

Chapter 2

History and Classification of Non-Siliceous Hybrid Materials

Abstract The exploration and creation of advanced materials make vital contributions to the development of human civilization. In other words, the human history is the unceasing innovation of materials since the ancient times. Indeed, our living system, Mother Nature, has provided us plenty of amazing presents such as water, food, and pristine tools. Among them, hybrid materials have gradually received our interest owing to the fantastic physicochemical properties constructed from the intimately integrated organic and inorganic units. Noticeably, the exploration concerning the “organic–inorganic hybrid materials” did have a long history. The establishment of a research system started in the middle of last century. With the rapid development of science and technology, the cognition of hybrid materials can indeed reach the molecular level. Furthermore, organic–inorganic hybrids gradually play vital roles in scientific research, industrial production, and even our daily life. Therefore, it is quite necessary to present the history and development of hybrid materials.

Keywords Classification of hybrid materials • Non-siliceous • Metal phosphonates • Metal sulfonates • Metal carboxylates

2.1 Brief History of Hybrid Materials

Organic–inorganic hybrid materials are typically described as the intimate integration of organic and inorganic moieties at the molecular scale and thus fall within the category of nanocomposite material. Indeed, nature provides suitable conditions for the generation of organic–inorganic hybrids such as mollusk shells, crustacean carapaces, and bone [1]. Deliberate efforts to combine the favorable properties of inorganic units and organic moieties in a single composite material represent an old challenge that started at the beginning of the industrial era. However, the first hybrid material made by humanity appeared only very recently at the geologic time scale. Because of the inherited natural availability and the intrinsic properties including adsorption capability, ion-exchange ability, and

favorable chemical and physical stabilities, hybrid materials on the basis of the organically modified clays represented an indispensable part of human creation and were gradually employed along the history of artistic, social, industrial, and commercial uses [2, 3]. In America for instance, the ancient Maya site contained an impressive collection of fresco paintings characterized by bright blue and ocher colors, which was known as Maya blue. This pigment was resulted from the introduction of a natural organic dye (blue indigo) into the channels of microfibrinous clay (palygorskite) [4]. In China, hybrid clays allowed the production of very thin ceramics thanks to the intercalation of urea inside the interlayer space, facilitating the further delamination which enhanced the resulting plasticity [5].

Organic–inorganic hybrids presented a strong scientific and industrial development over the twentieth century, during which the refined analytical methods and techniques allowed researchers to understand the true natures and structures. The notion of mixing organic and inorganic components has been part of the manufacturing technologies since 1940s [6]. For example, silicones, nanopigments suspended in organic mixtures, and organically templated zeolites provided a diversity of functional hybrid materials that have found application potential in various industrial and scientific research fields. Nonetheless, the concept “hybrid materials” was not proposed at that time. At the end of 1950s, several scientific communities made valuable contributions to the domain of mixed organic–inorganic compounds, which concerned the intercalation of organic units inside the clay and inorganic lamellar compounds [7, 8]. With the establishment of “*chimie douce*,” Livage opened the gates toward a new galaxy of materials in the middle 1980s, namely hybrid materials [9–13], and the concept of “organic–inorganic hybrid nanocomposites” exploded in the 1990s [14, 15]. The period between 1980 and 1995 was particularly fruitful due to the scientific melting pot resulting from the establishment of solgel chemistry (Fig. 2.1). The meeting between material scientists committing to glass and ceramics with chemists mainly working on polymers promoted the tremendous growth in creating a mass of mixed organic–inorganic composites.

Due to the mild conditions involved in the solgel process, solgel-derived siliceous species can be further modified or functionalized with polymers,

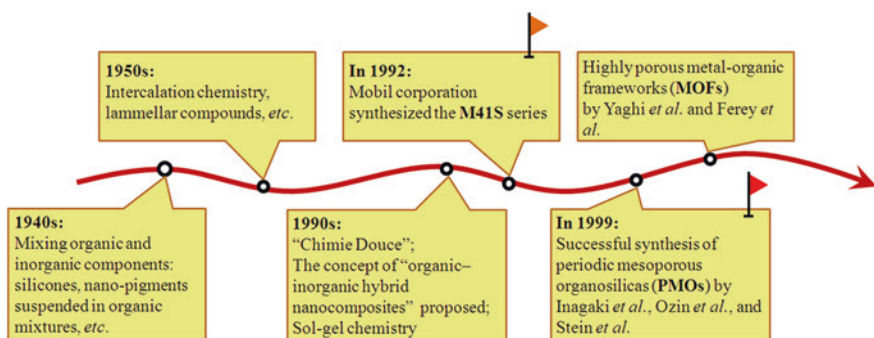


Fig. 2.1 Representative events of the development history for hybrid and porous materials

macromonomers, and numerous organic dyes or biomolecules, leading to the generation of two important materials known as “solgel optics” and biohybrids [16–20]. The synthesis of materials from the polymerization of organosilanes and metal alkoxides [21] and the design of transition-metal oxide-based composites particularly using nanobuilding block methodologies [22–24] represent major advances in the field as well.

The name of “hybrid materials” was evoked around the 1990s when the input of molecular chemistry was obviously creating a “scientific tsunami” in the domain of nanomaterials science [25]. In the period of 1990–1995, the feasibility of adjustment over the textures, structures, and compositions of hybrids was facilitated with the development of the chemistry of bridged and cubic polysilsesquioxane [26–30]. The 1990s were quite productive with the birth of two meaningful research directions depending on different strategies of hybrid chemistry. The first one concerned the synthesis of periodically organized mesoporous materials obtained through solgel condensation templated via the formation of micellar lyotropic assemblies generated by amphiphilic molecules or polymers. These vital works were pioneered by Inagaki et al., Ozin et al., and Stein et al. in 1999 [31–33]. Thereafter, Inagaki and co-workers successfully prepared an ordered benzene–silica via a surfactant-assisted method, showing a hexagonal array of mesopores with a lattice constant of 52.5 Å, and crystal-like pore walls that exhibit structural periodicity with a spacing of 7.6 Å along the channel direction (Fig. 2.2) [34]. The other domain is related to the very interesting family of hybrids known as metal–organic frameworks (MOFs) that can be categorized as nanoporous and crystalline hybrid coordination polymers. In fact, this kind of porous crystalline materials has a long history, and classical examples include transition metal cyanide compounds, such as Hofmann-type clathrates, Prussian blue-type structures, and Werner complexes, and the diamond-like framework *bis*(adiponitrilo)copper(I)

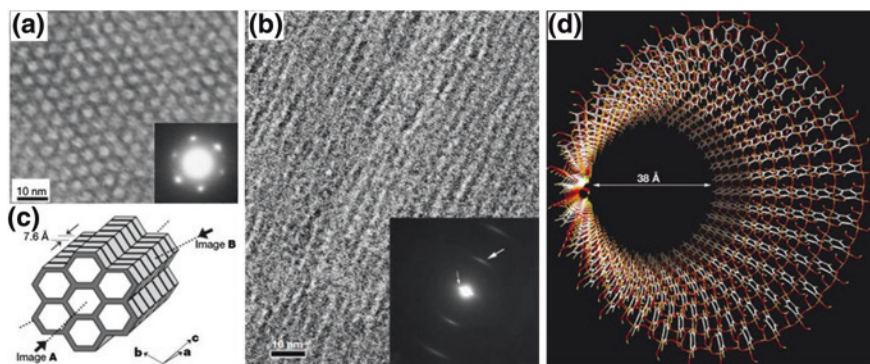


Fig. 2.2 TEM images, electron diffraction patterns, and the resulting structural model of mesoporous benzene–silica (a, b). Schematic model of mesoporous benzene–silica derived from the results of the TEM images and electron diffraction patterns (c). Model showing the pore surface of mesoporous benzene–silica (d). Reprinted with permission from Ref. [34]. Copyright 2002, Nature Publishing Group

organosulfonate groups has remained relatively unstudied, which can be due to the weak interaction or non-interaction capacity with the majority of transition metal ions or complexes.

Nowadays, the research of hybrid materials has shifted toward much more sophisticated nanocomposites with higher added values. The field of organic–inorganic material has been broadened to a multidisciplinary area, including organometallics, colloids and nanoobjects, soft matter and polymers, coordination polymers such as MOFs, sol/gel, aerosol/aerogel, catalysis and interfaces, porous materials, clays and lamellar compounds, nanocomposites, biomaterials, and bio-engineering. Furthermore, a very significant trend is the growing research interest in the rational design of functional hybrids, which extends the field even further. Hybrid materials represent an inexhaustible source of inspiration for us to explore and discover.

2.2 Classification of Non-Siliceous Hybrid Materials

Organic–inorganic hybrids can be defined as nanocomposite materials with intimately linked organic bridging groups and inorganic units. The versatile changes in composition and structure can bring various physicochemical properties that are not the simple sum of the individual contribution of both construction phases. As a result, the nature of the interface and the interactions between the organic and inorganic units can be employed to categorize the hybrids into two main classes [15, 40, 41]. Class I is associated with the hybrid systems that involve no covalent or weak chemical bonding. In this class, only hydrogen bonding, van der Waals or electrostatic forces are usually present. Conversely, Class II hybrid materials show strong chemical interactions between the components, which are formed when the discrete inorganic building blocks are covalently bonded to the organic polymer or inorganic and organic polymers are covalently connected with each other [42, 43]. On the other side, hybrids can also be characterized by the type and size of the organic or the inorganic precursors [15, 40]. Precursors can be two separate monomers or polymers and even covalently linked ones. Because of the mutual insolubility between inorganic and organic components, phase separation will occur. However, homogeneous or single-phased hybrids can be obtained through judiciously choosing bifunctional monomers that contain organic and inorganic components, or by combining both types of components in the phases where one of them is in large excess [44].

The chemical strategies to construct Class II hybrid frameworks are dependent on the relative stability of the interactions between the components and the chemical linkages that connect different components. PMOs represent the typical examples of Class II hybrids. The stable Si–C bonds under hydrolytic conditions allow for the easy incorporation of a large variety of organic bridges in the silica network during the solgel process. Nowadays, the potential of hybrid materials is further strengthened due to the fact that many of them are entering various

markets. From the academic and industrial point of view, the increasing impact of hybrid materials science can be summarized following the arborescent representation (Fig. 2.4). New systems should be aimed at high levels of sophistication and miniaturisation, recyclability, eco-friendliness, and cost efficiency.

Recently, the research focus has been turned toward metal phosphonates, sulfonates, and carboxylates. A diversity of organophosphonic, organosulfonic, and organocarboxylic acids and corresponding derivatives (i.e., salts and esters) has been discovered in nature. Judicious design of the organic bridging groups can introduce desirable properties into the hybrid frameworks. The different reactivity of coupling molecules leads to structural diversity and physicochemical peculiarities of the resultant hybrid materials and may provide decisive advantages in the

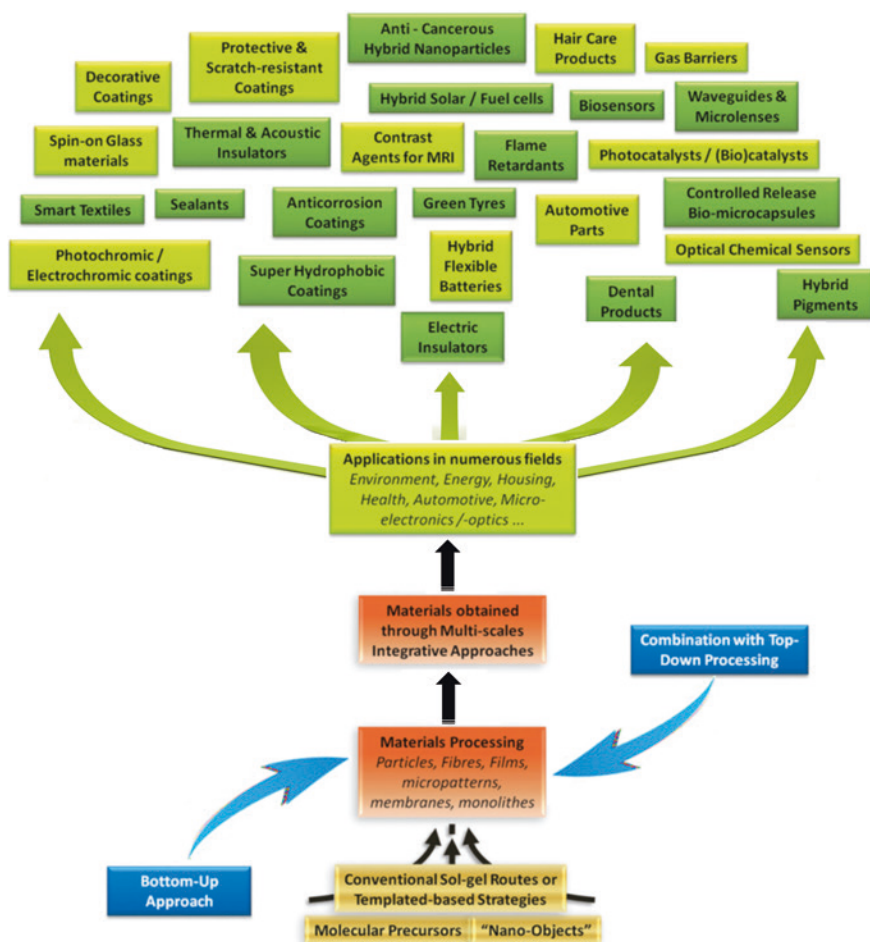


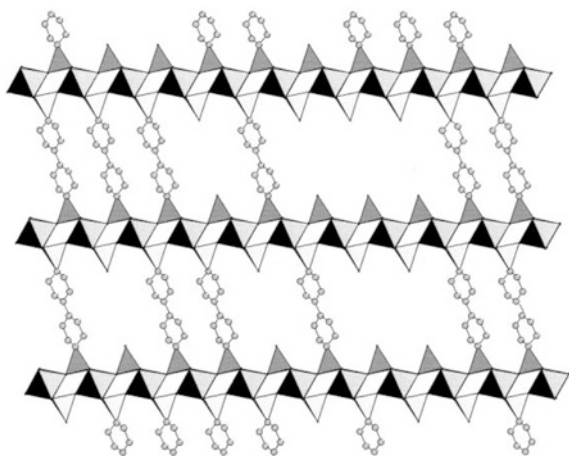
Fig. 2.4 Arborescence representation of hybrid materials. Reprinted with permission from Ref. [11]. Copyright 2011, Royal Society of Chemistry

synthesis of homogeneous hybrids. The homogeneous and efficient incorporation of organic functional groups into the framework of the materials can be realized, allowing for uniform physicochemical properties from the external surface to the internal skeleton.

Metal phosphonate chemistry is originated from the corresponding inorganic phosphate counterparts. In the beginning, gels were refluxed in strong H_3PO_4 and crystallized into what later came to be known as α -zirconium phosphate (α -ZrP) [45]. This compound has a clay-like structure in which the ZrO_6 octahedra are sandwiched between layers of phosphate tetrahedral. Dines et al. first conceived of producing porous materials by cross-linking the α -zirconium phosphate-type layers using diphosphonic acids, $\text{H}_2\text{O}_3\text{P-R-PO}_3\text{H}_2$, where R may be an alkyl or aryl group [46]. The strategy was to choose the cross-linking groups that are large and then space them such that different size of pores would result. However, the area subtended by a phosphate group on the α -ZrP layer was 24 \AA^2 . Given the fact that an alkyl or aryl group spaced every 5.3 \AA apart on the layer occupies most of the area between pillars, there should be no microporosity. To overcome this restriction, the Dines group used phosphorous acid as a spacer group, together with biphenyl as the R group. The idea was to space the biphenyl pillars two or three positions apart, thus creating microporosity. Clearfield and co-workers contributed a lot to the intimately relevant work concerning diphosphonate derivatives [47], which contains 2D sheets of ZrO_6 octahedra sandwiched between phosphate (or phosphonate) layers, which were akin to many other inorganic clays. Porous zirconium diphosphonates are synthesized by combining both a rigid diphosphonate (such as biphenylene bis(phosphonate)) and phosphite (HPO_3^-) or phosphate, where the average pore size could be adjusted by varying the ratio of acids used in the synthesis [48]. Figure 2.5 illustrates a possible structure for nanoporous zirconium diphenylenebis(phosphonate)/phosphate.

One important advantage of this approach is that materials with pores in the range of micropores and mesopores may be obtained. That is to say, an advantage

Fig. 2.5 An idealized structure of a porous zirconium phosphonate. ZrO_6 octahedra are shown in gray, PO_3C tetrahedra in light gray, and carbon atoms as light gray spheres



of the relatively small crystallite size and flat-plate morphology leads to the resulting materials with both nano- and mesoporosity. There has been some work to add functionality to these materials through the phosphonate used in the synthesis. Vermuelen and Thompson used viologens, rigid organic molecules of the formula $(\text{H}_2\text{O}_3\text{PCH}_2\text{CH}_2\text{-bipyridinium-CH}_2\text{CH}_2\text{PO}_3\text{H}_2)$, to bridge zirconium phosphonate layers [49]. These molecules have potentially useful photoinduced charge separation properties, and the presence of two positive charges on the amines in the bridge leads to the incorporation of anions into the framework for charge balance. Although the optical properties of the resulting phase were intriguing, the structure was dense and differed significantly from that normally encountered in zirconium phosphonate chemistry [50]. However, substitution of a fraction of the viologen diphosphonate with phosphoric acid resulted in porous materials [51] with ordered channels [52]. Owing to the tunable pore sizes, easy functionalization, and moderate thermal stability, metal phosphates/phosphonates become one of the most promising hybrid materials.

The metal-ligand coordinate bonds between donor and acceptor molecules have been exploited to generate infinite framework structures. For the synthesis of porous materials, networks are often envisioned where rigid organic molecules and metal atoms or clusters replace bonds and atoms in classical inorganic structures. Copper tetra(4-cyanophenyl) methane contains two types of tetrahedral nodes; Cu^+ coordinated to 4-cyano groups and the methane center in the organic ligand [53]. Together, these define a tetrahedral network with the same topology as the diamond structure with phenyl groups replacing carbon-carbon bonds. Yaghi has been instrumental in applying this methodology to carboxylate systems. But the inability of these solids to maintain permanent porosity and avoid structural rearrangements upon guest removal or guest exchange has been an obvious shortcoming. Carboxylate-based metal-organic frameworks that exhibit permanent porosity have now been prepared [54–56]. The first such solid was MOF-5, which consists of Zn^{2+} and 1,4-benzenedicarboxylate and has a microporous volume larger than any known zeolite [54]. There are now annually hundreds of papers describing MOFs, most of which possess highly complex structures. The Férey group has prepared many open framework carboxylates. The reactions carried out hydrothermally at 220 °C, and HF additions could achieve sufficient crystallinity for structure solutions from powders of new Cr(III) compounds [57]. Subsequently, Férey et al. [58, 59] prepared two additional chromium terephthalates containing pores of 25–29 Å and a surface area of about 3,100 m² g⁻¹ (Langmuir).

In addition to metal phosphonates and carboxylates, metal sulfonates represent another significant member of non-siliceous hybrid family. The coordination chemistry of the sulfonic groups has been less thoroughly investigated than that of carboxylic and phosphonic ones, probably due to the weakly coordinating behavior usually attributed to the sulfonate ligand. Nevertheless, the sulfonic group has a wide variety of possible coordinative modes and has been reported to form several types of layered or pillared layered compounds [60–62] with silver, alkali and alkaline earth metal ions, as well as transition metals and lanthanide(III) ions.

Noticeably, the majority of transition metal aqua complexes with sulfonate counter anions show that the sulfonate group cannot readily displace water from the coordination sphere of the metal ion [63]. However, a stable solid can be yielded when suitably soft metal cations are employed, including alkali ions, larger alkaline earth ions, and silver(I). The common feature of these ions is that none of them have stringent preferences with respect to coordination number or geometry.

As compared with the carbon atoms in the carboxylic groups, the central atoms of the sulfonic and phosphonic acids are able to accommodate more than eight electrons in the outer electron shell, which accounts for a greater bonding flexibility in these groups [64–66]. Nonetheless, the proton of the sulfonic group is more easily dissociable than the proton of the carboxylic and phosphonic functional groups and thus in this respect the sulfonic acids are stronger than their phosphonic and carboxylic counterparts. On the other hand, sulfonic acids can fully deprotonate at very low pK_a , causing serious problem with their stability. This implies the relatively weak coordination interactions between the sulfonate anions and metal cations, which make the frameworks insufficiently robust to sustain permanent porosity [39, 64]. In comparison with their sulfonate and carboxylate analogs, metal phosphonates exhibit much higher thermal and chemical stability due to the strong affinity of organophosphonic linkers to metal ions, making them promising in the fields of energy conversion, adsorption/separation, catalysis, biotechnology, and so forth [67, 68]. As to phosphonates and sulfonates, the coordination chemistry is quite similar, though the corresponding coordination is less predictable owing to more possible ligating modes and three probable states of protonation relative to the carboxylate bridging groups. Typical coordination modes between organic linkages and metal ions are illustrated in Fig. 2.6. For a single phosphonate/sulfonate group, each oxygen atom possesses the capacity to bridge more than one metal center. While formally a single phosphonate/sulfonate oxygen atom can bind to three metal centers, more typically, the oxygen

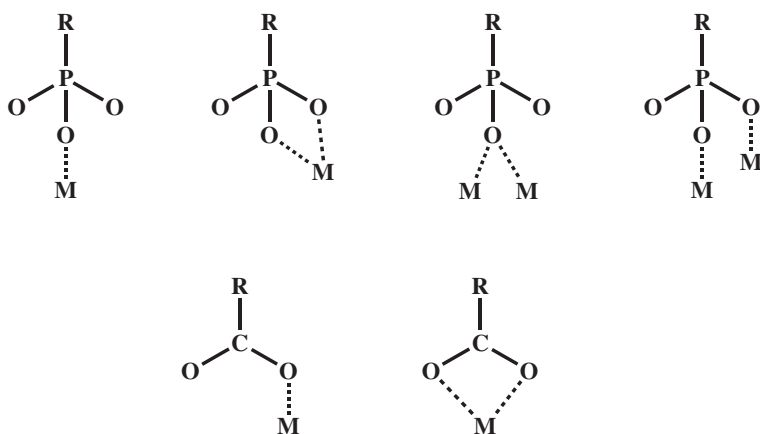


Fig. 2.6 Typical coordination modes of phosphonates and carboxylates

atoms of a phosphonate/sulfonate linker will bridge two metal ions maximum. The large bridging numbers are unattainable with other commonly employed classes of ligands such as carboxylates [69]. Noticeably, whereas the ligating directionality of a carboxylate group is confined to a plane, the spherical ligating shape of the electron density that encompasses a phosphonate/sulfonate group allows metal coordination to an additional dimension, which serves to further increase the connectivity of the network and favor the formation of a robust structure. This coordinative flexibility in terms of bridging modes, combined with the roughly spherical shape of the PO_3/SO_3 unit, has led us to draw the analogy between a phosphonate/sulfonate group and a “Ball of Velcro.” It should be noted that the chelation capacity of the organic linkages to metal ions usually follows the sequence of phosphonates > carboxylates > sulfonates [39, 64]. Therefore, the predisposition of simple metal phosphonates to a dense layered motif makes forming high surface area materials a challenge [70]. Numerous methodologies have thus been developed to incorporate considerable mesoporosity in the non-siliceous hybrid framework.

2.3 General Strategies of Incorporating Organic Groups

2.3.1 Surface Functionalization

Surface modification can have a significant influence on the materials behavior at the nanoscale and can lead to nano-/mesostructures with novel properties. Post-synthetic functionalization or grafting refers to the subsequent modification of the inner surfaces of mesostructured inorganic phases with organic groups (Fig. 2.7).

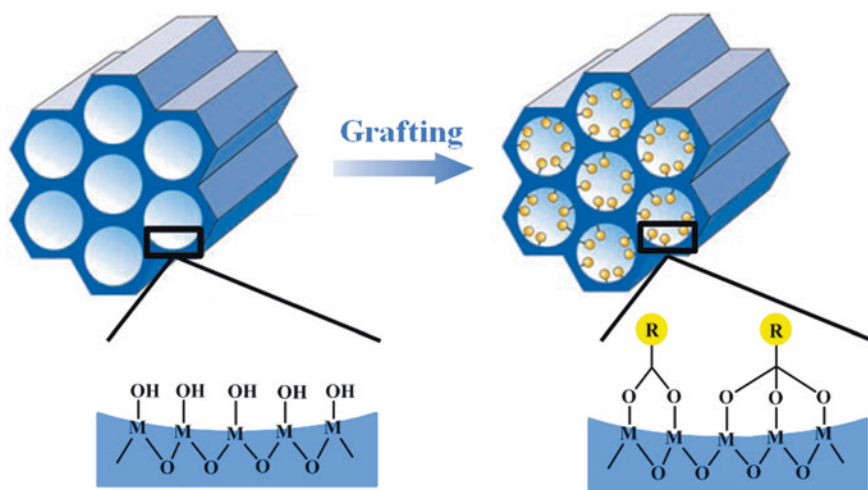


Fig. 2.7 Surface modification of mesoporous inorganic frameworks, R represents organic functional group

The absence of homocondensation between organic functional groups and the easy formation of organic–inorganic layers allows the straightforward and reproducible formation of robust monolayers on an extremely wide range of substrates. On one hand, the original physicochemical properties of the bulk materials can be preserved. On the other hand, diverse novel functional groups with special properties including bioactivity, electronic conductivity, and photochemical properties can be incorporated, showing the capacity to be further modified as well.

Mallouk et al. proposed to employ bisphosphonic acids for the formation of metal phosphonate multilayers on surfaces [71]. Later on, Guerrero et al. reported the anchoring of phosphonate and phosphinate coupling molecules on titania particles [72], with the use of six organophosphorous compounds: phenylphosphonic and diphenylphosphonic acids, their ethyl esters, and their trimethylsilyl esters. In the case of organophosphorus coupling molecules, reaction with the surface involves not only the condensation with surface hydroxyl groups but also the coordination of the phosphoryl on Lewis acid sites, and the cleavage of the M–O–M bonds depending on the anchoring conditions. The hydrolytic stability of organic monolayers supported on metal oxides was also investigated [73]. It was found that the monolayers of $C_{18}H_{37}P(O)(OH)_2$ demonstrated a better hydrolytic stability than other octadecyl organosilane modifiers. The high stability of these phosphonate monolayers is explained by the strong specific interactions of the phosphonic acid group with the surfaces of metal oxides. On the basis of the above-mentioned literature reports, the feasibility of grafting phosphonic acids onto metal oxides is fully confirmed. Soler-Illia et al. prepared organic modified transition metal oxide mesoporous thin films and xerogels by using dihexadecyl phosphate (DHDP), monododecyl phosphate (MDP), and phenyl phosphate (PPA) [74]. Dramatic differences were observed for the incorporation of organophosphonates in mesoporous versus non-mesoporous solids, demonstrating that the organic functions were incorporated inside the pore system. Incorporation behaviors were also observed depending on the mesostructure; cubic 3D mesostructures are more accessible than their 2D hexagonal counterparts [75]. Furthermore, the functionalized pores were found to be further accessible to other molecules (solvent and fluorescent probes) or ions (i.e., Hg^{2+}), opening the way for sensor or sorption applications.

Besides the monophosphonic acids mentioned above, Yuan and co-workers reported the use of a series of amine-based organophosphonic acids and their salts as organophosphorus coupling molecules in the one-step synthesis and the application exploration of oxide–phosphonates and metal organophosphonate hybrid materials with mesopores and hierarchical meso-/macroporous architectures [76, 77]. Claw molecules of ethylene diamine tetra(methylene phosphonic acid) (EDTMP) and diethylene triamine penta(methylene phosphonic acid) (DTPMP) were anchored to the titania network homogeneously. The synthesized titania–phosphonate hybrids showed irregular mesoporosity formed by the assembly of nanoparticles in a crystalline anatase phase. The synthesis process is quite simple in comparison with the previously reported two-step solgel processing involving first the formation of P–O–M bonds by non-hydrolytic condensation of a metal

alkoxide with a phosphonic acid and then the formation of the M–O–M bonds of the metal oxide network by hydrolysis/condensation of the remaining alkoxide group. The burdensome work to remove the residual organic solvent was not needed.

Organic “capping” agents containing terminal carboxylic groups have been widely used to prepare quantum dots or nanocrystals [78–81]. The capping agent limits the size of the nanoparticles by preventing further particle growth and agglomeration during synthesis and can also be useful in controlling the particle reactivity, imparting solubility or packing characteristics, and protecting both nanoparticle and its environment from destructive interactions. If different functional groups are anchored on the carboxylate linkages, variation of tremendous physicochemical properties can be realized. To date, reports regarding carboxylated mesoporous material are rare because the relatively low stability of C–O–M may prohibit their practical applications.

Anchoring of the functional groups is driven by condensation or by complexation. Correspondingly, grafting can be covalent (practically irreversible) or coordinative (partially reversible). Stronger grafting groups are needed for sensing and catalysis, while more labile functions are meaningful in the quest for controlled delivery or reversible signaling as well. The grafting strength will be also important for the even incorporation of the R function along the pore systems. Indeed, there are two key factors that control the homogeneous incorporation of organic functions: the accessibility of the pore systems; and the reactivity of the organic functional molecules toward the pore surface. The first factor will essentially depend on the possibility of pore interconnection, and the symmetry and orientation of the pore mesostructure. Noticeably, pore blocking can occur during the post-functionalization process.

2.3.2 *Direct Synthesis*

An alternative method to synthesize organically functionalized mesoporous hybrid is the cocondensation method (one-pot synthesis). It is possible to prepare mesostructured hybrid phases by the cocondensation of metallic precursors and organic functional groups in the presence or absence of structure-directing agents, leading to materials with organic residues anchored covalently and homogeneously in the pore walls (Fig. 2.8) [64, 65, 82]. By using structure-directing agents known from the synthesis of pure mesoporous silica phases (e.g., MCM or SBA silica phases), organically modified silicas can be prepared in such a way that the organic functionalities project into the pores. These will be elaborately discussed in Chap. 3.

Since the organic functionalities are direct components of the mesostructured hybrid matrixes, pore blocking is not a problem in the cocondensation method. Furthermore, the organic linkers are generally more homogeneously distributed than in materials synthesized involving the grafting process. The tendency toward homocondensation reactions, which is caused by the different hydrolysis and

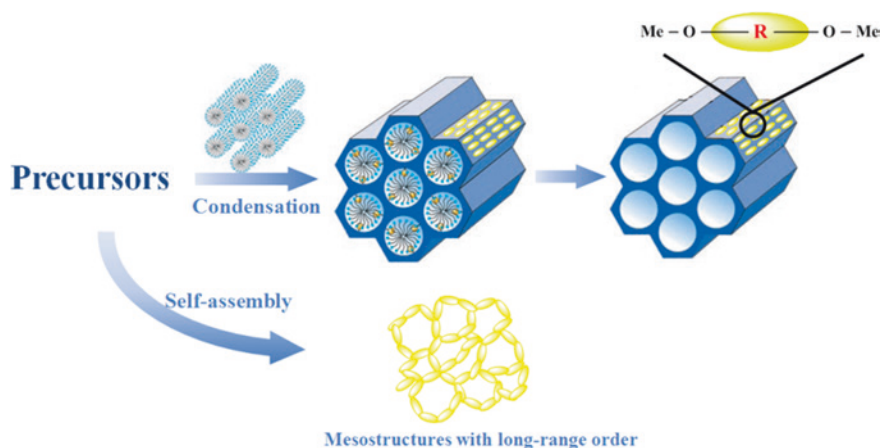


Fig. 2.8 General synthetic pathway to mesoporous non-siliceous hybrid materials

condensation rates of the structurally different precursors, is a constant problem in cocondensation because the homogeneous distribution of different organic functionalities in the framework cannot be guaranteed. Furthermore, an increase in loading of the incorporated organic groups and the complexity of organic linking groups can lead to a deterioration of the mesoporosity including the pore diameter, pore volume, and specific surface areas. Purely methodological disadvantage that is associated with the cocondensation method is that care must be taken not to destroy the organic functionality during the removal of the surfactant. This is why commonly extractive methods are favorable, while calcination is not suitable in most cases.

References

1. S. Mann, *Biomimetic Materials Chemistry* (Wiley-VCH, Weinheim, 1997)
2. E. Ruiz-Hitzky, P. Aranda, M. Darder, G. Rytwo, Hybrid materials based on clays for environmental and biomedical applications. *J. Mater. Chem.* **20**, 9306–9321 (2010)
3. F. Bergaya, G. Lagaly, *Handbook of Clay Science*, Elsevier Science, 2013
4. H. Berke, The invention of blue and purple pigments in ancient times. *Chem. Soc. Rev.* **36**, 15–30 (2007)
5. A. Weiss, A secret of Chinese porcelain manufacture. *Angew. Chem. Int. Ed.* **2**, 697–703 (1963)
6. B. Arkles, Commercial applications of sol-gel-derived hybrid materials. *MRS Bull.* **26**, 402–407 (2001)
7. M. Darder, P. Aranda, E. Ruiz-Hitzky, Bionanocomposites: a new concept of ecological, bioinspired, and functional hybrid materials. *Adv. Mater.* **19**, 1309–1319 (2007)
8. E. Ruiz-Hitzky, P. Aranda, M. Darder, G. Rytwo, Hybrid materials based on clays for environmental and biomedical applications. *J. Mater. Chem.* **20**, 9306–9321 (2010)
9. C. Laberty-Robert, K. Vallé, F. Pereira, C. Sanchez, Design and properties of functional hybrid organic-inorganic membranes for fuel cells. *Chem. Soc. Rev.* **40**, 961–1005 (2011)

10. D. Avnir, D. Levy, R. Reisfeld, The nature of the silica cage as reflected by spectral changes and enhanced photostability of trapped Rhodamine 6G. *J. Phys. Chem.* **88**, 5956–5959 (1984)
11. C. Sanchez, P. Belleville, M. Popalld, L. Nicole, Applications of advanced hybrid organic-inorganic nanomaterials: from laboratory to market. *Chem. Soc. Rev.* **40**, 696–753 (2011)
12. J. Livage, M. Henry, C. Sanchez, Sol-gel chemistry of transition metal oxides. *Prog. Solid State Chem.* **18**, 259–341 (1988)
13. C. Sanchez, J. Livage, M. Henry, F. Babonneau, Chemical modification of alkoxide precursors. *J. Non-Cryst. Solids* **100**, 65–76 (1988)
14. C. Sanchez, F. Ribot, Proceedings of the first European workshop on hybrid organic-inorganic materials. *New J. Chem.* **18**, 987–988 (1993)
15. C. Sanchez, F. Ribot, *New J. Chem.* **18**, 1007–1047 (1994)
16. F. Surivet, T.M. Lam, J.P. Pascault, Q.T. Pham, Organic-inorganic hybrid materials. 1. Hydrolysis and condensation mechanisms involved in alkoxysilane-terminated macromonomers. *Macromolecules* **25**, 4309–4320 (1992)
17. F. Surivet, T.M. Lam, J.P. Pascault, C. Mai, Organic-inorganic hybrid materials. 2. Compared structures of polydimethylsiloxane and hydrogenated polybutadiene based ceramics. *Macromolecules* **25**, 5742–5751 (1992)
18. T. Fournier, I. Salabert, T.H. Tran-Thi, H. Ali, J. Van-Lier, C. Sanchez, Charge transfer dynamics of donor-acceptor systems in solutions and sol-gel matrices. *J. Sol-Gel. Sci. Technol.* **2**, 737–740 (1993)
19. C. Sanchez, B. Lebeau, F. Chaput, J.P. Boilot, Optical properties of functional hybrid organic-inorganic nanocomposites. *Adv. Mater.* **15**, 1969–1994 (2003)
20. D. Avnir, T. Coradin, O. Lev, J. Livage, Recent bio-applications of sol-gel materials. *J. Mater. Chem.* **16**, 1013–1030 (2006)
21. P. Audebert, C. Sanchez, Modified electrodes from hydrophobic alkoxide silica gels-Insertion of electroactive compounds and glucose oxidase. *J. Sol-Gel. Sci. Technol.* **2**, 809–812 (1993)
22. G. Guerrero, J.G. Alauzun, M. Granier, D. Laurencin, P.H. Mutin, Phosphonate coupling molecules for the control of surface/interface properties and the synthesis of nanomaterials. *Dalton Trans.* **42**, 12569–12585 (2013)
23. C. Sanchez, G.J.A.A. Soler-Illia, F. Ribot, T. Lalot, C.R. Mayer, V. Cabuil, Designed hybrid organic-inorganic nanocomposites from functional nanobuilding blocks. *Chem. Mater.* **13**, 3061–3083 (2001)
24. L. Rozes, C. Sanchez, Titanium oxo-clusters: precursors for a Lego-like construction of nanostructured hybrid materials. *Chem. Soc. Rev.* **40**, 1006–1030 (2011)
25. L. Nicole, C. Laberty-Robert, L. Rozes, C. Sanchez, Hybrid materials science: a promised land for the integrative design of multifunctional materials. *Nanoscale* **6**, 6267–6292 (2014)
26. K.J. Shea, D.A. Loy, Bridged polysilsesquioxanes. Molecular-engineered hybrid organic-inorganic materials. *Chem. Mater.* **13**, 3306–3319 (2001)
27. K.J. Shea, J. Moreau, D.A. Loy, R.J.P. Corriu, B. Boury, in *Functional Hybrid Materials*, ed. by P. Gomez-Romero, C. Sanchez (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2004), pp. 50–85
28. G. Cerveau, R.J.P. Corriu, Some recent developments of polysilsesquioxanes chemistry for material science. *Coord. Chem. Rev.* **178**, 1051–1071 (1998)
29. R.M. Laine, Nanobuilding blocks based on the $[\text{OSiO}_{1.5}]_x$ ($x = 6, 8, 10$) octasilsesquioxanes. *J. Mater. Chem.* **15**, 3725–3744 (2005)
30. R. Duchateau, Incompletely condensed silsesquioxanes: versatile tools in developing silica-supported olefin polymerization catalysts. *Chem. Rev.* **102**, 3525–3542 (2002)
31. S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, Novel mesoporous materials with a uniform distribution of organic groups and inorganic oxide in their frameworks. *J. Am. Chem. Soc.* **121**, 9611–9614 (1999)
32. T. Asefa, M.J. MacLachlan, N. Coombs, G.A. Ozin, Periodic mesoporous organosilicas with organic groups inside the channel walls. *Nature* **402**, 867–871 (1999)
33. B.J. Melde, B.T. Holland, C.F. Blanford, A. Stein, Mesoporous sieves with unified hybrid inorganic/organic frameworks. *Chem. Mater.* **11**, 3302–3308 (1999)

34. S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, An ordered mesoporous organosilica hybrid material with a crystal-like wall structure. *Nature* **416**, 304–307 (2002)
35. Y. Kinoshita, I. Matsubara, T. Higuchi, Y. Saito, The crystal structure of bis(adiponitrilo)copper (I) nitrate. *Bull. Chem. Soc. Jpn* **32**, 1221–1226 (1959)
36. A. Clearfield, C.V.K. Sharma, B.L. Zhang, Crystal engineered supramolecular metal phosphonates: crown ethers and iminodiacetates. *Chem. Mater.* **13**, 3099–3112 (2001)
37. R.C. Finn, R. Lam, J.E. Greedan, J. Zubietta, Solid-state coordination chemistry: structural influences of copper-phenanthroline subunits on oxovanadium organophosphonate phases. Hydrothermal synthesis and structural characterization of the two-dimensional materials $[\text{Cu}(\text{phen})(\text{VO})(\text{O}_3\text{PCH}_2\text{PO}_3)(\text{H}_2\text{O})]$, $[\{\text{Cu}(\text{phen})\}_2(\text{V}_2\text{O}_5)(\text{O}_3\text{PCH}_2\text{CH}_2\text{PO}_3)]$, and $[\{\text{Cu}(\text{phen})\}_2(\text{V}_3\text{O}_5)(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2(\text{H}_2\text{O})]$ and of the three-dimensional phase $[\{\text{Cu}(\text{phen})\}_2(\text{V}_3\text{O}_5)(\text{O}_3\text{PCH}_2\text{PO}_3)_2(\text{H}_2\text{O})]$. *Inorg. Chem.* **40**, 3745–3754 (2001)
38. D.B. Mitzi, Thin-film deposition of organic-inorganic hybrid materials. *Chem. Mater.* **13**, 3283–3298 (2001)
39. G.K.H. Shimizu, R. Vaidhyanathan, J.M. Taylor, Phosphonate and sulfonate metal organic frameworks. *Chem. Soc. Rev.* **38**, 1430–1449 (2009)
40. P. Judeinstein, J. Rault, B. Alonso, C. Sanchez, Macroscopic–microscopic mechanical relaxation behavior of hybrid organic–inorganic materials. *J. Polymer Sci. Part B Polymer Phys.* **39**, 645–650 (2001)
41. R.J.P. Corriu, Chimie douce: wide perspectives for molecular chemistry. A challenge for chemists: control of the organisation of matter. *New J. Chem.* **25**, 2–2 (2001)
42. T.Z. Ren, Z.Y. Yuan, L.B. Su, Thermally stable macroporous zirconium phosphates with supermicroporous walls: a self-formation phenomenon of hierarchy. *Chem. Commun.* 2730–2731 (2004)
43. E.G. Vrieling, T.P.M. Beelen, R.A. van Santen, W.W.C. Gieskes, Mesophases of (bio)polymer-silica particles inspire a model for silica biomineralization in diatoms. *Angew. Chem. Int. Ed.* **41**, 1543–1546 (2002)
44. C. Sanchez, L. Rozes, F. Ribot, C. Laberty-Robert, D. Grosso, C. Sassoie, C. Boissiere, L. Nicole, “Chimie douce”: a land of opportunities for the designed construction of functional inorganic and hybrid organic-inorganic nanomaterials. *C. R. Chim.* **13**, 3–39 (2010)
45. A. Clearfield, Z. Wang, P. Bellinghausen, Highly porous zirconium aryldiphosphonates and their conversion to strong bronsted acids. *J. Solid State Chem.* **167**, 376–385 (2002)
46. M.D. Dines, P.M. DiGiacomo, K.P. Callahan, P.C. Griffith, R.H. Lane, R.E. Cooksey, in *Chemically Modified Surface in Catalysis and Electrocatalysis*, ed. by J. S. Miller, Chap 12. ACS Symposium Series 192. American Chemical Society, Washington, DC (1982)
47. A. Clearfield, Unconventional metal organic frameworks: porous cross-linked phosphonates. *Dalton Trans.* **28**(44), 6089–6102 (2008)
48. A. Clearfield, Organically pillared micro- and mesoporous materials. *Chem. Mater.* **10**, 2801–2810 (1998)
49. L.A. Vermeulen, M.E. Thompson, Stable photoinduced charge separation in layered viologen compounds. *Nature* **358**, 656–658 (1992)
50. D.M. Poojary, L.A. Vermeulen, E. Vicenzi, A. Clearfield, M.E. Thompson, Structure of a novel layered zirconium diphosphonate compound: $\text{Zr}_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{-viologen-CH}_2\text{CH}_2\text{PO}_3)\text{F}_6\cdot 2\text{H}_2\text{O}$. *Chem. Mater.* **6**, 1845–1849 (1994)
51. L.A. Vermeulen, M.E. Thompson, Synthesis and photochemical properties of porous zirconium viologen phosphonate compounds. *Chem. Mater.* **6**, 77–81 (1994)
52. H. Byrd, A. Clearfield, D. Poojary, K.P. Reis, M.E. Thompson, Crystal structure of a porous zirconium phosphate/phosphonate compound and photocatalytic hydrogen production from related materials. *Chem. Mater.* **8**, 2239–2246 (1996)
53. M. O’Keeffe, M. Eddaoudi, H. Li, T. Reineke, O.M. Yaghi, Frameworks for extended solids: geometrical design principles. *J. Solid State Chem.* **152**, 3–20 (2000)
54. H. Li, M. Eddaoudi, M. O’Keeffe, O.M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **402**, 276–279 (1999)

55. B. Chen, M. Eddaoudi, S.T. Hyde, M. O'Keeffe, O.M. Yaghi, Interwoven metal-organic framework on a periodic minimal surface with extra-large pores. *Science* **291**, 1021–1023 (2001)
56. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Systematic design of pore size and functionality in isorecticular MOFs and their application in methane storage. *Science* **295**, 469–472 (2002)
57. F. Millange, C. Serra, G. Férey, Synthesis, structure determination and properties of MIL-53as and MIL-53ht: the first Cr^{III} hybrid inorganic-organic microporous solids: Cr^{III}(OH) center·{O₂C-C₆H₄-CO₂}·{HO₂C-C₆H₄-CO₂H}_x. *Chem. Commun.* 822–823 (2002)
58. K. Barthelet, J. Marrot, D. Riou, G. Férey, A breathing hybrid organic-inorganic solid with very large pores and high magnetic characteristics. *Angew. Chem. Int. Ed.* **41**, 281–284 (2002)
59. G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Suable, I. Margiolaki, A chromium terephthalate-based solid with unusually large pore volumes and surface area. *Science* **309**, 2040–2042 (2005)
60. D.J. Hoffart, S.A. Dalrymple, G.K.H. Shimizu, Structural constraints in the design of silver sulfonate coordination networks: three new polysulfonate open frameworks. *Inorg. Chem.* **44**, 8868–8875 (2005)
61. Q. Li, X. Liu, M.L. Fu, C.G. Guo, Two luminescent alkali-silver heterometallic sulfonates. *Inorg. Chim. Acta* **395**, 2147–2153 (2006)
62. Z.M. Sun, J.G. Mao, Y.Q. Sun, H.Y. Zeng, A. Clearfield, Synthesis, characterization, and crystal structures of three new divalent metal carboxylate-sulfonates with a layered and one-dimensional structure. *Inorg. Chem.* **43**, 336–341 (2004)
63. A.P. Côté, G.K.H. Shimizu, The supramolecular chemistry of the sulfonate group in extended solids. *Coord. Chem. Rev.* **245**, 49–64 (2003)
64. Y.P. Zhu, T.Z. Ren, Z.Y. Yuan, Mesoporous non-siliceous inorganic-organic hybrids: a promising platform for designing multifunctional materials. *New J. Chem.* **38**, 1905–1922 (2014)
65. Y.P. Zhu, T.Y. Ma, Y.L. Liu, T.Z. Ren, Z.Y. Yuan, Metal phosphonate hybrid materials: from densely layered to hierarchically nanoporous structures. *Inorg. Chem. Front.* **1**, 360–383 (2014)
66. V. Videnova-Adrabinska, *Coord. Chem. Rev.* **251**, 1987–2016 (2007)
67. A. Clearfield, Z. Wang, Organically pillared microporous zirconium phosphonates. *J. Chem. Soc. Dalton Trans.* 2937–2947 (2002)
68. M. Pramanik, A. Bhaumik, Self-assembled hybrid tinphosphonate nanoparticles with bimodal porosity: an insight towards the efficient and selective catalytic process for the synthesis of bioactive 1,4-dihydropyridines under solvent-free conditions. *J. Mater. Chem. A* **1**, 11210–11220 (2013)
69. G.K.H. Shimizu, G.D. Enright, C.I. Ratcliffe, K.F. Preston, J.L. Reid, J.A. Ripmeester, A layered silver sulfonate incorporating nine-coordinate Ag-I in a hexagonal grid. *Chem. Commun.* 1485–1486 (1999)
70. K. Maeda, Metal phosphonate open-framework materials. *Micropor. Mesopor. Mater.* **73**, 47–55 (2004)
71. H. Lee, L.J. Kepley, H.G. Hong, T.E. Mallouk, Phase transformations in mesostructured silica/surfactant composites: mechanisms for change and applications to materials synthesis. *J. Am. Chem. Soc.* **110**, 618–620 (1988)
72. G. Guerrero, P.H. Mutin, A. Vioux, Anchoring of phosphonate and phosphinate coupling molecules on titania particles. *Chem. Mater.* **13**, 4367–4373 (2001)
73. S. Marcinko, A.Y. Fadeev, Hydrolytic stability of organic monolayers supported on TiO₂ and ZrO₂. *Langmuir* **20**, 2270–2273 (2004)
74. P.C. Angelomé, G.J.A.A. Soler-Illia, Organically modified transition-metal oxide mesoporous thin films and xerogels. *Chem. Mater.* **17**, 322–331 (2005)
75. P.C. Angelomé, G.J.A.A. Soler-Illia, Ordered mesoporous hybrid thin films with double organic functionality and mixed oxide framework. *J. Mater. Chem.* **15**, 3903–3912 (2005)
76. X.J. Zhang, T.Y. Ma, Z.Y. Yuan, Titania-phosphonate hybrid porous materials: preparation, photocatalytic activity and heavy metal ion adsorption. *J. Mater. Chem.* **18**, 2003–2010 (2008)

77. T.Y. Ma, X.J. Zhang, Z.Y. Yuan, High selectivity for metal ion adsorption: from mesoporous phosphonated titanias to meso-/macroporous titanium phosphonates. *J. Mater. Sci.* **44**, 6775–6785 (2009)
78. G.H.T. Au, W.Y. Shih, W.H. Shih, High-conjugation-efficiency aqueous CdSe quantum dots. *Analyst* **138**, 7316–7325 (2013)
79. Z. Hu, M. Åhrén, L. Selegård, C. Skoglund, F. Söderlind, Maria Engström, X. Zhang, K. Uvdal, Highly water-dispersible surface-modified Gd₂O₃ nanoparticles for potential fuel-modal bioimaging. *Chem. Eur. J.* **19**, 12658–12667 (2013)
80. A. Hassinen, R. Gomes, K.D. Nolf, Q. Zhao, A. Vantomme, J.C. Martins, Z. Hens, Surface chemistry of CdTe quantum dots synthesized in mixtures of phosphonic acids and amines: formation of a mixed ligand shell. *J. Phys. Chem. C* **117**, 13936–13943 (2013)
81. M.H. Zarghami, Y. Liu, M. Gibbs, E. Gebremichael, C. Webster, M. Law, p-Type PbSe and PbS quantum dot solids prepared with short-chain acids and diacids. *ACS Nano* **4**, 2475–2485 (2010)
82. T.Y. Ma, Z.Y. Yuan, Metal phosphonate hybrid mesostructures: environmentally friendly multifunctional materials for clean energy and other applications. *ChemSusChem* **4**, 1407–1419 (2011)

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