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Periodic Mesoporous Organosilica Nanomaterials with Unconventional Structures and Properties

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Abstract: Periodic mesoporous organosilicas (PMOs) are high surface area organic-inorganic hybrid nanomaterials that have found broad applications in various fields of research such as in (bio)chemistry or material science. By choosing suitable organic groups in the framework of these materials, their surface properties such as polarity, optical/electrical characteristics and adsorption capacity can be tuned. This critical review provides an overview of the current state of the art in the developments and applications of some PMO nanomaterials in diverse fields of research. This is placed in the context of four leading areas of PMO nanomaterials, including chiral PMOs, plugged PMO nanomaterials, Janus PMOs and PMO-based nanomotors. The review briefly discusses the recent and key findings on these PMO nanomaterials as well as their potential applications for future developments.

1. General Description

Since the discovery of periodic mesoporous organosilicas (PMOs) more than two decades ago,^[1] a series of attractive applications were found for them, in particular in the fields of heterogeneous catalysis, adsorption/separation, nano(bio)medicine, as well as electronic and optical devices.^[2] The major characteristics of PMOs compared to classical mesoporous silica is the use of organo-bridged alkoxysilanes in the synthesis, which can be described as (R'O)₃Si-R-Si(OR')₃. Herein, R' are usually methyl or ethyl groups and R indicates the bridging organic moieties that are finally integrated into the framework of the hybrid pore walls. This leads to the formation of a new class of nanomaterials with unique properties that possess periodically ordered pores of 2-30 nm diameters^[3] and a nano-sized pore walls thickness. Unlike to conventional organically modified mesoporous silicas, PMOs offer an enhanced number of surface functionalities as well as an improved and adjustable surface polarity due to the uniform coverage and distribution of organic groups on the surface. Moreover, the functional groups are attached to the surface with stable covalent bonds on both sides of the R groups, which strongly reduces the leaching of the surface functionalities.^[2,3]

Probably, the most common applications of PMOs are found in heterogeneous catalysis with a focus on fine-chemical synthesis.^[2g,j] Some other interesting features of PMOs can be addressed to the preparation of bifunctional PMOs,^[4] biodegradable PMOs,^[5] yolk-shell PMOs,^[6] multiple-shelled PMOs,^[7] single-atom catalysts on PMO matrices,^[8] and POSS–PMOs (POSS = polyhedral oligomeric silsesquioxane)^[9] providing a wide range of shapes and morphologies.^[2a,10] The latter example was presented by Ozin et al.,^[9] who published the synthesis of a hvbrid POSS-PMO thin film containing octa(triethoxysilylethyl)POSS. They investigated its application as a low-k

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dielectric material for microelectronics. Alternatively, diblock and triblock PMO nanocomposites were fabricated and employed as well-designed nano-carriers for controllable photothermally induced drug delivery systems, for example for the release of anticancer drugs such as doxorubicin.^[11]

PMO nanomaterials are also used for the production of organic-inorganic nanocomposites that have extraordinary reinforcement and swelling/deswelling properties with improved biological properties.^[12] In 2016, Khashab et al. synthesized а composite comprising of а hydrophobic poly(etherimide) doped with an ethylene-pentafluorophenylene-based PMO material and studied its application for water desalination (Figure 1a,b).[13] The hydrophobic nature of the synthesized PMO facilitates the loading of antimicrobial and antioxidant agents onto the pores of material. The resulting PMO-based composite showed a 140% increase in water vapour production compared to a



Figure 1. a) Schematic representation of the poly(ether imide) PMO (PEI–PMO) nanofiber containing 10% of PMO nanoparticles and b) its corresponding TEM image. Reproduced with permission.^[13] Copyright 2017, American Chemical Society. c) Preparation of a silicon-based composite comprising an atomic-scale distribution of carbon atoms. Reproduced with permission.^[14] Copyright 2019, John Wiley and Sons.

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commercial polytetrafluoroethylene membrane in combination with additional benefit that is the reduction of bacterial colonisation by up to 70%.

A PMO nanomaterial was also introduced into battery technology to prepare a silicon-carbon nanocomposite anode. Silicon-based anodes are among the most prominent anode systems in battery design. Unfortunately, they suffer from a significant volume expansion during the lithiation process that causes large tensile hoop stress, which initiates surface cracks. This issue results in the loss of electrical contact and rapid capacity fading. The preparation of silicon-based anodes that still contain carbon atoms was postulated to be a promising approach to solve this problem. While traditional methods (e.g. grafting of organic compounds) lead to a non-uniform distribution and agglomeration of carbon atoms, Zhang et al. found that PMO-derived nanoparticles can be used as highly stable anode materials.^[14] The synthesis of this material is shown in Figure 1c. Herein, 1,4-bis(triethoxysilyl) benzene (BTEB) was selected as the silicon precursor to prepare the nanoparticles. The benzene ring has similarities to the structure of graphite and provides a high C/Si atomic ratio to the resulting PMO matrix. The materials were calcined at different temperatures under an atmosphere of argon to form the porous carbon-silicon nanocomposites. The best electrochemical performance was found in a material, which was calcinated at 800 °C. Under these conditions, the PMO nanomaterial delivered the highest discharge capacity of 501 mAhg⁻¹ after 300 cycles.

Beyond experimental advances in the synthesis and applications of PMOs, some efforts have been made, albeit to a

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lesser extent, to understand and predict some structural features of PMOs using theoretical models.^[15] In an interesting study, Lee et al. investigated the assembly structure of the surfactants in PMOs by means of solid-state NMR spectroscopy accompanied by molecular dynamics simulation.^[16] They found that in mesoporous silica (SiO₂), the long hydrocarbon chain of the surfactant adopts a stretched conformation with the heads oriented towards the pore wall. In PMOs, the head of the surfactant has a weaker interaction with the pore wall and present a gauche-rich conformations (Figure 2). Such gauche-rich conformations might be responsible for the smaller pore sizes of PMOs compared to those found for mesoporous SiO₂.

In the following, this short review summarizes recent findings on underdeveloped branches of PMO chemistry and discusses their structural differences compared to the classical PMOs. These differences are the basis of the special properties of these materials and hence provide access to novel applications. We are focussing on four fundamental topics: chiral PMOs, plugged PMO nanomaterials, Janus PMOs and PMO-based nanomotors. At the end, an outline for possible further developments is given.

2. Unconventional PMOs

2.1. Chiral PMOs

The simplest method for preparing (chiral) organosilica materials is the grafting of chiral functional groups that bear a condensable silane group onto a preformed porous silica species in a high boiling point solvent, such as toluene. This is an efficient and fast route to generate organically modified functional materials. However, following this route, the loading of the organic component on the surface is comparably low and the chiral ligands are not uniformly distributed on the surface. In contrast, more uniform incorporation can be achieved by the addition of the target silane precursor during the polycondensation process in the presence of a structure-



Figure 2. The proposed structure of surfactant with a straight aliphatic tail in mesoporous silica (SiO₂) versus the gauche-rich conformation in PMOs. Reproduced with permission.^[16] Copyright 2022, American Chemical Society.

directing agent (SDA). Employing silane precursors with more than one condensable site give the opportunity to achieve a high and uniform loading of the chiral sites in the derived PMO nanomaterial. Under these conditions, the resulting PMO usually have a high degree of porosity as well as a high surface area and pore volume.

Chiral (also known as helical) mesoporous silicas are a new class of materials that, unlike to classical mesoporous silica (e.g. MCM-41 or SBA-15) with straight channels, have twisted channels and thus can be considered as a warped version of the conventional silica-based mesoporous materials. The synthesis of this material is mimicked from natural systems with helical structures (such as DNA)^[17] by employing either chiral^[18] or achiral surfactants.^[19] The interest in chiral PMOs led to significant discoveries in the preparation of new material with versatile properties. In the 2000s, pioneering results on the synthesis of chiral PMOs with either helical or non-helical morphologies were reported.^[20]

However, applications of chiral mesoporous silica are not sufficiently extended and thus this emerging field still needs to be developed. A highly interesting feature of such helical geometries is their ability to induce selectivity in chemical reactions due to the presence of a chiral environment. In some studies, chiral PMOs were applied as catalysts for the diastereoselective Mannich reaction,^[21] enantioselective separations,^[22] and the enantioselective addition of diisopropylzinc to pyrimidine-5-carbaldehyde.^[23]

Synthesis of PMOs with helical architectures and variable pore morphologies ranging from longitudinal to helical and then to concentric circular structures by employing achiral cationic surfactants as the structural directing agent was reported recently.^[24] However, the first report for the preparation of helical PMOs with achiral surfactants led to achieve a 1:1 ratio of left-/right-handed helical particles.^[25] In contrast, by employing different isomers of amino acid-based surfactants, Tatsumi et al. could prepare left-/right-handed PMOs with 100% selectivity.^[26] Typical SEM and TEM images of the 100% right-handed chiral mesoporous organosilica are shown in Figure 3a and b.^[26]

Another strategy for preparation of a chiral PMO is to employ chiral mesoporous silica nanorods as a hard template and to allow a subsequent growth of an organosilane shell on the surface of these nanorods.^[27] The authors showed that the internal chiral mesoporous silica template could successfully be etched and dissolved with retention of the helical morphology. A schematic illustration for the preparation of the chiral PMO nanotubes from the helical hard nanorod template is shown in Figure 3c. The amphiphilic nature of the resulting material makes it a suitable candidate to form a Pickering emulsion. The material showed a higher activity than mesosilica nanotubes and MCM-41 in the removal of organic contaminants from water.

It was found that the morphology of the PMO with an ethenylene functionality is sensitive to the applied reaction conditions such as the stirring rate or the ammonia concentration.^[28] For example, the length and helical pitch of the nanorod are higher under stirring compared to static



Figure 3. a) SEM and b) TEM images of the surfactant-free 100% righthanded chiral PMO nanomaterial. Reproduced with permission.^[26] Copyright 2011, American Chemical Society. c) Schematic illustration of the formation of helical ethylene-bridged PMO nanotubes from helical mesoporous silica nanorods as a hard template. Reproduced and adapted with permission.^[27] Copyright 2016, Royal Society of Chemistry.

conditions. In addition, a relatively low concentration of ammonia led to the formation of PMO particles with decreased length and larger diameters.

One of the most interesting features of helical PMOs is that the un-functionalized material can induce chirality in organic transformations. Consequently, a heterogeneous catalytic system based on a helical PMO accompanied by an immobilized chiral catalyst can show better (or improved) selectivity than either the neat helical PMO or a chiral catalyst attached to the surface of a non-helical mesoporous silica. A considerable note here is that this type of "structural-induced-chirality" should not be confused with chirality arising from an immobilized chiral organocatalyst or a chiral metallic complex on the surface of a non-helical support. Chirality can be induced to PMO hybrid materials by employing various chiral bis(trialkoxysilane) precursors. However, this may not always lead to the formation of helical geometries. Such materials can also be formed as nonhelical chiral PMOs. Some of these PMO materials having chiral bis(trialkoxysilanes) precursors found applications in asymmetric catalysis.^[29] The structures of some bis(trialkoxysilanes) that were reported as precursors for heterogeneous asymmetric catalysts are shown in Figure 4, compounds a-d. By using CATB as the surfactant and the binaphthalene precursor e in combination with 1,4-bis(triethoxysilyl)benzene as the bulk silica source, Crudden and co-workers reported the synthesis of an ultra-small mesoporous helical PMO.[30] They found that increasing the amount of the chiral dopant e led to an increase of the curvature of the resulting PMO materials.

In an interesting example reported in 2014, a comparison between the selectivity of a chiral compound derived from a bissilylated tartramide that was immobilized on the surface of MCM-41 and a chiral PMO material for a diastereoselective synthesis was carried out.^[21] The catalyst comprising of the

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Figure 4. Some examples of bis(trialkoxysilane) precursors used for the synthesis of chiral PMOs.

chiral ligand that was grafted on the surface of MCM-41 showed 76% selectivity for *anti*-isomer in the Mannich reaction between benzaldehyde, aniline and cyclohexanone (Scheme 1). Interestingly, the selectivity of the catalyst with the chiral tartramide compound in the framework of the chiral PMO material reached up to 95% for the *anti*-isomer. This is a 19% enhancement of selectivity induced by employing a chiral PMO material as a support of a helical ligand.

2.2. Plugged PMO Nanomaterials

The term "plugged PMO" refers to a PMO material with channels containing an uneven surface. The surface's crest that is composed of microporous silica is called "plug". Fabrication of plugged hexagonal templated silicas was first reported by Van Der Voort et al. in 2002^[31] and the concept was further



Scheme 1. Diastereoselective Mannich reaction.

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developed to plugged PMO materials in 2009.^[32] These plugs can partially or fully block the channels of the material. The silicon:template molar ratio, the acidity of the reaction mixture and the use of an alcoholic co-solvent are among the major factors that should be considered for controlling the plug formation in PMOs.[32,33] It was also shown that the formation of plugs depends on the hydrolysis rate of the precursors and hence the degree of the plugs can be adjusted by changing the sequence of the addition of the (organo)silica precursors.^[33] However, the formation and controlling of plugs in PMO structures is less studied and developed compared to other mesoporous materials such as SBA-15. In the latter case, it was previously shown that formation of the plugs can be controlled by employing various parameters such as the silicon (TEOS)/ Pluronic P123 molar ratio, a two-step silica addition, a one-step TEOS addition, a dual templating strategy, pH control and partitioned cooperative self-assembly.[34]

Nitrogen adsorption-desorption analysis is the most useful method to study the presence of plugs in these materials. The typical characteristic for a plugged PMO displayed by this method is the observation of a two-step N₂ desorption (or evaporation) in the nitrogen physisorption isotherms. The desorption step at higher pressures belongs to the desorption of N₂ from open pores and the delayed one at relatively lower pressures belongs to the desorption of N_2 from the (partially) blocked mesopores (Figure 5). The fractions of open and closed mesopores can be determined from the pore size distributions.^[34c] Fully plugged pores (i.e. blocked channels) seem to be useless for most of the applications due to the inaccessibility of the active centres that are located inside the pores. In contrast, PMOs with partially plugged pores have found some applications for the selective adsorption of macromolecules^[35] as well as in asymmetric organic synthesis by improving the chiral induction in the confined spaces of the



Figure 5. A typical N₂ adsorption/desorption isotherm of an ethenylenebridged plugged PMO showing two steps of desorption, which is related to the presence of both open and blocked pores in the material. Reproduced with permission.^[32a] Copyright 2009, Royal Society of Chemistry.

plugged material.^[36] However, synthesis and applications of plugged PMOs are not suitably developed compared to other mesoporous silica such as SBA-15.^[34a]

A plugged PMO with bridging ionic liquid units was recently prepared and used to stabilize palladium nanoparticles.^[37] The material was applied as a heterogeneous catalyst for the aerobic oxidation of benzylic alcohols to yield aldehydes and carboxylic acids (Scheme 2).^[37] The highest conversion of the starting material was observed by employing a catalyst having ionic liquid and organic group functionalities due to the balanced polarities of the channels for the adsorption of the lipophilic organic compounds. The results furthermore indicated that in the case of using the unplugged PMO palladium catalyst, the major product is benzaldehyde while the reaction proceeded further to produce benzoic acid in the plugged PMO catalyst through the overoxidation of the resulting aldehyde. A



Scheme 2. A general demonstration for the aerobic oxidation of benzylic alcohol and the effect of a plugged/unplugged support for product distribution. Overoxidation reactions were mostly observed in the plugged material, which is assigned to longer retention time of the substrates.

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plausible explanation for this phenomenon is a longer retention time of the benzaldehyde intermediate inside the plugged channel and thus an increased time of exposure to the catalytic environment leading to overoxidation of the benzaldehyde to benzoic acid. A bifunctional plugged PMO with mixed polar ionic liquid groups and hydrophobic ethyl functionalities was employed for the extraction of chlorophenol derivatives having different polarities.^[38] It was suggested that the material possesses a balanced polarity and various types of non-covalent interactions such as π - π interactions (with the bridging ionic liquid), hydrophobic interactions (with bridging ethyl groups) and hydrogen bonds. The plugs composed of amorphous silica with high concentration of silanol groups.

2.3. Janus PMOs

The term Janus(-type) materials refers to particles that possess an anisotropic distribution of at least two distinct surface functionalities. Janus materials may have different shapes and morphologies with chemical compositions having organic, inorganic or organic-inorganic hybrid characteristics.[39] Since the introducing of this forefront family of materials, they found broad applications in various fields of science.^[40] According to the definition, it is possible to prepare Janus materials with various surface polarities, which gives the opportunity to prepare bipolar materials that are capable to stabilize Pickering emulsions.^[41] Recently, periodic mesoporous organosilicas have also found applications in the preparation of materials with anisotropic Janus morphology for biphasic interfacial catalysis and drug delivery in cancer cells.^[42] The anisotropic properties for example allow Janus particles consisting of PMO/carbon sphere pairs to improve the laser desorption/ionization mass spectrometric detection of both hydrophobic and hydrophilic molecules.^[43]

The Janus PMO particles can persist in different forms and shapes. For example, Janus PMO-Au nanomaterials could be fabricated that employ various morphologies of gold nanoparticles.^[44] It was shown in this study that the geometry of the gold nanoparticles dictates the shape and growth of the Janus PMO-Au nanostructures. In addition, by tuning the reaction parameters such as solvent ratios, various shapes of Janus PMO-Au nanomaterials were successfully synthesized. With a solvent ratio of 15:1 (v/v) of H₂O:EtOH, the organosilica source grows anisotropically on the surface of Au nanoparticles to form Janus nanostructures, while at a ratio of 3:1 (v/v) of H₂O:EtOH, a core-shell morphology was obtained. The surface characteristics such as morphology, porosity and thermal stability in phenylene-bridged PMOs could be adjusted by selecting 1,4-bis(triethoxysilyl)benzene over the 1,3-bis(triethoxysilyl)benzene isomer.[42b] The para-phenylene-bridged PMO nanoparticles that show a higher molecular periodicity and had higher porosity and thermal stability. In addition, the formation of a multipodal geometry in the PMO with the 1,4-bis(triethoxysilyl)benzene precursor is a key feature to prepare a PMO with anisotropic Janus morphologies. Janus dumbbell-shaped PMO/mesoporous carbon particles with 1-5 nm platinum nano-

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particles loaded on the surface of the mesoporous carbon spheres were used as an efficient catalyst for the reduction of some nitroaromatic compounds under static conditions (without stirring) and by using NaBH₄ as the reducing agent. The material is capable to form a stable Pickering emulsion in a water/toluene system.^[45] The mesoporous carbon spheres in this catalyst were prepared by carbonization of mesoporous resorcinol-formaldehyde spheres under an inert atmosphere. Recently, Janus phenol-formaldehyde/PMO nanoparticles were prepared and used to remove heavy metal ions and organic dyes from polluted water.^[46] The high adsorption capacity of this material is attributed to the hydroxyl groups on surface of the phenol-formaldehyde resin microspheres and the large specific surface area of the PMO component. A Janus PMO/ mesoporous SiO₂ hybrid material was prepared by growing mesoporous silica on the surface of PMO nanoparticle seeds. The surface of the material was modified with acidic and basic species and employed in a cascade deacetalization/Henry reaction.[47]

In 2020, Li et al. prepared a Janus-type PMO-based material named "nanotruck" by an anisotropic growth of PMO nanorods on the surface of spherical, rough SiO₂ (rSiO₂) particles.^[48] It is believed that the rSiO₂ head acts as an "engine" to improve nano-bio interactions, while the high surface area PMO with adjustable length and diameter has a role as "trailer" for drug loading. The authors showed that by changing the initial amount of rSiO₂ as well as by tuning the concentration of 1,2bis(triethoxysilyl)ethane the growth and shape of the PMO can be controlled (Figure 6). In addition, in the presence of a very low concentration of ammonia (1 vol.-%), uniform core-shell nanostructures were formed and by slightly increasing the concentration of ammonia up to 3.5 vol.-%, the growth of PMO nanorods became dominant. In a typical application, dual-mode up-down conversion luminescent nanoparticles were embedded on the rSiO₂ heads, and the resulting nanotrucks were used for near-infrared (NIR) bio-imaging-guided controllable drug release.

The preparation of Janus materials with different surface functionalities using the selective functionalization of hollow silica particles is a simple, efficient and relatively low-cost procedure that was developed in our group.^[49] Quite recently,

we established a novel and highly selective method for the preparation of a Janus bifunctional PMO with two different groups on opposite faces of hollow particles using a modified Stöber method for the preparation of silica particles.^[50] A schematic presentation of the synthesis of such a Janus PMO is shown in Figure 7a. To summarize the process briefly: In a onepot procedure the hollow particles 1 possessing organic and hydrophobic 1,2-bis(triethoxysilyl)ethane (BTSE) groups at the inner side of the shell are prepared. Subsequently, the outer surface is modified by addition of a hydrophilic ionic liquid precursor that is added to the initial mixture to form material 2. This step is followed by crushing of the hollow particles resulting into the desired amphiphilic Janus PMO nanosheets 3. The selective surface bifunctionalization of the material was analyzed by means of scanning electron microscopy (SEM), transmission electron microscopy and elemental mapping. The material was also subjected to a selective surface labelling with Fe₃O₄ nanoparticles.^[49c-e] By means of SEM, it was found that the Fe₃O₄ nanoparticles are mainly interacting with the outer ionic liquid surface while the inner organic BTSE surface almost remained untouched (Figure 7b). In addition, the Janus PMO 3, is able to form a stable Pickering emulsion with water/toluene. Our findings show that after the formation of the Pickering emulsion, the Janus PMO nanosheets are slowly migrating to the interface of the two solvents. The behaviour of this Janus PMO material in the Pickering emulsion system was further studied using a sedimentation analysis technique.^[50] The results proved the upward and downward movements of the Janus nanoparticles, which ended up at the interface of the immiscible solvents.

2.4. PMO-Based Nanomotors

Due to their extraordinary movement, diffusion behaviour and properties, (self-propelled) nanomotors have found considerable attention in recent years. There are ongoing efforts to use these materials in combination with chemical and biological systems.^[51] In general, such nanomotors (or nanovehicles) consume energy from chemical substances in their environment, resulting in a movement of the particles. One challenging



Figure 6. a) SEM and b) TEM Images of Janus-type PMO "nanotruck". Reproduced and adapted with permission.^[48] Copyright 2020, Elsevier.



Figure 7. a) Schematic presentation of the synthesis of a Janus PMO nanomaterial. b) SEM image Janus PMO 2 in the middle of the crushing process. The particles are comprised of a rough outer surface with ionic liquid units and a smooth inner BTSE surface face (black arrow). The material was labelled with Fe₃O₄ nanoparticles that mostly interact with the outer ionic liquid face (red cycles), while the BTSE surface remained almost untouched. Reproduced and adapted with permission.^[50] Copyright 2022, Royal Society of Chemistry.

issue for the design of such nanomotors is a precise speed control. Very recently, Li et al. employed the Janus strategy to fabricate a nanoarchitecture with core-shell SiO₂@Au nanospheres and enzyme-modified PMO nanocomposites that can be considered as a new generation of PMO-based nanomotors (Figure 8a).^[52] In this work, an amino-functionalized PMO was used as a host (support) for the selective covalent immobilization of glucose oxidase and catalase on the surface of the material. The PMO domain acted as the glucose-powered engine that consumes glucose under the catalysis of enzymes (glucose oxidase/catalase). On the other hand, the Au nanoshell at the SiO₂@Au domain is capable to produce a local thermal gradient under a NIR irradiation (Figure 8b) (Figure 8). NIR has the advantage of excellent biocompatibility and allows remote manipulation among other developed propulsion modes.^[53] Thanks to the unique Janus nanostructure, the resultant of these two forces goes in opposite direction and hence the particle movements can be controlled with a so-called "NIR optical brake". By adjusting the power density of the applied NIR light at different glucose concentrations, the speed of the nanoparticles can be regulated. This phenomenon has a strong potential for application in controlling the speed of the enzyme-based nanomotors and in designing intelligent PMObased nanovehicles for various applications such as in nanobiomedicine.

MicroRNA (miRNA) are short, single-stranded and noncoding RNA molecules that persist in human body fluids such as serum and urine. The presence of dysregulated miRNA is a sign of various diseases such as cancer. Consequently, the precise detection of miRNA is considered as a non-invasive diagnosis of tumors in a very early stage before the tumor tissues being detectable by medical imaging scans. For this aim, Janus Au nanorod/PMO nanomotors were reported as a highly sensitive method for a direct and quantitative detection of miRNA in serum and cell media without requiring an additional amplification process to improve the detection efficiency.^[54] The TEM image of the as-synthesized material is shown in Figure 9a. The particles have no noticeable Brownian motion in the



Figure 8. a) TEM images of the Janus PMO/SiO₂@Au nanomotor and b) schematic illustration of the proposed speed regulation mechanism of the Janus PMObased nanomotor. Reproduced and adapted with permission.^[52] Copyright 2022, American Chemical Society.



Figure 9. a) TEM image of Au nanorod/PMO material used as nanomotor. b) Image of the particle movement in exposure of NIR irradiation. Reproduced and adapted with permission.^[54] Copyright 2023, American Chemical Society. The video of the particle movement is also available in Ref. [54].

absence of NIR irradiation. However, by exposure to NIR radiation, they start to diffuse in the aqueous suspension, which was detected by dark field microscopy (Figure 9b). The particle movement is a key parameter to recognize and capture miRNA-21 in reaction media with high sensitivity and selectivity.

3. Conclusion and Outlook

In this critical short review, recent findings in the field of less developed but nevertheless high-potential PMO nanomaterials having unusual structures and properties are described. In spite of desirable efforts in the synthesis of helical PMOs, their applications are still limited. The fact that a pure helical PMO nanomaterial can induce chirality in a chemical reaction is a very important finding that should not be disregarded, since it opens up new opportunities to design novel heterogeneous catalysts for asymmetric organic synthesis.

One of the most important properties of the plugged PMO compared to unplugged ones is the higher retention time of the molecules that diffuse inside their pores. Catalysts based on the plugged PMOs may for example have a significant positive influence in (gas-phase) polymerization reactions as well as an effect on the structural features of their products (branched/ linear chains, molecular weight of the polymers, etc.). Another remaining challenge is a controllable synthesis of plugged PMOs with smaller window sizes (i.e. smaller pore entrances) as a promising strategy for "ship-in-a-bottle synthesis" of metal complexes for catalytic applications.^[55] Here, small precursors of complexes that are larger than the window sizes will diffuse inside the pores and the complex can be built inside the channel. This would significantly improve the local concentration, activity, and selectivity of the catalytic species. Furthermore, leaching of the immobilized catalyst from the pores could dramatically be reduced thanks to the sterical hindrance of the "tight interior". The effect of the reaction conditions for plug formation in PMOs is less developed compared to the plugged mesoporous materials such as SBA-15^[34a] and future efforts in other research should address this issue. The same effort should also be made for new synthetic strategies of helical PMOs by employing the synthetic experiences for the preparation of mesoporous materials. $\ensuremath{^{[56]}}$

For Janus PMOs it is already foreseeable that they will have a high potential for applications. It is possible to anisotropically graft two (or more) different groups with tunable polarity and chemical composition to the surface of these systems. Of particular importance is the fact that Janus PMOs can act as the heterogeneous version of molecular surfactants. Since it is possible to rationally design such Janus PMO nanomaterials, it should in the future be possible to perform catalytic reactions in either water, organic solvents or in a Pickering emulsion. The particles can simply be separated from the reaction mixture by filtration at the end. Janus PMO hollow particles can also act as gas reservoirs. A Janus hallow PMO with for example perfluoroalkyl groups at inner surface can be considered as an oxygen nanoshuttle for tumor oxygenation in cancer treatment.^[57] This can be combined with their ability for drug delivery for more efficient cancer treatments. However, for working in living systems, information about biocompatibility/toxicity of the bis(trialkoxysilane) precursors, especially the synthetic ones is requested. These data are currently rather limited. For practical purposes, having a library of biological half-life and developing a standard method for the assessment of the toxicity of the silane precursors as well as the corresponding PMOs is crucial. Interesting efforts are developed for the synthesis and applications of biodegradable organosilica nanoparticles made from the precursor bis[3-(triethoxysilyl)propyl] tetrasulfide for cancer therapy.^[58] A considerable point for designing biodegradable PMOs is that the bridging R group in the (R'O)₃Si-R-Si(OR')₃ precursor should contain chemical bonds that are responsive under redox, acidic or enzymatic conditions.^[5a]

The field of Janus PMOs is in close relationship with PMObased nanomotors, taking advantage of their anisotropic morphologies. However, a rational design of PMO-based nanomotors with efficient cellar uptake is still a remaining challenge. One solution is to develop smart materials with deformable hollow PMO parts.^[59] In this type of material, the morphology of the PMO changes during the passage through the cellular membranes.^[59] The periodically distributed organic groups in hollow silica are responsible for its lower Young's modulus compared to rigid PMO nanoparticles. Since metal-organic frameworks (MOF) and covalent organic frameworks (COF) can show different surface functionalities,^[60] (Janus) PMO–MOF and (Janus) PMO–COF nanocomposites may be the next generation of unconventional PMO-based nanomaterials.

We hope that this review could make clear that the above mentioned topics offer a series of important yet hidden applications of PMOs that should be considered for future progress.

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The authors declare no conflict of interest.

Data Availability Statement

This is a review article. For additional data, readers may refer to the original works that are cited in the references section.

Keywords: chiral nanomaterial · Janus PMO · nanomotors · periodic mesoporous organosilica · PMO

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