Assembly of exfoliated α-zirconium phosphate nanosheets: Mechanisms and versatile applications

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Abstract

α-Zirconium phosphate (Zr(HPO4)2⋅H2O, α-ZrP) is an inorganic layered compound. Since the first report of crystalline α-ZrP in 1964, thanks to its simple synthesis and unique physicochemical properties, α-ZrP has found widespread application in many fields including mechanical reinforcing, barrier improvement, flame retardancy, anti-corrosion, catalysis, environment, energy, and medicine. Because of the ease of exfoliation of α-ZrP to obtain single-layer nanosheets, as well as its rich surface chemistry thanks to the high density of orderly arranged surface acidic hydroxyl groups, α-ZrP single-layer nanosheets are ideal building blocks for self-assembly or assembly with other chemicals. The assembly of α-ZrP nanosheets could form a randomly dispersed structure (isotropic), roughly ordered structure (nematic), or highly ordered structure (smectic) within liquid colloids or solid hybrids (including hydrogels). Thanks to the combination of the unique structures and the novel functions of the components, the assembled materials have found a wide verity of applications due to their excellent properties. In this article, the methods to synthesize α-ZrP, the approaches and mechanisms to exfoliate α-ZrP, and the strategies to assemble α-ZrP nanosheets to form various structures, as well as the applications of the assembled materials are reviewed. The emerging prospects of α-ZrP nanosheets as a key material in next-generation functional applications are envisioned.

KEYWORDS

application, assembly, exfoliation, nanosheets, α-zirconium phosphate

1 | INTRODUCTION

α-Zirconium phosphate (Zr(HPO4)2⋅H2O, α-ZrP), a layered material, has been a focus of research for many years thanks to its extraordinary properties including ion-exchange capability,[1–4] proton conductivity,[5–8] flame retardancy,[9–12] lubricating ability,[13–15] and bio-compatibility.[16–17] Crystalline α-ZrP was first synthesized by Clearfield and Stynes through the refluxing of gelatinous α-ZrP with phosphoric acid (the reflux method) back in 1964.[11] Highly crystalline α-ZrP could be prepared through the refluxing of gelatinous α-ZrP with phosphoric acid at the presence of hydrofluoric acid (the HF method)[18] or reacting zirconyl chloride with phosphoric acid under a hydrothermal condition (the hydrothermal method).[19] and a higher concentration of phosphoric acid used leads to larger lateral dimensions and higher crystallinity of the resultant α-ZrP.[19–20] New methods were reported to synthesize much smaller sized α-ZrP[21–22] and α-ZrP prisms,[23] which showed some unique features.

The crystal structure of α-ZrP was determined after its discovery[24] and then refined after the development of the HF method,[25] as shown in Figure 1A.[26] For each layer of α-ZrP, the zirconium atoms are on the same plane, and each zirconium atom is bonded to four oxygen atoms from the phosphate groups. Each phosphate group, possessing four oxygens, with three attached to the zirconium atom to construct the layer and the remaining one pointing toward the interlayer space and bonding with a H atom to form a hydroxyl group.[25,27,28] The interlayer distance of α-ZrP is 7.56 Å, with one mole of crystal water intercalated.[26] By adopting different methods, α-ZrP crystals with lateral dimensions ranging from ca. 20 nm to 5 μm can be synthesized, which creates a high versatility for various applications.

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FIGURE 1  (A) Crystal structure of $\alpha$-ZrP (hydrogen atoms not shown). Reproduced with permission: Copyright 1982, the Academic Press. Scanning electron microscope (SEM) images of (B) nanosized $\alpha$-ZrP synthesized in ethanol. Reproduced with permission: Copyright 2011, the American Chemical Society. Micro-sized $\alpha$-ZrP synthesized through (C) the hydrothermal method and (D) the HF method. Reproduced with permission: Copyright 2007, the Royal Society of Chemistry

FIGURE 2  (A) Number of articles published after the discovery of crystalline $\alpha$-ZrP in 1964. (B) Radar chart of the number of articles published on $\alpha$-ZrP in different disciplines. (Source: Scopus, searched using “zirconium phosphate” as the keyword, data collected on November 21, 2021)

Moreover, single-layer $\alpha$-ZrP nanosheets with various aspect ratios can be obtained after exfoliating $\alpha$-ZrP crystals with different lateral dimensions, providing building blocks with different sizes for assembly.

Since the first report of crystalline $\alpha$-ZrP in 1964, thanks to its simple synthesis, rich surface chemistry, ease of intercalation and exfoliation, and unique physicochemical properties, $\alpha$-ZrP has found widespread application in many fields including mechanical reinforcing, barrier improvement, flame retardancy, anticorrosion, catalysis, environment, energy, and medicine. Figure 2A presents the number of papers published on $\alpha$-ZrP every half a decade since 1964, which clearly shows that the number of papers has been soaring, covering many disciplines (Figure 2B).

Intercalation and exfoliation have been two key processes to investigate the properties and explore the applications of $\alpha$-ZrP. Intercalation is the phenomenon that guest species are inserted into the galleries of the layered materials and usually leads to a higher interlayer distance. The well-positioned acidic hydroxyl groups with a high density ($\sim 4$ groups per $\text{nm}^2$) on the top and bottom surfaces of each $\alpha$-ZrP layer facilitate the intercalation of $\alpha$-ZrP. These acidic hydroxyl groups are easy to deprotonate when encountered with bases, for example, amines. The intercalation of $\alpha$-ZrP based on the acid–base reaction has been thoroughly explored and widely reported in the literature, which can be exemplified by the intercalation by alkyl monoamines. As shown in Figure 3, the alignment of the guest monoamine molecules
METHODS AND MECHANISMS TO EXFOiliate α-ZrP

The exfoliation of α-ZrP can be achieved using various chemicals in different solvents, which are summarized in Table 1.

The aqueous exfoliation is most common, and exfoliation in organic phases could occur in some scenarios. Compared to many other layered compounds, α-ZrP is easy to be completely exfoliated into single-layer nanosheets via a quick process. For example, it takes only minutes to exfoliate α-ZrP into single-layer nanosheets using tetrabutylammonium hydroxide (TBAOH) or propylamine (PA) (Figure 4A). The exfoliated α-ZrP colloid is translucent to transparent (Figure 4B), which can be detected by the Tyndall effect under laser irradiation. α-ZrP single-layer nanosheets can be well characterized by transmission electron microscopy (TEM) (Figure 4C) and atomic force microscopy (AFM).

2.1 Intercalation leading to exfoliation

Followed by intercalation of certain amines into the galleries of α-ZrP, exfoliation could be realized by long-time equilibrium (4–7 days)[3,38] or subjected to agitation (vigorous stirring[76] or ultrasonication[77]). A widely used amine to exfoliate α-ZrP in this way is propylamine (PA)[3,38,54,56] PA is intercalated into α-ZrP following the process illustrated in Figure 3. A colloidal phase of the intercalation was observed when the PA/α-ZrP ratio is between 0.75 and 1.36,[3] which can be converted to an exfoliated state with the help of ultrasonication.[78] Understandably, a minimum amount of PA is needed for the exfoliation to occur. However, a maximum value also exists, exceeding which causes the recrystallization of α-ZrP and generates only compounds with an intercalated structure.[38] It should be noted that each mole of α-ZrP contains two moles of hydroxyl groups that could react with amino groups, and a bilayer intercalation compound with all the hydroxyl groups reacted (e.g., $n_{PA}/n_{α-ZrP} = 2$) is stable and may not proceed to reach an exfoliation. A similar phenomenon was also reported for methylvamine.[38,54,55] The formation of an exfoliated state was observed when $n_{MA}/n_{α-ZrP}$ is in the range of 1.05–1.81. The range difference could be related to the size and the hydrophilicity of MA and PA molecules. Since MA is in a gas state at room temperature while PA in a liquid state, PA is usually favored for the ease of handling and accessibility for the exfoliation of α-ZrP. With a similar structure and size to PA, allylamine with the carbon-carbon double bond could exfoliate α-ZrP in an aqueous dispersion ($n_{allylamine}/n_{α-ZrP}=1:1$) and go through polymerization afterward for more functions.[57] It is noteworthy that only MA and PA were reported to exfoliate...
**TABLE 1** Different chemicals for the exfoliation of $\alpha$-ZrP

| Exfoliating agent | Solvent                  | $\beta$_{exfoliating agent}/$\beta$$_{\alpha$-ZrP} for exfoliation (based on the available literature data) | References |
|-------------------|--------------------------|-------------------------------------------------------------------------------------------------|------------|
| Methylamine (MA)  | Water                    | 1.05–1.81                                                                                       | [38, 54–55]|
| Propylamine (PA)  | Water                    | 0.75–1.36                                                                                       | [3, 38, 54, 56]|
| Allylamine        | Water                    | 1                                                                                               | [57]       |
| Alkanolamine      | Water                    | 0.3–3.0                                                                                         | [58–62]    |
| Tetramethylammonium hydroxide (TMAOH) | Water | >0.70                                                                                           | [63–65]    |
| Tetraethylammonium hydroxide (TEAOH) or tetrapropylammonium hydroxide (TPAOH) | Water | >0.50                                                                                           | [65]       |
| Tetraalkylammonium hydroxide (TBAOH) | Water | >0.50                                                                                           | [66–69]    |
| Polyetheramine (Jeffamine®) | Water or organic solvent | >0.75                                                                                           | [19, 35, 70–72]|
| 2-(2-aminoethoxy)ethanol & ionic liquid | Ionic liquid | Very large (small molecule-assisted)                                                             | [73]       |
| 2-(2-aminoethoxy)ethanol & functionalized elastomer | Melt | Very large (small molecule-assisted)                                                             | [74]       |
| TBAOH & methanol  | Methanol                 | >0.80 (methanol-assisted, only in nanosized $\alpha$-ZrP)                                      | [75]       |

**FIGURE 4** (A) Schematic of aqueous exfoliation of $\alpha$-ZrP using tetraalkylammonium hydroxides (TXAOH) or propylamine.[65] Reproduced with permission: Copyright 2020, the American Chemical Society. (B) Digital image of an aqueous dispersion containing PA exfoliated $\alpha$-ZrP nanosheets exhibiting decent transparency.[77] (C) TEM image of PA exfoliated $\alpha$-ZrP nanosheets.[27] Reproduced with permission: Copyright 2017, the Royal Society of Chemistry. (D) Schematic of the aqueous intercalation/exfoliation of $\alpha$-ZrP using TBAOH as the exfoliating agent, with the dots representing TBA molecules, the curves water molecules, and the straight lines $\alpha$-ZrP layers.[66] Reproduced with permission: Copyright 2007, the American Chemical Society

$\alpha$-ZrP effectively among all the alkyl monoamines. The intercalation of ethylamine or butylamine into $\alpha$-ZrP does not lead to exfoliation regardless of the load. This might be due to the slight difference in the alignment between the odd-number and even-number carbon chains. [38]

Alkanolamines, amines with hydroxyl groups, could also serve as the exfoliating agents for $\alpha$-ZrP. [58,59] The load range for the exfoliation is wider, and therefore the exfoliation is easier to achieve, compared with alkyl monoamines. Furthermore, the extra hydroxyl group increases the hydrophilicity of the amines and possibly favors the aqueous exfoliation. [58,60] The minimum amount of the alkanolamines needed for exfoliation is less than that of monoamines, resulting from the larger size of the alkanolamine molecules, especially when tris(hydroxymethyl)aminomethane (TRIS) is used to exfoliate $\alpha$-ZrP. [62] It was reported that the partial hydrolysis of $\alpha$-ZrP brought up by the hydroxyl groups could be another factor promoting the exfoliation of $\alpha$-ZrP. [58,60] With the reduced basicity, the ease to achieve exfoliation, and variety of choices of alkanolamines, alkanolamines could be excellent candidates for the exfoliation of $\alpha$-ZrP for different applications. However, the detailed mechanisms from intercalation to exfoliation in $\alpha$-ZrP are not yet fully uncovered, and therefore more explorations are in need.
2.2 | Cation–cation repulsion

Another agent widely used for the exfoliation of α-ZrP is a strong base tetrabutylammonium hydroxide (TBAOH).[66–69] Because of the high basicity of TBAOH, hydrolysis of α-ZrP under high pH needs to be intentionally suppressed by lowering the temperature.[69] The high quality of the hydrolysis-free α-ZrP single-layer nanosheets exfoliated by TBAOH are ideal building blocks to assemble into orderly stacked layers. Instead of proceeding from the complete intercalation to exfoliation as previously discussed when a weak amine is utilized, the exfoliation of α-ZrP by TBAOH takes a different route with the intercalation/exfoliation occurring concurrently and gradually from the edge to the center of α-ZrP layers, as illustrated in Figure 4E.[66] The TBA cations would enter the galleries gradually and form a bilayer structure. The local double layer of cations with the cation–cation repulsion makes the intercalation compound unstable to reach exfoliation.[67] Therefore, unlike weak amines, the excessive highly basic and bulky TBAOH does not cause intercalation.

Tetramethylammonium hydroxide (TMAOH) was also explored to exfoliate α-ZrP,[63–65] assuming the same mechanism as TBAOH. A further look into the exfoliation of α-ZrP using tetraethylammonium hydroxide (TEAOH), tetrapropylammonium (TPAOH), and a combination of TMAOH and TBAOH clears up the mechanism more.[65] For tetraalkylammonium (TxA) cations in α-ZrP, the small ones are kinetically preferred to diffuse into the interlayer galleries. However, large ones are thermodynamically favorable to open up the galleries and facilitate the intercalated cations to move forward by recurring substitution reactions.

2.3 | Very large interlayer distance

As one would expect, the exfoliation of α-ZrP should be achieved when the interlayer distance is so large (e.g., from originally 7.56 to 73.27 Å)[70] that the nanosheet-nanosheet attraction is overcome. Hence, the intercalation of excessively large amines (e.g., polyetheramine with molecular weights of hundreds or thousands of g/mol) into α-ZrP, or the intercalation of large amines followed by the intercalation of polymers could lead to exfoliation.[35,66,71,72] The quality of the exfoliation product could be controlled by adjusting the addition rate of the large amines and the agitation method (stirring or ultrasonication).[71] A fast addition rate usually leads to poor exfoliation, while a slow rate leads to either a moderate exfoliation (through stirring overnight) or a good exfoliation (through ultrasonication followed by stirring overnight).

Using a combination of polyetheramine (Jeffamine® M600) and TBAOH during the exfoliation of α-ZrP could create a porous pathway within the galleries due to the size and shape difference of the two species, which facilitates to create voids and thus the further diffusion of guest species into the galleries and the subsequent exfoliation.[35] One main drawback of using polyetheramine is the difficulty in removing it from the system. Even with the assistance of ultracentrifuge, it is hard to completely remove polyetheramine after achieving exfoliation, and thus may affect the following application of the exfoliated α-ZrP nanosheets.[72]

However, the possibility of using organic solvents (e.g., methylethylketone,[70] acetone,[71,72] etc.) instead of water as the dispersion media endows this method as a favorable way to prepare α-ZrP/polymer hybrids because most polymers are water-insoluble.

2.4 | Aqueous to organic exfoliation system

The dispersion of α-ZrP nanosheets in an organic solvent is desired for applications like assembly with polymers or self-assembly in an organic phase. The direct exfoliation of microcrystalline α-ZrP in various organic solvents with TBAOH was screened, and the best outcome was partial exfoliation in acetonitrile.[68] A different approach is to exfoliate α-ZrP in water and subsequently exchange the water in the aqueous dispersion with the desired organic solvent. For the low-boiling-point water-miscible organic solvent (e.g., acetone, alkanols, etc.), the replacement of water could be realized through multiple cycles of centrifuge-rinse; for the high-boiling-point water-miscible organic solvent (e.g., 1-methyl-2-pyrrolidone, N,N-dimethylethamide, etc.), heating could be used to remove water from the mixture.[28,66,78,79] The similar solvent replacement could be repeated aiming for other organic solvents (e.g., water to miscible acetone, to acetone miscible toluene, although water and toluene are not miscible), which further broadens the applications of α-ZrP nanosheets.[66,71,80] These methods give satisfactory results but usually take multiple steps and use a large amount of chemicals.

Alternatively, small-molecule (e.g., 2-(2-aminoethoxy)ethanol)-assisted exfoliation of α-ZrP is achievable in an ionic liquid[73] or an elastomer melt.[74] The affinity of the ionic liquid to the small molecules intercalated is believed to be the driving force of exfoliation of α-ZrP, while the elastomer melt will react with the small molecules, leading to the exfoliation in a similar fashion. This method offers a new approach to prepare α-ZrP single-layer sheets in a nonaqueous environment.

Pica and coworkers invented a method to synthesis nanosized α-ZrP in alkanols.[71] The nanosized α-ZrP has a smaller size than microcrystalline α-ZrP and some danging groups on edge.[29,81] The direct exfoliation of nanosized α-ZrP in methanol is possible mainly because of the preintercalation of methanol molecules. This opens up a new opportunity to conduct assembly in methanol or methanol miscible solvents to form versatile hybrids.

3 | ASSEMBLY OF EXFOLIATED α-ZRP NANOSHEETS

Because of the ease of exfoliation of α-ZrP to obtain single-layer nanosheets, as well as the rich surface chemistry thanks to the high density of orderly arranged surface acidic hydroxyl groups, α-ZrP nanosheets are ideal building blocks for assembly either with themselves or with other chemicals. The assembly of α-ZrP nanosheets could form a randomly dispersed structure (isotropic), roughly ordered structure (nematic), or highly ordered structure (smectic) within liquid colloids[82] or solid hybrids (including gels) (Figure 5).[72] Note that the presence of single-layer nanosheets, especially the ones with a high aspect ratio, usually leads to a significantly increase viscosity of the
dispersion system. Therefore, solvents are usually added to maintain a low viscosity during the early stage of process to facilitate the assembly, and are usually removed at a late stage.

In solvents, the self-assembly behavior of α-ZrP nanosheets, as a result of the unique geometry and charge distribution, is promising for fundamental research on colloidal phases and applications, such as formulation base for coatings, electrical-optical devices, and even coloring. The solid hybrids from the assembly of inorganic nanosheets and other chemicals have always been a spotlight because of their excellent properties. The dispersion and orientation of α-ZrP nanosheets greatly affect the properties of the resultant hybrids (Figure 5). The morphologies and physicochemical properties of the hybrids assembled with α-ZrP nanosheets have been comprehensively studied. For the most-studied α-ZrP nanosheets/epoxy hybrids, a high concentration of α-ZrP nanosheets is favored for the orientation of nanosheets due to the space confinement effect of the neighboring nanosheets, while a low concentration usually leads to random orientations. The orientated structure brings a number of benefits, including maintained transparency, improved mechanical properties, and enhanced barrier and other associated properties. A large-scale ordered coating of α-ZrP nanosheets in epoxy has been achieved through a spray-coating process, which makes the assembled products more applicable.

In addition to regular solids, α-ZrP nanosheets were also assembled with other chemicals to form hydrogels. High-functionality crosslinkers within the tough hydrogel are an example. The exposure of the high density of hydroxyl groups on α-ZrP nanosheets ensures the high amount of weak interactions to disperse energy during deformation. A gradual alignment of the assembled α-ZrP nanosheets could also be observed during the stretching of the hydrogel, which contributes to the strain-hardening.

3.1 Self-assembly of exfoliated α-ZrP nanosheets in solvent

Numerous fundamental studies on liquid crystal phase transitions were reported for suspensions of polydisperse plate-like particles, for example, gibbsite and α-ZrP. The colloidal dispersion of TBAOH-exfoliated α-ZrP nanosheets with an identical thickness could be stabilized in different states with various nanosheets’ alignments under different concentrations (Figure 6A). The birefringence under a cross-polarizer is a good indication of the formation of liquid crystal phases. A diluted dispersion showed a disordered isotropic (I) phase, and an increase in the concentration of nanosheets caused the self-assembly of the α-ZrP nanosheets into orientationally ordered nematic (N) phase and layered ordering of smectic (S) phase. The columnar phase was not observed because of the polydispersity of the nanosheets. Furthermore, the phase behavior of α-ZrP nanosheets in water is strongly dependent on the ionic strength of the dispersion, including the TBA cations used during exfoliation and additional common salts (like NaCl) added. As Figure 6B shows, in addition to liquid crystal phases, samples with high salt concentrations and low nanosheet concentrations would enter a gelled phase (verified by the air bubbles in the image). For reentrance to a liquid crystal phase, a higher concentration of nanosheets is needed for a larger salt concentration.

For alkanolamine-exfoliated α-ZrP nanosheets, similar liquid crystal phases were observed through centrifugation, freeze drying, and redispersion (Figure 6C). Tactoids (microdomains nucleated in the isotropic phase) would form first from the assembly of a few single-layer nanosheets when the fraction exceeds 2 vol.% (Figure 6D). Then the tactoids with a few layers of nanosheets already stacked may further pile and align hierarchically as building blocks to generate the nematic phase upon the freeze drying, because the empty space between the tactoids tends to be occupied.

In addition, by replacing water with organic solvents, as previously discussed, the self-assembly behavior of single-layer α-ZrP nanosheets in organic solvents was also investigated. The birefringence from the alignment of α-ZrP nanosheets could be controlled by electric stimuli, and acetone was the most suitable solvent for the low viscosity of the dispersion. More interestingly, researchers also found that, with careful control, the liquid crystal phase α-ZrP dispersion in acetone would show desired structural colors (Figure 6E). A higher sheet concentration makes the average nanosheet–nanosheet distance shorter, and therefore a blue-shift is expected in color. The closer nanosheets also contribute to a better aligned assembly, so the reflection intensity also increases with the sheet concentration. When more TBA cations are added into the structural-colored liquid crystal, a blue-shift in color would also occur, because the electrostatic repulsion between the nanosheets is weakened, leading to a smaller nanosheet–nanosheet distance.

It is noteworthy that when α-ZrP is exfoliated with polyetheramine, smectic phase could also be achieved (Figure 6F). The long-range orientation of the nanosheets in epoxy is observed in many other cases and will be discussed in detail in the following sections.

3.2 Layer-by-layer assembly

As α-ZrP nanosheets contain a high density of orderly positioned acidic hydroxyl groups on both top and bottom surfaces, they are ideal building blocks for layer-by-layer (LBL) assembly, because the acidic hydroxyl groups can form hydrogen bonding, be deprotonated to form a negative charge, or be functionalized to generate a positive charge to offer broad versatilities.
The first LBL assembly of α-ZrP nanosheets with other cations was reported in 1997. As Figure 7A shows, the substrate was functionalized to possess positive changes on surface and then alternately deposited in dispersion of α-ZrP nanosheets and solution of poly(allylamine hydrochloride, a linear polycation) followed by drying and rinsing after each deposition step, to create a multilayered thin film based on the electrostatic attractions in between the layers. The LBL assembled film resembles an intercalated structure, and it offers a simple and effective way to fabricate α-ZrP containing thin films with various sizes.

Instead of linear polycations widely used in LBL assembly, bulky molecules could also be LBL assembled with α-ZrP nanosheets. A luminescent film with bulky photo active cation \(N,N'-\text{dimethyl-9,9'}\)-bisacridinium sandwiched by α-ZrP nanosheets was fabricated in this way (Figure 7B), and the lifetime of the luminescence was prolonged, which suggests that the nanostructure of the resultant LBL assembled hybrid could affect the performance of the guest molecules through the reduced agglomeration due to the isolation by the α-ZrP nanosheets and the delayed energy decay of the chromophore due to the confinement by the rigid α-ZrP nanosheets. Even larger molecules such as polyhedral oligomeric silsesquioxane (POSS) were also successfully LBL assembled with α-ZrP nanosheets (Figure 7C).

In addition to molecular cations, other positively charged species have been adopted for the LBL assembly with exfoliated α-ZrP nanosheets, such as alumina-coated silica nanoparticles (Figure 7C). Note that when fibers were used as substrates for LBL assembly, aggregations of
different sizes and shapes were observed, which was probably due to the island growth and washing procedure (carryover between baths).

A further manipulation of the LBL assembly of α-ZrP nanosheets with cations is the control of the repeat unit of the layers. Unlike the traditional LBL strategy of two alternating layers, a quadlayer assembly was achieved using one type of cationic layer (poly(dimethyl diallyl ammonium chloride) [PDDA]) and two types of anionic layers (polyacrylic acid [PAA] and α-ZrP nanosheets) on polyethylene terephthalate (PET) films (Figure 7D) to form the nanobrick wall structure (Figure 7E).[99] The quadlayer assembly strategy allows for the incorporation of extra components but still maintaining a highly ordered layered structure, potentially serving broader application needs.

### 3.3 One-step assembly for ordered structures

The LBL assembly conducted step-by-step allows for the creation of a highly ordered structure, while the one-step assembly is also possible to achieve a layered structure thanks to the 2D structure and large aspect ratio of the exfoliated α-ZrP nanosheets, and additional driving forces like share stress, etc. One typical example is the assembly of α-ZrP nanosheets and epoxy in acetone upon the removal of solvent due to shear.[66,70,71,88,96] The exfoliation of α-ZrP was first achieved in acetone using polyetheramine (Jeffamine® M600), and the epoxy precursor was dissolved in acetone as well and then mix with the dispersion of α-ZrP nanosheets. After removal of acetone and curing of epoxy, the final structure of the α-ZrP nanosheets within epoxy can be secured.

As seen in Figure 8A, the α-ZrP nanosheets exhibited a rough orientation (i.e., nematic) within epoxy.[88] The alignment of the α-ZrP nanosheets is related to the concentration of the nanosheets: a higher concentration leading to a better aligned structure due to the space confinement effect of the neighboring nanosheets, while a lower concentration leading to a more random structure. It is noteworthy that even though a rough orientation of the nanosheets could be observed under imaging, the nematic phase may not be easily confirmed by XRD, but small-angle X-ray scattering (SAXS).[72]

One similar work is a freestanding hybrid film of α-ZrP/polyetheramine. The aqueous dispersion containing α-ZrP nanosheets and the exfoliating agent Jeffamine® M600 was directly dropcast into a polystyrene petri dish, and the film could be peeled off when dried.[100] The SEM image of the cross-section of the assembled α-ZrP/polyetheramine hybrid is shown in Figure 8B, displaying a nacre-like structure.

A spray coating method was developed to form an α-ZrP/epoxy hybrid film using an acetone dispersion of polyetheramine (Jeffamine® M1000) exfoliated α-ZrP and epoxy precursor, followed by spray coating, drying, and curing (Figure 8C).[72] The α-ZrP nanosheets assembled to a smectic phase during the removal of solvent, and the
alignment was maintained by the curing of the epoxy matrix (as seen in the TEM image of the cross-section in Figure 8D). More detailed three-dimensional (3D) electron tomography (ET) characterization showed that the nanosheets were aligned parallel to the substrate, with only a few defects observed (Figure 8E), which helped researchers understand how the nanosheets were misaligned under the coassembly process. One intriguing part of this method is the discrepancy in mean interlayer distance, which was 6.3 nm, far smaller than that of the bulk sample cast after solvent removal via a rotary evaporation treatment (17.1 nm). It was proposed that during the drying of the spray coated hybrid thin film, the rapidly increasing concentration forces the assembly of random nanosheets into a smectic phase with the help of depletion interactions between the \( \alpha \)-ZrP nanosheets, thus making the interlayer distance small. Meanwhile, for the bulk liquid, the shear stress arising from the rotation and fast solvent evaporation drives the epoxy into the space between the nanosheets, enlarging the interlayer distance. This spray coating method is simple and takes a short time, which makes the assembly of \( \alpha \)-ZrP nanosheets with viscous polymers like epoxy more accessible.
Besides polymers, inclusion of small molecules within α-ZrP nanosheets is also achievable. However, direct intercalation of certain bulky molecules into layered α-ZrP is usually impossible because of steric hindrance. A potential solution is to “swell” α-ZrP with small molecules first\(^{101}\) or use θ-ZrP (hydrated α-ZrP with a larger interlayer distance).\(^{102,103}\) Both approaches target on expanding the interlayer distance to counter the steric hindrance, but they could not be universal because of the limited expansion. Assembly of exfoliated α-ZrP nanosheets with bulky molecules is an ideal way to sandwich guest molecules that normally cannot be intercalated, and the structure of the resultant hybrid is usually well aligned.

The assembly of bulky molecules with α-ZrP nanosheets to form a restacked layered structure usually includes several steps: exfoliation of α-ZrP, removal of exfoliating agents (this step could be skipped depending on the application requirements\(^{104,105}\)), dispersing exfoliated α-ZrP nanosheets with desired guest molecules, and one-step assembly of the nanosheets with the guest molecules during removal of solvent. One typical example following all these steps is the immobilization of 1-n-butyl-3-methylimidazolium chloride (BMIMCl), an ionic liquid, within restacked α-ZrP nanosheets,\(^{106}\) as shown in Figure 8F. The assembly of nanosheets and guest molecules is driven by the 2D structure of nanosheets upon gravity and ion–ion electrostatic interactions during removal of solvent. The resultant layered structure with guest molecules sandwiched could be verified with an increasing interlayer distance compared to that of pristine α-ZrP (7.6 Å) or restacked exfoliated α-ZrP with exfoliating agent only, depending on if the exfoliating agent is removed.

### 3.4 One-step assembly for disordered structures

Researchers also made use of the exfoliated α-ZrP nanosheets to build disordered structures through one-step assembly, mainly via in situ polymerization of monomers within the exfoliated nanosheets\(^{57,107,108}\) or drying dissolved polymers. The idea is simple: the diluted α-ZrP nanosheets in liquid has a random orientation at relatively low concentrations, and a solidified matrix could maintain that disorder.

Du et al. fabricated an α-ZrP/polyaniline (PANI) hybrid with randomly distributed α-ZrP nanosheets. The TBAOH exfoliated α-ZrP nanosheets were mixed with an aniline aqueous solution with salt. The hybrid film was fabricated by depositing the hybrid onto a polyaniline oligomer layer that was precoated on the surface of a Au plate by the electrochemical synthesis (Figure 9A).\(^{107}\) This method differs from a previous fabrication of an α-ZrP/PANI hybrid, which formed an intercalated structure.\(^{68}\) As Figure 9B shows, the prepared hybrid has a porous 3D network with interwoven polyaniline fibers and α-ZrP nanosheets. It should be noted that the amine groups on aniline could interact with the hydroxyl groups on α-ZrP nanosheets, which facilitates to stabilize the porous structure.

Similarly, dopamine, which also has an amine group, could assemble with α-ZrP nanosheets followed with polymerization to form a hybrid. As Figure 9C shows, after aqueous exfoliation of α-ZrP using TBAOH, dopamine and tris(hydroxymethyl)aminomethane were introduced into the dispersion, and the polymerization of dopamine started slowly in air and formed an α-ZrP/polydopamine (PDA) hybrid. Subsequently, a coassembly of α-ZrP/PDA/Ag hybrid was achieved through the in situ reduction of Ag⁺ ions.\(^{108}\)

While the exfoliating agents to prepare α-ZrP nanosheets are often either removed or ignored (if they do not negatively impact the assembly process or the properties of the resultant hybrids), a more desirable scenario is to take advantage of the exfoliating agent to promote the assembly process. To achieve this goal, allylamine, an amine with a carbon–carbon double bond was selected to exfoliate α-ZrP. The allylamine-exfoliated α-ZrP nanosheets were then mixed with acrylamide and a crosslinker (N,N′-methylenebisacrylamide) to copolymerize allylamine together with α-ZrP nanosheets into a hybrid hydrogel with the nanosheets well dispersed (Figure 9D).\(^{37}\) The orientation of the α-ZrP nanosheets increases during the elongation of the hydrogel, which could play an important role in the mechanical properties of the hydrogel.

### 3.5 Assembly after proper surface modification

Exfoliated α-ZrP nanosheets could be further surface modified with different functional groups for targeted uses.\(^{28,77,79,108,109}\) However, it is worth mentioning that after surface modification, α-ZrP nanosheets could exhibit different assembly behaviors.

After aqueous exfoliation of α-ZrP by TBAOH (or PA), a subsequent acid treatment could remove the residual TBA cations on α-ZrP nanosheets. To further functionalize the nanosheets with organic reactants, a solvent exchange process could be carried out as described previously.\(^{78}\) Zhou et al. grafted thiol groups (-SH) onto the α-ZrP nanosheets by reacting with (3-mercaptopropyl)trimethoxysilane (MPTMS), followed by a further oxidation to convert -SH groups to sulfonic acid groups (-SO₃H) (Figure 10A).\(^{79}\) It was found that when the α-ZrP nanosheets were functionalized with -SH groups, the nanosheets assembled to form a random porous structure (Figure 10B), while functionalized with -SO₃H groups, the nanosheets assembled to a layered structure (Figure 10C). This is believed to be a result of the formation of strong hydrogen bonding from the sulfonic acid groups, while the thiol groups could not. The hydrogen bonding in between the layers facilitates the alignment of the nanosheets through lowering the total energy.

Another effect of the functionalization of α-ZrP nanosheets is changing their hydrophilicity. By reacting the surface hydroxyl groups with octadecytrichlorosilane, long carbon chains were attached to α-ZrP nanosheets (Figure 10D).\(^{110}\) In a water–oil interface, the unfunctionalized α-ZrP nanosheets assembled with luminescent species would aggregate in the aqueous phase, while the functionalized ones assembled in the oil phase (Figure 10E). The transformation from hydrophilicity to hydrophobicity without a doubt changes the assembly behavior of the α-ZrP nanosheets in different solvents, which allows for serving different applications.

In addition to assembly behavior, the surface modification on α-ZrP nanosheets can also impact the properties of the assembled hybrids. In the assembled α-ZrP nanosheet/epoxy...
hybrids, when long-chain amines are used as the exfoliating agent, the detachment of the amines from the nanosheets could significantly influence the curing of epoxy and cause a huge drop in glass transition temperature ($T_g$) of the final assembled hybrids. To tackle this problem, dual epoxy was functionalized to the surface of $\alpha$-ZrP nanosheets (Figure 10F). As a result, the reduction in $T_g$ is largely suppressed, compared with the unfunctionalized sample. The functionalization of $\alpha$-ZrP nanosheets also led to a stronger adhesion with epoxy during assembly and subsequent curing, resulting in a higher mechanical performance.

Most modifications of $\alpha$-ZrP are based on the reactions with the surface hydroxyl groups on $\alpha$-ZrP nanosheets as discussed above. An alternative approach is to synthesize ZrP phosphate–phosphonate hybrids by the reaction between zirconyl chloride and a mixture of phosphoric acid and phosphonic acid (e.g., alkylphosphonic acid, phenylphosphonic acid, etc.).\textsuperscript{111–114} The formed ZrP phosphate–phosphonate hybrids contain both hydroxyl groups and desired functional groups on the layer surface, which facilitates the assembly with guest species without any further modification. Sun et al.\textsuperscript{115} synthesized a hybrid by reacting zirconyl chloride with a mixture of phosphoric acid and methylphosphonic acid, leading to the formation of an $\alpha$-ZrP derivative containing both hydroxyl groups and methyl groups on layer surface (Figure 10G). The presence of methyl groups improves the hydrophobicity of the product, leading to a much better dispersion with nonpolar solvents and intercalation by such solvents, and eventual exfoliation and assembly with guest species soluble in nonpolar solvents.

4 | PROPERTIES AND APPLICATIONS

Thanks to the combination of the unique structures and the novel functions of the components (i.e., $\alpha$-ZrP nanosheets and guest species), the assembled hybrids have found widespread application due to their excellent properties.

4.1 | Mechanical properties

The assembled hybrids containing $\alpha$-ZrP nanosheets exhibited greatly improved mechanical properties.\textsuperscript{88,100,116–118} Boo et al.\textsuperscript{88} mixed $\alpha$-ZrP nanosheets with epoxy monomers. After curing, the assembled hybrid possessed simultaneously improved mechanical strength, stiffness, and toughness compared to the neat epoxy, which has rarely been achieved, thanks to the excellent mechanical properties of $\alpha$-ZrP nanosheets and their uniform dispersion and rough
orientation (see Figure 8A). As discussed early, a high concentration of α-ZrP nanosheets led to a high level of alignment due to the space confinement effect generated by the neighboring α-ZrP nanosheets, which helped further improve the mechanical properties thanks to the orientation effect.

Hybrids containing well-aligned α-ZrP nanosheets were also explored to potentially maximize the reinforcing effect. Li et al. assembled α-ZrP nanosheets with epoxy using a simple, energy-efficient film casting process. Their morphological characterizations revealed that the α-ZrP nanosheets formed a smectic phase with a highly aligned lamellar order and helical organization in the epoxy matrix (see Figure 6F). The assembled α-ZrP/epoxy film containing 8.2 vol.% α-ZrP demonstrated superior tensile strength (210 MPa) and Young’s modulus (22 GPa), much higher than the neat epoxy. The obtained mechanical results of the α-ZrP/epoxy
film were compared with several theoretical micromechanical models, and the experimental data at 8.2 vol.% α-ZrP loading were found to be close to the model predictions. An α-ZrP/epoxy coating with similar structural attributes was prepared by Lei et al. to evaluate its scratch resistance. [119]

With the incorporation of α-ZrP nanosheets, the assembled α-ZrP/epoxy coating showed significantly enhanced antiscratch performance, including a lower scratch coefficient of friction (SCOF) and considerably higher resistance to microcracking and plowing damages. Such improvements in scratch resistance were believed to be originated from the highly ordered and layered smectic structure of α-ZrP nanosheets.

Inspired by “hook and loop fasteners”, a highly stretchable and compressible hydrogel composed of α-ZrP nanosheets was fabricated by Ding et al., [57] where the high density of acidic hydroxyl groups on α-ZrP nanosheets served as “hooks” and the amine functional groups on polyacrylamide-co-allylamine (PAM-co-AA) chains acted as “loops” (see Figure 9D). Due to the interactions of the hooks and the loops, numerous nano hook-and-loop fasteners were generated in the hydrogel structure, leading to superior mechanical properties. The hydrogel containing α-ZrP nanosheets-based “hook and loop fasteners” (PAM-10ZrP-C) exhibited outstanding tensile strength (0.680 MPa), Young’s modulus (0.200 MPa), and stretchability (>2100% tensile strain), as well as remarkable resilience to cut (Figure 11A) and compression (Figure 11B). In contrast, after gentle compression, the control sample without α-ZrP nanosheets (PAM-C) was found to be shattered (Figure 11C). Moreover, hydrogel PAM-10ZrP-C also depicted exceptional resistance to simultaneous compression and torsion even in a 37°C protein buffer solution (mimicking synovial fluid), suggesting that it was promising for demanding applications such as artificial articular cartilage.

4.2 Barrier properties

The “tortuous pathway” strategy has largely been adopted to impart barrier properties of the assembled hybrids containing inorganic nanosheets, which are generally considered impermeable for guest molecules. [53,85-86,120-126] α-ZrP is a particularly ideal candidate because it can be completely exfoliated into single-layer nanosheets and the aspect ratio of the nanosheets can be well-controlled by synthesizing layered α-ZrP crystals with various lateral dimensions as discussed above. When single-layer α-ZrP nanosheets are well dispersed, their concentration, aspect ratio, curvature, and orientation dictate the barrier properties of the assembled hybrids.

Sun et al. explored these effects on the barrier properties of α-ZrP/epoxy hybrids, where α-ZrP nanosheets were randomly assembled with epoxy. [127] As respectively shown in Figure 12A and B, the hybrids containing 1.0 and 2.0 vol.% α-ZrP nanosheets with an aspect ratio of ca. 100 (ZrP-100) exhibited different levels of orientation, although the authors did not intentionally control their alignment. The increased orientation is believed to be owing to the space confinement effect from the neighboring nanosheets. As such, the hybrid containing 2.0 vol.% α-ZrP nanosheets exhibited a much higher barrier performance. In contrast to the low aspect ratio α-ZrP nanosheets that maintained to be flat in the assembled hybrids, high aspect ratio (ca. 1000) α-ZrP (ZrP-1000) nanosheets depicted significant curvature in epoxy even at a lower concentration of 0.7 vol.% (Figure 12C), which should be owing to their much lower buckling strength. The authors studied a number of barrier models to correlate with their experimental findings. At 0.7 vol.% of ZrP-1000 nanosheets, the models suggested that the effective aspect ratio should be between 230–730 (instead of ca. 1000, Figure 12D), reasonably close to the diameter of the dashed circle (i.e., “hydrodynamic diameter”) shown in Figure 12C divided by the thickness of the nanosheets.

It is intuitively understandable, as well as predicted by models and proved by experiments [127] that a higher level of nanosheets orientation normal to the penetration direction will lead to higher barrier properties. Sue and coworkers prepared a thin epoxy film by assembling well-exfoliated α-ZrP nanosheets into a lamellar orientation parallel to the substrate via a spray coating method (see Figure 8C). [172] Due to the highly aligned and overlapping arrangement of

**Figure 11** (A) Pictures of a cylindrical PAM-10ZrP-C hydrogel sample (6 mm in diameter and 40 mm in length) being aggressively pressed by a brand-new razor blade, remaining intact, and exhibiting no visible cracking after being stretched immediately. (B) Pictures of a cylindrical PAM-10ZrP-C sample (23 mm in diameter and 5 mm in height) before, during, and immediately after being compressed by 90.0%. (C) Pictures of a cylindrical PAM-C control sample (23 mm in diameter and 5 mm in height) before and after being gently compressed. [157] Reproduced with permission: Copyright 2021, the American Chemical Society.
α-ZrP nanosheets (see Figure 8D), the α-ZrP/epoxy hybrid film possessed superior barrier properties at both low and high humidity levels. In another report, Jeffamine® M600 exfoliated α-ZrP nanosheets were self-assembled and organized to form a unidirectional layered structure (see Figure 8B). The enhanced exfoliation induced by Jeffamine® M600 facilitated an efficient self-assembly, which resulted in highly ordered alignment of α-ZrP nanosheets and led to significant improvement in gas barrier properties.

The LBL technique was also adopted to assemble α-ZrP nanosheets with PAA and PDDA to form a highly ordered nanobrick wall structure on PET films (25 μm in thickness), in which PDDA interacted with PAA and α-ZrP nanosheets, forming a quadlayer of PAA/PDDA/α-ZrP/PDDA (see Figure 7E). The film contained well-aligned α-ZrP nanosheets. The ion-crosslinked network between PDDA, PAA, and α-ZrP nanosheets resulted in a highly packed nanobrick wall structure, which in turn led to a superior barrier performance. The PET film with 19 quadlayers exhibited an oxygen transmission rate (OTR) of 0.87 cc/m²/day at 23°C under dry conditions, much lower than that of the uncoated PET film (57 cc/m²/day).

4.3 Flame retardancy

Inorganic nanosheets have been adopted to assemble with other chemicals for flame retardancy applications because they can effectively block the diffusion of oxygen, etc., to slow down the combustion. Compared with many other inorganic nanosheets, α-ZrP nanosheets are particularly attractive for flame retardancy applications, because phosphorus compounds have long been used as a group of effective flame retardants. α-ZrP nanosheets can very effectively improve the barrier properties as discussed above. Therefore, the combination of the chemical flame retardant nature and physical barrier of α-ZrP nanosheets has created a unique synergy to generate effective flame retardancy.

Because well-exfoliated α-ZrP nanosheets can be much more effective in improving barrier properties compared to the layered α-ZrP microcrystals, effective exfoliation and uniform dispersion of α-ZrP nanosheets are the basic strategies to enhance flame retardant performance. Alongi et al. incorporated partially exfoliated α-ZrP into polyamide 6 and achieved effective flame retardance as evidenced by the reduction of the total heat release and the heat release rate (HRR) during the combustion.

Considering other flame retardant additives can be coassembled with α-ZrP nanosheets, researchers have explored this strategy to further enhance the flame retardancy of the assembled hybrids. Luo et al. prepared a flame retardant PVA aerogel through coassembling α-ZrP nanosheets, ammonium polyphosphate (APP), and PVA, followed by freeze-drying. The neat PVA aerogel surface depicted a smooth structure (Figure 13A), whereas hybrid α-ZrP/APP/PVA (2/13/85 wt.%) aerogel demonstrated a pore structure with ribbon-like short ligaments, which were ascribed from the aligned and continuous composite aerogel mainframes (Figure 13B). These ligaments were probably formed because the partial α-ZrP nanosheets were captured by the rapidly advancing ice fronts that connected adjacent aligned α-ZrP nanosheets. At 2 wt.% α-ZrP loading, synergistic improvement in flame retardancy was achieved, resulting in a 43.7% improvement in limiting oxygen index (LOI). Other tests including, cone calorimetry method, also
confirmed the noteworthy enhancement in flame retardant performance of the PVA hybrid aerogel. Further analysis on the sample residues disclosed that the compact structure of the hybrid aerogel served as a physical barrier to protect it from burning.

The LBL strategy was also adopted to construct a coating on flexible polyurethane (PU) foam to achieve flame retardancy. The coating was deposited through the electrostatic attraction and hydrogen bonding between α-ZrP nanosheets, chitosan, and alginate (Figure 13C and D). The XRD characterization revealed that the distance between the α-ZrP nanosheets ranged from 0.75 to 1.04 nm. The results suggested that both a higher trilayer number and a higher concentration of α-ZrP were favorable to lower the HRR during combustion. At 9 trilayers and 0.8 wt.%, α-ZrP dispersion (for LBL coating) led to a 71% drop in HRR compared to that of the neat PU foam, which was mainly owing to the increased barrier of the coating.

A similar LBL technique was employed to coat PET textiles to impart flame retardancy. α-ZrP nanosheets were LBL assembled with polydiallyldimethylammonium chloride, or POSS, or alumina coated silica nanoparticles to coat PET textiles. The coating on PET textiles exhibited significant flame retardant effect in terms of time to ignition and combustion kinetics.

4.4 | Anticorrosion

Owing to their high barrier performance, the coatings assembled with α-ZrP nanosheets are also highly promising for anticorrosion applications. Li et al. assembled α-ZrP nanosheets with epoxy via spray coating on an aluminum (Al) substrate to prepare an α-ZrP/epoxy anticorrosion coating. The long-range orientational and positional organization of the assembled α-ZrP nanosheets were in smectic order, revealed by TEM imaging (Figure 14A). Furthermore, it was observed that the smectic structure of the α-ZrP nanosheets was originated from the metal/liquid interface, indicating that the nanosheets were able to wet the metal surface. The corrosion resistance of the α-ZrP/epoxy coatings was determined by electrochemical impedance spectroscopy (EIS), where the magnitude of impedance was analyzed to measure the resistance of the coating to the transportation of electrons and charges. The closely packed structure of the nanosheets and aligned smectic order favored corrosion resistance, contributed to the decrease in charge transfer and surface charging, thus increasing the magnitude of impedance. The authors proposed a “tortuous pathway” model, as briefly illustrated in Figure 14B. It is suggested that increasing the level of alignment of the nanosheets through using high aspect ratio α-ZrP nanosheets should improve corrosion resistance. Similarly, α-ZrP nanosheets were assembled with other polymers to prepare α-ZrP/polybenzoxazine and α-ZrP/PU anticorrosion coatings. Besides, α-ZrP nanosheets were surface functionalized to achieve a potentially higher affinity with epoxy or higher level of orientation during assembly in epoxy to prepare anticorrosion coatings.

4.5 | Catalysis

α-ZrP nanosheets contain a high density of acidic surface hydroxyl groups, which can be easily modified. As such, α-ZrP nanosheets can be potentially used as a support to assemble with various catalytic species to form heterogeneous catalysts. Because α-ZrP nanosheets can be well dispersed in many solvents, α-ZrP nanosheet supported catalysts can possess advantages of both homogeneous and heterogeneous catalysts.

As discussed early, sulfonic acid-modified α-ZrP nanosheets were synthesized and assembled (see Figure 10A), which can be used as a solid acid catalyst. The solid acid demonstrated excellent dispersibility in polar solvents and reactants, thus endowing high accessibility to the sulfonic acid groups. This solid acid catalyst was evaluated in the Baeyer–Villiger oxidation of cyclohexanone to ε-caprolactone at 80°C for 24 h, achieved a yield of 83.3% for ε-caprolactone and showed a high recyclability. This α-ZrP-based solid acid catalyst was also explored for esterification reaction of oleic acid to produce biodiesel. Thanks to its high catalytic behavior, the solid acid led to a high conversion rate (89%) of oleic acid through esterification with methanol, exhibiting a higher catalytic activity than the commercial catalyst Amberlyst. Overall, the α-ZrP nanosheet-based solid acid catalyst can be uniformly dispersed in the reaction media but remain heterogeneous and thus can be easily separated and recycled.

Besides sulfonic acid groups, Zhou et al. also managed to graft 1-(triethoxy-silyl-propyl)-3-methyl-imidazolium chloride (SiIL) onto α-ZrP nanosheets through the reaction between the surface hydroxyl groups on α-ZrP and the triethoxy silane groups on SiIL. The assembled SiIL-functionalized α-ZrP nanosheets (ZrP-SiIL) can also serve as a heterogeneous catalyst. The catalytic performance of the assembled ZrP-SiIL was evaluated in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate under a solvent-free condition. Catalyst ZrP-SiIL exhibited an outstanding performance (equivalent to the free ionic liquid BMIMCl). A high yield of 99.7% was obtained, which...
could be attributed to the high dispersion of ZrP-SiIL in the reaction system. Moreover, ZrP-SiIL could be easily recycled, and still achieved a yield of 92% after 11 cycles. The excellent performance of ZrP-SiIL is mainly owing to its highly accessible active sites thanks to its homogeneous dispersion in polar organic reagents. A Zn complex was similarly grafted onto α-ZrP nanosheets, which can serve as a catalyst to synthesize poly(lactic acid).[138]

Moreover, Au nanoparticles (NPs) were assembled with α-ZrP nanosheets to form another heterogeneous catalyst.[109] Because Au has a particularly strong interaction with thiol groups, thiol groups were first grafted onto α-ZrP nanosheets by reacting MPTMS with the hydroxyl groups on α-ZrP nanosheets (ZrP-SH). HAuCl4 was then mixed with the dispersion containing the thiol-modified α-ZrP nanosheets. Au NPs were synthesized via in situ reduction and subsequently assembled with the thiol-modified α-ZrP nanosheets to form an assembled nanostructure (ZrP-SH(Au)). As the microscopy images in Figure 15 show, ZrP-SH and ZrP-SH(Au) possessed a porous structure, and Au NPs with a size distribution of 2.0 ± 1.0 nm were uniformly dispersed on the α-ZrP nanosheets with few aggregations. The lattice planes of Au NPs exhibit no stacking faults or twins, suggesting the formation of a single crystalline lattice structure inside AuNPs. The assembled ZrP-SH(Au) catalyst showed the ability to effectively reduce 4-nitrophenol to 4-aminophenol in the presence of sodium borohydride.[109]

Similarly, other catalytic species, including silver NPs[108,139] and TiO2-x clusters,[77] were assembled with α-ZrP nanosheets to form heterogeneous catalysts for various applications. For further reading, Pica has well summarized the use of α-ZrP in the field of catalysis.[140]

### 4.6 Energy-related applications

α-ZrP is highly proton conductive and thus can be assembled with various polymers to form hybrid proton exchange membranes (PEMs) for fuel cell applications.[7,141-143] For direct methanol fuel cells (DMFCs), because methanol crossover remains a serious problem, the presence of α-ZrP nanosheets can also effectively improve the barrier properties of PEMs to lower the permeability of methanol, thus an extra major benefit. Besides, α-ZrP nanosheets can also help improve the thermal, dimensional, and oxidative stability of PEMs.[7]

Kuan et al. assembled TBAOH-exfoliated α-ZrP nanosheets with Nafion® to form a hybrid PEM, which achieved simultaneous improvements in proton conductivity and barrier against methanol permeation.[141] The proton conductivity and permeability test results showed that with 1 wt.% α-ZrP nanosheets, a slight increase in proton conductivity (from 6.0 × 10^{-2} to 6.1 × 10^{-2} S/cm) and significant drop in methanol permeability (from 2.6 × 10^{-5} to 0.9 × 10^{-6} cm²/s) were achieved. With an increase in α-ZrP nanosheets content to 3 wt.%, the resultant membrane exhibited a slight drop in proton conductivity (5.6 × 10^{-2} S/cm), whereas the methanol permeability was further decreased to 0.6 × 10^{-6} cm²/s. α-ZrP nanosheets were assembled with other polymers including sulfonated poly(etheretherketone) (SPEEK)[143] and sulfonated poly(flourene ether ketone) (SPFEK)[7] and achieved similar performance improvements.

To enhance the proton conductivity of α-ZrP nanosheets and thus potentially bringing a further benefit for fuel cell applications, Hu et al. grafted sulfonic acid groups onto the surfaces of α-ZrP nanosheets to synthesize sulfonated α-ZrP...
nansheets (ZrP-SO$_3$H), which were subsequently assembled with SPFEK to prepare membranes for PEM fuel cell applications.[8] The grafting of sulfonic acid groups was found to enhance the proton conductivity of the assembled PEM as they offer additional protogenic groups for forming acid–water clusters. At 2 wt.% loading of ZrP-SO$_3$H, the assembled PEM exhibited simultaneous improvements in proton conductivity and oxidative and thermal stability, as well as a lower water uptake and methanol permeability. The DMFC test showed a peak power density of 61 mW/cm$^2$, much higher when compared with the DMFC using neat SPFEK (38 mW/cm$^2$) or Nafion$^\circledR$ 117 (41 mW/cm$^2$).

Besides fuel cells, $\alpha$-ZrP nanosheets also emerge as a potential candidate to improve the electrode performance of lithium-ion batteries. It was found that assembling $\alpha$-ZrP nanosheets on LiMn$_{1.5}$Ni$_{0.5}$O$_{0.4}$ (LMNO) greatly suppressed the interfacial side reactions between cathode and electrolyte at elevated temperatures and voltages. The electrochemical experiments revealed that $\alpha$-ZrP nanosheet/LMNO hybrid electrode (containing 2 wt.% $\alpha$-ZrP) exhibited a higher performance than the pristine LMNO, achieving a 94.6% capacitance retention after 200 cycles at 55°C.[118]

4.7 | Environmental applications

Hybrids containing $\alpha$-ZrP nanosheets hold potential to sense certain toxic metal ions such as Pb(II). Wang et al. coated $\alpha$-ZrP nanosheets on a glassy carbon electrode surface for selective detection of Pb(II). In the batch adsorption study, four different commonly used heavy metal ions (Zn(II), Cd(II), Cu(II), and Hg(II)) were utilized together with Pb(II). Their results suggested that all five metal cations were adsorbed by the $\alpha$-ZrP nanosheets, but Pb(II) exhibited the most prominent signals among the five cations (Figure 16A). This could be due to the highest binding affinity of Pb(II) toward the surface of $\alpha$-ZrP nanosheets, which was further confirmed by the energetic data obtained from density functional theory (DFT) calculations, where Pb(II) showed the highest relative binding energy (198.3 kcal/mol), compared to other metal cations.[64]

In addition to sensing heavy metal cations, hybrids assembled with $\alpha$-ZrP nanosheets were also utilized to remove heavy metal cations from aqueous solutions. Du et al. prepared a 3D porous hybrid assembled from fibrous PANI and $\alpha$-ZrP nanosheets (see Figure 9A and B), which possessed responsive ion-exchange properties.[107] The 3D porous structure of the hybrid film and the abundantly exposed active sites on $\alpha$-ZrP nanosheets resulted in a capability to quick uptake/release Pb$^{2+}$ cations from an aqueous solution. The mechanism of the potential-induced ion exchange effect on the elimination of Pb$^{2+}$ ions is illustrated in Figure 16B. The porous $\alpha$-ZrP/PANI film demonstrated an ion exchange capacity of as high as 123.5 mg/g, a 9 times higher than the compact $\alpha$-ZrP/PANI, and an 85.2% retention in capacity was found after 1000 cycles.

Apart from sensing and removal of heavy metal cations, hybrids assembled with $\alpha$-ZrP nanosheets have found other environmental applications such as CO$_2$ capture. Zhou et al. assembled $\alpha$-ZrP nanosheets with an ionic liquid, BMIMCl, to form hybrid with a sandwich structure to capture CO$_2$.[106] As the instant CO$_2$ capture curves as a function of temperature (Figure 16C) show, the coassembled $\alpha$-ZrP/BMIMCl hybrid (containing 70 wt.% ZrP) showed two peaks with an increasing temperature, while pure BMIMCl exhibited a virtually constant CO$_2$ capture amount of ca. 0.03 mmol/g. The first peak at ca. 40°C could be attributed to the coexistence

FIGURE 16  (A) Voltammetric peak current of metal ions at the $\alpha$-ZrP nanosheets modified glassy carbon electrode in the presence of Pb(II), Cd(II), Hg(II), Zn(II), and Cu(II).[64] Reproduced with permission: Copyright 2013, the American Chemical Society. (B) Schematic of the electrochemically switched ion exchange process with potential-induced ion exchange effect on the removal of Pb$^{2+}$ ions.[107] Reproduced with permission: Copyright 2016, Elsevier. (C) Instant CO$_2$ capture amount of BMIMCl and ZrP/BMIMCl as a function of temperature.[106] (D) Kinetic data of CO$_2$ capture of ZrP/BMIMCl at various isothermal temperatures.[106] Reproduced with permission: Copyright 2016, the American Chemical Society.
of the physical and chemical sorption of CO$_2$, and the second peak at ca. 60°C is owing to the chemical absorption of CO$_2$. The CO$_2$ capture behavior of the $\alpha$-ZrP/BBMIMCl hybrid under a flow of CO$_2$ (100 ml/min) at various isothermal temperatures are displayed in Figure 16D. The trend matched the instant CO$_2$ capture behavior well, and the highest CO$_2$ capture capacity reached 0.73 mmol/g at 60°C. Overall, the CO$_2$ capture capacity of the $\alpha$-ZrP/BBMIMCl hybrid was ca. 6 times higher than that of the neat BBMIMCl, which was mainly owing to the high accessibility of the BBMIMCl in the assembled hybrids in comparison with the slow diffusion of CO$_2$ inside the neat BBMIMCl.

5 | SUMMARY AND OUTLOOK

It has been almost 60 years since the first synthesis of crystalline $\alpha$-ZrP$^{11}$ but $\alpha$-ZrP did not catch high attention until about 20 years ago. The widespread interest in 2D materials stimulated by graphene helped promote the research on $\alpha$-ZrP nanostructures. Compared with other 2D materials, $\alpha$-ZrP is very easy to synthesize and scale up. $\alpha$-ZrP can also be easily completely exfoliated into single-layer nano-sheets, which can serve as an ideal building block for fabrication but especially for assembly. Assembly using $\alpha$-ZrP nanostructures is still a new field of research but has attracted very high attention in recent years. One particularly unique feature of $\alpha$-ZrP single-layer nano-sheets is the high density of orderly positioned acidic surface hydroxyl groups on both top and bottom surfaces. These surface hydroxyl groups bring three key benefits: (1) unique properties such as ion exchange and proton conductivity; (2) numerous possibilities for surface functionalization; and (3) interactions with guest species to facilitate assembly. For future assembly research using $\alpha$-ZrP nanostructures, proper tailoring of surface functionality is expected to lead to well-preserved structures and tunable interface with other components, thus unique properties for broader and more advanced applications.

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CONFICT OF INTEREST

The authors declare no competing interests.

DATA AVAILABILITY STATEMENT

None.

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ABBREVIATIONS

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