



Functionalization of mesostructured inorganic–organic and porous inorganic materials

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ABSTRACT

The capability to functionalize the interior channels and/or high internal surface areas of mesostructured inorganic–organic or porous inorganic solids with specific organic or inorganic moieties has dramatically expanded the potential applications for these versatile materials in catalysis, separations, optical and optoelectronic devices, drug delivery, sensors, and energy conversion. Key to the widespread application of these materials are the various synthetic schemes that have been developed to provide control over the types of species incorporated and, more importantly, their distributions within the mesostructured hosts. Furthermore, multiple active species can often be independently incorporated and collectively optimized to yield multifunctional properties that widen application prospects. Several recent developments and examples in this rapidly growing field of materials chemistry and engineering are highlighted and discussed.

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Mesoporous inorganic materials have been synthesized with various mesophase structures (e.g., hexagonal, cubic, lamellar Fig. 1a–c) and macroscopic morphologies (e.g., powders [1*,2–4*,5*], fibers [6*,7], thin films [8*,9*,10], and monoliths [11*] Fig. 1d–f). In general, ordered mesostructured materials are formed from solution by the co-assembly and cross-linking of network-forming inorganic species (typically oxides) in the presence of structure-directing organic agents [13]. The structure-directing agents are typically amphiphilic surfactants or block-copolymers that self-organize into mesoscale (2–50 nm) structures, according to the solution composition and processing conditions used. Such structure-directing species can be retained in the product materials to yield mesostructured inorganic–organic composites or be removed by oxidation or solvent extraction to introduce porosity and thereby yield mesoporous inorganic materials with high internal surface areas (500–1000 m²/g) and large uniform pore dimensions (2–50 nm). The diverse properties of these materials originate from the ability to control the sizes and periodic order of the mesochannels and macroscopic morphology, while also tailoring the inorganic framework and internal pore surface or channel compositions to influence macroscopic adsorption, reaction, transport, photo-response, or other properties.

1. Co-assembly of functional species

One general approach to the modification of the macroscopic properties of mesostructured materials is to incorporate species with the desired functionalities simultaneously during initial self-assembly and material syntheses. Often this takes advantage of the selective partitioning of the functional components between the different

locally separated domains, such as between the hydrophilic or hydrophobic regions of self-assembling block-copolymer species and accompanying network-forming hydrophilic oxide (or other) species. Such co-assembly syntheses generally involve either co-condensation of functional species that form covalent bonds with the self-assembling components or physical interactions that result in preferential solubilization of the functional species within the different self-assembled regions.

1.1. Co-condensation of inorganic framework moieties

Extensive efforts have been directed toward the co-condensation of functional moieties with the network-forming inorganic precursor species during formation of the inorganic framework. Typically, this is accomplished by modifying the initial reaction mixture that contains the structure-directing organic agent and inorganic precursor species (e.g., hydrolyzable alkoxysilanes or other inorganic precursor species) to include one or more additional network-forming species (e.g., soluble alumina, titania, other metal oxides, epoxy monomers) with the desired functionalities. These species subsequently co-assemble and condense into the inorganic framework, although often with distributions of species that are difficult to establish and control. When conditions allow it, the primary advantage of this approach is its simplicity, because the incorporation of the functional moieties and the formation of the mesoporous material occur in a single synthetic step (commonly referred to as a ‘one-pot’ synthesis). Limitations of this approach are that the functional components must be compatible with the synthesis conditions, must not disrupt the mesophases self-assembly process, and must distribute the functional species to the desired locations within the final product. For example in aqueous solution syntheses, this depends greatly on the choice of the

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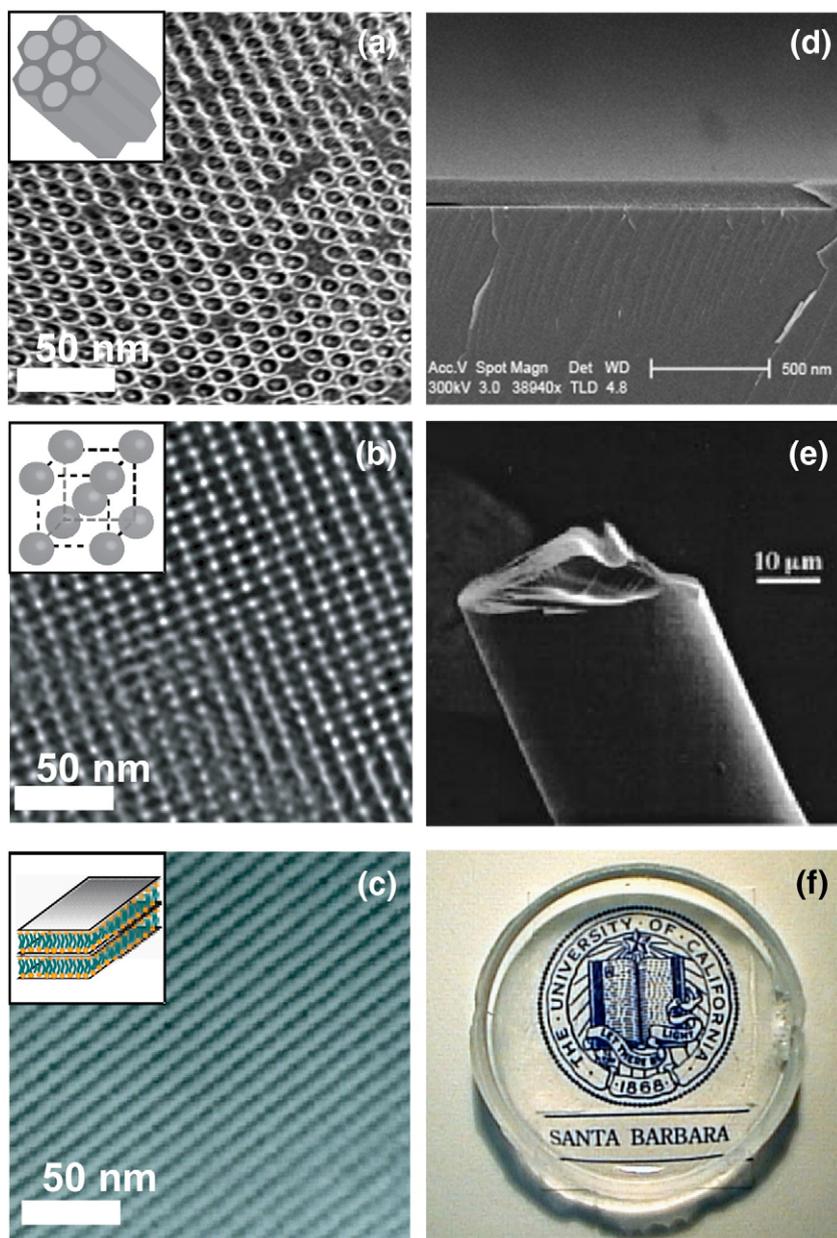


Fig. 1. Transmission electron micrographs of (a) hexagonal, (b) cubic, and (c) lamellar mesostructured silicas, with pore channel or gallery configurations shown schematically in the insets. Mesostructured materials can be processed into a variety of different morphologies, including (d) films, (e) fibers, and (f) monoliths [adapted with permission from Refs. [7,11,12]].

functional species: hydrophilic components tend to be distributed within the inorganic framework walls, hydrophobic components tend to associate with the organic structure-directing moieties in the mesochannels, while amphiphilic components can be incorporated at the interface(s) between the two regions. Where the functional guest species ultimately reside has a significant influence on the ultimate properties of the material. For example, if the functional moieties are co-condensed or embedded within the rigid inorganic framework walls, they may be stable against chemical attack or leaching, but may also be less accessible to other diffusing or reacting guest molecules in the mesopores.

Co-condensation functionalization has generally been focused on the formation of mesoporous materials containing mixed metal oxide frameworks [17,14–17]. An important example includes Al-containing mesoporous silicas [17,18], which incorporate four-coordinate aluminosilica moieties to introduce Lewis or Brønsted acidity into the inorganic frameworks. Hydrolyzable sources of networking forming

Al precursor species, such as NaAlO_2 , $\text{Al}(\text{OH})_3$, aluminum isopropoxide, or aluminum sulfate, co-condense with silica in the presence of structure-directing surfactant or block-copolymer species into highly ordered mesostructured solids. The choice of solution pH depends on the structure-directing agent that is used and also influences the processability, i.e., whether rapid precipitation occurs to form powders or whether slower co-condensation occurs to allow fibers, films, or monoliths to be prepared.

Many other types of functional heteroatoms have been incorporated into the frameworks of siliceous mesoporous materials by co-condensation to modify the adsorptive and/or catalytic characteristics (e.g., acidic or redox properties) of the inorganic walls. For example, isomorphic substitution of trivalent Al, Ga, or Fe in mesoporous silica frameworks has been shown to yield Brønsted acid sites of varying strengths [19,20]. Mesoporous silicas have also been co-condensed with oxides of transition metal elements, such as Ti, V, and Cr to form oxidation catalysts [20,21]. In addition, rare-earth elements, such as

trivalent europium and terbium, have been doped into mesoporous oxidic frameworks to capitalize on their photoluminescence properties [22,23]. In general, mesoporous mixed metal oxide systems synthesized under basic pH conditions are capable of a more effective co-condensation and thus higher metal heteroatom loadings in the silica frameworks, compared to those synthesized under acidic solution conditions. Such mesoscale materials synthesis strategies can be combined with zeolite synthesis protocols, i.e., using both surfactants (e.g., cetyltrimethylammonium, CTA⁺) and small-molecule structure-directing agents (e.g., tetrapropylammonium, TPA⁺, or tetraethylammonium, TEA⁺, cations) to assemble and cross-link protozeolitic nanoclusters into mesostructured materials with nanocrystalline frameworks [24,25,26,27]. Such materials have mixed oxide frameworks with higher stabilities and zeolite-like adsorption/reaction properties, compared to conventional mesostructured materials with amorphous walls. An important recent advancement reported by Smarsly, Antonietti, and coworkers relies upon the use of thermally stable poly(ethylene-co-butylene)-*b*-poly(ethyleneoxide) block-copolymer species to maintain mesostructural ordering during calcination and crystallization of the inorganic framework [28]. This approach has recently been used to prepare mesoporous mixed oxide frameworks comprised of rutile titania nanocrystals in an amorphous Ta₂O₅ matrix, which exhibits photocatalytic properties [29].

Organically functionalized mesoporous materials may also be prepared by co-hydrolysis and condensation of tetraalkoxysilanes [Si(OR)₄], along with a terminal trialkoxysilane [RSi(OR')₃], in the presence of suitable structure-directing agents, as shown in Fig. 2. A variety of organosilanes have been used in this way. For example, thiol-functionalized mesoporous silica has been prepared by the co-condensation of tetraethoxysilane (TEOS) with 3-mercaptopropyltrimethoxysilane (MPTMS) to introduce selective adsorption properties for heavy metals such as mercury(II) [30]. Thiol-functionalized mesoporous silicas can also be transformed into solid acid catalysts through conversion of the thiol groups into sulfonic acid moieties by using a suitable oxidizing agent, such as H₂O₂ [31]. Oxidation of the thiols can occur subsequent to the formation of the thiol-functionalized mesoporous silica or *in situ* by the addition of H₂O₂ to the initial co-condensation solution [32]. Sulfonic-acid-functionalized silica can similarly be synthesized by *in situ*

oxidation/co-condensation to yield mesoporous materials containing arene-sulfonic acid species, which exhibit increased acid strengths compared to their alkyl counterparts [33,34a]. Furthermore, mesoporous silicas may be synthesized with trialkoxysilane derivatives that contain different functional groups. Their co-condensation has been used to produce acid- and base-bifunctionalized mesoporous silica for use in heterogeneous catalysis [34b,34c].

The conversion of co-condensed reactive organosilane species into moieties with desirable functional properties has been extended to other surface species in mesoporous materials. For example, vinyl-functionalized mesoporous silicas have been synthesized using triethoxyvinylsilane, followed by sequential modification of the anchored vinyl species to form a variety of other functionalities, such as alcohol, epoxide, or diol functional groups [35]. In all of these systems, care must be taken to avoid decomposition of the reactive organosilane moieties both during the initial self-assembly/co-condensation step (often undertaken in solutions of extreme pH) and when removing the structure-directing agent from the mesopores. For this reason, solvent extraction is often the method of choice for removing the structure-directing species, because the conditions are milder than can be used in thermal oxidation or UV/ozone treatments.

Another class of organically functionalized mesoporous materials, also referred to as periodic mesoporous organosilicas (PMOs), are formed by the hydrolysis and condensation of bis-silylated precursors of the form (R'O)₃Si-R-Si(OR')₃. In contrast to organically functionalized mesoporous materials formed from terminal organosilanes, which tend to yield products with a majority of the organic moieties residing at the mesopore surfaces, in PMOs, the organic moieties may be incorporated more uniformly within the inorganic (typically silica) pore walls [36–38]. Such materials have been synthesized with a wide range of organic bridging units, a number of which are depicted in Fig. 3. These generally result in mesostructured materials with frameworks that are more hydrophobic and less brittle than their wholly siliceous analogs.

Of particular interest are PMOs generated by the condensation of aromatic-bridged silanes, such as 1,4-bis(triethoxysilyl)benzene or 4,4'-bis(triethoxysilyl)-1,1'-diphenyl (Fig. 3, left column, second and third from the top, respectively, with -CH₂CH₃ as the R group) in the presence of cationic structure-directing surfactant species, which yield mesoporous materials with both ordered mesopores and high degrees

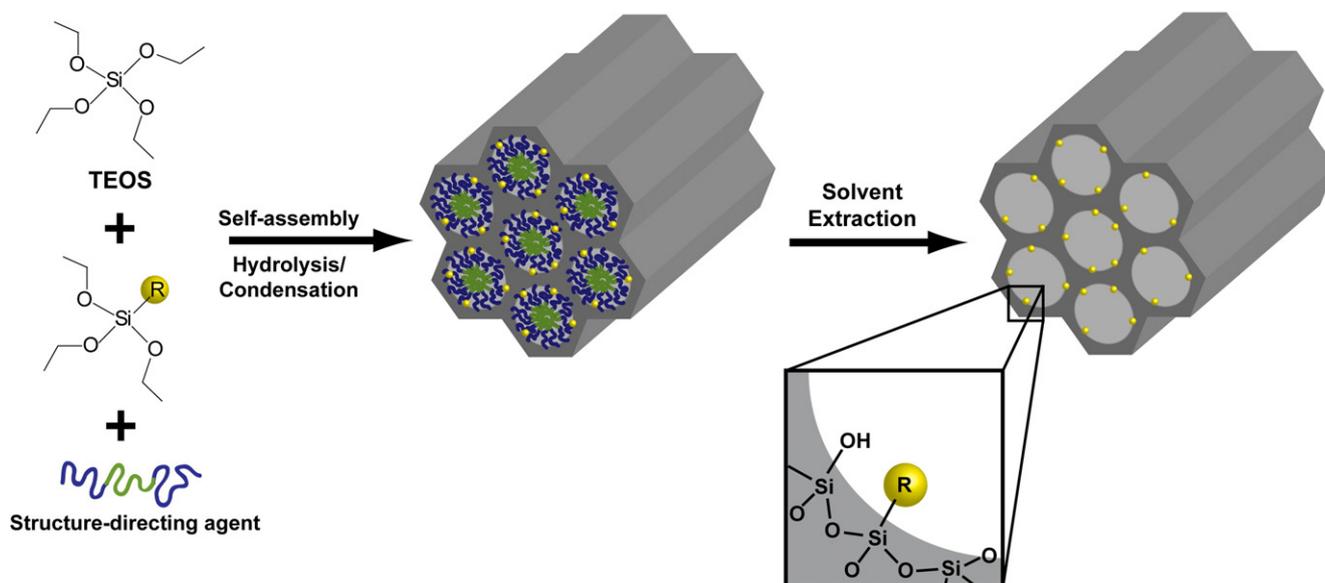


Fig. 2. Co-condensation approach to the functionalization of mesoporous inorganic materials by direct co-assembly and incorporation of the functional moiety (R) species during synthesis.

co-assembled system is that it provides opportunities to adjust the mechanical properties of the resulting mesoporous material, according to the relative proportions of resin and silica in the framework. Compared to wholly organic mesoporous polymers (e.g., phenolic resins) or wholly mesoporous silica, hybrid resin-silica frameworks combine the mechanical robustness of silica with the greater elasticity of the partially polymerized resin component. Furthermore, either the silica or resin can be selectively removed from the cross-linked material, as shown in Fig. 5, to produce mesoporous carbon or silica, respectively, often with additional nanoscale porosity in the walls. Non-covalently bonded functional species, such as organic dyes or surfactant-passivated nanoparticles, have also been directly incorporated during the syntheses of mesostructured inorganic materials. In these syntheses, the incorporated functional components are often hydrophobic and thus interact with the hydrophobic moieties of the surfactant or block-copolymer structure-directing species and are dispersed within the hydrophobic regions of the as-synthesized mesostructured product materials. Examples include the incorporation of laser and photochromic dyes (e.g., rhodamine 6G, spiroxazine, spiroxyran, etc.) [46,47,48], including the combined incorporation of rare-earth and organic dye species to introduce multiple photo-responsive functionalities [49,50]. Advantages of organic dye incorporation in mesostructured organic-inorganic materials are the capacity for high dye loadings, while maintaining high dye dispersions, promoting high interfacial contact with the inorganic framework (e.g., titania), with robust mechanical and photophysical properties. An example is the incorporation of porphyrin dye species into block-copolymer-templated mesostructured silica. Tetraphenylporphyrin (TPP) guest species exhibit optical-limiting behavior in solution [51] and are desirable to incorporate in high concentrations in transparent matrices that can be used as optically responsive coatings. In this case, the porphyrin guest species can be more effectively dispersed in mesostructured silica host films than in silica glass, because of favorable interactions with the amphiphilic triblock-copolymer species that significantly reduce undesirable dye aggregation [52]. These TPP-doped mesostructured triblock-copolymer-silica com-

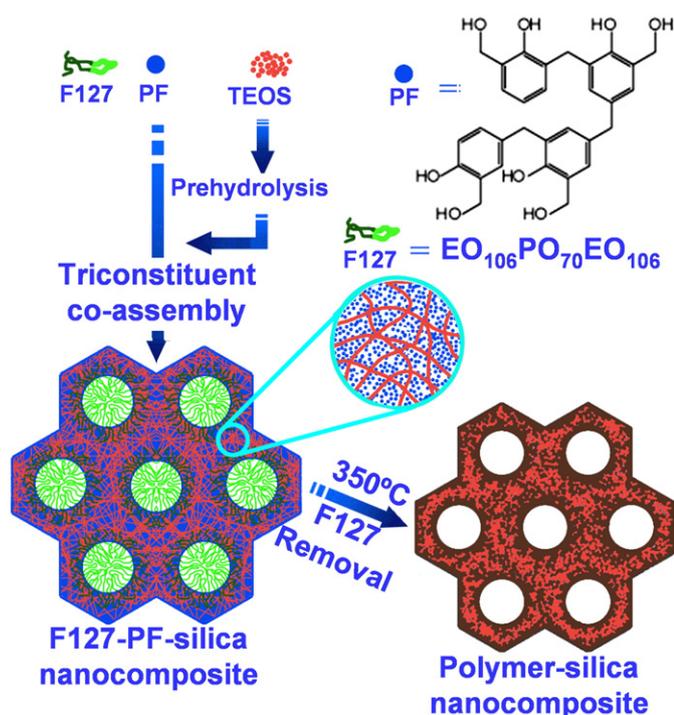


Fig. 5. Schematic diagram showing a synthesis approach for the preparation of mesoporous polymer-silica nanocomposites [adapted with permission from Ref. [45]].

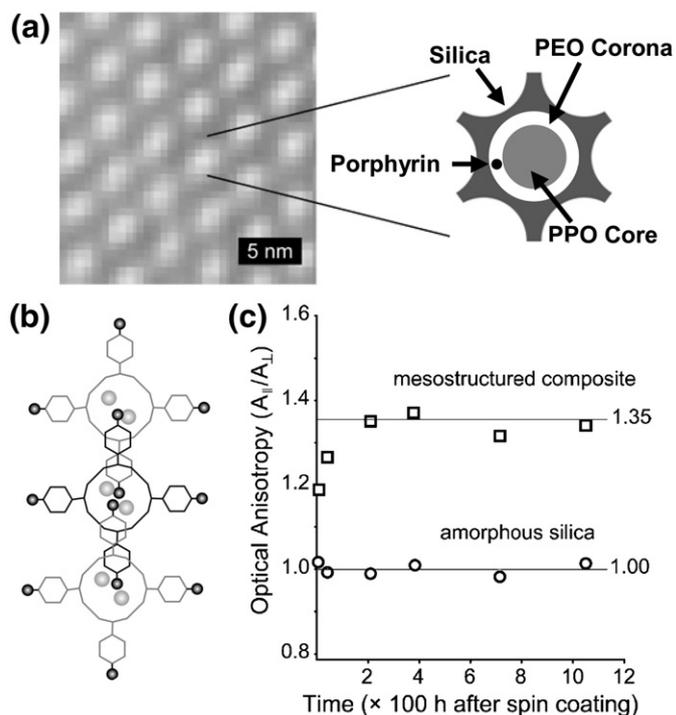


Fig. 6. (a) TEM image of a hexagonal mesostructured silica/EO₂₀PO₇₀EO₂₀ block-copolymer composite and a schematic diagram showing the locus of J-aggregate solubilization principally within the hydrophilic PEO corona regions surrounding the more hydrophobic PPO cores. (b) Schematic diagram of a supramolecular J-aggregate assembly of porphyrin dye molecules. (c) Anisotropic optical absorption measured at 490 nm for 1 wt.% H₂TPPS₂⁻ J-aggregates incorporated into an orientationally ordered 1- μ m-thick hexagonally mesostructured silica/EO₂₀PO₇₀EO₂₀ composite film and an amorphous silica glass film for comparison [adapted with permission from Ref. [53]].

posites combine the benefits of the high dye solubilities characteristic of polymers with the mechanical robustness of inorganic oxide glasses. Furthermore, the use of mesostructured silica-block copolymer thin films provides an orientationally ordered matrix which allows for the stable alignment of co-assembled porphyrin J-aggregates which exhibit anisotropic optical properties [53]. Fig. 6a shows a TEM image and accompanying schematic diagram of a mesostructured silica framework containing porphyrin J-aggregate assemblies (Fig. 6b). Separate solid-state 2D NMR measurements establish that the porphyrin assemblies are located preferentially within the PEO corona regions of the mesostructured silica films. Inclusion of the porphyrin dye within the aligned mesoporous silica results in anisotropic optical absorption properties, as shown in Fig. 6c.

Other non-covalently bonded functional species introduced by co-assembly into mesostructured inorganic-organic host matrices include surfactant-passivated nanoparticles, and conjugated polymers. For example, alkylthiol-stabilized gold nanoparticles mixed with surfactants in water form nanoparticle-containing micelles. Upon subsequent addition of a cross-linking silica source, such as tetraethoxysilane, these co-assemble to form an inorganic network around the nanoparticle-containing hydrophobic regions [54]. Similarly, conjugated polymers have been incorporated during syntheses of mesostructured materials to introduce electronic and optoelectronic functionalities. Under principally non-aqueous conditions, for example using tetrahydrofuran as a solvent, highly hydrophobic poly-[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) conjugated polymer species have been co-assembled and incorporated into the hydrophobic regions of block-copolymer-directed silica or titania films [55–57]. Mesostructured titania/MEH-PPV composites are promising materials for photovoltaics or displays. Such

materials can be synthesized by post-synthetic modification procedures (see below), as demonstrated by Wu et al. [58,59] although diffusion limitations, etc. often limit their performance properties. By using co-assembly synthesis strategies and adjusting the solvent and structure-directing block-copolymer species, the conjugated polymer guests can be incorporated to enhance interfacial contact with the continuous mesostructured titania network (Fig. 7a), thereby promoting carrier transport to the electrodes. A schematic representation of a titania/MEH-PPV-based photovoltaic device and accompanying current–voltage plots are shown in Fig. 7b. The latter clearly demonstrates that inclusion of MEH-PPV in the titania mesostructure improves photovoltaic properties of the device. Co-assembly of non-covalently bonded functional species generally requires that they be compatibly soluble with the solvent, inorganic precursor and/or structure-directing components. In such cases, favorable solution and colloid thermodynamics allow the functional species to be co-processed in ‘one-pot’ syntheses and distributed within the mesostructured host, according to their often preferential interactions with one or more of the self-assembling components.

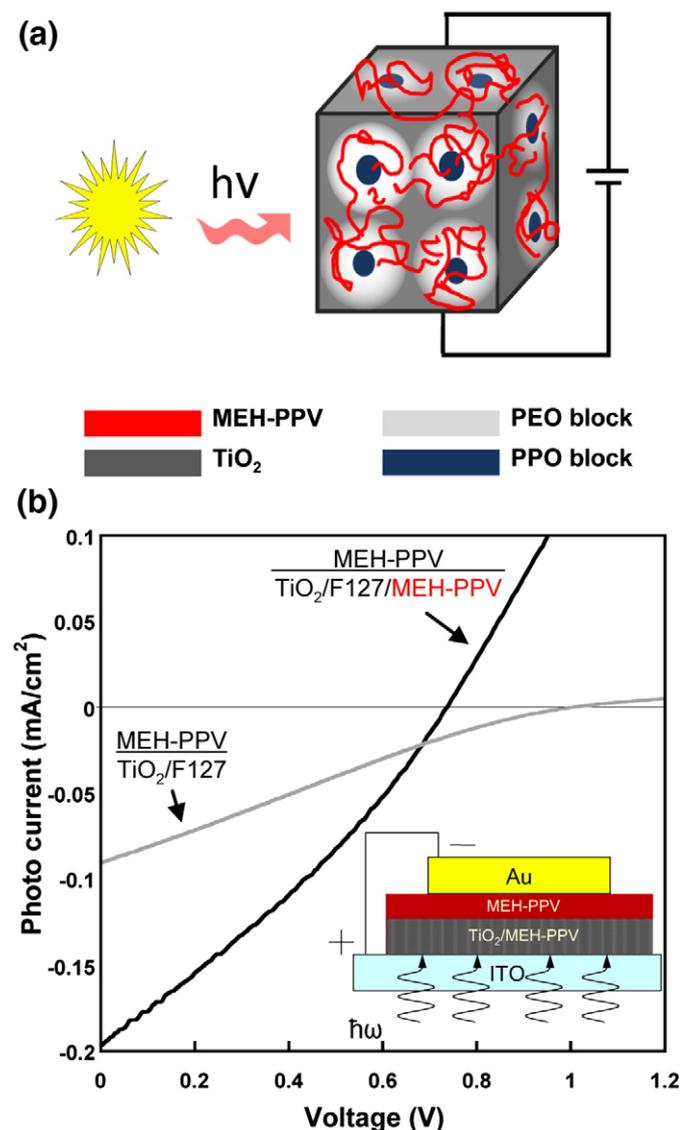


Fig. 7. (a) Schematic diagram of a mesostructured cubic TiO₂/block-copolymer/MEH-PPV composite, integrated into a photovoltaic device. (b) Plot of the photocurrent generated as a function of applied voltage for photovoltaic devices based on different block-copolymer-directed titania films with (black line) and without (grey line) MEH-PPV [adapted with permission from Ref. [57]].

1.3. Post-synthetic modification

Often, it is difficult or impossible to find conditions that are simultaneously compatible with all of the necessary composition, structural, or processing requirements to prepare functionalized mesostructural materials with the desired properties in a single synthetic (“one-pot”) step. However, protocols have been developed whereby mesostructured materials can be prepared and subsequently modified in a sequence of steps to improve a material’s macroscopic properties. This is usually referred to as ‘post-synthetic modification,’ and imparts desired functionality after the initial synthesis step, following formation of the mesostructured framework. This generally involves removal of the structure-directing species (by oxidation or solvent extraction) and subsequent introduction of the functional species into the resulting mesopores of the material in one or more adsorption or pore-inclusion steps [60]. Such modifications exploit the relatively large pore dimensions of mesoporous solids that allow large molecular species, including enzymes and moderately sized polymers, to be introduced into the channels, compared to nanoporous systems (e.g., zeolites). For organic functional species, post-synthetic functionalization often involves the reaction of alkoxy silanes [RSi(OR’)₃] or chlorosilanes [RSiCl₃] with silanol species on the interior mesopore surfaces. In the case of inorganic functional species, post-synthesis incorporation can occur via reactions with silanol species, ion-exchange at charged surface sites, or incipient-wetness impregnation. Post-synthetic functionalization offers the advantage of allowing sequential incorporation of multiple functionalities that would otherwise be incompatible in a single co-condensation step. In addition, relatively high surface loadings of functional species can be incorporated into the material with minimal effect on overall mesostructural ordering. Such approaches are generally limited to functional species that are sufficiently small to diffuse or imbibe into the mesopores (2–50 nm, depending on the structure-directing agent used). Species that are larger than the mesopore dimensions of a given material will either not enter and/or be concentrated near the external particle, film, fiber or monolith surface, precluding in most cases the introduction of beneficial functional properties.

Prior to post-synthetic functionalization of mesoporous inorganic materials, it is common for surface compositions (e.g., hydroxyl concentration) and pore size distributions of as-synthesized materials to be altered to facilitate subsequent functionalization steps. Reducing the concentrations of surface hydroxyl groups is often achieved by high temperature treatments in dry atmospheres and can yield more isolated sites to which functional groups can be covalently grafted. By comparison, post-synthetic heat treatments, in conjunction with pH-controlled washing, provide a facile method for modifying mesopore surfaces and structures. One example is the treatment of MCM-41 mesoporous silica powders in alkaline (pH 10) solutions to increase pore size regularity and improve hydrothermal stability [61]. Similar post-synthesis thermal and/or alkaline treatments have been used to modify the porosities of SBA-15-type materials [62,63]. Calcination of the block-copolymer-directed silica at 450 °C has been shown to yield a bimodal distribution of pore sizes comprised of relatively unordered nanopores within the siliceous frameworks that form the hexagonal mesopore array [62]. Further treatment with alkaline solutions results in the enlargement of such pores, which can be controlled by adjusting solution pH and time of contact. In contrast, mild thermal treatment in water (≤ 100 °C) has been reported to close the nanopores and thereby yield monomodal mesoporosity [62]. Extended thermal treatment of synthesis mixtures up to 130 °C in the presence of hydrophobic swelling agents have been shown to yield hexagonal mesoporous silica with larger pore dimensions up to 16 nm [63]. Such structural modifications allow the mean pore sizes and distributions of the inorganic host framework to be adjusted to increase or otherwise influence the diffusion of guest species within the pores.

Independent of such pore-modifying treatments, the compositions and structures of mesoporous inorganic materials may be modified to

incorporate diverse surface functionalities to introduce desirable physical and chemical properties. Much recent effort has focused on the post-synthetic functionalization of calcined or solvent-extracted mesoporous silica or metal oxides to covalently graft a wide variety of organic or organometallic moieties with applications in separations and catalysis [64]. For example, aminopropyl-functionalized mesoporous silica has been shown to adsorb carbon dioxide [65], while aminosilane-functionalized mesoporous silica has been used to sequester soluble chromate and arsenate species for purification of groundwater [66]. Similarly, mesoporous silicas have been post-synthetically modified with organic groups that preferentially adsorb heavy metals from solutions. Mesoporous silica containing post-synthetically grafted imidazole moieties (e.g., by using *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole) selectively binds Pt^{2+} or Pd^{2+} species for precious metal separation and recovery [67]. Modification of mesoporous silica to incorporate surface thiol groups (e.g., by grafting tris(methoxy)mercaptopropylsilane) results in high uptakes of metals, such as Hg^{2+} , Pb^{2+} , Cd^{2+} , and Ag^+ , from contaminated water streams [68]. Recently, Brunel and coworkers demonstrated the immobilization of organic ion species onto the surfaces of mesostructured organosilicas, which act as heterogeneous analogs to homogeneous ionic liquids [69].

It is increasingly common that functionalized mesoporous inorganic materials are used to control mass transport, particularly in controlled release applications, such as for drug delivery. One way of controlling drug release is to alter the desorption rate of an adsorbed species by organic functionalization of the mesoporous silica surface to modify surface-binding properties. For example, the release of ibuprofen from mesoporous silica can be modified significantly by the presence of various organic functionalities on the interior mesopore surfaces [70,71–74]. Grafted organic moieties alter the hydrophilicity of the mesopore surfaces, thus affecting the strength of ibuprofen binding and consequently its desorption rate. For example, hexamethyldisilazane- [72] or amine-functionalized [71,72] mesoporous silicas show slower ibuprofen release rates that are consistent with their reduced surface hydrophilicities.

An alternate method of controlling release is to use stimuli-triggered species that act as molecular gates to control transport of guest species out of (or into) mesopore channels. For example, coumarin moieties readily undergo reversible photodimerization when exposed to UV light and display similar properties when anchored near mesopore openings in mesoporous silica. Light-triggered dimerization of such grafted coumarin species has been demonstrated and used to release weakly adsorbed compounds filling the silica mesopores [75]. Similarly, azobenzene derivatives grafted post-synthetically near mesopore channel ends have been shown to act as photo-responsive molecular barriers in mesoporous silicas, as depicted schematically in Fig. 8a [76,77]. Such properties exploit the light-induced *cis-trans* isomerization about the $\text{N}=\text{N}$ bond in azobenzene moieties to control diffusion of guest molecules within and from the mesopores. For example, Fig. 8b,c demonstrates the photo-controlled release of dye species from azobenzene-functionalized mesostructured silica reported by Angelos et al., which was initiated as a result of the *cis-trans* conformational changes induced by exposure to 457 nm light. Interestingly, the dye release was halted by cessation of the light exposure and resumed upon subsequent re-illumination. Such properties demonstrate the potential of mesostructured materials functionalized with photo-responsive species to regulate transport of guest species for diverse delivery or adsorption applications.

The high surface areas, large adjustable pore sizes, and modifiable surface properties make mesoporous inorganic solids well suited for use as supports for catalytically active organometallic or enzyme moieties. Motivated by environmental concerns and separation challenges associated with homogeneous catalysts and conditions, there has recently been substantial effort devoted to the development of heterogeneous analogs of homogeneous catalysts. A number of catalytically active organometallic species that have previously been used under homogeneous conditions have been grafted onto mesoporous inorganic supports. These include organometallic complexes of Cu [78], Mn [79,80], Mo [81], Ir [82], Pd [83], and Rh [84,85], which have been covalently anchored onto mesoporous silica, aluminosilica,

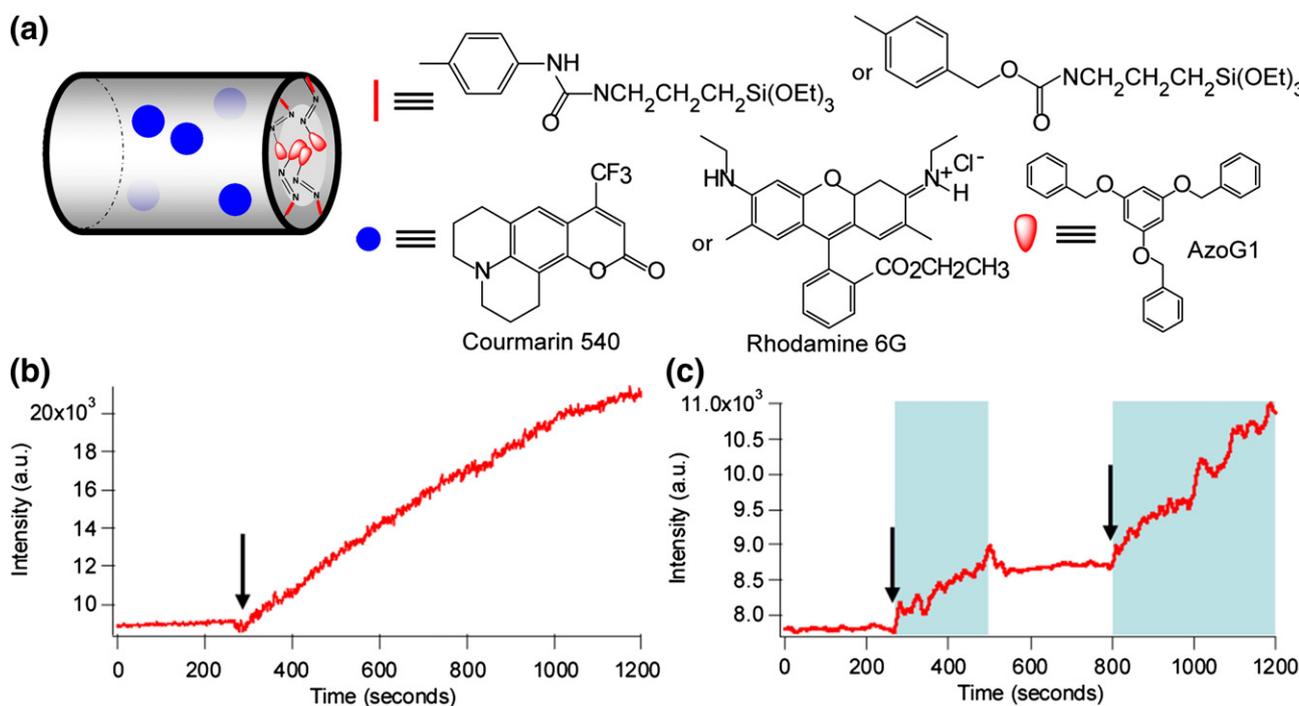


Fig. 8. (a) Schematic diagram of a single mesopore channel functionalized with photo-responsive molecular guests, such as post-synthetically grafted species that include azobenzene groups, AzoG1 end species (red tear drops), and more weakly bonded guest species (blue circles) whose transport properties are to be controlled. (b,c) Release profiles of Coumarin 540A dye species from AzoG1-azobenzene-modified mesoporous silica, as measured by luminescence intensity in solution as functions of time. The arrows indicate when illumination with 457 nm light was initiated to induce the *cis-trans* conformational changes of the azobenzene moieties that account for the release of the dye guest molecules into solution [adapted with permission from Ref. [77]].

and/or alumina supports to promote diverse reactions, such as Friedel–Crafts hydroxylation [78], epoxidation [81], hydrogenation [82–85], etc. These heterogeneous catalysts are not only easier to recover and recycle, but in several cases exhibit improved catalytic properties and stabilities, compared to their homogeneous counterparts. For example, Pd complexes with various chiral triaza ligands have been incorporated into hexagonally mesostructured MCM-41 silica powders and shown to yield higher hydrogenation reactivity and selectivity than homogenous analogs; this has been attributed to favorable interactions between the active metal complex and the mesoporous support [83]. Similarly, metal complex–support interactions have been shown to increase enantioselectivity of asymmetric organometallic catalysts, as demonstrated by the asymmetric hydrogenation of the C=O bond of methyl benzoylformate by Rh and Pd complexes tethered within porous silica supports [84]. These considerations also influence the properties of immobilized enzymes on mesoporous supports for which a large and growing body of work exists [86]. Recent examples include the demonstration of an enzymatic (chloroperoxidase) catalyst that exhibits high activity, stability, and reusability for removing organosulfur compounds from fossil fuels [87]. The modification of mesoporous silica to incorporate hydrophobic alkyl moieties in the framework has been shown to promote lipase-catalyzed trans-esterification activity in organic solvents [88]. Furthermore, mesocellular silica foams with immobilized enzymes, such as thrombin, on their interior surfaces have been shown to promote blood-clotting, with promising applications in biomedicine [89]. The large and uniform mesopore sizes allow large organometallic or enzyme species to be incorporated post-synthetically onto interior pore surface sites, which can modify their dynamics, activities, and stabilities under different conditions and in the presence of different reactants and products.

Considerable research efforts have been directed toward functionalizing mesoporous inorganic materials with acidic moieties for catalysis and ion-exchange-membrane applications. Mesoporous silica materials such as SBA-15 may be selectively functionalized to produce solid acid catalysts with adjustable acid strengths. For example, surface hydroxyl groups in mesoporous silicas have been functionalized to incorporate $-\text{COOH}$, $-\text{PO}_3\text{H}_2$, or $-\text{SO}_3\text{H}$ moieties, yielding weak, moderate, and strong solid acids, respectively [90]. Other strong solid acids include perfluoroalkylsulfonic-acid-functionalized mesoporous silicas, produced by post-synthetic grafting of 1,2,2-trifluoro-2-hydroxy-1-trifluoromethyl-ethane-sulfonic-acid- β -sultone to surface silanol groups [91]. The solid acid catalysts showed high activities and selectivities for both esterification and Friedel–Crafts acylation reactions. The same sulfonic acid species were similarly grafted to mesoporous aluminosilica films for use as fuel cell membranes with enhanced proton conductivities at elevated temperatures (80–200 °C) [12]. Whereas polymeric proton-exchange membranes often dehydrate and exhibit reduced proton conduction properties at these temperatures, sequential functionalization of cubic mesoporous silica films leads to materials that remain hydrated and ion-conducting at higher temperatures and lower humidities. Post-synthetic grafting of aluminate species under alkaline conditions increased the hydrophilicity of mesostructured silica pore surfaces, resulting in significantly increased membrane hydration at elevated temperatures (80–200 °C). Subsequent additional post-synthetic steps, including under non-aqueous conditions, were shown to incorporate perfluorosulfonic-acid moieties that led to high acidities and high proton conductivities [12]. Fig. 9a shows a schematic diagram and TEM image of such an acid- and aluminosilica-functionalized cubic mesoporous silica film. Fig. 9b compares the temperature-dependent proton conductivities of otherwise identical cubic mesostructured silica membranes after different functionalization steps with respect to Nafion® 117, a commercial perfluorinated sulfonic-acid polymer membrane. The combination of acid- and aluminosilica-functionalization of mesoporous silica films yields proton conduction properties that are less

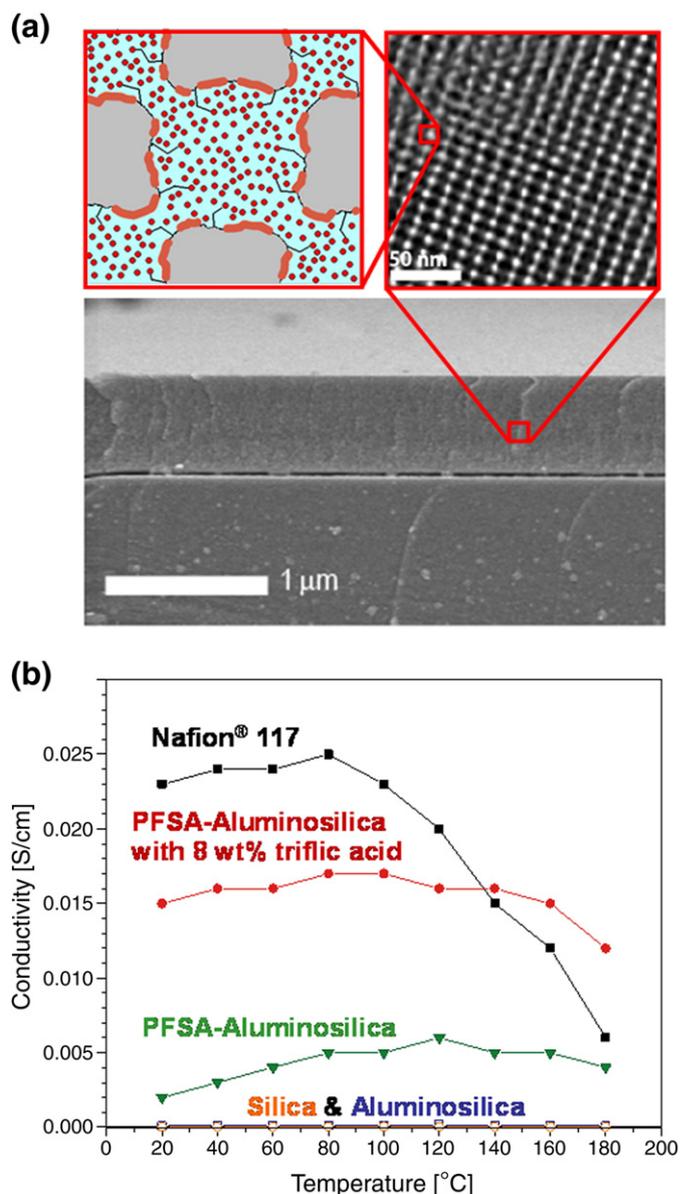


Fig. 9. (a) Schematic diagram of a single cubic mesopore and TEM image of sulfonic-acid-grafted, aluminosilica-grafted mesoporous silica. The grey regions correspond to the mesostructured silica framework, the orange regions to surface-grafted aluminosilica, the red dots to fluorinated sulfonic acid species, and blue background to intrapore water. (b) Temperature-dependent proton conductivities measured at 50% relative humidity for cubic mesostructured silica (yellow) and after functionalization with aluminosilica (blue), perfluorinated sulfonic-acid (PFSA) and aluminosilica (green), and PFSA, aluminosilica, and triflic-acid (red). Results for commercially available Nafion® 117 are shown for comparison [adapted with permission from Ref. [12]].

temperature- and humidity-dependent than Nafion® 117, achieving higher conductivities above ca. 135 °C at 50% relative humidity.

Post-synthetic incorporation of inorganic functional species into mesoporous materials has been widely practiced to introduce oxides, metal complexes, or metal clusters onto the interior surfaces of mesoporous silica. For example, surface grafting of alumina or aluminosilica moieties onto mesoporous silica yields high surface area materials with acidic surface properties. This can be achieved by reacting anhydrous AlCl_3 or $\text{Al}(\text{NO}_3)_3$ with surface silanol groups to form surface aluminosilica moieties [92]. Such grafted aluminosilica species provide surface Brønsted or Lewis acid sites that are more accessible to diffusing reactant species, compared to those obtained by co-condensation (i.e., one-pot) syntheses, which tend to yield sites that are distributed within the frameworks [93–95]. Mesoporous

silicas grafted with titania (TiO_2) moieties similarly exhibit Lewis acid properties that make them promising catalysts [96]. Other common metal oxide functionalities that have been post-synthetically incorporated onto mesoporous silica include zirconia, tungsten oxide, manganese oxide, and vanadia, which often exhibit superior structural integrities, acidities, and catalytic activities to materials prepared by co-condensation [97,98]. Along with common metal oxide functionalities, mesoporous silicas have also been functionalized with rare-earth species, including Eu^{3+} , Er^{3+} , and Yb^{3+} that interact electrostatically with anionic surface sites and which have shown potential as heterogeneous catalysts [99,100]. Post-synthetic incorporation of metal oxides can be further improved by utilizing atomic-layer-deposition methods. Through sequential functionalization of the mesoporous silica surfaces, single layers of various metal oxides may be deposited onto the mesoporous silica framework. Dai and coworkers have demonstrated the use of surface sol-gel processes to deposit sequential layers of different metal oxides, including titania, zirconia, alumina, iron oxide, and germanium oxide, onto mesoporous silica [101,102]. For example, Fig. 10a,b shows schematic representations of hydrolytic and non-hydrolytic processes, respectively, involved in the sequential deposition of sol-gel-derived oxides on hydroxylated surfaces, such as found on the interior of a representative mesopore channel. Using such an approach to control surface and near-surface compositions in mesopore channels is expected to provide substantial versatility toward tuning surface and macroscopic material properties.

A primary advantage of these post-synthetic functionalization methods is that the incorporated inorganic species are localized at the mesopore surfaces, allowing for increased accessibility of the active sites in subsequent catalytic reactions. This is particularly important when the inorganic functional species being incorporated is a precious metal or other expensive compound. For example, Yang et al. recently reported the selective functionalization of nanopore surfaces in mesoporous SBA-15 silica with palladium nanoparticles through a sequence of post-synthetic treatments [103]. Their functionalization steps involved the initial removal of a portion of the structure-directing species with an acid treatment, followed by functionalization of the mesopore surfaces with trimethylchlorosilane, then removal of the remaining structure-directing species from the nanopores, and finally deposition and reduction of dichlorobis(acetonitrile)palladium [$\text{PdCl}_2(\text{MeCN})_2$] to form Pd nanoparticles [103]. Numerous other nanoscale metal clusters or complexes of Pt [104], Rh [105], Os [106], Co [107–109], Mo, W [110], and Ni [111], have also been post-synthetically incorporated into mesoporous materials, frequently with catalysis as the primary motivating interest(s) [112]. An interesting example is the recent report of robust, nanoscale Pt clusters prepared on mesoporous silica that was pre-treated to form a layer of titania on the interior mesopore surfaces [113]. The resulting mesoporous silica- TiO_2 -supported Pt clusters were shown to be active as diesel

oxidation catalysts and were notably thermally stable against sintering at temperatures up to 850 °C.

Similar strategies have been used to prepare nanoscale semiconductor clusters supported on mesoporous silicas. Generally, precursor ions or adsorbed complexes are introduced into the mesopore spaces and subsequently converted into their functional forms. For example, adsorption of germanium hexahydride [Ge_2H_6] at surface silanol groups and subsequent thermal treatment has been shown to lead to the formation of nanometer-size germanium clusters in mesoporous silica [114]. Compound semiconductor clusters, such as PbS [115], CdS [116], and GaN [117,118], have similarly been prepared inside pre-formed mesoporous silica pores by post-synthetic treatments. Such clusters will generally be on the internal mesopore surfaces and accessible to other diffusing and reacting species in the pore channels. In general, functional species that are introduced post-synthetically to surface sites in mesoporous solids may, however, be more prone to leaching or poisoning compared to co-condensed moieties within the inorganic framework.

Finally, a number of important innovations have used mesoporous silica materials as templates for ‘nanocasting’ a diverse range of other materials that do not lend themselves to solution-phase self-assembly syntheses. An important example, first reported by Ryoo and coworkers [119,120,121], demonstrated the use of mesoporous silica frameworks as templates for the synthesis of mesoporous carbon materials. This was achieved by back-filling the mesopores of a calcined silica framework with organic precursor species, followed by pyrolysis in the absence of oxygen to carbon, and acid-etching to remove the silica template. By using aromatic carbon precursors, such as acenaphthene and other substituted naphthalenes, mesoporous carbon materials with graphitic framework structures have been synthesized [121]. Such materials have been used as supports for highly dispersed Pt as anode and/or cathode catalysts in fuel cell applications [122,123]. Mesoporous carbons in general are well suited for a variety of applications, including as conductive catalyst supports, adsorbents for separation processes, and as electrodes or supercapacitors in electrochemical devices [124]. Similar ‘nanocasting’ strategies have been used to prepare an increasingly wide range of materials with mesoporosities [125], including NiO, CeO_2 , Cr_2O_3 , Fe_2O_3 , Mn_2O_3 , and NiFe_2O_4 [126].

2. Summary and outlook

The diversity and combinations of functional species that can be incorporated into a similarly diverse range of compositions of mesostructured inorganic materials is enormous and continuing to grow. Such growth is driven by a wide range of potential applications for these materials, which is also continuing to expand. Both inorganic and organic functional species have been incorporated into mesoporous inorganic materials using co-assembly/co-condensation and/or post-

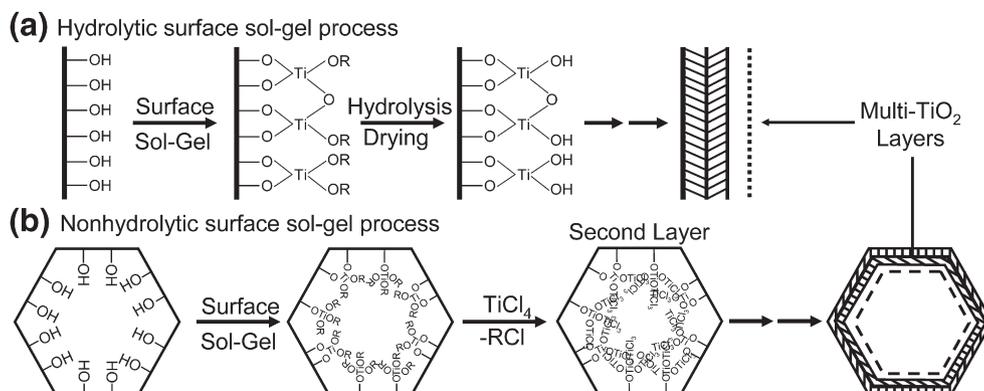


Fig. 10. Schematic diagram of hydrolytic surface sol-gel processes involved in depositing sequences of molecular layers with specific oxide surface compositions (a) on a surface with terminating surface hydroxyl groups and (b) on similar surfaces in a representative mesopore channel [reproduced with permission from Ref. [101]].

synthetic functionalization approaches that rely upon a variety of physicochemical interactions and, especially, interface chemistries. Whether one approach or the other is preferable depends on numerous interrelated considerations, such as the compatibilities of the functional components with the solution or post-synthetic processing conditions, where the functional components are to be distributed and active, and the ultimate applications for which they are intended. Through careful selection of species and conditions, functional moieties can be selectively incorporated within the mesoscale channels, on the internal mesopore surfaces, or within the inorganic frameworks of the mesopore walls. Increasingly, such synthetic control is being exercised in combination with several functional components, including mixed and synergistic organic and inorganic species. The versatility of these expanding functionalization options is providing increased opportunities for the design, development, and control of material compositions, structures, and properties, especially at the molecular level.

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