

Metal/Metal Oxides/Silsesquioxanes as Fillers for Functional Polymer Composites

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Abstract: Integration of properties of inorganic filler and polymer matrix provides fascinating and economic approach for tailoring the desired high performance materials. Due to unique capability of metal/metal oxides/silsesquioxanes as nanofillers, they have attracted much attention to reinforce polymer matrices. We discuss here the influence of these nanofillers dispersion, interactions with polymer matrices, and consequent properties modification on technological applications. Homogeneously dispersed fillers led to improve physiochemical and biological properties of the materials, such as mechanical strength and biocompatibility. Additionally, they act as scaffolds for tissue engineering, maintaining their characteristics even under adverse conditions. Extending their utility in various biomedical applications, researchers are examining their potential in stimuli-responsive systems, drug delivery, gene vectors, and biological imaging.

1. Introduction

In the past decades, nanomaterial with one dimension less than 100 nm attracted much attention due to novel and promising applications in different area of interest. This is because combination of polymer and nanofillers afford a number of possibilities for the design of new materials with technological importance. Macroscopic performance of the new materials from synergy of polymer and nanofillers strongly depend on the later

dispersion in the former. Different approaches are used to overcome nanofillers aggregation either by functionalization or by selection of a decent processing method (e.g. ultrasonication, mechanical blending, rapid precipitation, to name a few)^[1]. To make nanofillers capable for different applications, control on the geometrical distribution is necessary, which require compatibility with polymer matrix, external fields, templates or polymer modification. The dispersion of these nanofillers takes place both in water (hydrosols)



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or organic solvents (organosols), depending on the conditions and capping agent in the surrounding [2]. To avoid irreversible growth and agglomeration of the metal oxide nanoparticles we should protect its reactive surface-by-surface ligands. Thus, the fabrication of nanofillers with proper dispersion and controlled structure is indispensable and dependent on the selection of the ligands. A variety of motifs can be used for this purpose which includes surfactants, oligomers, polymers etc., and different combinations and motifs can be achieved through non-covalent interactions (e.g. electrostatic forces, acid-base proton transfer, hydrogen bonding and other van der Waal forces) [3]. Metal oxide particles display interesting application potential which stem from their exciting size dependent optoelectronic and physicochemical properties [4,5]. Recently intensive technological and scientific efforts are being carried out to uniformly disperse metal oxide nanoparticles into organic polymer matrix and thereby fabricating organic-inorganic (O-I) hybrid materials [6,7]. For this purpose different strategies are used, but one of the successful strategy is the colloidal dispersion and encapsulation of nanoparticles with silica shells or polyhedral oligomeric silsesquioxane (POSS) cubes [8]. POSS, with hydrophobic moieties that can be linked to hydrophilic surfaces either of metal/metal oxides or polymers, for the development of ordered structures like self-assembly in bulk, solution, and thin films such as core shell micelles, vesicle, cylinders, microphase separated nanostructures [9-15]. These moieties have the additional advantages of controlling distance between the core particles in the assemblies, biocompatible, permeability, ease of functionalization, bioconjugation, oxidative stability, flame retardancy, and non-covalent modifiers [8,15-21]. Coalescence of properties of inorganic filler and polymer matrix provides fascinating and economic approach for tailoring the desired high performance materials [22,23]. A variety of polymer-metal oxide nanocomposites that offer attractive thermal, mechanical, electrical, and optical properties has been extensively studied [24-29]. Polyhedral oligomeric silsesquioxane (POSS) are three-dimensional, molecular level organic-inorganic architectures consisting of alternate Si-O bonds forming the cage structures with R forming the periphery. The peripheral moieties can be exploited for mono and multi-functional POSS preparation. Based on the

compatibility, structure and reactivity of the peripheral moieties, POSS can be incorporated homogeneously into polymer matrices.

Properties of POSS related composite materials are dependent on well dispersed and uniform incorporation of POSS particles into polymer matrices of interest. Usually two approaches are used to afford nanocomposites with well-dispersed POSS particles i.e. (i) chemical cross-linking and (ii) physical blending [15,30-32]. Very little is known about metal oxide/POSS nanocomposites. Some researchers have studied metal/POSS nanocomposites for antimicrobial and catalytic applications [3,8,33-37]. Different technological properties of the developed nanocomposites are dependent on the coating, of the nanoparticles with suitable coating agent. Covalent attachments of nanoparticles and polymer backbones are found to enhance the thermal and mechanical properties [1,18,38-41]. Some researchers have studied the optical, electronic, and magnetic properties to be dependent on the inter-particles spacing and ordered assemblies [42,43]. To cut short due to stable, ease of isolation, molecular and variously functionalization chemistry of POSS, its composites with metal are preferred over metal/polymer composites [44-46]. Keeping these in view different properties of metal/metal oxides/silsesquioxane based polymer composites are reviewed here.

2. Metal/Metal Oxide/Silsesquioxane Nanoparticles Chemistry

The two key properties of nanoparticles i.e. large number of unsaturated surface atoms and quantum size effects compared to bulk materials make its chemistry interesting for different technological applications [47]. Due to their high surface energy, aggregation is the major challenge in achieving these desired applications. Different researchers have tried to overcome these challenges as reviewed follows:

2.1 Stable Dispersion of Nanoparticles in Aqueous and Non-aqueous Media

Scientific implementation, utilization of nanoparticles into different commercial products ranging from catalysts, food safety, clinical diagnosis, environmental monitoring, UV-blocking coating, sunscreens, composite materials require robust and cost-effective homogenous dispersion, compatibility with different organic polymer matrices, and surface functionalization

in aqueous and non-aqueous media^[48,49]. To make these particles effective as nanofillers, they are stabilized in the carrier liquid and prevented from air oxidation, agglomeration by their surface modification with different additives^[50-54]. NP-mediated applications requires surface functionalization that not only affects their solubility, dispersion, stability, and compatibility but also provide the cationic, anionic and neutral functional groups or charges that are exploited for intermolecular, van der Waals, ligand exchange and other interactions. Nanoparticles are mostly used in nanofluids e.g. iron nanoparticles used as ferrofluids due to their greater saturation magnetization. Iron nanoparticles can be stabilized in the carrier liquid to avoid agglomeration and air oxidation by coating with a surfactant or a polymer^[55-57]. D. Maity, D.C. Agrawal have studied iron oxide nanoparticles in aqueous as well as non-aqueous media^[58]. Qiao, Ruirui, *et al.* grafted iron oxide nanoparticles with bromomaleimide and PEG brush polymers in non-aqueous medium for biomedical applications^[59]. Hola, Katerina, *et al.* have highlighted different covalent and non-covalent strategies for the functionalization and stabilization of iron oxide nanoparticles^[60]. They have discussed three aspects of functionalization by incorporating common functional groups i.e. chemical modification of amine groups, bioactive substances, and carboxyl groups for enzyme immobilization on iron oxide nanoparticles surface. Lee, S.H., Nishi, H., & Tatsuma, T. have tuned the plasmon resonance of molybdenum oxide nanoparticles in non-aqueous media for visible range electronic harvesting materials^[61]. Patil, R.M., *et al.* have functionalized iron oxide nanoparticles with oleic acid to reduce their agglomeration followed by treatment with betaine-HCl to increase their hydrophilicity and stability for hyperthermia application^[62]. In another study collagen fibers are cross-linked with oleic acid functionalized iron oxide nanoparticles and were employed for oil removal application in non-aqueous media^[63]. Kharisov, Boris I., *et al.* have reviewed the recent trends in solubilization and stabilization of iron nanoparticles in aqueous and non-aqueous media^[64]. Some researchers have adopted dodecylamine protected silver nanoparticles using tin (II) acetate as reducing agent and SnO₂ nanoparticles for electronic ink formulation in non-aqueous medium^[65,66]. Kharissova, Oxana V., Boris I. Kharisov, and

Edgar Gerardo de Casas Ortiz. have reviewed dispersion of carbon nanotubes in aqueous and non-aqueous media with great emphasizes on physical techniques and using surface agents^[67]. Kaushik, Madhu, and Audrey Moores. reviewed nano-cellulose as support for functional metal nanoparticles for catalytic applications^[68]. Wang, Shunzhi, *et al.* have reported the progress in metal organic frameworks as functional nanomaterials for sensing, membranes applications based on porosity, and diverse chemical functionalities^[69]. Park, Jong-Won, and Jennifer S. Shumaker-Parry. have studied citrate and thiol co-adsorbed layer and their chemistry for functional gold nanoparticles^[70]. Burrows, Nathan D., *et al.* have highlighted the chemistry of nanoparticles anisotropy, regiospecific functionalization and also discussed surface chemistry of gold nanorods with an outlook for surface chemistry toolbox development of the synthetic nanoparticles^[71,72]. Rossi, Liane M., *et al.* have reviewed the role of surface functionalization/capping of metal nanoparticles in catalysis with the perspective of surface tuning for the activity and selectivity^[73]. Some researchers have highlighted polydopamine surface chemistry and primary, secondary functionalization role in biomedical applications^[74,75]. Gao, Chuanbo, Fenglei Lyu, and Yadong Yin. have discussed the encapsulation of metal nanoparticles in nanopores or nanoshells and their subsequent stabilization. They have also discussed encapsulation in nanoshells role catalysis in context of inorganic oxides, porous materials, organic frameworks, dendrimers, and organic cages^[76]. Soriano, Gustavo Bonomi, *et al.* have used block copolymer to stabilize silver nanoparticles and studied their interactions with cellular membrane model^[77]. M. Sahoo and S. Sabbaghi, have reported the stability and dispersion of CuO Nanoparticles in ethylene glycol-water mixture using pH, temperature and weight percent effects as the factors. They have studied the optimum properties when the nanoparticles are more dispersed and stabilized^[78]. Shadpour Mallakpour and Atefeh Jarahiyan have reported the dispersion of CuO nanoparticles surface functionalized with ascorbic acid and citric acid. They have studied improved thermal properties for poly (vinyl alcohol) /CuO nanocomposites with well dispersed nanoparticles^[79]. C. Karuppiah *et al.* have reported ZnO nanorods CuO nanospheres

(ZnO-CuO) heterostructures. They have confirmed their formation through SEM, energy dispersive X-ray spectroscopy, X-ray diffraction and cyclic voltammetry^[80]. Some researchers have stabilized and functionalized TiO₂, ZnO, CeO₂ Nanoparticles for transparent catalytic, UV-protecting coatings, sunscreens, thermomechanical properties improvement etc. with different additives^[81-83]. Zhou, Li, *et al.* have reported the synthesis of organic functional group decorated molybdenum disulphide (MoS₂) nanosheets by exploiting chemical conjugations of thiol ligands with MoS₂ bulk crystals^[84].

Based on the siloxane core both silsesquioxane and silica have some similar physical properties, but the peripheral functional groups in silsesquioxane and one-half difference of oxygen in silsesquioxane structure allow for its different charging behaviour, ease of functionalization, colloidal stability, pH and temperature response. These fascinating properties of silsesquioxanes helpful in surface modification are reviewed here. Wang, Dan, *et al.* have chemically linked carbon dot carboxylic acid groups with the amine functional POSS to achieve composite filler with enhanced photoluminescence and thermal stability for sensing applications^[85]. Dong, Fuping, Liangyu Lu, and Chang-Sik Ha. have highlighted the developments in POSS containing hybrid materials including their structures and chemical reactions in context of catalysis, polymer composites, adsorption, sensing and biomedical applications^[86]. Sun, Di, Wei Wang, and Dan Yu. have reported alkyl functionalized POSS achieved via click-chemistry (photochemical thiol reaction), employed for cotton fabric super-hydrophobic modifications, fluorine free, durable and most effective with four dodecyl and four triethoxysilyl groups^[87]. Przybylak, Marcin, Hieronim Maciejewski, and Agnieszka Dutkiewicz. have reported bifunctional fluorinated POSS prepared via sol-gel and dip coating methods, applied for cotton fabric hydrophobic modifications, and durability^[88]. Wang, Wen-Jing, *et al.* have reported octa-aminopropyl POSS (OA-POSS) functionalized carbon dots for cell imaging. The amino groups on OA-POSS form amide bond with carboxylic groups on carbon dots to afford water soluble inorganic-organic hybrid carbon dots^[16]. Ge, Qian, and Hongzhi Liu. have reported amine-functionalized POSS as adsorbent for heavy metals removal via

nucleophilic substitution of octa(3-chloropropyl) silsesquioxane with triaminoethylamine silsesquioxane. They have studied improved thermal stability and hydrophilicity for the as synthesized silsesquioxanes with an ease of regeneration and potential for water purification^[89]. Zhang, R.L., *et al.* have reported the preparation of hierarchical carbon fiber achieved by the co-grafting of POSS and CNTs, and have investigated increased interfacial adhesion, improved mechanical performance for the as prepared co-grafted fiber-resin composite^[90]. Yang, Xiaoru, and Hongzhi Liu have reported porous ferrocene functionalized POSS and porous pyrene-functionalized POSS via Friedel-Crafts reaction of octavinyl silsesquioxane with ferrocene and pyrene respectively. They have investigated regeneration and water purification performances of the as prepared functionalized POSS^[91,92]. Chuo, Tsai-Wei, and Ying-Ling Liu. have utilized methacrylated-POSS and furfurylamine to achieve methacrylated furan Diels-Alder adducts in the composite structure exhibiting thermally stable self-healing ability and thermal reversibility^[93]. Akbari, A., Naderahmadian, A., and Eftekhari-Sis, B. have reported preparation of catalysts using OA-POSS and ionic liquid followed by copper and silver nanoparticles immobilization for click reaction in aqueous medium and nitro-phenol reduction with easy recovery and recyclability^[94]. Song, Shasha, *et al.* have investigated dispersion state, thermal conductivity and thermal stability of PVDF composite membranes incorporated with POSS functionalized CNTs^[95]. Shi, Mengni, *et al.* employed gamma-radiation induce grafting under mild conditions to achieve functionalization of graphene oxide with octavinyl POSS. They have reported improved thermal stability and hydrophilicity with green chemistry approach^[96]. Selvaraj and Alagar have stabilized and functionalized silver nanoparticles by amino-functionalized POSS, with diverse shaped nanoparticles for glucose oxidation by the chemical reduction of AgNO₃ using glycerol as reducing agent^[8]. Dell'Erba *et al.* have reported silver nanoparticles coated with OH-functionalized organic groups as nanofiller for different applications^[1]. J. Zheng *et al.* have reported Ag Nanoparticles (Ag NPs) through common chemical reduction by interface regulation between AgNO₃ and graphene oxide (GO) using hydrophobic POSS^[34]. Zhang, Jingyan,

et al. have reported unique chain architecture of star shape polymers with outer cross-linking using octa(3-azidopropyl) POSS by click reaction^[97].

3. Effect of Fillers Dispersion: Functional Polymer Composites

Homogeneous dispersion of nanoparticles (3D

fillers, nanotubes and nanofibers, plate like fillers, silsesquioxanes, and metal/metal oxides) is the key step in nanotechnology industrialization and functional materials development. Different strategies adopted for homogeneous dispersion of fillers have been discussed and the schematic is shown in **figure 1**.

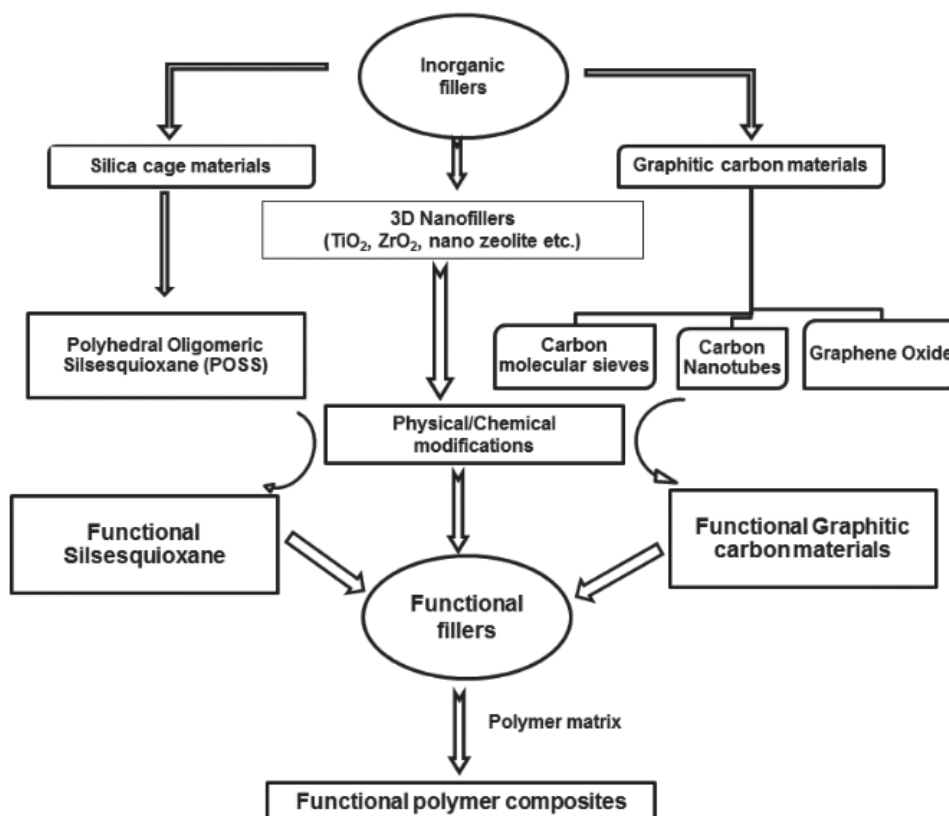


Figure 1. Fillers for Functional Polymer Composites

Ag and Au nanoparticles can be dispersed by the reduction of organometallic compounds in polymer matrix for optical property modification^[8,56,98-100]. They have reported the absorption spectra of Ag and Au film at different treatment duration^[32]. Klaus Mullen *et al.* have studied different dispersion dependent properties of the ZnO/PMMA transparent UV-protective nanocomposites. They have reported dispersion and re-dispersion in the toluene hydrophobic medium^[101]. Zong, Peisong, *et al.* have achieved homogeneous dispersion and interfacial interactions by preparing aminopropylisobutyl POSS (Ap-POSS) covalently grafted with graphene. They have investigated that the as prepared graphene-Ap-POSS nonhybrids have interfacial interactions with epoxy polymer matrix through non-covalent and covalent bonds that promote

dispersibility, compatibility in the composites as demonstrated by the improved thermal conductivity and decreased thermal interfacial resistance^[102]. Liu, Konghua, *et al.* have reported homogeneously dispersed silver nanoparticles decorated graphene by utilizing poly(amidoamine) as stabilizing and reducing agent for the preparation of conducting polymer composites^[103]. Ben-Sasson, Moshe, *et al.* have reported surface functionalization of polyimide reverse osmosis (RO) membrane with copper nanoparticles (Cu NPs) by employing the electrostatic interactions between polyethyleneimine capped positively charged Cu NPs and negatively charged polyimide RO membrane^[104]. Kanahara, M., Shimomura, M., and Yabu, H. have fabricated gold nanoparticles (Au NPs) polymer composite particles by employing the electrostatic

interactions between citrate stabilized Au NPs and amino-terminated polymer particles^[105]. They have investigated the adsorption and diffusion of the Au NPs on the polymer particles based on glass transition temperature and molecular weights of the polymer particles. Huang, Qiang, *et al.* have reported the synthesis of molybdenum disulphide (MoS₂) polymer composite by the self-polymerization of levodopa in weak alkaline medium on the surface of MoS₂ for adsorption of methylene blue from aqueous solution^[106].

The dispersion of fillers in functional polymer composites is a crucial factor that affects the mechanical, thermal, and electrical properties of the composite material. The homogeneous dispersion of nanoparticles such as 3D fillers, nanotubes, and nanofibers, platelike fillers, silsesquioxanes, and metal/metal oxides is essential to achieve the desired properties. Several studies have been conducted to explore practical examples demonstrating the homogeneous dispersion of these fillers. For instance, a study by Wang *et al.* demonstrated the homogeneous dispersion of carbon nanotubes in a polymer matrix using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).^[107] Another study by Liu *et al.* investigated the dispersion of graphene oxide in a polymer matrix using SEM and TEM.^[108] These studies provide valuable insights into the methods employed to achieve homogeneous filler dispersion in polymer composites.

The future is now open to the synergistic integration of nanocomposites with 3D printing, which is soon projected to eclipse its competition with conventional production methods. Preparing a nanocomposite resin for polymerization-based 3D printing, which involves the agglomeration of nanoparticles, has always been a challenge. The nanoparticles cluster in the composite matrix as a result of the high surface-area-to-volume ratio, which influences the final characteristics. In an effort to examine the mechanical and thermal properties of 3D-printed nanocomposites, Mussadiq *et al.* dispersed graphene oxide (GO) in it. For this purpose, high and poor GO dispersions were analyzed along with their influence on various attributes using a well-dispersed sonication dispersion technique.^[109] Microscopy was used to examine the fracture surfaces of the control and poorly and highly scattered printed

composite tensile specimens. A typical microstructure of brittle materials, as reported in the literature^[110,111], is shown in **Figure 2a**. The reference samples were standard acrylates that failed in a brittle manner. A river-like flow that intensifies as the cracks spread is what starts the series of cracks in the microstructure. The literature^[111-113] provides evidence of incomplete polymerization resulting from experimental error, which accounts for part of the dark voids seen in the sample. These voids were probably created during the 3D printing process since it's possible that either the specimens failed during testing, or the resins weren't fully cured by the 3D printer's laser source. However, this building structure was taken into consideration in the study and had no bearing on the comparison and evaluation of the results that were presented in this study because all the sections were tested in the same settings and with the same built structure. The fracture surface of a printed nanocomposite that is poorly scattered is shown in **Figure 2c**. GO's wrinkly morphology is visible on certain smooth, hazy surfaces.

Furthermore, gaps between the GO and the polymer matrix are also visible on the fracture surface, suggesting that the nanofiller–matrix interface is weak, which causes debonding and a multitude of river-like formations. The fractures occur after a failure that resembles brittleness but leans toward ductility.^[114] There are additional gaps or black surfaces, which are also caused by the nanofiller aggregating inside the polymer matrix. This leads to inadequate mechanical characteristics and insufficient polymerization. The increase in GO loading further impacted the brittleness of printed nanocomposites in tensile testing. Consequently, the voids were the primary cause of the brittle behavior.

Consequently, the voids were the primary cause of the brittle behavior. As the tensile strength increases, these gaps allow abrupt fracture, leading to brittle fractured surfaces, as shown by.^[114] When the stress surpasses the composite interface strength, the weak nanofiller–polymer matrix interface causes the GO to be pulled as the micro-cracks spread. The rough fracture surface is proof that the exfoliation or pullout of GO encourages local plastic deformation of the polymer matrix to release the fracture energy. Comparably, as seen in **Figure 2e**, the highly scattered printed nanocomposite has a rather smooth and layered

fracture surface, indicating the cracks propagated. Here, the GO is contained inside the matrix by the

strong nanofiller polymer matrix interface.

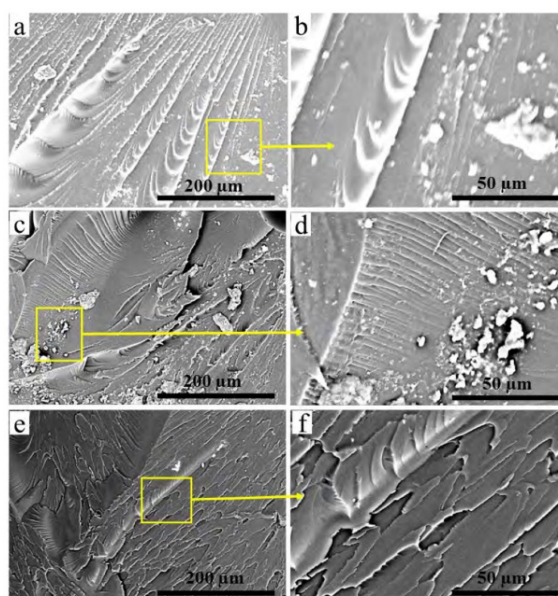


Figure 2. The fracture surface of (a,b) control specimens and (c,d) poorly dispersed and (e,f) highly dispersed nanocomposites.^[109]

4. Conclusions and future outlook

This perspective discusses the synthesis and role of functional fillers for polymer composites, with a focus on their dispersion, stability, compatibility, non-covalent, and covalent interactions. The performance of the functional polymer composites is mainly influenced by the polymer matrix's porosity, general thermomechanical stability, and nanoparticle dispersion within the nanocomposites. The stable dispersion of the nanoparticles with intrinsic characteristics intact in the functional polymer composites will be necessary for these materials to be commercialized in the future. Functional metal/metal oxide nanofillers or POSS nanocages, which have favorable biocompatibility, non-toxicity, and cyto-compatibility, could be used as desired nanocarrier candidates to encapsulate hydrophobic drugs into self-assembled cavities, resulting in improved aqueous solubility and a controlled drug release profile. Similarly, POSS-based complex systems for gene therapy have been developed by numerous research groups with the goal of increasing transfection efficiency. The successful application of POSS-based hybrid materials in biomedical imaging plays a crucial role in the diagnosis/detection of diseases and the assessment of

therapeutic effect due to the superior physicochemical properties (such as excellent biocompatibility and simple design for surface multifunctionalities). Due to their strong biocompatibility, osteo-conductivity, and osteoinductivity, silica-based nanoparticles have shown promise in clinical use and for bone tissue restoration. As compared to ordinary nanomaterials, POSS-incorporated hydrogels displayed a homogeneous system without a phase boundary, which resulted in increased structural stability when exposed to external stress. They may also serve as an inorganic cross-linker in an otherwise organic hydrogel network due to their versatility, which helped to firmly anchor them in the network and improve its properties through molecularly controlled mechanisms. Numerous investigations have demonstrated that POSS-incorporated hybrid hydrogels were cytocompatible and facilitated chondrocyte adhesion, dissemination, and proliferation.

Conflict of Interest

Declaration of conflict of interest.

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