Design and development of novel layered nanostructured hybrid materials for environmental, medical, energy and catalytic applications
Potsi, Georgia

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CHAPTER 5

Carbon Nanostructures containing Polyhedral Oligomeric Silsesquioxanes (POSS)

This review chapter describes the synthesis and properties of carbon nanostructures containing organic-inorganic cage-like polyhedral oligomeric silsesquioxane (POSS) nanoparticles. The physical and chemical functionalization of carbon nanomaterials such as graphene, graphene oxide, carbon nanotubes, and fullerenes with POSS towards the development of novel hybrid nanostructures is described in detail. Special emphasis is given to the potential impact of these hybrid nanostructures on various technological applications.

5.1. Introduction
Silsesquioxanes belong to the family of silicone resins\[1\] that have been used in a plethora of applications due to their exceptional properties such as thermal and photo stability, electric insulation, chemical stability and functionalities. Silsesquioxanes with a general formula \(\text{RSiO}_{3/2}\) possess a pronounced aptitude to form three-dimensional (3-D) cage-like highly symmetric frameworks known as polyhedral oligosilsesquioxanes (POSS). Several structures are known for silsesquioxanes, including random, ladder, partially condensed and cage (e.g. T8, T10 and T12) types.\[2\] These cubic, hexagonal, octagonal, decagonal, dodecagonal or even open cage-like structures derive from hydrolytic condensation reactions of trifunctional organosilicon monomers\[3\] with formula \(\text{RSiOH}_3\), where \(R\) is an organic group covalently attached to the silicon chain. POSS with the general formula \(R_n\text{Si}_{11n}O_{1.5n}\), where \(R\) is a vertex group including hydrogen or organic functional groups,\[2,4\] consist of an inorganic silica-oxygen core and polar or non-polar organic substituents attached at the edges of the cage (see cubic analogue in Figure 5.1). This multiple functionality of POSS – in addition with their nanopore size that varies between 1-3 nm depending on the length of the \(R\) groups\[5\] - make them chemically compatible with many nanocomposite constituents like polymers, nanocarbons, inorganic layered materials, biological systems, or DNA.\[6, 7, 8, 9, 10, 11, 12, 13, 14, 15\] POSS can be attached to these systems\[16\] mainly via covalent linking on the surface or physical blending. After the discovery of the first POSS in 1946\[17\] a wide variety of stable 3-D polyhedral oligosilsesquioxane frameworks have been reported, with an immense variety of functional groups imparting new interesting properties to the silica cage structure.\[18, 19\]

![Figure 5.1. Molecular structure of a cubic polyhedral oligomeric silsesquioxane (POSS).](image)
Polyhedral oligomeric silsesquioxanes appear highly promising candidates for the synthesis of hybrid nanomaterials suitable for a wide range of applications. The incorporation of POSS has been first applied into polymer matrices with the aim to improve the polymer properties in terms of higher thermal stability, mechanical stiffness and viscosity.\cite{20} Moreover, immense efforts have been made worldwide over the last decade to incorporate 3D silsesquioxanes into carbon nanomaterials in order to enhance the characteristics of the resulting nanohybrids for various technological sectors such as energy storage,\cite{21, 22} environmental applications\cite{23} and biomedicine.\cite{24, 25, 26} This mini-review focuses on the most recent experimental scientific endeavours to create novel materials combining cubic POSS (most common polyhedral structure) with carbon nanostructures such as graphene, carbon nanotubes and fullerenes. The design and development of these novel systems is of high importance for optical,\cite{24, 27, 28, 29, 30} and thermal\cite{31, 32, 33, 34} applications as well as in the fields of electronics\cite{21, 29, 35, 36} and solar cells.\cite{23, 37}

5.2. Fulleren functionalization with POSS and their derivatives
In 2008, David J. Clarke and coworkers\cite{24} reported for the first time polyhedral oligomeric silsesquioxane bound to fulleropyrrolidines. These derivatives were proposed as suitable optical limiters, expected to find applications in various scientific, industrial, medical and military fields, where lasers are utilized. It is well known that the protection against pulsed tunable lasers is a great challenge. C\textsubscript{60} solutions have been identified as effective optical limiters.\cite{24} However, in order to extend the optical limiting behaviour of C\textsubscript{60} to the solid phase (for example in a polymeric matrix), which is preferred for practical applications, David J. Clarke et al.\cite{24} covalently linked fullerene derivatives to POSS even though these two nanoparticles are generally immiscible and own different molecular shapes. They proposed two quite long synthetic pathways\cite{24} for the functionalization of
fulleropyrrolidines with POSS as depicted in Figures 5.2 and 5.3. The characterization of the two POSS derivatives in solution confirmed the presence of the fulleropyrrolidines and an optical power limiting essentially identical to that of C$_{60}$. Since the optical properties of C$_{60}$ were retained in the final compounds, the authors proposed that the incorporation of the POSS-C$_{60}$ in a polymeric matrix through the synthesis of a N-functionalized amino glycine and its reaction with POSS-C$_{60}$. The combination of the two classes of material (POSS and C$_{60}$) leads to a successful integration of the properties of the two components in the new hybrid materials. Apart from the laser-focused applications proposed by the authors, the derived hybrids present important features for various nanotechnological fields including polymer reinforcement, solar cells, sensors, etc.

![Synthesis of POSS/fulleropyrrolidines](image)

**Figure 5.2.** Synthesis of POSS/fulleropyrrolidines (synthetic pathway 1). (Reproduced with permission from Ref.[24])
To avoid the long synthetic route followed to obtain the POSS-fulleropyrrolidine described above, one year later, the same group of researchers synthesized and characterized a POSS-iminofullerene compound\cite{27} shown in Figure 5.4. Their purpose was to prepare POSS-fullerene derivatives with short phenyl groups and optical limiting capacity, which could be incorporated into polymers. The study of the optical
limiting properties of POSS-iminofullerene in solution showed that also in this case the optical power limiting of the compound was the same as that of C\(_{60}\).

Hao-Jan Sun et al.\(^{[21]}\) synthesized and characterized a sphere-cubic shaped amphiphile composed of an inorganic-organic POSS-C\(_{60}\) dyad. Since POSS has insulating and C\(_{60}\) semiconducting properties in the solid state, crystals of this dyad can find application in nano-capacitors. POSS and C\(_{60}\) were connected with a short and single covalent linkage in order to prevent a macroscopic phase separation. More specifically, the POSS-C\(_{60}\) dyad was synthesized by Steglich esterification\(^{[21, 38]}\) of a carboxylic acid-functionalized C\(_{60}\) and hydroxyl-functionalized POSS. The esterification was carried out in a mixed solvent of CH\(_2\)Cl\(_2\)/DMF. The resultant dyad exhibits polymorphism with two crystal lattices: orthorhombic and hexagonal. Both crystalline forms present a bi-layered structure, which contains double layers of C\(_{60}\) and double layers of POSS moieties. The C\(_{60}\)-C\(_{60}\) interaction is stronger in the case of the hexagonal lattice than in the orthorhombic one. A comparison between the two crystalline forms in terms of thermodynamic stability and structural formation kinetics showed that the hexagonal phase is thermodynamically more stable (higher melting point), while the orthorhombic phase was found to be kinetically more favourable and easier to form.

In 2012, Fafu Yang et al. claimed that the POSS-C\(_{60}\) derivatives with short phenyl groups are not favourable for homogeneous dispersion in polymers.\(^{[39]}\) For this reason they designed and synthesized dumbbell-shaped POSS-C\(_{60}\) dyads where POSS and C\(_{60}\) are linked with long and flexible aliphatic spacers. These POSS-fullerene dyads possess great flexibility and compatibility with polymers. Figure 5.5 presents the synthetic route that was followed to obtain the POSS-C\(_{60}\) dyads in multiple steps with a total yield around 40%.

Two years later, Cheng and his colleagues\(^{[40]}\) reported the design of an asymmetric giant amphiphile by combining two isobutyl POSS (BPOSS) and one C\(_{60}\). This amphiphile is prepared by the Bingel reaction\(^{[41]}\) and its structure consists of two different layer thicknesses of C\(_{60}\) and BPOSS, while the C\(_{60}\) layer is sandwiched
between two BPOSS layers. After the coupling of the two BPOSS to the C\(_{60}\), the total symmetry of the molecule reduces from I\(_h\) (C\(_{60}\)’s symmetry) to C\(_{2v}\) (diBPOSS-C\(_{60}\)).\(^{[42],[43]}\) The possibility of altering the sizes and shapes of the molecular units which are used in order to obtain the giant amphiphiles, as well as the control of the thickness of the resulting layers, are two interesting characteristics that could lead to practical application as nano-capacitors.\(^{[44]}\)

Important progress in the incorporation of POSS and fullerene into polymers was made in 2008 when Weihua Kai \textit{et al.} succeeded in linking these compounds to both ends of the same polymer chains (poly(\(\epsilon\)-caprolactone), PCL).\(^{[45]}\) In this way, the poor solubility of C\(_{60}\) could be (partially) overcome and the final polymers presented improved optical limiting and thermomechanical properties. Inoue and coworkers prepared three different materials: a fullerene double end-capped PCL, a POSS single end-capped PCL and a fullerene and POSS double end-capped PCL (see Figure 5.6). They found that both POSS and C\(_{60}\) moieties aggregate in small particles onto the ends of the PCL chains creating a network structure. The confinement effect of POSS and C\(_{60}\) on the crystallization behaviour of PCL resulted in a decrease of the crystallization enthalpy (\(\Delta H\)) from the DSC analysis (Table 5.1). As it is shown, the \(\Delta H\) value of POSS single end-capped PCL is almost the same as that of double end-capped one, while that of fullerene and POSS double end-capped PCL decreases.

\textbf{Figure 5.5.} Synthesis of POSS-C\(_{60}\) dyads. (Reproduced with permission from Ref.\(^{[39]}\))
Nevertheless, the value of such decrease is much smaller compared to that of PCL with fullerenes at both ends. This can be ascribed to the formation of the network structure by the aggregation of the fullerene moieties at both the ends of the PCL, while in the case of the fullerene and POSS double end-capped PCL the network structure is formed by two types of aggregates (fullerene and POSS moieties). Consequently, the confinement effect of the fullerene aggregates on the crystallization of PCL is stronger than that of POSS aggregates. Therefore, Weihua Kai et al. concluded that depending on the fullerene and POSS end cappings, it is possible to synthesize various kinds of aggregated polymeric materials with different network strengths.

**Figure 5.6.** Synthetic pathway for fullerene and POSS double end capped PCL. (Reaction 1: Chlorobutyryl chloride, pyridine, room temperature; Reaction 2: Sodium azide, DMF, 65 °C. (Reproduced with permission from Ref.[45])
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Table 5.1. Thermal properties of PCL and its fullerene (F) and POSS (P) capped derivatives.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>DPCL</th>
<th>FPCLF</th>
<th>PCLP</th>
<th>FPCLP</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH (J g⁻¹)</td>
<td>72.2</td>
<td>51.1</td>
<td>75.5</td>
<td>69.9</td>
</tr>
<tr>
<td>T mc (°C)</td>
<td>27.3</td>
<td>22.7</td>
<td>27.9</td>
<td>29.9</td>
</tr>
<tr>
<td>POSS content %</td>
<td>-</td>
<td>-</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Fullerene content %</td>
<td>-</td>
<td>12.7</td>
<td>-</td>
<td>7.0</td>
</tr>
</tbody>
</table>

a. The crystallization enthalpy (ΔH) and melt crystallization temperature (T mc) were determined from DSC and normalized with the PCL content. b. The weight content of POSS calculated from TG results. c. The fullerene weight content determined from the TG at a temperature about 600 °C. [45]

In 2012 Wen-Bin Zhang and coworkers[23] prepared and applied a POSS-C₆₀ dyad as a novel electron acceptor for bulk heterojunction polymer solar cells with an inverted device configuration. The conducting polymer chosen to be mixed with POSS-C₆₀ was poly[4,4’-bis(2-ethylhexyl)dithienol[3,2-b:2',3’-d]silole]-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5’-diyl] (SiPCPDHTBT). The incorporation of POSS into electro-active materials results in improved stability and device performance,[37] while C₆₀ derivatives are commonly employed as electron acceptors in bulk heterojunction polymer solar cells. POSS-C₆₀ dyads provide the benefits of both molecular moieties: electronic properties and versatile functionalization. Wen-Bin Zhang et al.[23] studied the ability of these bulk heterojunction materials to generate increased short circuit current and open circuit voltage for high power conversion efficiencies. The characterization of POSS-C₆₀ with various techniques showed that the presence of POSS did not change the C₆₀ electronic properties. The same group also studied the power conversion efficiencies of the bulk heterojunction polymer solar cells made by the same polymer (SiPCPDHTBT) mixed with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM). To compare the difference in device performances between PCBM and POSS-C₆₀, bulk heterojunction polymer solar cells with an inverted device configuration were fabricated (Figure 5.7). The use of POSS-C₆₀
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**Figure 5.7.** (right) Molecular structures of POSS-C$_{60}$, PCBM and SiPCPDDBT. (left) polymer solar cell device configuration. (Reproduced with permission from Ref. [23])

improved the performance and the overall device efficiency by increasing the short circuit current value by 2.22 mA cm$^{-2}$ and the power conversion efficiencies by 0.58 % compared to PCBM. These results proved that POSS-C$_{60}$ is a potentially useful electron acceptor in bulk heterojunction polymer solar cells.

5.3. Functionalization of carbon nanotubes with POSS and derived hybrids

In 2009, Jong-hwan Jeon et al.\cite{46} developed a new approach for the preparation of hybrid nanocomposites of Pd nanoparticles and multi-walled carbon nanotubes (MWCNTs) destined to be used in hydrogen sensing devices.\cite{46} The hybrid Pd-POSS and MWCNT-COOH nanocomposites were synthesized by a self-assembly method via ionic interaction between positively charged Pd-POSS and negatively charged MWCNT-COO$^-$. as described in Figure 5.8. The palladium nanoparticles (Pd-POSS) were synthesized by using the cubic silsesquioxanes (POSS-NH$_3^+$) as a cross-linker for the self-organization of the isolated palladium nanoparticles.\cite{46}
A year later, Anandhanatarajan Gomathi et al.\textsuperscript{[22]} investigated the functionalization of MWNTs with POSS to enable their dispersion in polar solvents for polymer composite preparation and Qi-Fang Li et al.\textsuperscript{[29]} synthesized composite fillers based on MCWNTs functionalized with POSS. More specifically, MWCNTs were grafted with aminopropyl isooctyl-POSS, creating novel hybrids named MWCNT-g-POSS (g for grafted), as filler (Figure 5.9) for poly(L-lactide) (PLLA). The hybrid composites were studied for the optical transmittance, electrical, and electromagnetic interference shielding properties in comparison with PLLA/MWCNT composites.\textsuperscript{[29]} The authors showed that for the hybrid PLLA/MWCNT-g-POSS composites the electrical threshold was 0.8 wt\%, which was lower than that for composites without POSS (1.4 wt\%). The PLLA/MWCNT-g-POSS composite also exhibited a better nanotube dispersion and less alignment of the nanotubes in the polymer, giving rise to better mechanical properties and to higher electrical conductivity and electromagnetic interference shielding.\textsuperscript{[29]}
New hybrid reinforcements of carbon fiber with POSS-functionalized MWCNTs were fabricated by Feng Zhao and co-workers\cite{47} in 2011. Octaglycidyldimethylsilyl POSS and MWCNTs were uniformly grafted on the carbon fiber surface to enhance the interfacial properties between carbon fibers and epoxy cast (Figure 5.10). Mechanical property test results demonstrated the improvement of the interlaminar shear strength and impact toughness.\cite{47}

In 2012, Shahid Majeed et al.\cite{48} created a hybrid system of pyrene and POSS which, when grafted onto MWCNTs, improves the dispersion of MWCNTs in organic solvents such as tetrahydrofuran, toluene, and n-hexane. The functionalized MWCNTs with pyrene-POSS (Figure 5.11) were used to fabricate polydimethylsiloxane (PDMS) nanocomposite membranes by solvent evaporation, reducing the likelihood of electrostatic discharges in gas separation applications.\cite{48}
Aaron Tan et al.\textsuperscript{[49]} in the same year, functionalized MWCNTs with a novel nanocomposite polymer of POSS and poly carbonate-urea (POSS-PCU) for biological and medical applications. A major concern for the use of carbon nanotubes in biological systems was their insolubility and their inherent toxicity. The amphiphilic nature of POSS-PCU increased the dispersibility of carbon nanotubes in biological systems as well as their biocompatibility. More importantly, when exposed to near-infrared radiation the nanocomposite increased the temperature and this effect was demonstrated to be exploitable in a biomedical setting to destroy cancer cells via photothermal ablation (Figure 5.12).\textsuperscript{[49]} Apart from the biomedical purposes, these nanocomposites seem to have great potential for several other nanotechnological applications including nanoelectronics.

Yong Tang and coworkers\textsuperscript{[50]} grafted POSS onto CNT’s as to achieve \textit{improved flame retardant} and super-hydrophobic properties in the resulting hybrid. Actually, this was a follow-up on their previous study where POSS and Carbon Nanofiber (CNF) were deposited to form a coating sheet on polymer composites in order to improve the
latter’s performance as a fire retardant; that combination turned out not to be efficient enough because of the aggregation and low thermal stability of POSS particles.\textsuperscript{[50]} To improve this MWCNTs were used and POSS covalently attached on them, then the resulting hybrid material was processed into buckypaper, which improved the thermal stability of POSS particles.\textsuperscript{[50]} The results reported so far are very promising and in this area there will be a growing interest in the near future toward efficient industrial use of these hybrid nanostructures.

Like \textit{C}_{60} discussed above, also carbon nanotube suspensions exhibit optical limiting behaviour, which strongly depends highly on the concentration of MWCNTs. In this case functionalization with POSS can improve the solubility and hence the optical power limiting as shown by Bin Zhang \textit{et al}.\textsuperscript{[30]} These authors demonstrated that a hybrid MWCNT-POSS-NH\textsubscript{2} performs as active element in an optical limiter for nanosecond laser pulses at 532 nm. MWCNTs were treated with acids (HCl, H\textsubscript{2}SO\textsubscript{4}, HNO\textsubscript{3}) in order to functionalize them with -COOH groups and then washed with excessive SOCl\textsubscript{2} for the -COCl groups to appear. Optical observation of the hybrid product in THF indicated that MWCNT-POSS with a POSS concentration 44 wt\% gave rise to a black dispersion which was stable for at least one month.\textsuperscript{[30]} Dispersions of the hybrid material show a pronounced nonlinear optical response - strong scattering at high intensities, followed by a decrease in transmission. Since POSS is a non-optically active material, it acts as a solubility promoter for the carbon nanotubes, responsible for the nonlinear optical response.

![Figure 5.12. Illustration of photothermal ablation when MWCNTs functionalized with POSS-PCU are exposed to near infrared. (Reproduced with permission from Ref.\textsuperscript{[49]})](image-url)
The POSS functionalization of MWCNTs was also investigated by Guang-Xin Chen and Hiroshi Shimizu,[51] who first treated MWCNTs with acids in order to remove impurities and shorten them while grafting at the same time hydroxyl and carboxyl groups. They then reacted these nanotubes with excess of SOCl₂ to produce MWCNT-COCI, which they mixed with aminopropylisooctyl-POSS to obtain the MWCNT-g-POSS hybrid material. When this MWNT-g-POSS was dispersed in PLLA by solvent casting (chloroform) or simply by melt compounding, a homogeneous dispersion of MWNTs throughout the composite was obtained and the mechanical properties of the composite improved with respect to pure PLLA.[51]

An elegant new strategy to graft POSS onto MWCNTs by click-chemistry was developed by Santosh Kumar Yadav et al.[52] These authors first prepared azide moiety-functionalized POSS by a simple reaction with sodium azide in the presence of ammonium chloride and alkyne-functionalized MWCNTs via a solvent-free diazotization reaction and a coupling reaction between MWCNTs and p-aminophenyl propargyl ether. Then they linked the two via Cu(I)-catalyzed azide-alkyne cycloaddition with a product yield of 75-80%.

Also POSS derivatives can be grafted on carbon nanotubes: Abdollah Omrani et al.[53] functionalized MWCNT and octa(phenol) octasilsesquioxane (OP-POSS) to fabricate a hybrid nanocomposite, by linking hydroxyl groups of OP-POSS and carboxyl acid groups of functionalized MWCNT–COOH. The hybrid MWCNTS/OP-POSS nanocomposite showed improved solubility and thermal stability compared to OP-POSS.

Celina Maria Damian and colleagues investigated the functionalization of MWCNTs with aminoethyl aminopropyl and POSS (POSS-NH₂) as reinforcing agent in epoxy nanocomposites.[54] The functionalization of MWNTs consisted in a three step reaction of oxidation, amidation and acylation with thionyl chloride (Figure 5.13). When the product was dispersed in a diglycidyl ether bisphenol (DGEBA) epoxy matrix, SEM studies showed that the POSS-functionalized MWNTs acted as fracture retardant within this nanocomposite material.[54]
A pilot procedure for coating MWCNTs with POSS was reported by Wenjing Zhang et al.\textsuperscript{[35]} in 2014. This procedure combined the Diels–Alder cycloaddition with atom transfer radical polymerization. MWCNTs were functionalized with furfuryl-2-bromoisobutyrate (FBB) and used to induce the polymerization of octa-acrylate POSS on the MWCNT surface as described in Figure 5.14. Finally, the POSS-coated MWCNTs was dispersed in a polyvinylidene fluoride (PVDF) matrix to obtain a conductive composite with high dielectric constant and low dielectric loss.\textsuperscript{[35]}

\textbf{Figure 5.13.} Functionalization of the MCWNT with POSS-NH\textsubscript{2}. (Reproduced with permission from Ref.\textsuperscript{[54]})

\textbf{Figure 5.14.} Functionalization of MCWNT with FBB and coating with octa-acrylate POSS. (Reproduced with permission from Ref.\textsuperscript{[35]})
An alternative method for coating MWCNTs with Methacrylate-POSS by \textit{in situ} free-radical polymerization was developed by Da Sun \textit{et al.}\cite{55} in the same year. The thickness of the POSS layer in the core–shell structure could be varied between 5 nm and 40 nm. The POSS-MWCNT hybrids showed excellent dispersion in organic solvents and also good electrical performance (from 0.75 Ω cm to 2505 Ω cm, depending on the thickness of the coating layer).\cite{55} This synthetic method may become important for exploring and creating a rich variety of hybrid nanostructures for device applications.

To obtain new cobalt based materials, in 2013 Zhijun Ruan and co-workers,\cite{56} used for the first time the solid-state pyrolysis (SSP) of POSS group-containing organometallic precursors to generate carbon nanotubes (MWCNTs) based nanocomposites for magnetic applications. With the presence of POSS and the control of $[\text{Co}_2(\text{CO})_6]$ moieties the size and the shape of nanocomposites could be regulated.\cite{56} However, many aspects (including a screening of various other metals) still have to be studied before the SSP method can be widely applied to produce CNT magnetic hybrid nanostructures.

POSS can also be used to synthesize MWCNT/SiO$_2$ hybrids. An interesting approach for the development of MWCNT/SiO$_2$ hybrids was proposed by Xu’s group\cite{57} by using a CVD method. Carbon nanotubes were grown from ethanol with the help of PSS-(2-(trans-3,4-cyclohexanediol)ethyl)-heptaisobutyl-substituted POSS acting as a metal-free catalyst. The two reagents were mixed, nebulized and brought inside the CVD reactor using hydrogen as carrier gas. Since POSS looses its ligands under CVD conditions, the produced CNTs were decorated with SiO$_2$ nanoparticles. Several parameters of the reaction such as growth temperature, concentration of POSS and amount of water in ethanol were examined with respect to their influence on the morphology of the produced MWCNTs and the SiO$_2$ nanoparticles attached to them.\cite{57}
5.4. POSS immobilization on graphene and graphene oxide and resulting hybrids
The functionalization of graphene with POSS was first investigated by Anandhanatarajan Gomathi, et al.\cite{22} in 2010. Graphene, prepared by thermal exfoliation of graphitic oxide, was acid-treated to generate surface carboxyl and hydroxyl groups providing in this way the necessary environment for covalent binding of the POSS molecules. The graphene-POSS hybrid material was easily dispersed in polar solvents allowing for the preparation of polymer composites with polyvinyl alcohol and nylon-6,6. This method can be used for the deposition of any POSS derivative on a oxidized graphitic structure as long as the functional groups of the POSS derivatives are appropriate (mainly primary or secondary amines, or thiol groups) for covalent binding with the oxygen-containing groups decorating the graphene layers; it therefore has great potential for the functionalization of graphene-based materials with various POSS.

Just one year later, Xiaofang Shen and coworkers\cite{58} described the preparation of an electrochemical sensor based on graphene oxide nanoribbons (GON) where, in order to overcome aggregation between graphene layers, they inserted octa(3-aminopropyl)octasilsequioxane octahydrochloride (OA-POSS) nanocages between the graphene layers. GON/OA-POSS films were used to modify an electrode for pre-concentrating and sensing of 1-hydroxypyrene (1-OHP), a metabolite of polycyclic aromatic hydrocarbons widely used as biomarker for the evaluation of human exposure to these molecules.\cite{58}

The functionalization of graphene oxide (GO) with amine-functionalized POSS has been adopted by several groups.\cite{59, 60, 61, 62} In that approach, POSS was linked via amide formation with the epoxy (via a ring opening reaction) and carboxyl groups of the graphene oxide sheets to change the chemical properties of GO, to separate the GO layers in a physical way or to enhance the dispersibility of the sheets in organic solvents, such as hexane, THF, chloroform, acetone and toluene. More specifically, POSS-graphene appears to be soluble in THF at a relatively high concentration of 30 mg/mL, without formation of precipitates.\cite{59} The resulting hybrid could be prepared
as a thin film (by solution casting),\textsuperscript{[59]} which showed superhydrophobic properties with a water/air contact angle of \( \sim 157^\circ \). POSS-graphene powder was shown to form liquid freestanding marbles on hydrophobic or hydrophilic surfaces as a small reactor for different applications. When POSS-graphene hybrids were incorporated into PMMA at low percentage (1 wt%), the glass transition temperature \( T_g \) of the composite material increased by more than 10 \(^\circ\)C, which identifies these hybrids as ideal reinforcing agents for polymer matrices.

Luca Valentini \textit{et al.}\textsuperscript{[63]} went one step further in the engineering of nanostructures by first immobilizing GO sheets on a (3-aminopropyl)triethoxysilane (APTES) layer on a Si substrate and then grafting POSS-NH\textsubscript{2} onto them. APTES layer was successfully self-assembled on the oxygen plasma-treated Si substrate as confirmed by IR spectroscopy. The reaction between the -NH\textsubscript{2} groups of POSS and the -COOH groups of GO, led to a change of the GO surface properties from hydrophilic to hydrophobic. Tribological measurements on the POSS-GO-APTES tri-layer revealed a reduced friction coefficient, making it suitable for application as lubricant coating.

In another report Luca Valentini \textit{et al.} pursued the goal to graft POSS to the GO film when POSS is offered in the form of vapour.\textsuperscript{[64]} The authors showed that amino-functionalized POSS can be brought in to the gas phase via thermal evaporation and easily interacts with GO’s functional groups. A comparison of the morphology of the hybrids obtained by the evaporation of POSS-NH\textsubscript{2} and neat POSS onto GO evidenced clear differences in wrinkling and bending of the graphene sheets. Light ON/OFF tests on GO sheets treated with amino-functionalized POSS showed a variation of the conductivity under illumination. In a follow-up paper\textsuperscript{[65]} the same group proved that when POSS-NH\textsubscript{2} was coupled with graphene oxide sheets in tetrahydrofuran (THF), a solvent capable of completely solubilizing the silsesquioxane molecules and dispersing GO, the photoconductivity response of the hybrid to visible-light stimulus was 50 times stronger.

In the same year Xin Wang and coworkers\textsuperscript{[66]} developed a synthetic protocol for the functionalization and reduction of GO with octa-aminophenyl polyhedral oligomeric
silsesquioxane (OapPOSS) by simple refluxing in THF, as described in Figure 5.15. When this hybrid was used incorporated in an epoxy resin, the thermal oxidative resistance and thermal stability improved as compared to the neat resin. The authors assigned this improvement to the good linkage between the OapPOSS-GO hybrid and the epoxy matrix and to the fact that graphene retards the permeation of heat and the escape of volatile degradation products. These experiments identified the novel hybrid material OapPOSS-rGO as an efficient graphene-based flame retardant additive for epoxy resin materials.\(^{[66]}\) The results so far reported in this field are very promising, however, the properties of these new materials have been disclosed only partially.

The grafting of OapPOSS to GO was further developed by Wenqi Yu et al.\(^{[67]}\) who employed a simple *in situ* reduction method for the surface functionalization of GO instead of exploiting the interaction between amino groups on POSS and carboxyl groups on the GO sheets as presented so far\(^{[59, 64, 68]}\) (Figure 5.16).

![Figure 5.15. Schematic representation of graphene oxide reduction and functionalization with octa-aminophenyl polyhedral oligomeric silsesquioxane. (Reproduced with permission from Ref.\(^{[66]}\))](image-url)
In the same year Kumari Pallathadka Pramoda and coworkers\textsuperscript{[34]} prepared a polylactide (PLA)-based nanocomposite combining functionalized-GO nanosheets and oligomeric silsesquioxane (POSS) nanocages as nanofillers to enhance thermal and mechanical properties of PLA. The authors compared the structure-property relationship of PLA mixed with (1) functionalized GO, (2) functionalized POSS, (3) a physical mixture of functionalized GO and functionalized POSS, and (4) the GO-g-POSS (with eight hydroxyl groups) and demonstrated that the new GO-g-POSS hybrid nanocomposite exhibited a better/enhanced thermal and mechanical behaviour than the dispersed other nanofillers in PLA matrixes.\textsuperscript{[34]}

Titash Mondal, Anil K. Bhowmick and Ramanan Krishnamoorti\textsuperscript{[69]} went one step further by recently reporting a method towards covalent modification of graphene in order to produce novel inorganic-organic hybrid materials. Their purpose was to achieve the grafting of POSS to graphene in a scalable manner with a limited use of chemicals and in milder reaction conditions that the ones used when linking amine-terminated POSS to carboxylated graphene as described above. For this they decided
to exploit the intrinsic topological defects of graphene, namely heptagons and pentagons situated close to the edges of the graphene layers; these defects show a higher reactivity because of the higher strain in these rings and their non-aromatic nature. Expanded graphite was brought in contact with n-butyl-lithium (n-BuLi), which attracts protons from the defects (nucleophilic attack) and produced anionic centers. The latter were reacted with epoxycyclohexylethyl-POSS with cyclopentane as substituent. Furthermore, a molar excess of n-BuLi also leads to a nucleophilic reaction between graphene sheets and butyl groups, resulting in bi-functionalized graphene where the covalently grafted butyl groups prevent the graphene layers from re-agglomeration. This functionalization protocol therefore has the added benefit of inducing exfoliation.

5.5. Conclusions
In conclusion, in this work we reviewed all the recent achievements concerning the grafting of polyhedral oligomeric silsesquioxanes (POSS) to carbon nanostructures including graphene, graphene oxide, nanotubes and fullerenes. The aim of this effort was to give a clear overview of all the synthetic procedures applied until now as well as to illustrate the improvements of chemical and physical properties that can be achieved by the combination of POSS with different carbon nanostructures. Thus, we reported improved solubility of carbon nanostructures through functionalization with POSS, as well as the utilization of the synthesized hybrid organic/inorganic nanostructures as nanofillers in polymers to attain enhanced thermal and mechanical behaviour, modify the electronic properties or, to improve flame retardancy. New frontiers are open taking advantage of new properties of these hybrid nanostructures that still under investigation.
Carbon Nanostructures containing Polyhedral Oligomeric Silsesquioxanes (POSS))

References


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