New Opportunities for Functional Materials from Metal Phosphonates

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ABSTRACT: Hybrid functional materials and their derivatives are propelling a technological revolution in chemistry, materials science, and other disciplines. The performance of hybrid materials touches many fundamental aspects of energy conversion and storage, sustainable environment, and life sciences. Based on their rich chemistry, diverse metal phosphonates and their derivatives can be synthesized. These materials manifest various structures and enable new functionalities, which are hardly attainable in simple mixtures or other multicomponent materials. Here, we highlight and discuss the fascinating materials design innovations that organophosphonates can enable, with an eye on energy, environment, and biological applications involving specific functionality under different stimuli.

Designing advanced materials based on organic and inorganic chemistry has historically promoted the innovation and development of a spectrum of fields in science and technology. Organic (*e.g.*, polymers and plastics) and inorganic materials (*e.g.*, ceramics and glasses) are omnipresent in every corner and every aspect of our daily life.[1] We are in the process of a scientific revolution in environment, energy, sustainability, and information technology, and many of these classical materials are gradually approaching their performance limits. Therefore, new engineered materials are needed for these emerging applications, which can be achieved by combining the organic and inorganic components to generate new functionalities.

Organic-inorganic hybrid materials feature molecularly intimate conjunction of diverse organic and inorganic components (**Figure 1**).[1,2] In sharp contrast to additive functionality of physical composites and multicomponent materials, the framework homogeneity and structural periodicity of hybrid materials constitute a crucial scientific realm straddling the chemical, physical, and material disciplines, wherein fundamentally new functions can be created via taking advantage of interaction modes and strengths of organic linkages.[3-5] Besides traditional ligands like carboxylic acids, sulfonic acids, alkoxy groups, and polyazaheteroaromatic ligands (*e.g.*, triazolates, tetrazolates), the role of organophosphonic acids in generating hybrid materials is considerably attractive, since organophosphonic acids can form stronger bonds and more coordination modes than the former ligands do with metal nodes or metal-based clusters.[6,7] The robust metal phosphonate frameworks, in terms of thermal/mechanical stability and insolubility even in highly acidic medium, ensure the feasibility of pre- or post-

functionalization, thereby ensuring their applications in relatively harsh conditions, *e.g.*, in heterogeneous catalysis, ion exchange, proton conductors, corrosion protection, and selective adsorption/separation.[8-14]

Given the uniform topology schemes and controllable geometries of building blocks for metal phosphonates and their corresponding derivatives, the "design rules" dominating the structure-performance relationship lie in the fundamental chemistry and materials science of organophosphonic acids.[15,16] From the chemistry point of view, the control over the solubility difference, reaction activity, molecular dimensions, and chemical compositions for different organophosphonic acids can deliver various materials with designable skeletons and porosity. From the materials science perspective, metal phosphonates can potentially perform as a platform to gain the mechanistic insights of the related hybrid systems, in which the confined space initiates the host-guest interactions involving ions and molecules, carriers, and excitons. Herein, based on the organophosphonic chemistry, we discuss the design methodologies of metal phosphonates and the derivatives as well as the cutting-edge functionality development, accompanied with the identification of the fundamental issues and the potential applications.

PROPERTIES OF ORGANOPHOSPHONIC LIGANDS

To be specific, each phosphonic group ($-PO_3H_2$) of the organophosphonic ligands contains three oxygen atoms that can coordinate with up to nine metal atoms, the versatile coordination modes of which lead to diverse metal phosphonates with different structural types and fascinating properties.[17,18] Moreover, the reaction degree
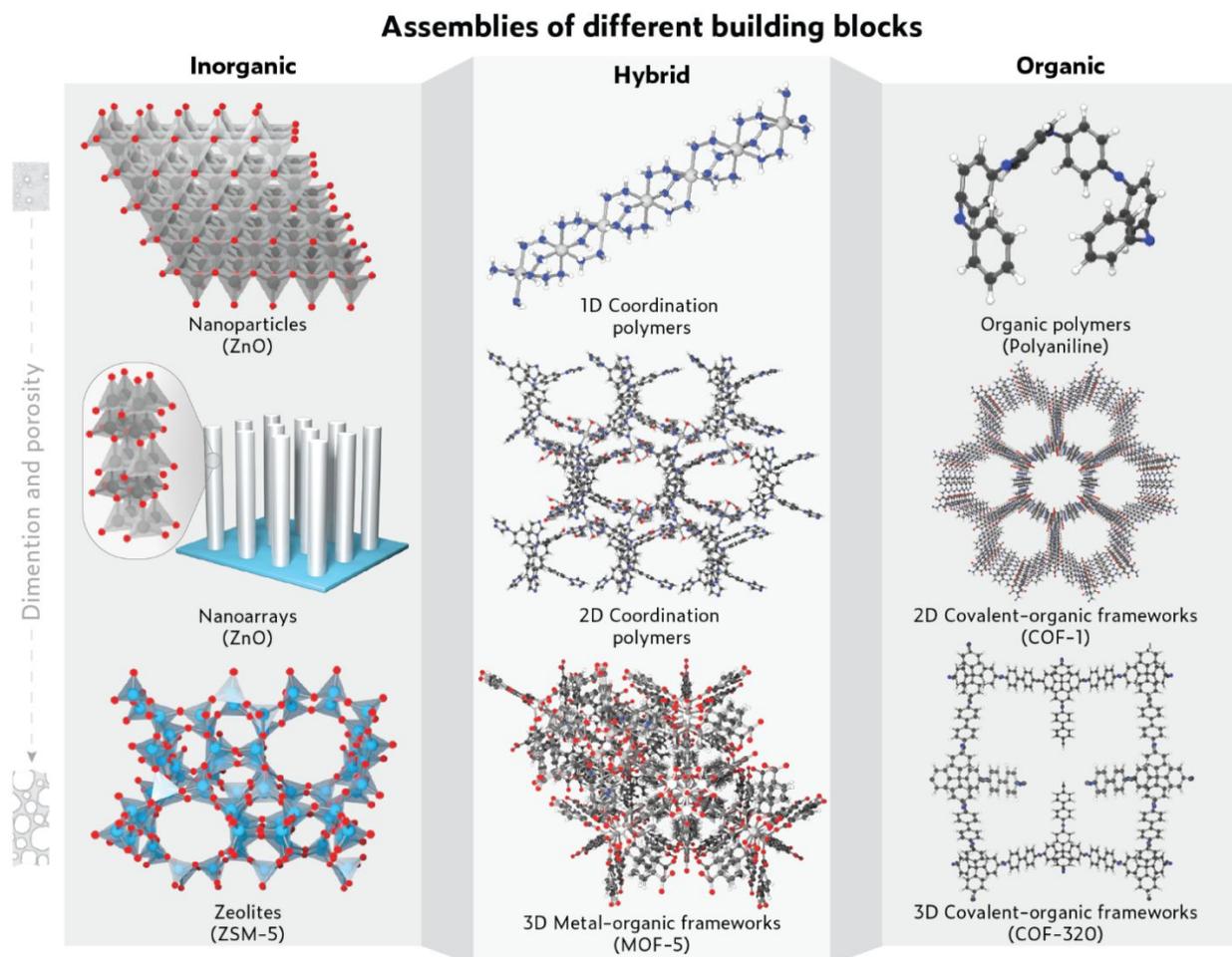
Figure 1. Schematic showing diverse building units that can be used to construct different architectures: inorganic, organic, and organic-inorganic hybrid structures. Many related systems like mesoporous (organo)silicas, active carbons, and supermolecules are not demonstrated herein.

/rate between organophosphonic groups and metal ions relies on the following factors: synthetic conditions (*e.g.,* temperature, pH value), substituents on the ligands, and the nature of organophosphonic acids (*e.g.,* protonation/deprotonation degree).[19-21] The changes of these conditions can result in diverse coordination modes and arrangements that the resulting structures can take, further revealing the difficulty in predicting the coordination chemistry of organophosphonic ligands.

On the other hand, the strong binding ability of organophosphonic groups can deliver promising stability of metal phosphonates against air, water, and thermal treatment, which ensures their long-term stability in different applications. For some applications like aqueous energy conversion and storage (*e.g.,* supercapacitors, batteries) and liquid adsorption and separation, their stability against water matters. Generally, the stability depends on the valence of metal ions,[7,8] as the reactivity and coordination ability of metallic salts increase with the valence of metal ions. In aqueous media, the hydrolysis rate and the simultaneous polymerization reaction with organophosphonic acids become less controllable upon increasing the valence of metal ions, thus leading to the insolubility increase of the final metal phosphonates. Monovalent metal phosphonates are highly soluble in water, while the solubility of divalent metal phosphonates is significantly depressed, even though they can potentially crystalline as supramolecular structures. The solubility decreases with the increase of valence of incorporated metal centers. For example, trivalent and tetravalent metal phosphonates are highly insoluble, even in highly acidic solutions. Accordingly, compared to monovalent or divalent metal phosphonates, trivalent and tetravalent metal phosphonates have attracted more attention to be developed for stable and efficient energy storage, sensors, liquid-phase catalysis, *etc*. However, in terms of their synthesis processes, trivalent and tetravalent metal phosphonates tend to precipitate easily in the form of poorly ordered materials with much less crystallization. This can not only pose a challenge to obtain sufficient lattice structures due to the limited reaction reversibility during the synthesis, but also make the illustration of structure-performance relationship highly challenging.

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SYNTHETIC REACTIONS AND METHODOLOGIES

Typically, metal phosphonates are termed as unconventional metal-organic frameworks (MOFs) due to their similarities in chemical compositions and functionalities, whereas metal phosphonates are poorly crystalline and structurally less characterized.[6-8] It should be noted that the greater thermal stability and lower solubility even in acidic solutions for metal phosphonates endow them with the ability for easy post-functionalization, thus finding applications in the field of ion exchange, catalysis, and adsorption. These features make metal phosphonates "unconventional" compared to the conventional MOFs that are highly crystalline and structurally well-characterized but less stable. The bottom-up strategy starting with pristine organophosphonic acids and metallic salts has been used to prepare metal phosphonates frequently and widely. To improve on the structural features (*e.g.*, porosity, crystallinity) of metal phosphonates, the key is to take advantage of the physicochemical properties of these precursors to achieve their modification and thus to control their self-assembly process.

Regarding periodic molecular or lattice structures of metal phosphonates, the synthesis experience and design principles extracted from the non-phosphonate MOFs and even covalent organic frameworks (COFs) might be applied to the metal phosphonates (**Figure 1**). Assembly of building moieties to construct well-developed topology for metal phosphonates is easier than that to construct COFs, as the formation of COFs involves the covalent bonds with the least reaction reversibility.[22] Compared to non-phosphonate MOFs, generating well-defined topology and porosity for metal phosphonates become more difficult due to the stronger binding ability of the organophosphonic acids with metal units.[6-8] As such, several chemical strategies have been proposed to resolve the synthesis difficulty: (1) tuning the molecular structures of organophosphonic acids to adjust their reactivity to metallic sources,[23] such as introducing phosphate esters in the organophosphonic linkers to enable partial acidification, which can weaken their reactivity with trivalent or tetravalent metal precursors; (2) employing anchillary ligands to decrease the number of free coordination sites and inhibit the formation of layered frameworks, which can enhance the reaction reversibility and the solubility of the resultant complexes with appropriate substituents incorporated in the metal phosphonates;[24] (3) the enlarging effect of small-cluster precursors with replaceable ligands after interacting with the organophosphonic groups;[25] and (4) extending the geometry of the organic linkers (*e.g.*, organophosphonic acids with sterically hindered lipophilicity or bulky functional groups).[26]

Additionally, the control over the reactivity (*e.g.*, hydrolysis, condensation) of metallic precursors is another significant way to tune the resultant properties of the organic-inorganic networks (*e.g.*, composition uniformity, stability) of metal phosphonates. For example, a fast reaction rate, particularly for those transition metal salts with high valences (*e.g.*, V^{4+}, Ti^{4+}), can result in forming discontinuous phases like composites of metal oxides and phosphonates or hybrid interphases.[27] Generally, the reactivity of metal precursors in aqueous media follows the sequence: inorganic metal salts > metal alkoxides with alkoxy moieties > metal alkoxides with bulky moieties (*e.g.*, methyl > ethyl > propyl). In order to decrease the reaction rates of metal precursors and to improve the reaction reversibility, a step beyond is to utilize organic reagents with chelating capacity like acetic acid, ethylenediamine, crown ether, and catechol, as well as to use mixed or even pure non-aqueous systems.[28,29] The reactivity balance between organic linkages and inorganic metal precursors significantly influences crystallization, compositional continuity, structural regularity, and skeleton stability. Accordingly, the combination of building blocks with specific geometries and metal precursors with controlled reactivity can generate various metal phosphonates with different porosities and compositions, thus delivering the molecular designability to achieve a material platform for architectural and functional design. Herein, we discuss the recent progresses of design methods and designable physicochemical properties of metal phosphonates, and also focus on the optimization of their performance in the area of adsorption/separation, catalysis, and energy conversion and storage.
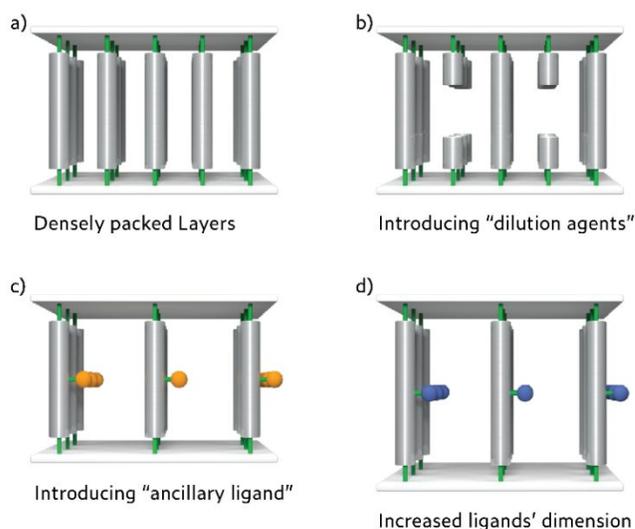

Figure 2. Schemes of metal phosphonates and the different strategies that can be used to increase their porosity. (a) Conventional layered metal phosphonates with limited space or porosity due to the densely packed organophosphonic pillars (shown as the long cylinders that connect the two layers of metal phosphonates). (b) Introducing "dilution agents" (demonstrated as short cylinders) between the organophosphonic pillars. (c) Grafting ancillary ligands (orange balls) onto the organophosphonic ligands to prevent the close-pillar disposition. (d) Increasing the dimensions of the rigid organophosphonic linkers to create porous structures (blue balls: additional ancillary ligands).

DESIGN ON A HIERARCHICAL SCALE

Combining the aforementioned synthetic chemistry with the topological characteristics allows for the design of different metal phosphonates on a hierarchical scale, *i.e.*, targeted frameworks (atomic scale), pores with controllable symmetry and connectivity (nano-/mesoscale), and distinct surface chemistry and functionality (macroscale). In this context, metal phosphonates featuring different physicochemical properties can be synthesized, ensuring a complicated yet well-defined surface chemistry. This determines the functions for specific applications.

Porosity along with skeleton adjustment. One of the defining characteristics to synthesize metal phosphonates for potential practical applications is their porosity (**Figure 1** and **2**), the improvement of which can provide channels for enhanced diffusion within the bulk of metal phosphonates and expose abundant active sites. Unfortunately, organophosphonic groups in the frameworks of the metal phosphonates studied at the early stage are too crowded to leave free space, affording densely packed layered structures with poor or even no porosity (**Figure 2a**).[30,31] This largely prohibits the direct utilization and the functional design of metal phosphonates because of the hardly accessible active sites with the bulk. Generally, there are three strategies to improve their porosity: (1) phosphoric and small alkyl/aryl organophosphonic acids can perform as "dilution agents" that are inserted in between the organophosphonic linkers to create interlayer porosity (**Figure 2b**);[32] (2) ancillary ligands grafted on the phosphonates can overcome the "close-pillar disposition" to provide intralayer voids (**Figure 2c**);[33] and (3) upon increasing the molecular length of the rigid organophosphonic linkers, extended porous structures can be created, while shape of the building blocks determines the pore topology (**Figure 2d**).[34] According to experimental results, the porosity could be continuously adjusted from micropores (using phosphoric/organophosphonic intercalation molecules) to mesopores (usually less than 5 nm through extending the geometrical dimension of organophosphonic acids). However, multifold interdigitation engenders interpenetrated structures, low porosity, and reduced stability upon further enlarging the dimensions of organophosphonic acids.[35,36] Developing new strategies to prohibit structural penetration and enhance porosity are highly promising to design the functionality of metal phosphonates.

Inspired by the templating strategy for designing microporous zeolites and mesoporous (organo)silicas, micellar lyotropic assemblies depending on sol–gel chemistry can direct the ordered packing of metal phosphonates, thereby providing a highly adjustable pore size and symmetry at the mesoscopic level after removing templates.[37] In other words, the size of mesopores depends on the hydrophobic/hydrophilic volume ratios of the supermolecular templates. Compared to the aforementioned template-free methods, the templating method can significantly push the limit of pore size

without deteriorating the frameworks. Generally, oligomeric/ionic surfactants and Pluronic block copolymers direct the formation of mesoporosity in the range of 2–10 nm, while polystyrene-based colloidal templates can generate pores of 20–50 nm. Moreover, swelling the dynamic liquid-crystal using aromatic or aliphatic hydrocarbons can tune the mesopores in a different way, filling the gap between 10–20 nm.[37-39] Modulating the packing parameters and interaction modes between metal phosphonates and surfactant molecules, through adjusting parameters like protonation degree of phosphonates and hydrophobic segments of the polytopic bridging blocks, can control the phase diagram of the surfactant molecules and thus the pore symmetry, for instance, 2D (*e.g.*, lamellae, hexagonal), 3D (body/face-centered cubic), and even bicontinuous mesophases.[40,41] Importantly, the pores in the synthesized metal phosphonates can be utilized for efficient insertion and diffusion of guest species with internal active sites being accessible. As such, metal phosphonates can be designed to feature a broad range of pore sizes from micropores, mesopores to even macropores using aforementioned template-free and templating methods. In the following part, we discuss how the porosity and pore environment of metal phosphonates can influence their applications in CO_2 capture, heavy metal ion adsorption, and selective separation.

CO_2 capture/separation is critical for developing low-carbon economy, while porous metal phosphonates represent a promising candidate with designed functionality to realize the goals. Intracrystalline microporosity (Figure 2) stabilized by phosphonate monoesters or high-valence metal nodes can provide a moderate CO_2 uptake capacity (1.2–2.5 mmol $g_{adsorbent}^{-1}$ at 1 bar).[42,43] Although the pore walls of these metal phosphonates have not been chemically modified, the small size of intracrystalline pores (< 2 nm) created by ancillary functional groups or extended organophosphonic ligands reveals that they have decent CO_2 capture capacities due to the high surface area. Incorporation of basic functional groups like azine and amine in the organophosphonic ligands can not only improve the CO_2 uptake amount (~ 3.0 mmol $g_{adsorbent}^{-1}$ at 1 bar), but also enhance the CO_2 selectivity in the presence of either methane or N_2.[44] This is due to the increased adsorption enthalpy and affinity towards CO_2. Nonetheless, the small size of micropores limits CO_2 transport kinetics. In fact, the optimization of uptake ability, kinetics, and selectivity can be potentially achieved on hierarchically porous metal phosphonstes, *i.e.*, preserving micropores with pore width similar to the kinetic diameter of N_2 or methane to simulate molecular sieving effect while creating hierarchical porosity (mesopores or even macropores through the templating methods) to provide open frameworks for enhanced mass transfer.[37,45] Nonetheless, the investigation of mesoporous or hierarchically porous metal phosphonates for CO_2 capture has been scarcely investigated to the best of our knowledge. In comparison with the state-of-the-art MOFs and COFs, there remains a

long way to go for porous metal phosphonates in terms of capacity enhancement, kinetics model establishment, control over the pore environment to improve CO_2 adsorption capacity and efficiency, and the exploration of high-pressure CO_2 adsorption.

Different from gas phase adsorption, the competitive behaviors from different solutes and solvents make liquid-phase adsorption process more complicated. The hydrophilicity of the pore surface should be the first case to be concerned, otherwise pores cannot be accessed and refilled effectively. Functional groups, such as hydroxyl, amino and sulfonic,[46,47] can be pre- or post-anchored onto organophosphonic ligands, which can increase the hydrophilicity, act as active sites for adsorption, and be used for further functionalization (*vide infra*). Here, we take the removal of environmentally unfriendly heavy metal ions (*e.g.*, Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Cr^{3+}) as an example using porous metal phosphonates as the solid adsorbents. These heavy metal ions can be coordinated by these functional groups on the surface of porous metal phosphonates, following a Langmuir behaviour.[48] This is an indicator of monolayer adsorption behavior. Therefore, a well-developed porosity (mesoporosity and/or hierarchical porosity) together with large surface areas are the prerequisites for high uptake capabilities (generally falling in the range of 5–50 μmol $g_{adsorbent}^{-1}$ at room temperature) and fast adsorption kinetics. Thanks to their robust frameworks, metal phosphonates can be easily regenerated through proton exchange and reused multiple times. The stability and recycling performance of metal phosphonates are obviously superior to the other MOFs counterparts. Noticeably, there remains a lot of underdeveloped areas. For example, different heavy metal ions show different hydrated structures, leading to a variety of hydration diameters (normally < 1 nm). A precise control over the micropore size using the strategies demonstrated in Figure 2 can potentially realize the ion screening effect so as to maximize the adsorption capacities. Furthermore, these metal ions are adsorbed by porous metal phosphonates through the coordination interaction with the organic functional groups exposed on the pore surface, though the active functional groups for specific heavy metal ions remain unclear. Future studies can be focused on the adjustment of organophosphonic ligands with designed compositions and functionalities so as to control pore environment. This can help to illustrate the adsorption mechanism of heavy metal ions, thus making the optimizations of adsorption capacities and selectivity possible.

In regard to the adsorption of organics (*e.g.*, biomolecules, small molecule organics), it is of scientific significance in developing biotechnology, medicine, and analytical technology. Similar to heavy metal ion adsorption, organics adsorption/separation involves liquid phase adsorption processes. Accordingly, surface chemistry concerning charge states, hydrophobicity/hydrophilicity, and polarity should be tailored via designing organophosphonic acids with specific functions, aiming at high adsorption efficiency and selectivity. For example, pH-responsive piperazine group (switching between cationic and neutral network upon changing pH conditions) could achieve a controlled release of anionic photosensitizer for photodynamic therapy of tumors.[49] Under pH conditions close to the isoelectric points, the corresponding adsorption turns to be governed by host–guest hydrophobicity (metal phosphonates)–hydrophobicity (*e.g.*, proteins, enzymes) interactions. Upon using divalent metal (*e.g.*, Ca^{2+}, Mg^{2+}) phosphonates with relatively high solubility, a pH-driven dissolution process of the metal phosphonates could realize controlled release of anti-osteoporosis bisphosphonate drugs.[50] Furthermore, hydrophobicity/hydrophilicity for metal phosphonates can be modulated through different chemical strategies. For example, lengthening the alkyl chains or using aromatic structures can increase the hydrophobic interaction between the channel walls and the nonpolar side chains of biomolecules, leading to increased adsorption/separation capacity.[37] Since biomolecules possess distinct spatial sizes and isoelectric points, the biomolecules can be selectively separated by changing surface states, pore diameters, and even pore structures of metal phosphonates.

The porosity and the corresponding chemical environment inside the metal phosphonates render an interface for the interactions with liquid/gas molecules, ions, and organics. Both periodic and disordered porosity have been successfully introduced into metal phosphonates. According to our experience, periodic porosity provides controllable textual property, large surface area, and abundant active sites, ensuring fast diffusion and high efficiency for adsorption/separation. In contrast, disordered porosity is usually from the random assembly of metal phosphonate nanoparticles, suggesting the straightforward synthesis protocols. The well-developed sol-gel chemistry can be used to control the disordered pore size from mesopore to macropore. However, to the best of our knowledge, the property difference between periodic and disorder porosity and their influence on applications like adsorption and separation have been scarcely studied. Future work can be done using the combination of experimental characterizations and theoretical simulations, aiming at achieving better performing porous metal phosphonates.

Particularly, regulating the pore size and dimension and introducing functional groups into the organophosphonic linkers is critical for designing high-performance adsorbents. Pore surface engineering (*e.g.*, click reactions) is an efficient strategy to functionalize the pore walls with desired functional groups and controlled densities of active sites, which would tune the interaction types and strength between the metal phosphonates and guest adsorbates, thus controlling the adsorption/separation efficiency and selectivity. Furthermore, high-pressure gas uptake, dynamic adsorption models, and *in-situ* experiments involving the metal phosphonate adsorbents are still underdeveloped compared to the conventional MOFs, but worthy of further and deep exploration.

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Complementary design of compositions and functionality. The fundamental principles discussed above focus on the controllable synthesis of porous metal phosphonates with well-structured frameworks. Particularly, the complementary design of chemical compositions and functionalities offers a promising approach to integrate the compositional and structural peculiarities, thereby attaining synergistic effects and optimizing the target functionality to a different level. Further concerns on how to introduce additional functional moieties into metal phosphonates should be paid attention.
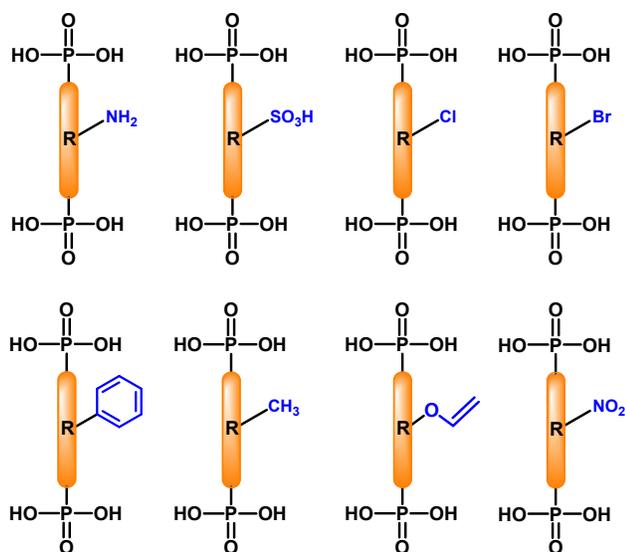

Figure 3. A series of organophosphonic ligands with different functional groups, where R represents the organic functional group in the ligands. Some of them (*e.g.*, –NH$_2$ and –SO$_3$H) have been successfully introduced into the metal phosphonate hybrid frameworks. It is reasonable to envision that others remaining and new functional groups can be incorporated through controllable synthesis or post treatment to extend the functionalities of metal phosphonates even further.

The bottom-up method is straightforward but challenging to introduce functionality into metal phosphonates, in which the functional moieties need to be directly grafted onto the organophosphonic ligands prior to the preparation of metal phosphonates. In this respect, it is advantageous to make the functional moieties (*e.g.*, –NH$_2$, –SH, –SO$_3$H$_2$, –X) (**Figure 3**) be homogeneously distributed on the pore walls without disturbing the structural regularity significantly. For this purpose, the design principles for porosity and framework stability should be fulfilled simultaneously. Unfortunately, this brings difficulties in rational synthesis of organophosphonic ligands with exceptional functions without sacrificing the framework chemical/hydrothermal stability. Aiming at the diversity-oriented design of functional metal phosphonates, a modified bottom-up strategy and even a post-modification method should be developed to introduce desirable functional groups with preferred densities.

The organic-inorganic hybrid nature and inherent porosity of metal phosphonates make them a unique platform for functionality design, through which synergistic effects and optimized performance for energy storage and heterogeneous catalysis can be achieved. Here, we first discuss the proton conductivity of pristine metal phosphonates prepared from the bottom-up method. It is well know that better proton-conducting materials can be used as hydrogen fuel cell electrolytes, especially when these proton-conducting materials are resistant to water.[51,52] Herein, a designable materials platform for alternative proton conductors can be realized on metal phosphonates with tunable and robust frameworks. However, two shortcomings that prohibit the enhancement of proton conductivity occur to the classical metal phosphonates: (1) microporosity with a confined space can spatially lock the proton carriers; and (2) intrinsic proton carriers (*e.g.*, defective P–OH sites from uncoordinated organophosphonic ligands) only afford the proton conductivities at the level of 10^{-5}–10^{-4} S cm^{-1}, still too low to satisfy practical application needs like hydrogen fuel cells and direct-ethanol fuel cells (DEFC).[53] Incorporating mesoporosity or hierarchical porosity through ligand extension or template-assisted methods can not only allow high-content loading of proton carriers to generate hydrogen-bonding networks, but also ensure an optimal proton transportation distance between any donor-acceptor pairs for accelerated H$^+$ ion conduction. Typically, there are three strategies to improve the pristine proton conductivity. The first one is using chemically removable reagents (*e.g.*, organoamines or esters) to protect the P–OH sites ahead of the reaction between organophosphonic acids and metal precursors. The second method is post-modification (*e.g.*, sulfonation to introduce –SO$_3$H$_2$). The third method is introducing proton-containing sites like pyridine and bipyridine units onto the pore surface of metal phosphonates. These three ways can synergistically improve the intrinsic and extrinsic proton conductivities. These strategies can improve the proton conductivity to the level of 10^{-3}–10^{-2} S cm^{-1}.[54-57] Noticeably, the overall functionalization should be conducted in a controlled manner to ensure the efficient condensation between organophosphonic acids and metal precursors, *i.e.*, ensuring the framework stability of the metal phosphonates.

The robust framework and the capability to offer intrinsic proton source sources, either by partial protonation of the phosphonate linkers at a low pH value or by incorporating acidic group, make metal phosphonates promising alternatives as proton conductive materials to the classical polymers (*e.g.*, commercial Nafion) and less stable MOFs. Due to their thermal stability, metal phosphonates can perform well even at high temperature (*e.g.*, 150 °C), and their proton conductivity at elevated temperature can reach the level of 10^{-1} S cm^{-1}.[51-57] To further enhance the intrinsic proton conductivities of metal phosphonates,
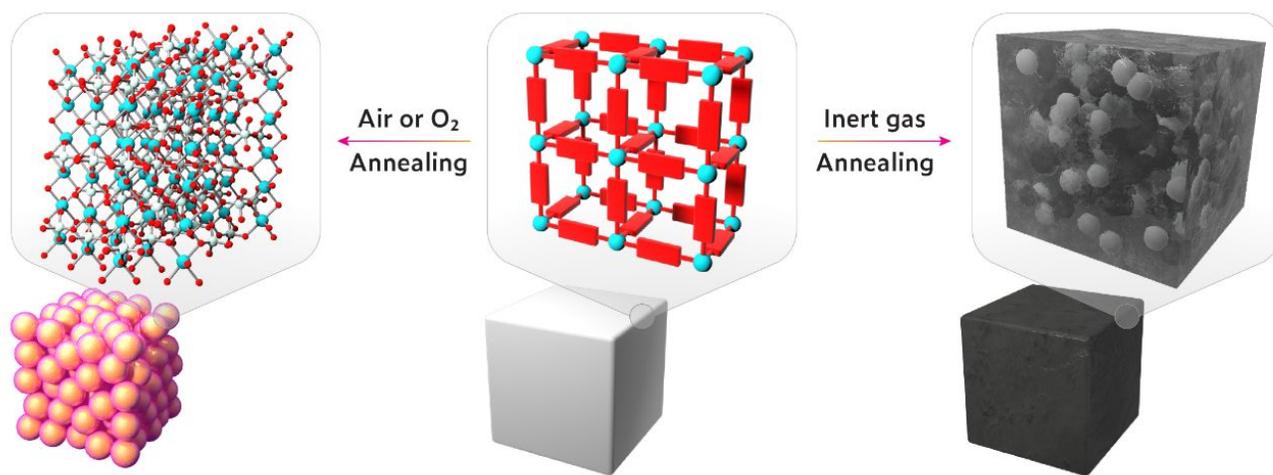
Figure 4. Scheme used for designing metal-phosphonate-related functional materials. Metal phosphonates can perform as sacrificial templates to synthesize (right) carbon composites using inert gas annealing, and (left) metal compounds or single metal compound nanostructures (using $TiPO_4$ as an example) by air or O_2 annealing.

increasing the concentration and the mobility of proton carriers (*e.g.*, uncoordinated P–OH, –COOH, $–SO_3H_2$)[58] may provide a feasible pathway. Noticeably, the concentration of proton carriers relies on the overall acidity of the proton sources, while the proton mobility can be facilitated by the existence of a continuous hydrogen-bonding network that contains protic sites. These can be potentially realized by introducing an appropriate amount of coordination/structural water, hydrophilic guest species, and an open framework with high surface area, and three-dimensional pore connectivity. Another problem needed to be fixed is the lack of crystallinity especially in tetravalent metal phosphonates,[59,60] which makes it difficult to illustrate the exact proton transportation pathways at the atomic scale due to the absence of long-range periodic order. On one hand, using the chemical strategies discussed in the Section of "Synthetic reaction and methodologies" would improve the crystallization degree of the resultant tetravalent metal phosphonates and the periodicity of the structural pores. In this way, the proton transfer pathways and mechanisms can be determined because of the ordered arrangement of the proton-conducting functional groups in the organophosphonic linkers of the metal phosphonate frameworks. On the other hand, featuring facile fabrication processes and mild reaction conditions, amorphous tetravalent metal phosphonates show many promising opportunities for practical applications, either as new proton-conducting host materials or facilitating other processes, though this direction remains undeveloped. The combination of molecular dynamics simulation, neutron scattering, and X-ray synchrotron will help to infer the short-range ordering of the amorphous framework, which provides the opportunities to illustrate the proton-conduction mechanism of the high-valence but stable metal phosphonates. The illustration of proton diffusion mechanisms in both crystalline and amorphous metal phosphonates will provide insightful guidelines to design

better performing proton-conducting metal phosphonates.

Another way to functionalize metal phosphonates through modifying their compositions is to introduce catalytic sites or active components into metal phosphonates, which can produce a novel pattern of heterogeneous catalysts, wherein nanopores perform as nanoreactors. Different from pure inorganic or organic catalysts, such organic-inorganic frameworks of metal phosphonates with controllable chemical compositions at the molecular scale can allow separate reaction steps to occur in close proximity at spatially different active sites and synergistically expedite catalysis. For instance, bifunctional organophosphonic linkages with both acidic P–OH and basic $–NH_2$ could activate aziridine and CO_2, respectively, resulting in considerable conversion and regioselectivity for the CO_2 cycloaddition reaction to yield oxazolidinones.[61] Adjusting the interfaces of the hybrids enables bottom-up tuning of the materials chemistry and even energetics, which can take full advantage of the surface-chemistry-dependent properties in heterogeneous catalysis.

It is well known that MOFs constructed by the most frequently used ligands like carboxylic and polyazaheteroaromatic ligands have been developed as alternative heterogeneous catalysts to traditional catalysts, such as zeolites.[62,63] The catalytic activity of MOFs can be either from the organic ligands, the open metal sites or both. A step further is to embed active guest species, including active metal ions, small metal clusters, and nanoparticles, into the functional empty pores. This post-functionalization method ensures the high accessibility of catalytically active sites, facilitates the efficient transfer of reactants and products, and provides shape- and size-selective catalysis. Compared to conventional inorganic supports like microporous molecular sieve materials with remarkably high chemical and thermal stabilities, MOFs
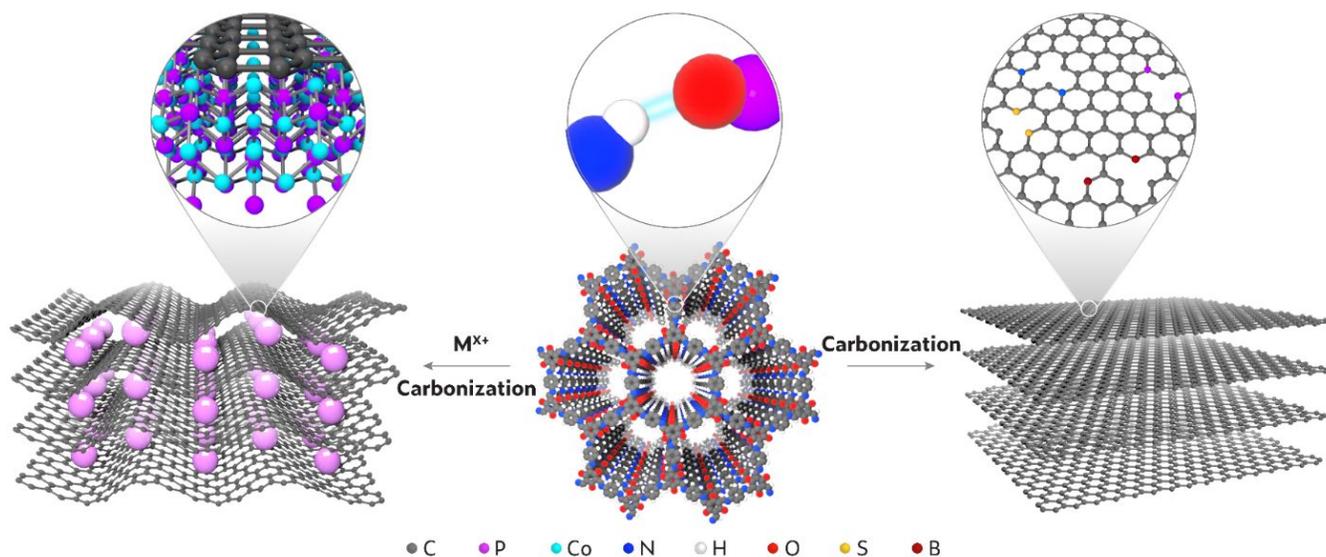
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Figure 5. Based on the acid-base coordination interaction, the organophosphonic and organic base species could induce the formation of polymer-like materials, which can be directly carbonized to chemically doped carbon nanostructures. If metal ions are introduced before the carbonization process, the final products can be metallic compounds that are highly dispersed on the carbonaceous frameworks.

can offset the stability limitations with structural diversity. This allows the introduction of new physiochemical properties, such as strong host-guest interaction to improve catalytic activities. Importantly, the homogeneous distribution of organic linkers in the framework of MOFs together with the controllable porosity allows the uniform loading of identical catalytic species. This is a crucial strategy to enhance activity, yield, selectivity, and stability as well as to achieve the "atomic economy". Importantly, the porosity and organic functional groups (*e.g.*, ethylenediamine bridging) from the organophosphonic linkers promote the efficient insertion and immobilization of catalytically active metal cations, such as Zn^{2+}, Cu^{2+}, Pd^{2+}, and Au^{3+}. This way enables the precise control of the loading species and amount, reduces the risk of leaching during catalytic reactions, and realizes the preparation of versatile heterogeneous catalysts for target reactions, for instance, loaded Cu^{2+} for catalytic oxidation and immobilized Au^{3+} for alkyne hydroalkoxylation. Additionally, there are two approaches to further functionalize the loaded metal ions.[64-66] The first way is to oxidize them to produce metal oxides for photocatalysis (*e.g.*, Zn^{2+} to ZnO). The other way is *in situ* stepwise synthesis of single-atom catalysts, metal clusters, and even metal nanoparticles through precisely controlled chemical reaction method (*e.g.*, Pt^{2+} to Pt^{1+} and Pt clusters/nanoparticles). This way is extremely promising to decrease the reaction temperature and enhance the selectivity of conventional industrial catalytic reactions, such as water–gas shift reaction and alkene hydrogenations. However, using metal phosphonates as catalyst supports has been largely undeveloped compared to the classical MOFs. Promisingly, the higher framework stability and similar framework compositions for metal phosphonates ensure their application for efficient and

stable heterogeneous catalysis. To functionalize the stable framework of metal phosphonates, some chemical strategies, *e.g.*, post-bromination, have been successfully conducted to control the electronic structures of metal phosphonates for improved photocatalysis.[67,68] Furthermore, the host-guest interaction between the support and metal species together with the quantum confinement effect can endow the composite catalysts with the ability to trigger the thermodynamically unfavoured reactions like catalytic oxidation and hydrogenation,[62,69] which has been a long-term challenging topic using inorganic supports.

In comparison with the conventional MOFs and emerging COFs for catalysis,[3,70-72] heterogeneous catalysts based on metal phosphonates are still at their early stage. One reason for this is the difficulty in simultaneously maintaining permanent porosity, framework stability, and crystallinity. However, based on the organic chemistry, it is possible to design and synthesize various organophosphonic ligands with controllable reactivity and different catalytically active sites, such as chiral pyrrolidine organocatalytic sites, organic radical species, and redox-active moieties, which will further broaden the application range of the metal phosphonates. Integration of additional active components into metal phosphonates can generate a new type of heterogeneous catalyst. Since organic functional groups uniformly distribute on the pore surface of metal phosphonates, one can possibly tune the constituents and size of active particles loaded on to the metal phosphonates as well as the bonding/electronic interactions between components through precisely controlling reaction time/temperature or judiciously choosing protective agents, that is, controllability and functionality seem almost limitless.

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METAL-PHOSPHONATES-BASED DERIVATIVES

The adjustable compositions and structural peculiarities of metal phosphonates make them promising starting materials and templates to create interesting nanostructures with controllable compositions (*e.g.*, metal phosphates, carbonaceous materials) after high-temperature pyrolysis. In comparison with other methods for synthetizing nanostructures, the pyrolysis of metal phosphonates can precisely control the resulting dimensions, compositions, and structures. This feature holds promise for integrating various functionalities after one-step treatment, all of which play crucial roles in energy-related areas (*e.g.*, eletrocatalysis, electrochemical energy storage). There are two metal-phosphonate-templating methods: (1) self-templating strategy involving pyrolysis of sole metal-phosphonate precursors, and (2) external-templating method in the presence of other templates (*e.g.*, graphene, nanostructured carbons, graphitic carbon nitride, MXene, and conductive polymers).

Pyrolysis products strongly depend on the treatment conditions. Specifically, metal (pyro)phosphates formed in air/oxygen[73] and their composites with carbon substrates produced under the protection of inert gases (**Figure 4**).[74] The pyrolysis products from metal phosphonates are different from the conventional MOFs-derived materials, which are metals, oxides, carbides, or nitrides.[75] This is due to the high chemical stability of the as-formed metal phosphates, which can avoid the carbothermal reaction in inert atmosphere, the oxidation using air, and the self-decomposition at high temperature.

Metal (pyro)phosphates can be used as the electrode materials in efficient oxygen electrocatalysis and mobile-ion battery cathodes, while the *in-situ* formed carbon substrates can promote the overall electrode kinetics through increasing electronic conductivity and promoting the mass transfer due to the introduction of abundant porosity.[76-81] Take aqueous oxygen evolution reaction as an example, metal phosphates could perform as stable, efficient electrocatalysts. The stability was related to the flexible coordination modes of phosphate groups that could stabilize intermediate states of metal sites (*e.g.*, Co), while the high efficiency (*i.e.*, activity and selectivity) is associated with unique metal-coordination environment induced by phosphate groups, which would favor reaction intermediate adsorption and thus decrease reaction energy barriers.[82-84] Compared to the conventional methods of synthesizing metal phosphates (*e.g.*, hydrothermal technique), the direct pyrolysis of metal phosphonates can easily control the particle size, crystallization degree, and phases. All of these are critical features to realize enhanced oxygen electrocatalysis through adjusting the electrochemically active surface areas and modifying the surface states to optimize the adsorption states of reaction intermediates.

Furthermore, heteroatom-containing feature (*e.g.*, P, N, and S) of organophosphonic acids can lead to the formation of heteroatom-doped nanostructures, resulting in the modification of geometric and electronic structures and even the fabrication of multi-component metal compounds.[85,86] This can not only facilitate host-guest interactions during electrocatalysis, but also introduce new active sites at the interfaces. Unfortunately, the influence of the changes of the resultant electronic and interfacial properties on the electrocatalysis remains elusive. It should be noted that under high-temperature and harsh conditions of pyrolysis, the metal phosphonates tend to be collapsed, resulting in featureless bulk materials (*e.g.*, carbons or metal phosphate), which greatly limits the materials' electrochemical performance.

In terms of the conventional MOF precursors, the pyrolysis strategy enables the rational design of various nanostructures with a range of sizes, shapes, and compositions through employing appropriate MOF precursors and synthesis techniques.[87,88] Typically, this method is limited to the well-known MOFs, such as MILs and ZIFs. However, their complicated synthesis procedures and high price of the precursors, especially organic ligands, significantly prohibits the economic viability of the products. In a sharp contrast, some cheap and widely available organophosphonic acids that have been used to synthesize multifunctional metal phosphonates are the main components in industrial detergents.[37,48] Upon further controlling the synthesis conditions like temperature, heating rate, gas atmosphere, and post-treatment, more derivatives, including metal carbides, metal phosphides, and metal chalcogenides, will be obtained. More systematic investigations should be conducted to reveal the materials evolution and transformation processes during pyrolysis using thermogravimetric analysis, spectroscopic tests, and electronic microscopes. The unveiled mechanisms can provide guidelines to synthesize metal-phosphonate-derived materials with controlled morphologies, compositions, and functionalities. The exploration in this area will further extend the selection range of relatively cheap but efficient materials for energy conversion and storage (*e.g.*, supercapacitors and mobile-ion batteries).

Inspired by the linking and acidic functions of organophosphonic ligands in the frameworks, we have developed a universal acid-base strategy to synthesize a series of carbon-based materials (**Figure 5**). Indeed, the metal knots in the hybrid framework could be substituted by other moieties with similar bridging functions, such as organic amines. The cross-linking reaction between organic amines and organophosphonic acids on the basis of acid-base interaction could make polymer-like networks (similar to COFs) come into being (middle part of **Figure 5**). This allowed one-step carbonization process to directly introduce heteroatoms into the carbon nanomaterials, where organophosphonic and amine species served as heteroatom sources.[89] The heteroatom dopants can be readily adjusted in terms of contents (controlling carbonization temperature and duration) and types (*e.g.*, P/N and P/S using different functional organic groups), which provides a way to investigate the structure-activity relationship in electrocatalysis. Take N,P-codoped carbon as an example,[90] the synergistic coupling effect between P

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(electron donor) and N (electron acceptor) can efficiently adjust the electronic state of the neighbouring C,[90,91] making it the active site towards electrochemical oxygen evolution reaction with low energy barriers and accelerated kinetics.

According to our previous experience, the nanostructures of organophosphonic-derived carbons are greatly related to the chemical properties of amine-based precursors, for instance, melamine for hierarchically porous graphene,[89] dopamine for microporous carbon nanospheres,[91] and aniline for carbon nanofibers.[90] Because of the enormous combinatorial space, it is essential to depend on the design heuristics to create better-performing and cost-effective carbon materials. Indeed, some of them have demonstrated competitive or even superior performance in electrochemical water/oxygen reduction compared to commercial noble metal catalysts.[75,89-93] However, it remains challenging to synthesize nanostructures with controllable characteristics that affect their physicochemical and electronic properties. In particular, the factors that can potentially influence the morphology of the derived nanostructures, including precursors (*e.g.*, components, nanostructures), heat treatment conditions (*e.g.*, temperature, rate and time of heating), and the introduction of guest components, should be investigated. There is a promising opportunity to gain various functional nanostructures with engineered properties based on the metal-phosphonate-templated strategy. Further research and development should focus on the understanding of the underlying mechanism during the pyrolysis process to make this methodology more versatile and convincing.

CONCLUSIONS AND PERSPECTIVES

Following a rational and feasible design process, the inherent properties of metal phosphonates, originating from their rigid configuration, homogeneous frameworks, and adjustable porosity, render a versatile platform for desired structures and functionalities. Advances in synthesis methodologies of advanced metal phosphonates could have significant impact in the fields of multiphase adsorption/separation, catalysis, and energy conversion and storage (**Figure 6**). Post modification and the feasibility of synthetizing carbonaceous nanostructures according to organophosphonate-based characteristics further extend the application possibility and feasibility.

The key to understanding the physicochemical properties of metal phosphonates lies in elucidating their structures. Future investigation should involve new techniques and methods to control the skeletons and pores as well as to improve their crystallinity. Besides the structural design, leveraging computational methods (*e.g.*, density functional theory) can enable precise and large-scale modeling of metal phosphonate with amorphous or (semi)crystalline frameworks. The predictions of theoretical properties like bandgap, electronic adsorption bands, charge-carrier mobility, and ion conduction will provide valuable feedback for designing the structures, which will further direct the future applications.
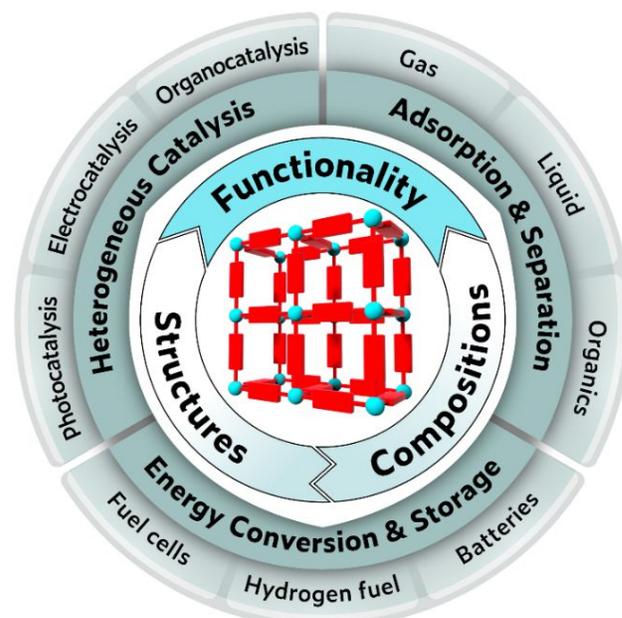

Figure 6. Schematic illustration of the functionality adjustment of metal phosphonates through controlling their structures and compositions, which can further make them promising in various areas.

From the economic point of view, metal phosphonates and their derivatives show various superiorities over conventional MOFs. For example, many cheap industrial detergents like etidronic acid and aminotris(methylenephosphonic acid) have been used as organophosphonic ligands to synthesize a series of metal phosphonates and their derivatives (*e.g.*, chemically doped carbons, metal phosphates) with controlled nanostructures, porosity, and functionality.[8,54,89,90,82,93] Accordingly, the low cost of precursors gives metal phosphonates and their derivatives great economic benefit. Importantly, the synthetic techniques and theories extracted from classical MOFs chemistry can be used to design new metal phosphonate chemistry. Nonetheless, compared to conventional MOFs, the greater stability of metal phosphonates makes them suitable for designing functional organic-inorganic chemistry for practical applications that even involve harsh conditions.

Although low-valence metal cations usually tend to crosslink with organophosphonic groups in a crystalline manner, amorphous or less crystalline metal phosphonates featuring high-valence metal knots and remarkable stability represent a unique opportunity to shed lights on the structure-property-performance correlations for a class of materials without regular structures. Instead of well-defined atomic/molecular coordination, the irregularity, defects and surfaces should be taken into account to deliver a general model of the structure before drawing conclusions regarding the relationships, while special attention should be paid on the nanoparticles with short-range order and their variants with pore sizes exceeding those predicted depending on the interlayer spaces.

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Secondly, tuning the reactivity of organophosphonic ligands through introducing appropriate substituents or additional co-ligands as well as changing molecular architectures can possibly direct the topological evolution and bring new functionalities. This type of metal phosphonates (*e.g.*, mixed carboxylate-phosphonate or sulfonate-phosphonate materials) will fill the gap between crystalline, periodic MOFs, and that of amorphous unconventional MOFs with robust frameworks. Thirdly, high-throughput synthesis techniques can be developed for fast and automated screening of synthesis conditions (*e.g.*, solvents, temperature, pressure), aiming at obtaining a scalable method to synthesize new metal phosphonates for practical applications. Last but not least, organophosphonic chemistry has been applied in the synthesis of inorganic nanomaterials including metallic compounds, carbons, and their composites, with good control over the nanostructures and compositions. Further optimization will bring more opportunities for applications in renewable energy utilization. Many more organophosphonic ligands with various functionalities remain to be explored through organic synthesis and examined for designing functional materials, reflecting that this area will continue to flourish.

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The manuscript was written through contributions of all authors.

Notes

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