid nanomaterials, particularly POSS composites, make them promising platforms for polymer composites, catalysts, sensors, energy, and biomedicine.[35]

3. Advanced Applications

3.1. Nanofillers for Polymer Nanocomposites

3.1.1. Enhancement of the Thermal Properties of Polymers

Though polymers are used widely in both daily life and industry, the thermal stability, mechanical properties, and electrical properties of polymers still need to be improved. SSQs, especially POSS, are attractive hybrid nanomaterials that can provide polymers with superior thermal properties.[11,26,36–49] SSQs with a rigid Si–O–Si framework show excellent thermal properties and SSQ-containing polymers exhibit good thermal properties even after a physical blending process.[38,49–53] As a kind of organic–inorganic hybrid nanomaterials with a nanocage structure, SSQs have good interface interactions with polymers and show excellent thermal and mechanical stability. The nature of SSQ substitutes plays a significant role in the level of compatibility between the SSQs and polymer matrix.[54,55] Interactions between POSS and a polymer play a key role in enhancing the thermal property.[45]

Phenyl group-functionalized POSS, with rigid benzene in the molecule, can usually be used to improve the thermal properties of a polymer matrix.[56,57] Octa phenyl substituted POSS(Ph-POSS), as inorganic/organic nanofillers, was incorporated into the polycarbonate (PC) matrix to improve the thermal stability. The improved thermal stability was attributed mainly to the formation of a silicon-containing heat shield layer at high temperatures.[58] Ph-POSS-TiO$_2$ organic–inorganic hybrid nanomaterials were incorporated into an epoxy resin to form epoxy/POSS-TiO$_2$ nanocomposites. The addition of POSS-TiO$_2$ improved the thermal stability of the epoxy resin matrix, which could be used in satellites to enhance their adaptability to the space environment and extend their service life.[59] The phenyl groups combined with the migration of SSQ to the surface as a shielding layer was found to be the main factor for the improved thermal stability. In the study of isotactic polypropylene(PP)/POSS hybrid nanocomposites, Barczewski et al. reported that the migration of POSS to the surface leads to agglomerated particles in the nanocomposites, which work as a shielding layer to suppress flammability.[60]

Phenyl-containing POSS also were incorporated into poly (vinyl pyrrolidone) (PVP) through free radical copolymerization. Akbari and Arsalani fabricated a series of hybrid nanocomposites with good thermal stability. The addition of small amounts of POSS could enhance the thermal stability of PVP due to good interactions between Ph-POSS and PVP matrix.[44] After the incorporation of phenyl-containing double-decker SSQs, the thermal decomposition temperature of the (Polybenzoxazine) PBZ/SSQ nanocomposites was observed at 500 °C, which is the highest thermal stability ever reported for membranes. The improved thermal and mechanical properties were attributed to covalent bonding between the rigid SSQ structure and benzoxazine matrix.[61] Octaphenyl-POSS(Ph-POSS) was utilized in a hybrid with resorcinol formaldehyde (RF) to form a resol-type Ph-POSS/RF ablative heat shielding material for a thermal protection system. The thermal properties were improved due to crosslinking between the OP-POSS units and RF resin. In addition, the formation of a hybrid inorganic–organic surface protection layer enhanced the thermal stability of the surface and bulk.[62] Zheng's group fabricated a macrocyclic oligomeric silsesquioxane (MOSS) starting from polyphenylsilsesquioxanes (**Figure 1**). These stereoregular epoxide groups containing SSQs were then incorporated into the PBZ thermoset. The final organic–inorganic nanocomposites exhibited enhanced glass transition temperatures (T_g) and improved thermal stability. The improved properties were attributed to the reinforcement of SSQs on the PBZ matrix as well as the additional crosslinking between PBZ and the SSQ macromer.[23]
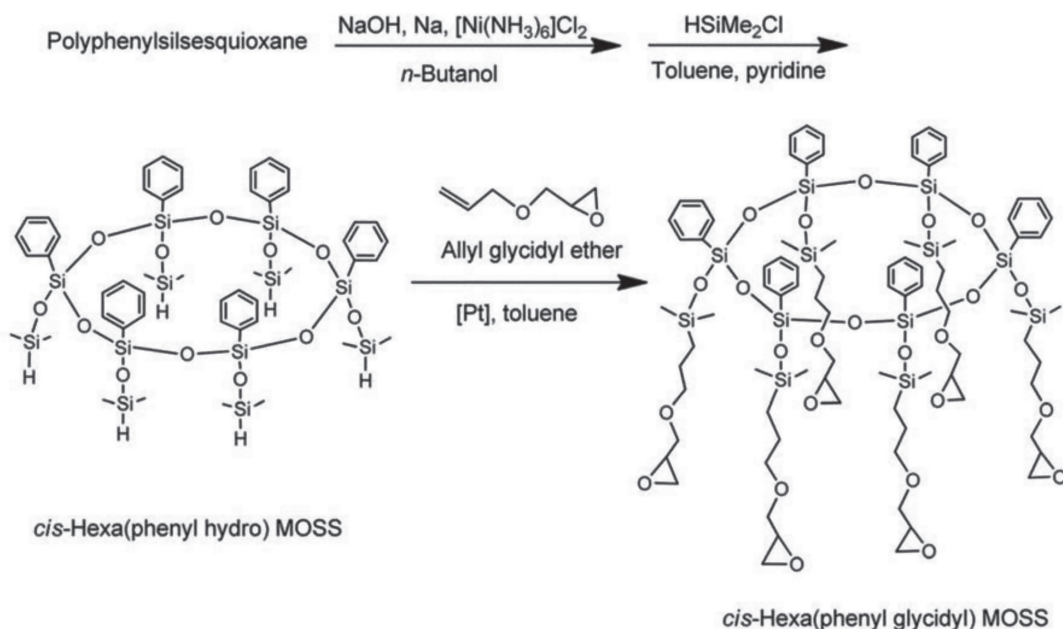
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Figure 1. Synthesis of cis-hexa(phenyl glycidyl) SSQ macromer. Reproduced with permission.[23] Copyright 2015, The Royal Society of Chemistry.

Glycidyl-POSS (GC-POSS) are often used to improve the properties of epoxy resin.[63] Epoxy resin usually has good adhesion and chemical resistance but the material is limited by the high viscosity, high shrinkage during the curing process, and low thermal stability.[25] Lee's group blended different contents of a glycidyl-POSS into an epoxy resin (diglycidyl ether of bisphenol-A) and cured them with an amine hardener at various temperatures and times to improve the thermal properties.[40] Glycidyl-POSS was used to form a hybrid with epoxy resin and the properties of the composites were studied by differential scanning calorimetry, thermal conductivity, and dielectric spectroscopy. Interestingly, they reported that low POSS contents are effective in improving the thermal conductivity due to the nanostructure from covalent bonding between POSS and the polymeric matrix.[64]

Aminopropyl isobutyl POSS (amine-POSS) molecules were incorporated into poly(ethylene terephthalate)(PET) fibers through the reaction between the amine group on POSS and the carboxyl group on PET. The thermal decomposition temperature of the composites measured at 5 wt% weight loss were 350 °C, which is much higher than that of neat PET. The high thermal stability of the PET/POSS nanocomposites resulted from the good dispersion of amine-POSS in the PET matrix, that is, the uniform dispersion of POSS in the polymer matrix due to the strong interfacial interactions between POSS and PET during polymerization.[26]

POSS nanofillers do not always improve the thermal stability of polymers. Khonakdar et al. prepared trifluoropropyl poly(lactic acid)(PLA)/POSS nanocomposites via melt blending and studied the influence of POSS on the thermal properties of the PLA/POSS nanocomposites. The presence of POSS reduced the thermal stability of the nanocomposites slightly compared to the neat PLA due partly to the large POSS agglomerates at high POSS contents caused by the strong interactions among the POSS particles.[65]

3.1.2. Enhancement of the Mechanical Properties of Polymers

As mentioned above, the organic functional groups in SSQs provide compatibility with the polymer and the inorganic silicon–oxygen cores provide the reinforcement during the composite formation process; hence, SSQs could be used to improve the mechanical properties of nanocomposites.[39,66,67]

Through a vacuum-assisted flocculation process, Huang et al. incorporated POSS-COOH nanoparticles into the structure of aramid nanofibers (ANFs) to fabricate nanocomposite membranes. The mechanical properties of the composite membranes could be controlled by changing the POSS content, in which POSS worked as a cross-linking agent between nanofibers. In addition to the high thermal stability of the membranes, excellent mechanical performance was also found. These POSS/ANFs hybrid nanocomposites may be promising materials for the practical applications of strong and heat-resistant membranes.[68] Qiu et al. used trisilanolisobutyl-POSS(tsib-POSS) to reinforce the mechanical properties of a poly(L-lactide) (PLLA) nanocomposite. The addition of POSS enhanced the crystallization behaviors of PLLA because of its nucleation agent effect. This tsib-POSS plays a key role as a reinforcing filler in the PLLA matrix and has a greater tensile modulus than neat PLLA.[69]

Li et al. prepared biodegradable poly(p-dioxanone) (PPDO)/octamethyl-POSS(ome-POSS) nanocomposites with various POSS contents via a simple solution casting method. The dispersion of POSS in the polymer matrix affected the mechanical properties of the hybrid materials significantly. As shown by the SEM images in **Figure 2**, POSS are dispersed randomly in the matrix, even when the POSS loading is 10 wt%. The mechanical properties of the PPDO/ome-POSS nanocomposites were enhanced compared to neat PPDO, which is due partly to the good dispersion of POSS in the matrix.[70]
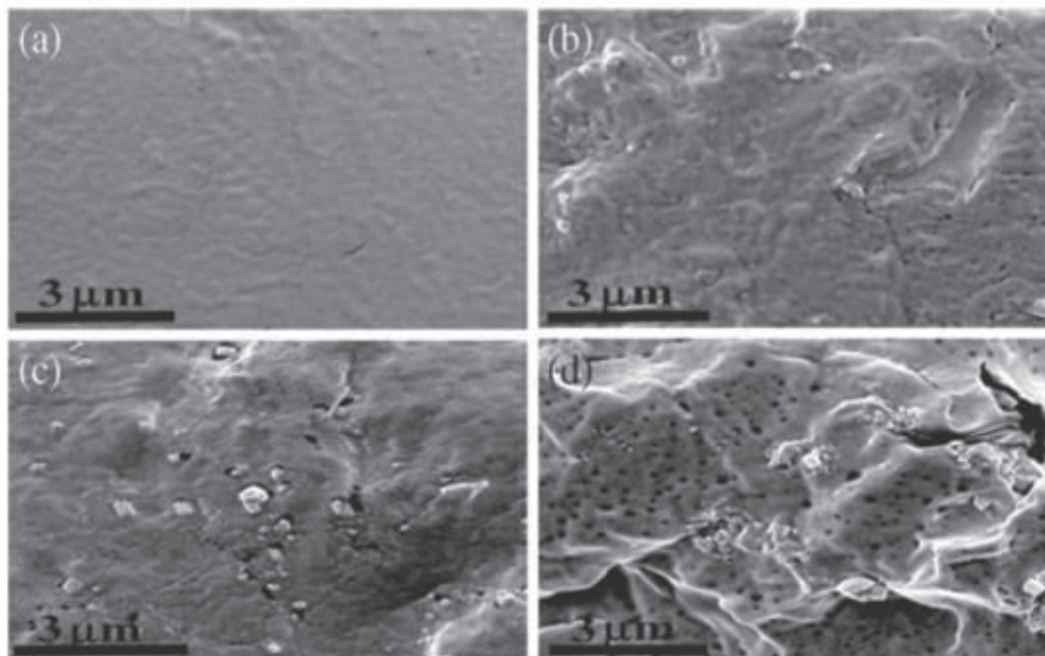
Figure 2. SEM images showing an overall morphology of fractured surface of a) PPDO, b) ome-POSS 1 wt%, c) ome-POSS 5 wt%, and d) ome-POSS 10 wt%. Reproduced with permission.[70] Copyright 2015, Indian Academy of Sciences.

The scratch resistance and healing ability of the polymers could be enhanced by POSS nanomaterials. Yari et al. modified a typical acrylic melamine clear coat with an OH-functional hyper-branched polymer and octa(3- hydroxy 3-methyl butyl dimethyl siloxy) POSS nanostructures. The modified clear coats showed superior healing ability, which was attributed mainly to the POSS nanostructures. POSS was found to improve the scratch resistance significantly via molecular-scale reinforcement of the polymers.[71]

3.1.3. Enhancement of Electrical Properties of Polymers

POSS molecules have a comparable size with the segments of polymer chains and can react with polymers with good solubility in many solvents. Therefore, dielectric polymer nanocomposites using POSS as a nanofiller have attracted attention for high voltage applications in the engineering dielectric and electrical insulation fields.[72,73]

Reactive POSS can be used to improve the dielectric properties of epoxy resin for high voltage insulation applications. For example, octa-aminophenyl POSS (OASQ) or glycidyl-POSS are commonly incorporated into epoxy to form hybrid materials with enhanced electrical properties. Tanaka incorporated OASQ into epoxy to fabricate dielectric epoxy/POSS nanocomposites.[74] The curing reaction occurred between the epoxide ring and acid anhydride as well as between the epoxide ring and POSS. The electrical properties were influenced significantly by the molecular dispersion of POSS in the epoxy, which was determined by the reaction degree of POSS with epoxy. Heid et al. used triglycidylisobutyl-POSS(TGIB-POSS), which has three epoxy groups surrounded by a cage-like silica core,

to react with epoxy matrix in the presence of a curing agent to form nanocomposites.[75] These epoxy groups are compatible with those of the epoxy system and can form covalent bonds with the matrix. When POSS was dispersed well at the molecular level at low contents, the composites showed improved resistance to corona discharges, increased dielectric breakdown strengths, and high thermal conductivities.

The incorporation of porous nanoparticles into polymer matrix by chemical grafting or physical blending was reported to be an effective and convenient way to decrease the dielectric constant of the polymer matrix significantly.[76,77] Geng et al. utilized octa-aminophenyl POSS to decrease the dielectric constant of fluoropoly(ether ether ketone)s (PEEK-CF$_3$-COOH). The dielectric constants (k) of the organic–inorganic nanocomposites were reduced drastically to as low as 1.71 (1 MHz). In addition, the thermal and mechanical properties of the nanocomposites were improved significantly by the incorporation of OASQ moieties due to covalent bonding between the OASQ nanoparticles and PEEK-CF$_3$-COOH matrix.[78] Thirukumaran et al. prepared eugenol-based PBZ/amine-POSS nanocomposites through the copolymerization of amine-containing POSS with allyl-containing benzoxazine compounds. The incorporation of POSS decreased the dielectric constant of the benzoxazines from 1.83 to 1.32. The thermal stability, crosslink density, and flame retardance of the nanocomposites increased when small amounts of POSS cores (5 wt%) were incorporated into the system. These nanocomposites could be used as ultra-low-k materials for advanced microelectronics.[79] Sadhasivam and Muthusamy incorporated amino-functionalized POSS into polyimide(PI) and obtained thermally stable PI nanocomposites with a low dielectric constant.[48] The reduced dielectric constant (from 3.5 for neat PI to 2.1 for PI/POSS hybrid

nanocomposite containing 5 wt% of POSS) of these PI–POSS hybrids can be explained by the porous POSS and loose PI networks.

Besides the porous structure, a new mechanism of the decreased dielectric constant by POSS addition was recently proposed from the viewpoints of the interfacial effect.[80,81] Huang et al. examined a typical polystyrene(PS)/POSS nanocomposite and reported that POSS molecules could form crystalline nanoplatelets in a PS matrix. They found that when the POSS is crystallized to form well-dispersed particles, the interfacial effect can influence the arrangement of polymer chains and further reduce the polarity and dielectric constant.[82]

3.1.4. Enhancement of Other Properties of Polymers

In addition to the enhancement of the thermal, mechanical, and electrical properties of polymers, SSQs and SSQs-containing polymer hybrid nanocomposites could also be used as antifouling membranes.[83] and UV-shielding coatings.[81,84,85] A cellulose/POSS hybrid nanocomposite film was prepared and used as a packaging coating that exhibited good UV aging resistance and high shielding performance.[86]

POSS and POSS-based hybrid nanomaterials have been used as lubricant additives to achieve high tribological performance owing to their steady inorganic Si–O–Si framework and excellent organic compatibility.[87–89] Liu et al. utilized octavinyl-POSS (OV-POSS) to react with alkyl mercaptan via a "thiol-ene click" reaction to obtain additives for lubricant oils. Only a very low content (0.40 wt%) of POSS hybrid nanomaterials in the lubricant oil could achieve very low friction coefficients (0.099). The fundamental friction reducing mechanism was attributed partly to the stable POSS films formed on the frictional surface.[90]

POSS also could be incorporated into polymers to protect satellites and other spacecraft in low earth orbit. Nouranian et al. first grafted PI onto the POSS nanoparticles and then dispersed them in the PI matrix to form nanocomposites. The PI with POSS nanoparticles was more resistant to atomic oxygen attack than the PI hybrid nanocomposites with carbon nanomaterials, such as graphene or carbon nanotubes. They attributed these results to the good dispersion of POSS nanoparticles in the PI matrix, which could reduce the amount of PI exposed on the material surface.[91]

3.2. SSQs for Catalyst

Suitable organic functionalized SSQs or SSQs-based hybrid nanomaterials could be used directly as catalyst. POSS-based-nanoparticles-supported organic-inorganic hybrid nanomaterials with a very high surface and internal organic content have potential catalyst applications. A chiral pyrrolidine-bridged POSS was fabricated and applied as a heterogeneous catalyst in an asymmetric Michael addition reaction under room temperature, giving the product in excellent yield (85–91%), diastereoselectivities (up to 99:1), and enantioselectivities (95–98%). The catalyst can be recycled by a simple filtration without significant loss in reactivity and selectivity.[92]

SSQs-based magnetic nanoparticles are suitable as heterogeneous catalysts because of their good stability, easy functionalization, high surface area, and facile separation using an external magnet. Aminopropyl-functionalized POSS with eight triethoxysilane arms (APTPOSS) were anchored successfully to the surface of Fe_3O_4 nanomagnetics to fabricate Fe_3O_4@APTPOSS magnetic nanocatalysts. These magnetic POSS nanoparticles were an efficient, easily available catalyst with high catalytic activity for the synthesis of pyrans. Only a small catalyst loading was needed because of the high catalytic activity of aminopropyl groups.[93]

Derivatives of POSS, including catalytic moieties also were prepared and employed as a catalyst. A rigid POSS-based porous cationic framework was fabricated from octakis(chloromethyl) silsesquioxane and rigid n-heterocyclic cross-linkers. The materials behaved as an efficient heterogeneous catalyst for the aerobic oxidation of benzene because they contained an enriched poly(ionic liquid)-like cation structure, tunable mesoporosity, and high surface area.[94]

POSS with suitable organic substitutes and porous structure could be used as a support for metal (oxide) nanoparticles. Nano-sized Mn oxide particles were loaded onto an agglomerated SSQs carrier and applied as an efficient catalyst for water oxidation. The composites showed great potential as a catalyst in artificial photo-synthetic systems for water splitting, due to the good dispersion of Mn on SSQ nanocomposites.[95] Gold nanoparticles (nAu) supported by octavinyl-POSS hybrid polymers were fabricated and used as a flow-through catalyst for aqueous liquid-phase reduction reactions. The highly efficient catalytic performance was attributed to the size of the nAu and the catalytically available gold surface.[96] Palladate-loaded POSS-Cl nanocomposites were prepared and used as a pre-catalyst for the Suzuki-Miyaura reaction in water at 100 °C at a low loading (0.08–0.16 mol%). The structure of the POSS was highlighted to play a key role in reaching higher yields in the Suzuki–Miyaura reaction.[97] Imidazolium-containing POSS was synthesized and used to stabilize Pd nanoparticles via both electrostatic interactions and imidazloe-N-coordination. The obtained Pd@POSS nanoparticles worked as an active heterogeneous catalyst for Suzuki–Miyaura cross-coupling reactions and Heck reactions with good reusability.[98]

Through a green synthetic methodology without the addition of an alkali solution, Mohapatra's group fabricated octakis(3-(1-methylimidazolium) propyl) octasilsesquioxane (POSS-MPIm)-supported palladium NPs. As shown in **Figure 3**, POSS-MPImCl reacted with Pd(OAc)₂ for 72 h at 100 °C via a solid state annealing process to form Pd(II)-MPIm-POSS (1). The final product, Pd(0)-nano-POSS (2), was fabricated from the in situ reduction of Pd(II)-MPIm-POSS (1) in the presence of PhB(OH)₂ under alkaline conditions. The obtained NP is a highly efficient and easily recyclable homogeneous catalyst for Suzuki–Miyaura cross-coupling reactions with a turnover frequency(TOF) up to 1670 h^{-1}.[99]

Bimetallic catalysts dispersed in SSQ-based nanomaterials have attracted enormous attention owing to their enhanced catalytic performance. Zhao et al. utilized aminopropyl isobutyl POSS to stabilize platinum–palladium (Pt–Pd) alloy NPs through a co-chemical reduction process using formaldehyde as the reductant.[100] With octa-maleamic acid SSQs as the
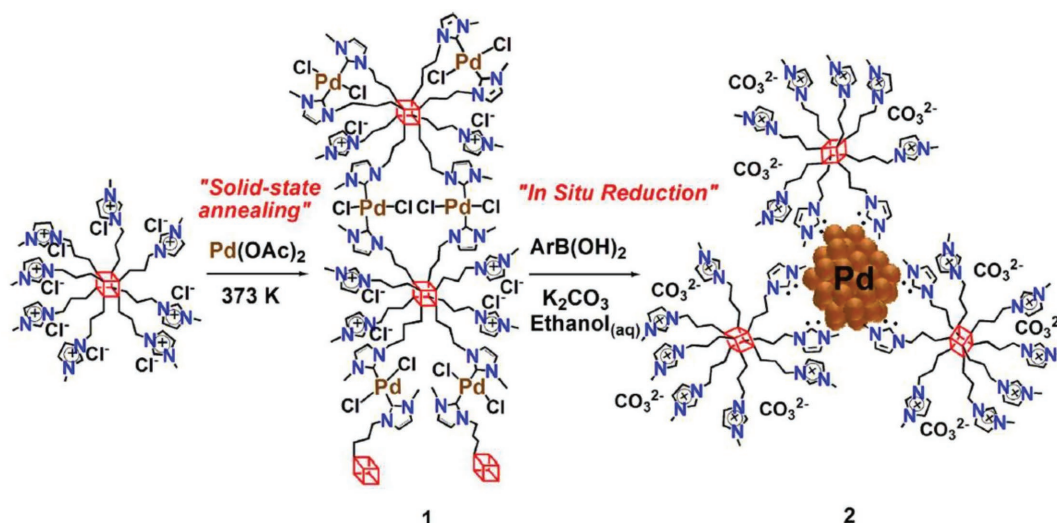
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Figure 3. Solvent-free synthesis of Pd(II)-MPIm-POSS composite (1) and a subsequent reduction to fabricate Pd(0)-nano-POSS nanocomposite (2) (red cube: POSS). Reproduced with permission.[99] Copyright 2016, Wiley-VCH.

stabilizing agent, the same group fabricated well-dispersed Pt–Pd NPs (mean particle diameter 6.5 nm) through a hydrothermal method. These well-dispersed Pt–Pd NPs exhibited enhanced electrocatalytic performance, stability, and tolerance to CO poisoning in formic acid oxidation.[101,102]

3.3. Sensors

SSQs are considered suitable candidates to construct porous polymers for loading photosensors and the obtained luminescent properties show the selective detection for chemicals. With octavinyl-POSS as the key building unit, Yu's group constructed a class of luminescent nanoporous inorganic–organic hybrid polymers through the Heck coupling reaction. The luminescence properties of these polymers were used for picric acid detection in an ethanol solution.[103] Zhang et al. also reported isopropyl-functionalized POSS bridged with reduced perylene bisimides for the rapid and selective detection of picric acid in a tetrahydrofuran solution.[104]

Li's group used POSS as a core bonded covalently with eight silole units to form dendritic organic–inorganic hybrid nanomaterials via a one-step hydrosilylation process. As shown in **Figure 4**, octakis(hydridodimethylsiloxyl)octasilsesquioxane (1) and octakis(vinyldimethylsiloxyl)octasilsesquioxane (2) were utilized as synthetic scaffolds and two different 2,3,4,5-tetraphenylsilole derivatives 3 and 4 were selected as the aggregation-enhanced emission (AIE) luminogens. The target organic–inorganic materials were synthesized by a hydrosilylation reaction in the presence of Karstedt's catalyst. These hybrid nanomaterials exhibited the AIE phenomenon, which could be quenched selectively by 2,4,6-trinitrophenol. Therefore, the POSS-based hybrid nanomaterials are quite promising as sensitive, selective, and stable sensors for the detection of explosives in aqueous media.[105]

With SSQs as a porous structured matrix, nanomaterials, such as gold, graphene, or magnetic particles could also be loaded

and work as sensors for the detection of chemicals. Chemosensors or immunosensors could be fabricated by soluble charged SSQs and gold nanoparticles (nAu). A sensor for the detection of o-nitrophenol and p-nitrophenol was built by depositing SSQ stabilized Au onto a glassy carbon electrode surface (**Figure 5**).[106] In this work, the soluble-charged SSQs (3-n-propyl-4-picolinium silsesquioxane chloride) was used as a stabilizing agent for the synthesis of nAu. The anionic metal complexes, such as $AuCl_4^-$ ions, could be adsorbed on the charged SSQs and the well-dispersed nAu could be obtained with a mean particle size of 4.5 nm. This SSQ-supported nAu also could be used as an immunosensor for the sensitive detection of troponin T (cTnT), a cardiac marker for acute myocardial infarction (AMI).[107] Pessoa et al. also used charged SSQs to stabilize nAu and deposited them on a glassy carbon electrode and then immobilized the horseradish peroxidase onto the electrode surface to build a biosensor. The modified electrode exhibited excellent performance for the determination of catechol and long-term stability owing to the SSQ framework in the structure.[108]

In addition to nAu, SSQ-based hybrid nanocomposites could be also prepared with other materials, such as graphene oxide (GO). Based on the POSS/reduced graphene oxide(rGO) nanocomposite, Zheng et al. reported an electrochemical sensor for the detection of nitrite.[109] The POSS/rGO nanocomposite was fabricated using a one-step hydrothermal synthesis method and showed a low detection limit and good selectivity as a sensor for nitrite.

3.4. Adsorption

SSQs-based hybrid nanomaterials could find interesting technological applications as sorbent materials. The large accessible surface area and pore volumes in the structure can facilitate adsorption through the diffusion of molecules in the porous structure. SSQs can be used to adsorb gas from the environment or adsorb pollution materials from wastewater.[110]
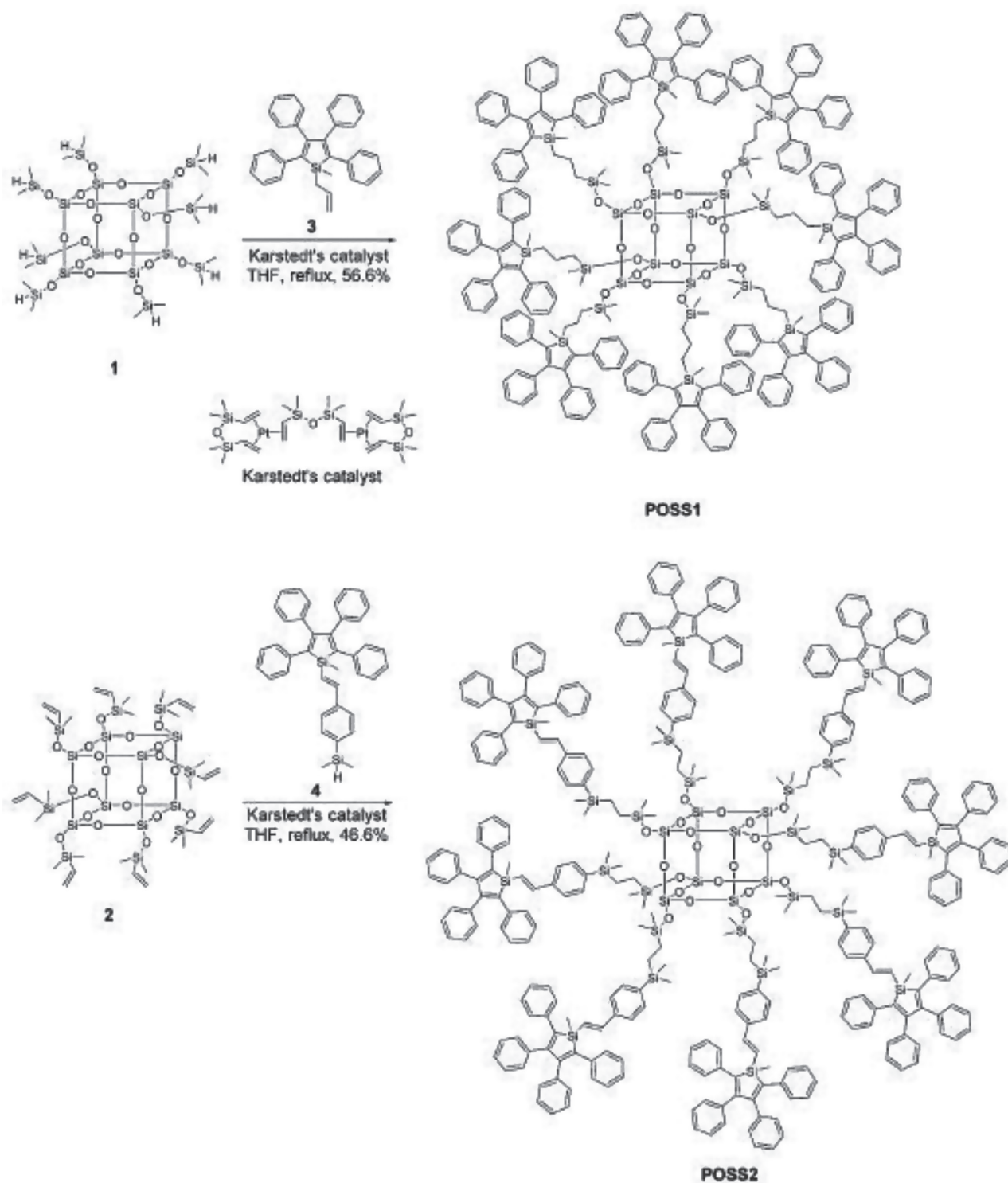
Figure 4. Synthetic routes to POSS1 and POSS2 for the detection of explosives in aqueous media. Reproduced with permission.[105] Copyright 2016, The Royal Society of Chemistry.

CO_2 capture is an important strategy for the protection of the environment and climate. SSQ aerogels with amine groups were synthesized using a single-step sol-gel process followed by supercritical drying.[111] The amine-SSQs possess a high surface amine content of 7.64 mmol g^{-1} and a porosity of 94.1%, which showed excellent CO_2 capture and regenerability. The rigid cage structures of the SSQs make it possible to form porous materials and the SSQ-containing porous polymers could be applied in gas adsorption, including CO_2 capture. Liu's group fabricated hyper-crosslinked PS as hybrid porous polymers through the
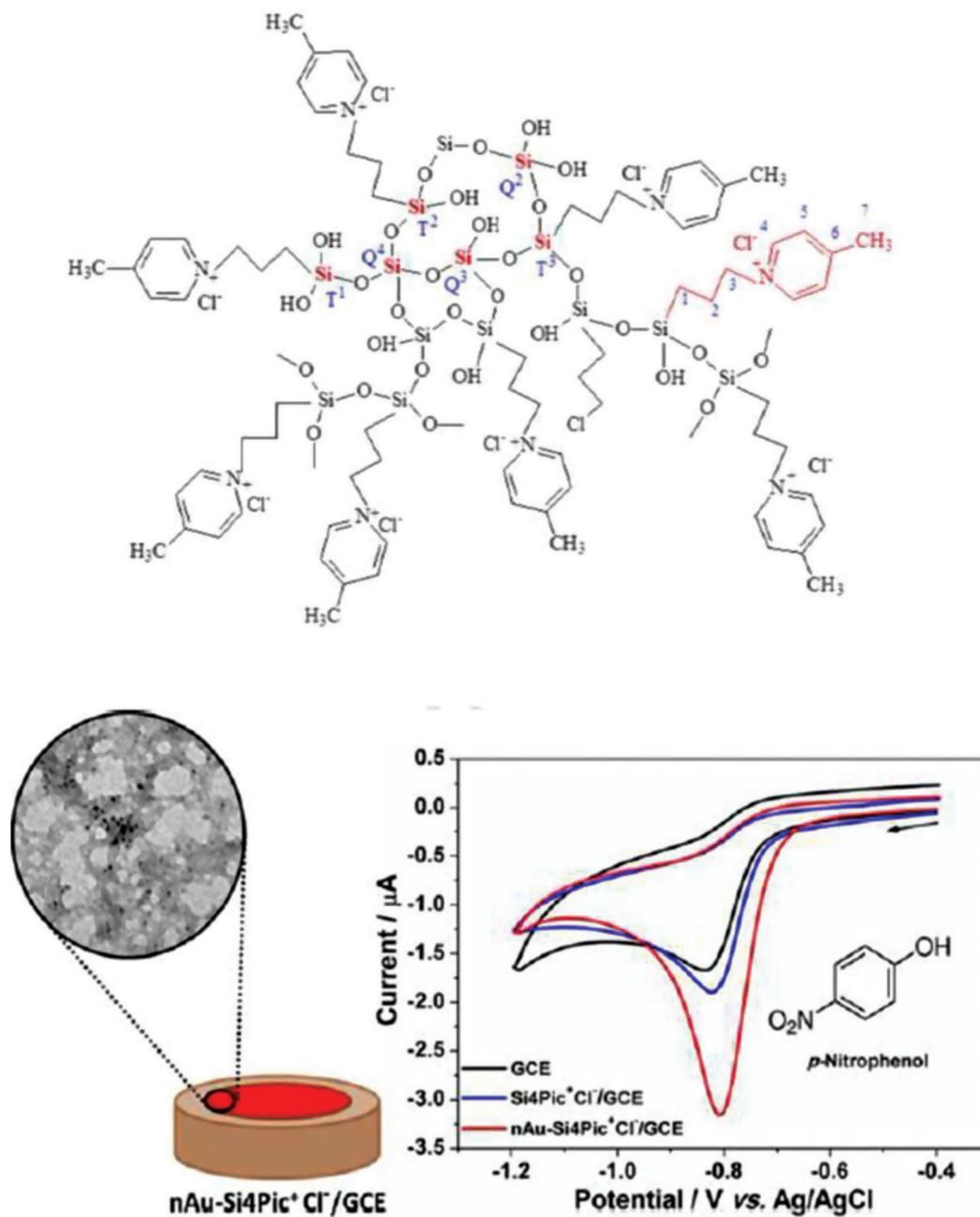
Figure 5. Chemical structure proposed for the charged SSQs (Si4Pic$^+$Cl$^-$) polymer. Transmission electron microscope(TEM) image SSQ stabilized Au nanoparticles (nAu-Si4Pic$^+$Cl$^-$) and cyclic voltammograms for 50 µmol L^{-1} p-NP in B-R buffer pH 7.0 at the GCE, Si4Pic$^+$Cl$^-$/GCE, and nAu-Si4Pic$^+$Cl$^-$/GCE sensors, $v = 50$ mV s^{-1}. Reproduced with permission.[106] Copyright 2014, Elsevier.

reaction of cubic octavinyl-POSS (OVS) and commercial PS via the Friedel–Crafts reaction (**Figure 6**).[112] The porosity of the resulting hybrid polymers could be fine-tuned by varying the ratio of PS and OVS. The gas sorption applications showed that hybrid polymers possessed high H$_2$ uptake and CO$_2$ uptake.

Liu's group further introduced the thiophene unit into the SSQ network by a reaction of OVS with dibromothiophene to form hybrid nanoporous polymers, which exhibited a high surface area, large pore volume, and unique hierarchical pores.[113] The resulting SSQ-based materials showed ultrahigh adsorption

capability of Rhodamine B and methylene blue as well as toxic metal ions, such as Hg^{2+}, Pb^{2+}, and Ag$^+$. This is due mainly to the existence of a large amount of sulfur and double bonds combined with the porous structure. Ha's group fabricated a series of SSQ hollow spheres with a high coverage of functional groups, including fluoroalkyl, phenyl, vinyl, and methyl groups, via a one-step hydrolysis-condensation process with alkyltrialkysilane as the sole precursor. The resulting hollow SSQ materials were used to adsorb benzophenone pollutant from wastewater. The hydrophobicity of SSQ was found to be
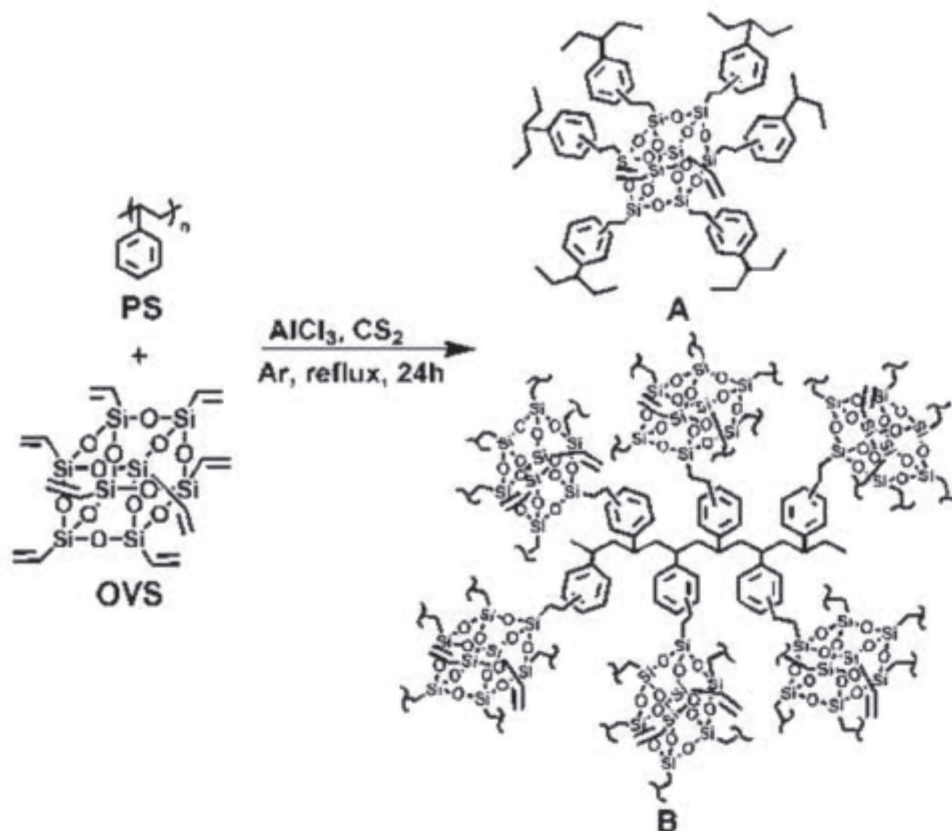
Figure 6. Synthetic routes for hyper crosslinking PS, and possible fragments A and B. Reproduced with permission.[112] Copyright 2015, The Royal Society of Chemistry.

an important factor that influenced the adsorption capacity.[114] Xu et al. fabricated hollow spheres based on cage-like methacryloxypropyl silsesquioxanes (CMSQs) using a facile emulsion-polymerization strategy (**Figure 7**). The preparation of capsules included the formation of a core/shell structure with PS as the removable core and SSQ as a shell. The materials demonstrated very high methylene blue adsorption capacity (95.1 mg g^{-1}). The pore sizes of the spheres were approximately 2–3 nm, which is related to the molecular symmetry and cage volume of SSQ. This uniform size of the pores is believed to be an important factor for providing the high and selective adsorption of methylene blue.[115]

Ha's group synthesized multi-functional magnetite-polysilsesquioxane (PSQ) hybrid nanoparticles in a one-pot approach. As shown in **Figure 8**, ferrous and ferric chloride were used to fabricate magnetite by a coprecipitation process and various silane monomers modified on the surface using a surface grafting method.[116] The results suggested that the magnetic SSQ hybrid nanoparticles have excellent and selectivity adsorption behavior for iron (Fe^{3+}) ions. In another report, a magnetic octavinyl-POSS composite (Fe$_3$O$_4$@POSS) was fabricated and then decorated with boronate to form a nanomagnetic organic–inorganic hybrid material.[117] The final materials exhibited high adsorption capacity of catecholamines due to the porous structure with a high surface area, higher pore volume, and high content of functional boronic acid groups.

Importantly, active vinyl groups from the SSQ enhanced the high content of functional boronic acid groups, which improved the adsorption capacity.

The advantage of SSQ is that they not only show high adsorption because of the intrinsic porous structure, but can also work as a matrix to load nanoparticles for the adsorption of molecules. Gómez et al. fabricated a pendant dodecyl group-functionalized SSQ film hybrid with goethite (Gt) or montmorillonite (MMT) nanoparticles and tested them as sorbents of contaminants from wastewater. Goethite and MMT have been used to remove contaminants from wastewater.[118] The SSQ films synthesized in that study could be recuperated easily after treatment. This means that the films could be applied as simple surface-contaminant trappers, which would facilitate the adsorption of contaminants.

Owing to the high flexibility to be functionalized and the compatibility with polymers, the SSQ nanoparticles also could be applied as a filler to the polymer membranes for the purification of water. Chung et al. first incorporated POSS into a nanofiltration (NF) membrane as a selective layer for the concurrent removal of Se and As ions, which are toxic to humans.[119] The resulting NF membrane had a mean effective pore diameter of 0.65 nm, and a superior pure water permeability of 5.4 L m^{-2} h^{-1} bar^{-1} with significantly high rejections of SeO$_3^{2-}$, SeO$_4^{2-}$, and HAsO$_4^{2-}$ toward 93.9%, 96.5%, and 97.4%, respectively. The function of POSS was found to decrease the adsorption of Se and As ions
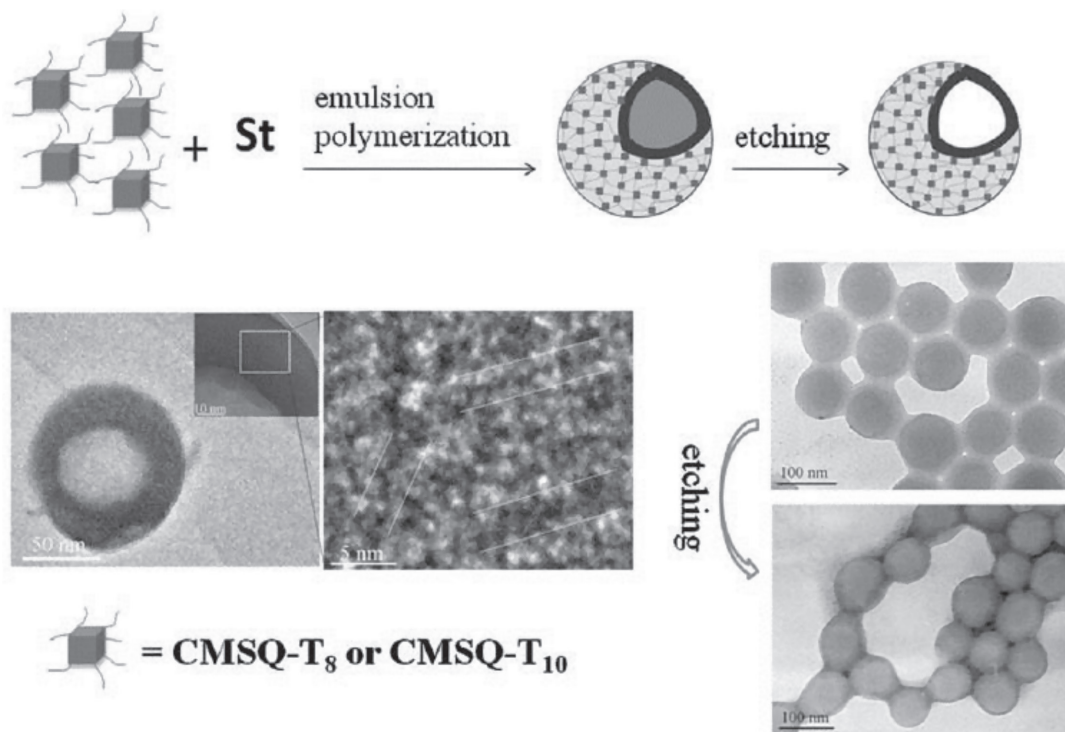
Figure 7. Formation of the PS/CMSQ core–shell particles by emulsion polymerization and the hollow nanosphere products. Reproduced with permission.[115] Copyright 2016, Wiley-VCH.

on the membrane nanocomposite surface, probably due to the large POSS molecules on the membrane surface that prevent the interactions between ions and the membrane.

3.5. SSQ for Energy

Porous carbon or polyaniline (PANI) materials with a high surface area are considered promising supercapacitor electrode materials. They exhibit high capability for charge accumulation at the electrode–electrolyte interface and are favorable for the rapid transport of electrolyte ions.[120]

SSQ hybrid nanomaterials could be applied in energy storage, taking full advantage of their porous structure and surface functionality.[121,122] Jiang et al. developed octa-aminophenyl POSS-derived nitrogen-doped well-defined nanoporous carbon materials and applied them as a supercapacitors electrode.[123] They mixed octa-aminophenyl POSS with phenolic resol to form a uniformly distributed, self-templated, and cross-linked copolymer. After carbonization and removal of the monodispersed silica domains, nanoporous carbon materials were obtained.[123] The materials exhibited high electrochemical performance and good stability as a supercapacitor electrode owing to their controllable nitrogen content, large surface area, and uniform nitrogen-doped nanoporous structure.

SSQ materials could be used as a support matrix and porogens to porous carbon electrodes. A series of polyacrylonitrile(PAN)/POSS nanofibers were fabricated using an electrospinning process. Porous carbon nanofibers were then obtained after a treatment with KOH to etch the carbon

and by hydrofluoric acid (HF) to remove the POSS. The final porous carbon nanofibers had a high specific capacitance and showed great potential as stable freestanding supercapacitor electrodes.[124] Octa-aminophenyl POSS (OASQ) was used to bridge carboxylated nanocarbon (CNF-COOH) and PANI through a polymerization process to form a unique CNF-conjugated polymer hybrid nanomaterial (**Figure 9**). The incorporation of SSQs onto the polymer led to a porous structure with loosely hyperbranched PANI nanobundles. The high conductivity, combined with the porous network, makes it promising for supercapacitor electrode applications.[125]

Gel polymer electrolytes (GPEs) for lithium-ion batteries (LIB) are usually fabricated by immobilizing liquid electrolytes in a polymer host. SSQ nanoparticles, when well dispersed in GPEs, can improve their ionic conductivity, electrochemical stability, and mechanical strength. POSS increases both the ionic conductivity and lithium transference number of the electrolytes significantly.[126] Ma et al. synthesized POSS-poly(methyl methacrylate)(PMMA) particles and used them to modify electrospun polyvinylidene fluoride (PVDF). The resulting hybrid nanocomposites were applied as GPEs for lithium-ion batteries.[127] POSS-PMMA hybrid particles were found to have improved thermal stability and mechanical strength of the GPEs without decreasing the electrochemical properties. The cells with POSS-PMMA-modified hybrid nanocomposite electrolytes showed good cycling performance. These results suggest that POSS-containing GPE hybrid nanocomposites are promising for LIB applications. Lu et al. fabricated electrospun polymer nanofibrous mats loaded with ionic liquids (ILs) and lithium
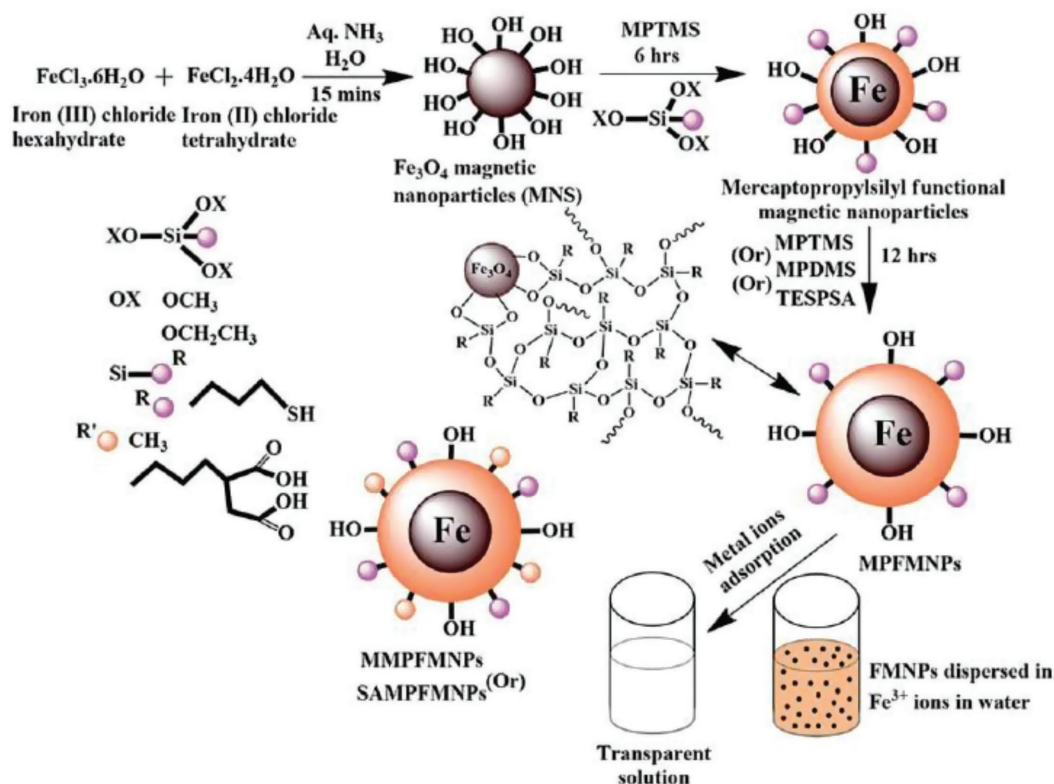
Figure 8. One-pot synthesis of functional polysilsesquioxane magnetite hybrid nanoparticles. Reproduced with permission.[116] Copyright 2017, The Royal Society of Chemistry.

salts for non-volatile electrolytes to take advantage of their high ionic conductivities.[128] They incorporated octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS (POSS-OH) into the electrospun poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-co-HFP) nanofibers on the nanometer scale (**Figure 10**a,b). POSS-OH can be considered the smallest silica nanoparticle, which contains a nanoscale silicon-oxygen cubic cage linked with eight alkylhydroxy groups. Figure 10 c–e shows the good dispersion of POSS-OH nanoparticles in the polymer matrix. This POSS-containing electrospun polymer mat has great potential for lithium ion batteries.

The porous hollow POSS cage structure can retain water molecules and increase the water uptake, leading to an increase in proton conductivity. Zhuang et al. developed hybrid nanocomposite membranes by immersing POSS-modified porous sulfonated poly(ether ether ketone) nanofibers into a Nafion solution.[129] The results showed that the introduction of POSS improved the proton conductivity, water swelling, and methanol permeability of the nanocomposite membrane. These POSS containing nanocomposite membranes could be used as proton exchange membranes for fuel cell applications.

3.6. SSQ in Biomedicine

SSQs containing hybrid nanomaterials have been applied to nanomedicine owing to their biocompatibility and ease of surface modification.[130] The successful utilization of these organic/inorganic hybrid systems for biomedical applications depends on their physicochemical properties. Kumar et al. examined the cell viability of SSQs and reported that the in vitro toxicity of SSQs nanoparticles are based on their size, shape, and surface properties.[131] The tremendous advancement of SSQs has been focused on the field of biomaterial applications, including tissue engineering, drug delivery, biomedical devices, and biosensors.

3.6.1. Bioimaging

To label a targeted object, techniques, such as fluorescent imaging, magnetic resonance imaging (MRI), and X-ray tomography (CT), have attracted considerable attention. Photosensor molecules usually show poor water-solubility and are easy to aggregate in aqueous solution. In addition, easy degradation and potential toxicity also are the main challenges for further applications. An ideal nanocarrier for photosensor applications is expected to have high biostability, low toxicity, and can prevent the photosensor from self-quenching. Two-photon excited photodynamic therapy (TPE-PDT) provides a potential perspective for cancer treatment. Through a sol-gel process, SSQs were synthesized with a two-photon photosensitizer and four triethoxysilyl groups for TPE imaging and PDT of cancer cells (**Figure 11**). The SSQ materials were used as a carrier to load gold nanospheres without the need of thiol linker. The addition of Au nanoparticles (NPs) to the SSQ matrix induced
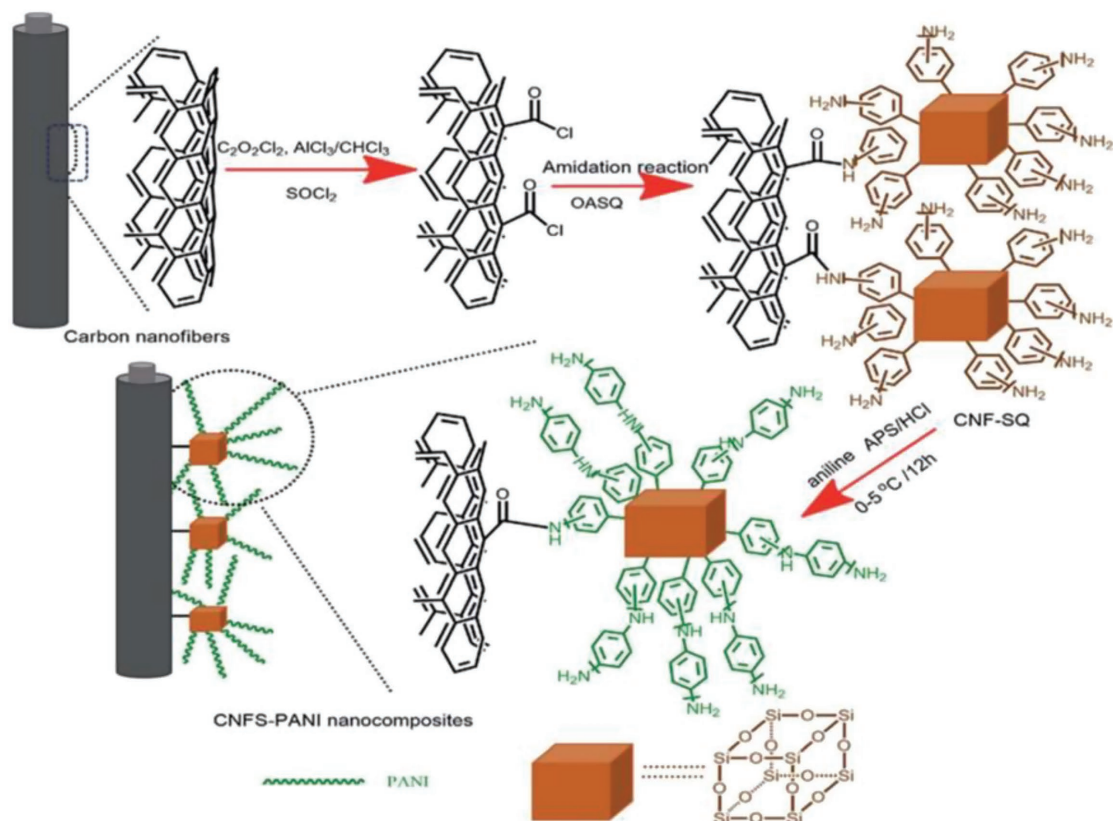
Figure 9. Schematic design for the preparation of CNFS–PANI hybrid nanocomposites by functionalizing CNF with OASQ through amidation followed by a reaction with aniline to form a hyperbranched PANI-grafted CNF. Reproduced with permission.[125] Copyright 2015, The Royal Society of Chemistry.
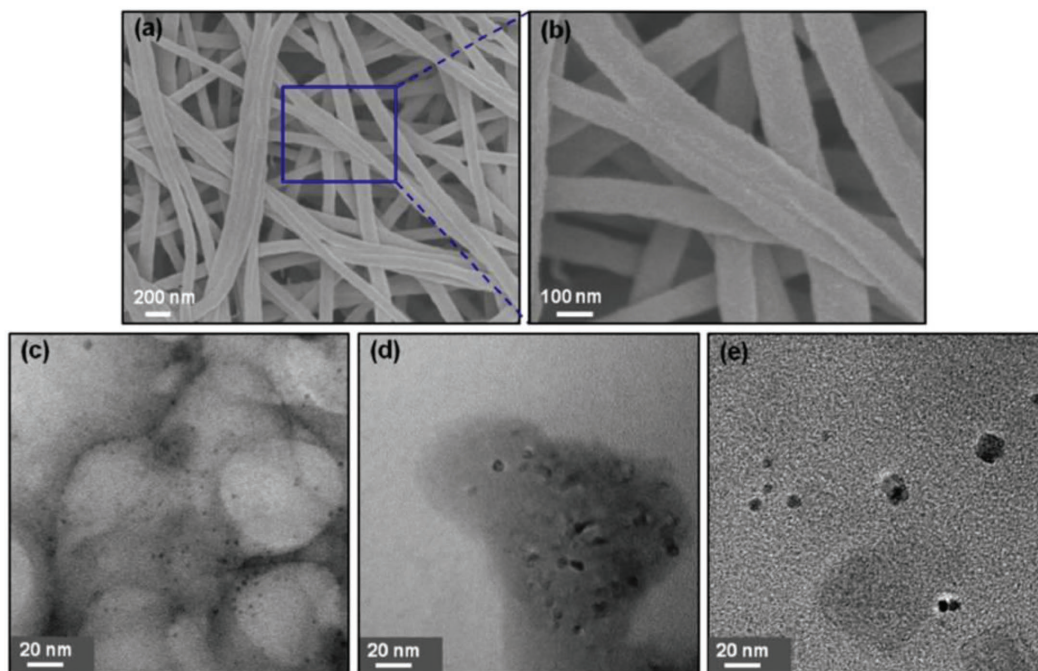

Figure 10. SEM images of the electrospun PVDF-co-HFP/POSS-OH mats with a,b) 5 wt% POSS-OH; TEM images of electrospun PVDF-co-HFP/POSS-OH mats with c) 2 wt%, d) 5 wt%, and e) 8 wt% POSS-OH, respectively. Reproduced with permission.[128] Copyright 2014, Elsevier.
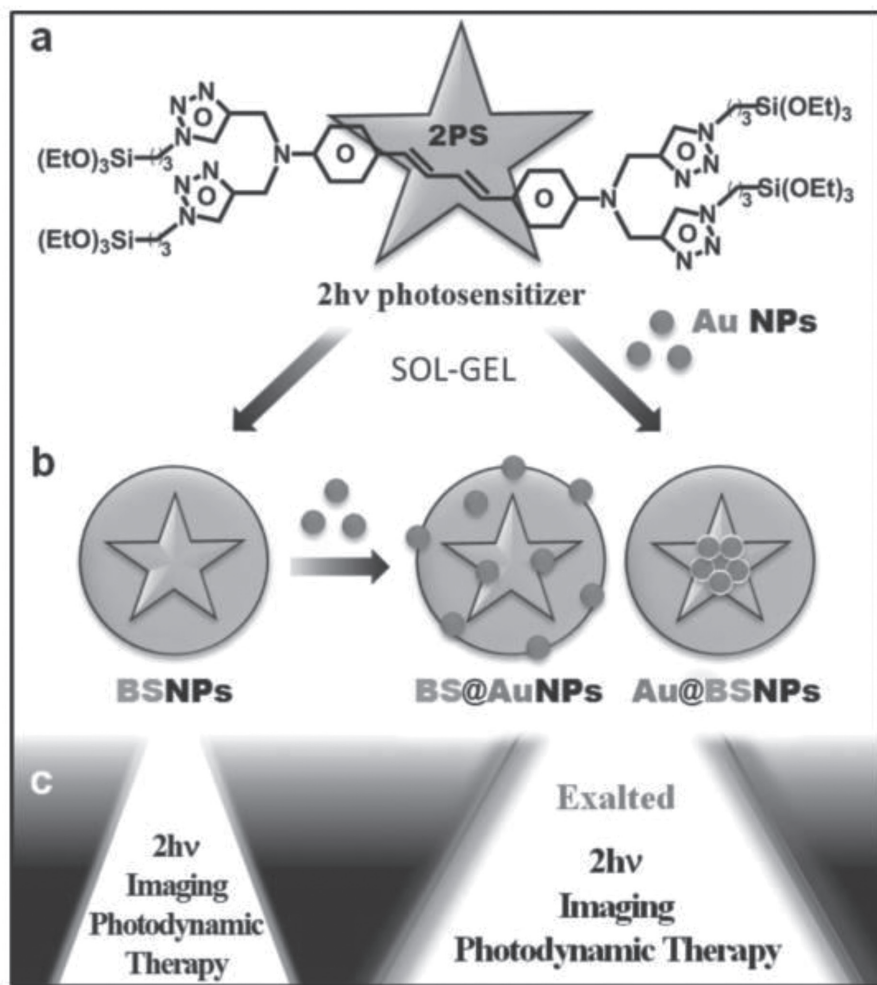
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Figure 11. a) A novel two-photon sensitizer (2PS) condensing via sol-gel chemistry in bridged silsesquioxane nanoparticles (BSNPs) and b) in Au@BSNPs or BS@AuNPs with the combination of gold nanospheres. c) The presence of gold exalts the nanomaterials TPE-PDT and fluorescence imaging. Reproduced with permission.[132] Copyright 2015, Wiley-VCH.

Bridged SSQ nanomaterials could be designed well by incorporating photo-sensitive moieties into the SSQ precursors.[133] Durand et al. developed a versatile process to design monodisperse tetra-alkoxysilylated diaminodiphenylbutadiene or porphyrin photosensitizer-based SSQ nanospheres, 30 to 50 nm in size.[134] In addition, one type of photosensitizer-disulfide-based biodegradable bridged SSQ nanomaterial was also fabricated for two-photon-excited imaging and the treatment of breast cancer cells. Such an organic–inorganic hybrid nanomaterial could be an efficient biodegradable theranostic for cancer treatment. The same group prepared porphyrin- or phthalocyanine-bridged SSQ nanoparticles that displayed a very high signal for photoacoustic imaging in mice.[135]

Utilizing commercially available octavinyl-POSS, Wei et al. developed cross-linked AIE-active fluorescent polymeric nanoparticles (FNPs).[136] As shown in **Figure 12**, octavinyl-POSS was introduced to crosslink a red fluorescence AIE dye (PhE) as the imaging signal and poly(ethylene glycol) methyl ether methacrylate (PEGMA) as the hydrophilic segment to fabricate PEG-POSS-PhE nanoparticles. The obtained core/shell structured amphiphilic copolymers (named as PEG-POSS-PhE) exhibited good water dispersity, strong red fluorescence, and a low critical micelle concentration (CMC) (0.0069 mg·mL^{-1}) in an aqueous solution. The POSS-based polymers have great potential for biological imaging applications, owing to their high water dispersity, uniform morphology, small size, as well as their excellent biocompatibility and cellular internalization.[136]

remarkable fluorescence. Enhanced TPE-excited fluorescence was observed with gold-doped nanosystems compared to a pure photosensitizer containing SSQ. Both SSQs and gold-doped SSQs are quite promising for bioimaging and cancer theranostics.[132]

Owing to the structural similarities with silica materials, SSQs are promising host precursors used to encapsulate rare
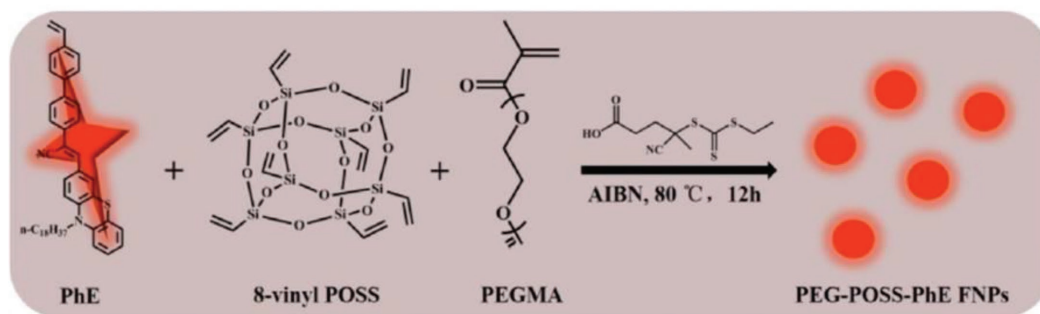

Figure 12. Schematic showing the preparation of PEG-POSS-PhE FNPs. Reproduced with permission.[136] Copyright 2017, Elsevier.

earth elements and form silica materials after thermolysis. Rare earth metal-doped silica nanoparticles have been developed by the thermolysis of Eu^{3+}-doped metallasilsesquioxanes.[137] This approach can be used to fabricate a range of nanostructured materials doped with rare earth elements for bioimaging applications. Carniato et al. constructed luminescent mesoporous silica through the self-assembly of POSS and europium (III) ions. The chemical combination of POSS and Eu^{3+} ions resulted in a robust mesoporous silica with interesting luminescent properties and good hydrothermal and photobleaching stability. These properties make them promising for the fabrication of stable and efficient luminescent devices for bio-imaging applications.[138] POSS could also be used to transfer rare earth-doped upconversion luminescent nanoparticles (UCNP) from hydrophobic to hydrophilic environments by coating the surface of the nanoparticles. The resulting POSS-UCNP exhibited high water solubility, low cytotoxicity, and excellent biocompatibility. The successful application of the particles for in vivo MRI demonstrated the potential of the materials for multimodal bioimaging.[139]

Quantum dots (QDs) are fluorescent nanoparticles with unique photophysical properties but are limited by the instability, toxicity, and hydrophobic surface. SSQ-based nanomaterials are expected to be the protecting materials to solve this problem. Seifalian et al. coated QDs with a new developed POSS/poly-(carbonate-urea)urethane (POSS-PCU) nanocomposite polymer for bioimaging applications.[140] The resulting nanocomoposites are promising for long-term bioimaging applications because they are biocompatible, highly photostable, and colloidally stable. The POSS-based polymer not only protected the QDs but also assisted in QD solubility in aqueous solution.[140]

POSS could be coated on magnetic particles as a shell to protect the guest molecules or nanoparticles inside. Selvan et al. utilized either polyethylene glycol (PEG) or octa(tetramethylammonium) (OctaTMA) functionalized POSS as a protection layer on small-sized (<10 nm), water-soluble, magnetic nanoparticles (MNPs) for magnetic resonance imaging (MRI). The POSS provided the magnetic nanoparticles with good colloidal stability at different pH and salt concentrations, and low cytotoxicity to MCF-7 human breast epithelial cells. The MR phantom images of the nanocomposite demonstrated promising applications in bioimaging.[141]

3.6.2. Antimicrobial Activity

SSQs could be hybridized with suitable polymers to form nanocomposites with stability, hydrophobicity, and antibacterial properties.[142,143] Trisilanolisobutyl POSS has been used to modify polyurethane (PU) to prepare POSS-PU nanofiber composite membranes by electrospinning technology.[144] The antibacterial activity of the nanofiber membranes was obviously improved after the addition of POSS, due partly to its hydrophobicity. The lower surface tension and hydrophobic groups by the incorporation of POSS are believed to lead to decreasing bacterial adhesion or resistance to bacteria contamination.

Amino-POSS materials were applied to functionalize a regenerated cellulose for antimicrobial purposes. The resulting well-dispersed hybrid-functionalized POSS/cellulose nanocomposites improved significantly the antimicrobial behavior against pathogenic bacteria as well as the optical transparency and thermal stability.[145] Through the melt spinning process, octa ammonium POSS nanoparticles were also filled into PP to form antimicrobial composite fibers. The resulting POSS/PP fibers had an antimicrobial effect against at least four different types of bacteria. The antibacterial effects of modified PP fibers increased with increasing POSS content.[146] The antimicrobial effectiveness of this ammonium POSS was attributed to the positive charge at the nitrogen atom. SSQ porous materials could be loaded with an antibacterial metal, such as silver, copper, or zinc to obtain stable antibacterial composites.[143,147,148] Spherical silver nanoparticles with a mean size of ≈5 nm were synthesized in aqueous media and loaded onto a charged SSQ-containing a quaternary ammonium group. The resulting silver-containing SSQs materials demonstrated excellent antibacterial performance.[148]

Using post-synthetic surface functionalization procedures, the antibacterial moieties also could be introduced into SSQ nanostructures.[149] In Yeganeh's report, the bactericidal 1,2,3-triazolium functional groups were anchored chemically to the surfaces of the hydrophobic triazolium POSS nanoparticles (as shown in **Figure 13**). The resulting nanocomposites were incorporated into a dental restorative system composed of ternary thiol-allyl ether-methacrylate resin and glass fillers. The triazolium-POSS-containing nanocomposite exhibited significantly higher bactericidal activity against *Streptococcus mutans*.[150]

3.6.3. Drug Delivery

Owing to the organic/inorganic hybrid structure, biocompatibility, and nontoxicity, the SSQ-containing nanomaterials could be applied to drug delivery.[151] Recently, the study of SSQ for drug delivery focused not only on the increased drug capacity, but also on various types of stimuli-triggered release.[152] Lin et al. developed nanoparticles comprised of polysilsesquioxane polymer crosslinked by a cisplatin prodrug (Cisplatin-PSQ) via a base-catalyzed sol-gel process.[153] The resulting nanoparticles had an exceptionally high cisplatin loading, and the release of cisplatin was triggered in the presence of L-cysteine (a model reducing agent).[153] Zhou et al. fabricated disulfide-bridged SSQ with an organic–inorganic hybrid hollow structure via a facile one pot process. The stability and biocompatibility of the obtained materials were improved after subsequent PEG modification. These SSQ-based hollow spheres showed high doxorubicin (DOX)-loading capacity and demonstrated both pH- and glutathione-triggered DOX release behaviors. Therefore, SSQ-containing hybrid nanomaterials have great potential as nanocarriers for drug delivery and theranostic applications.[154] Huang et al. reported POSS-based star polymer-drug conjugates that exhibited excellent loading capacity of hydrophobic drugs (docetaxel(DTX)) and stimuli-responsive DTX release under acidic lysosomal and reducing cytoplasmic environments.[155]

POSS with functional groups that could be bonded covalently with drug molecules are suitable for a drug delivery system. An amine-functionalized POSS was crosslinked
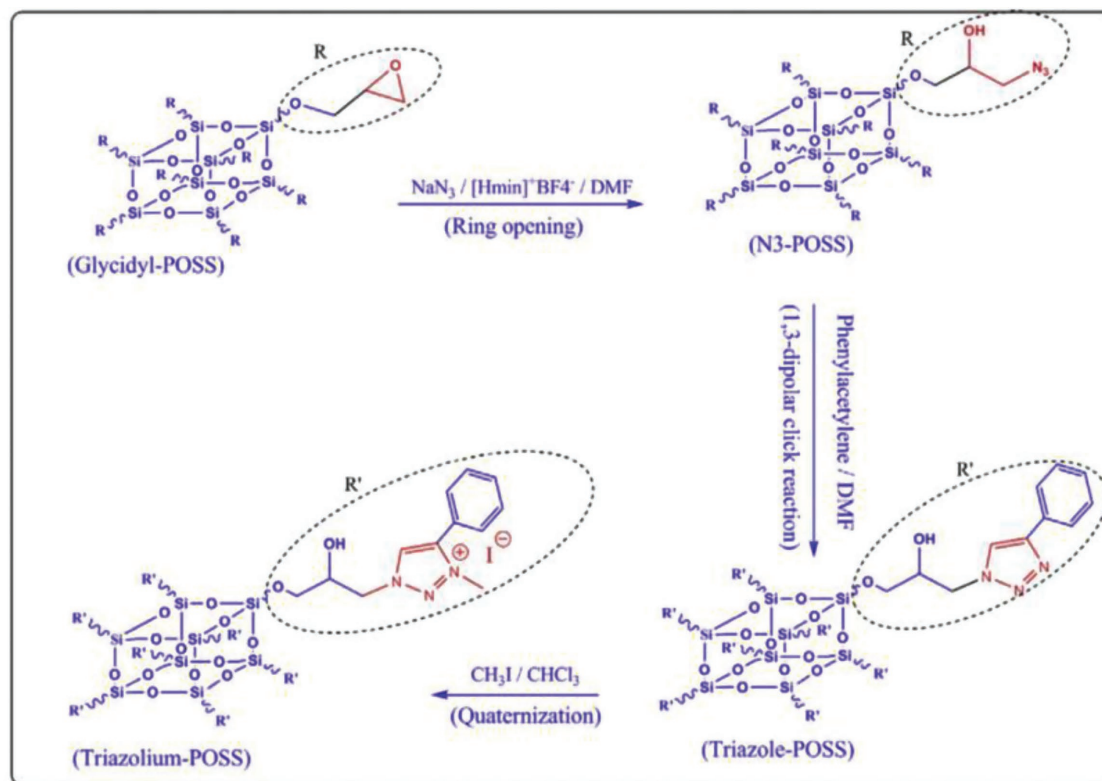
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Figure 13. Synthetic route for the preparation of triazolium-POSS. Reproduced with permission.[150] Copyright 2017, Elsevier.

with a carboxyl-containing photosensitizer (chlorin e6) via an amine-carboxyl reaction to form a 3D network through the 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC)/N-hydroxysuccinimide(NHS) coupling method. The obtained POSS-Ce6 nanocomposites were coated with PEG polymer to construct the final nanoagent (POSS-Ce6-PEG) (**Figure 14**). The resulting inorganic–organic hybrid nanocomposites showed high drug-loading capacity and superior chemical stability with enhanced photodynamic therapy (PDT).[156]

Fully functionalized amide-POSS was combined with ibuprofen or acetaminophen to construct a drug delivery system. In such a system, the drug molecules can be released under physiological conditions and at the same time, the POSS could be hydrolyzed and removed safely from the organism. The drug delivery system showed low toxicity and efficient cellular uptake with a nanoscale-sized 3D structure. These SSQ materials are quite promising as a kind of biocompatible drug carrier.[157]

Khashab fabricated o-nitrophenylene-ammonium bridged silsesquioxane (BS) nanoaggregated particles and hollow nanospheres with tunable morphologies. The BS formation process included the hydrolysis and condensation of a photoresponsive bridged alkoxysilane precursor in a NaOH aqueous-ethanol solution. Interestingly, hollow BS particles were also prepared, as shown in the TEM images in **Figure 15**. Such nanoparticles were applied to the on-demand delivery of plasmid deoxyribonucleic acid (DNA) in HeLa cancer cells via light actuation.[158]

SSQs could also be used as a modifier or stabilizer of nanoparticles for drug delivery.[159] Seifalian et al. utilized octaammonium POSS to modify single-walled carbon nanotubes (SWCNTs), imparting biocompatibility and water stability for drug loading. The resulting POSS-SWCNT worked as a paclitaxel (PTX) drug carrier that could deliver PTX to cancer cells. The combination of POSS, SWCNT, and PTX as a conjugate provides an efficient strategy for cancer drug delivery and therapy.[160]

3.6.4. Tissue Engineering

SSQs have good biocompatibility, cell compatibility, and suitable 3D nanostructure, which are favorable as tissue engineering materials.[161] For tissue engineering, biocompatibility and cytocompatibility should be the first aspect to consider. Lin et al. reported that mercaptopropylisobutyl-POSS and octahydroxypropyldimethylsilyl-POSS showed no significant toxicity to cell growth and proliferation. On the other hand, aminoethylaminopropylisobutyl-POSS decreased the cellular viability at high concentrations. The above three POSS nanomaterials demonstrated good ocular biocompatibility in most cases, making them promising for ocular biomedical applications.[162] More recently, POSSs have been applied as the components of ophthalmic biomedical devices, such as intraocular lenses or contact lenses, because of their chemical inertness and transparency.[162] By simple physically mixing, nanocomposites from
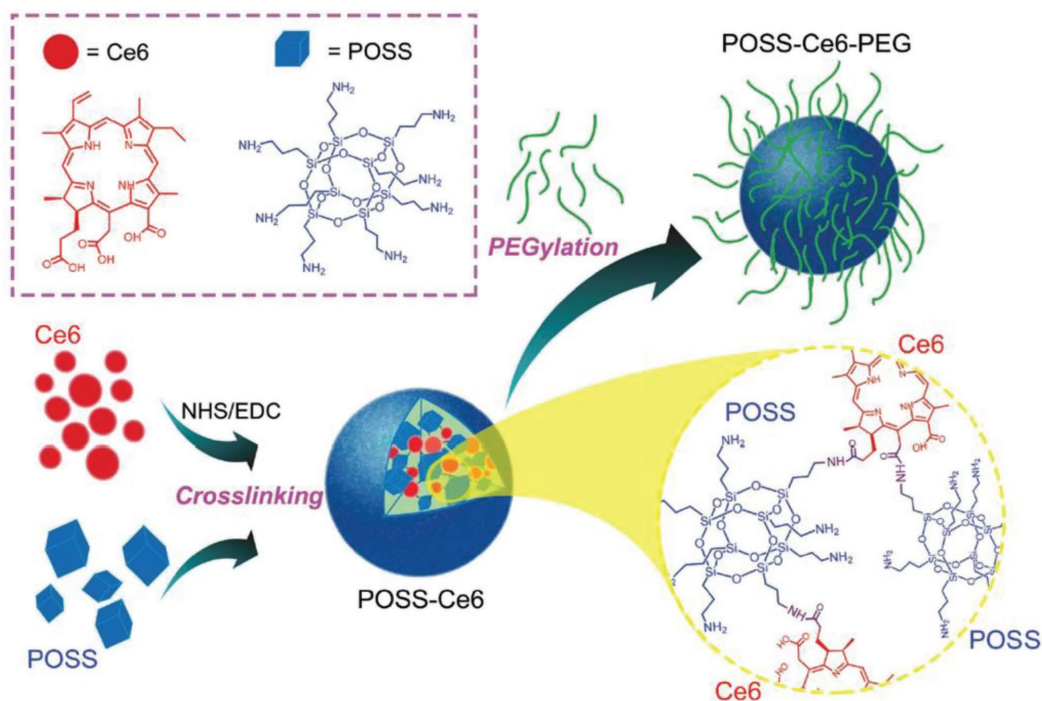
Figure 14. Schematic illustration showing the synthetic process of POSS-Ce6-PEG NPs. Reproduced with permission.[156] Copyright 2017, The Royal Society of Chemistry.

trisilanolisooctyl POSS (open-cage POSS) hybridizing with PU showed good biocompatibility because of its inert and low inflammatory response.[163]

A PU/POSS nanocomposite was fabricated by the Seifalian group by integrating trans-cyclohexanechloroydrinisobutyl-

POSS nanoparticles into the poly(ε-caprolactone urea) urethane backbone. The degradation kinetics of this POSS-contained nanocomposite was studied for tissue engineering. In the degradation process, the nanocomposites maintained the vital mechanical structures and elasticity rather than becoming stiff
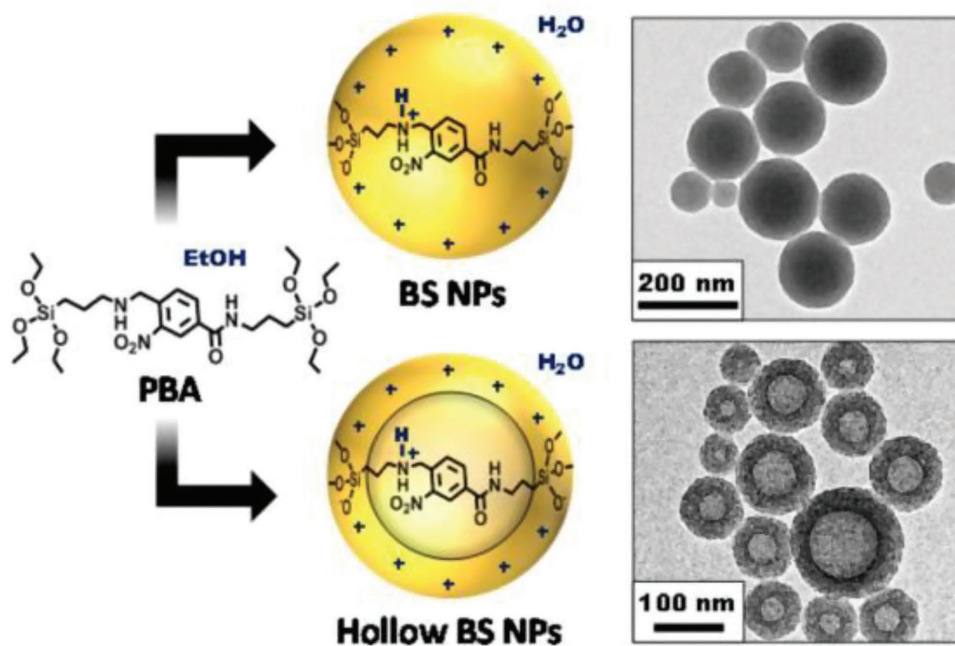

Figure 15. Design of bridged silsesquioxane (BS) and hollow BS (nanoparticles) NPs via the sol–gel reactions of the photoresponsive bridged alkoxysilane precursor, as shown by TEM images. Reproduced with permission.[158] Copyright 2015, The American Chemical Society.
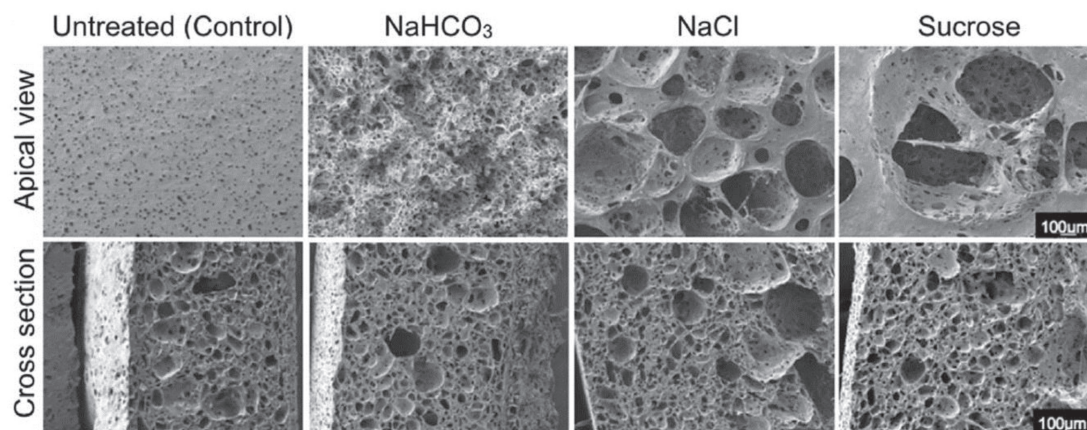
Figure 16. SEM images of the apical surface and a cross section of candidate bioscaffolds with porous structure utilizing $NaHCO_3$, NaCl and sucrose as porogens, respectively. (scale bar = 100 μm). Reproduced with permission.[165] Copyright 2016, Elsevier.

and brittle. This property is very important for tissue engineering applications, including tissues, such as the skin or vasculatures.[164]

To further enhance the performance of SSQs in tissue engineering, a 3D nanostructure and high porosity are needed. Poly(carbonate-urea) urethane (PCU)/POSS hybrid nanocomposites were fabricated, followed by topographical modifications as a bioscaffold.[165] Sodium bicarbonate ($NaHCO_3$), sodium chloride (NaCl), and sucrose were used as porogens dispersed onto the PCU-POSS nanocomposite surface to increase the surface porosity (as shown in **Figure 16**). This process provided additional opportunities for improved cellular and vascular growth. The experiments showed that surface modification with large porogens can improve the integration of a PCU-POSS nanocomposite scaffold.

3.7. Other Applications

SSQ-containing hybrid nanomaterials have also been reported to be a nanoscale etching barrier.[166] Recently, SSQs nanocomposites were used as antireflection coatings for optoelectronic devices to solve problems, such as unwanted light reflection, ghost images, stray light, and energy loss. Xu et al. fabricated a moth-eye-like antireflection surface with double-layer nano-wrinkled structures by coupling the polymeric surface onto a methacryl and aminophenyl-functionalized SSQ rigid template.[167,168] Fluorinated and octamethacrylated SSQ-based photoresist could be fabricated as an ideal high-performance material for ultraviolet nanoimprinting because of their properties, such as low surface energy, low viscosity, and high curing rate.[169]

Anti-ice films have been fabricated via an addition-curable process of octavinyl-POSS and fluorinated methacrylate/polymethylsiloxane. Octvinyl-POSS was used not only to strengthen the cross-linking structure, but also to build hierarchical micron/nano-structured surfaces. These anti-icing and icephobic coatings are promising for managing the issue of ice accretion.[170]

4. Summary and Outlook

SSQs, including particularly cage-like POSS hybrid nanomaterials, have attracted considerable interest in recent years because of their unique designable organic-inorganic nanostructure and good compatibility with polymer and biology systems. This review article summarized the recent research advances on SSQ-based hybrid nanomaterials with their fabrication, property, and applications. Different hybrid methods include physical blending and chemical reactions, such as covalent bonding or grafting process. The work present here showed the most recent development of SSQ-containing hybrid nanomaterials in the field of polymer nanocomposites, catalyst, adsorption, sensor, energy storage, and biomedicine. In the case of SSQs/polymer nanocomposites, SSQs work mainly as nanofillers, which could be well dispersed in a polymer matrix. In some other cases, SSQs usually play the role of a nanocarrier for guest molecules or ions due to the porous structure of SSQs.

Considerable effort has been made on the synthesis of SSQs with different functional groups and structures. Challenges still exist regarding the fabrication of novel SSQs and SSQ hybrid nanomaterials with unique properties and high performance. The structure–property relationship of these materials still needs to be examined. For further practical applications, SSQs with suitable organic moieties, controllable size and structures should be developed. The amazing applications of hybrid SSQ-based nanocomposites, such as catalysts, adsorption, energy, and biomedicine, need to be explored further.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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