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Zeolitic imidazolate framework materials: Recent progress in synthesis and applications

Binling Chen, Zhuxian Yang, Yanqiu Zhu and Yongde Xia[*]

College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter EX4 4QF, United Kingdom. E-mail: y.xia@exeter.ac.uk

Abstract

Zeolitic imidazolate frameworks (ZIFs) represent a new and special class of metal organic frameworks comprised of imidazolate linkers and metal ions, with structures similar to conventional aluminosilicate zeolites. Their intrinsic porous characteristics, abundant functionalities as well as exceptional thermal and chemical stabilities, have led to a wide range of potential applications for various ZIF materials. Explosive research activities ranging from synthesis approaches to attractive applications of ZIFs have been emerged in this rapidly developing field in the past 5 years. In this review, the development and recent progress towards the different synthesis strategies to generate both powder and membrane/film-based ZIF materials are analysed and summarised. Their attractive and potential applications in gas separation, catalysis, sensing and electronic devices, and drug delivery in the past years are discussed and reviewed. In addition, the prospect and potential new development of ZIF materials are presented.

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1. Introduction

For a long time, porous materials have continuously been the research focus not only in fundamental investigations but also in practical applications due to their intrinsic properties such as high surface areas, large pore volumes and tuneable pore sizes.[1] Noticeably, zeolite-type porous materials are technologically one of the most important nanoporous inorganic materials which have been widely used in large numbers of industrial processes including separation, catalysis and sensing.[2, 3] In addition to the well-known aluminosilicate zeolites, many other zeolite-like inorganic materials such as the aluminophosphates and transition metal phosphates discovered in the 1980s and 90s,[4] further riched the zeolite family. It is estimated that the econmic volume of zeolites in industries is annually up to 350 billion dollars worldwide.[5]

During the last decade, much efforts have been devoted to developing a new class of porous materials based on hybrid metal–organic frameworks (MOFs), which are also known as "hybrid organic inorganic frameworks" or "coordination polymers". The term MOFs was firstly introduced by Yaghi and his co-workers in 1995,[6] although it is worth noting that the first synthesis of a coordination polymer can be dated back in 1965.[7] MOFs are rapidly developed by the prospect of finding new structures, enhancing their functionalities, exploring new gas sorption and catalytic properties and expanding pore sizes.[8-10] The modular nature of MOFs and the mild conditions for their synthesis have permitted the rational structural designs of numerous MOFs and the incorporation of various functionalities by applying the concept of secondary building unites (SBUs), which have well-defined geometrical shapes in the synthesis. MOFs consist of metal clusters that are joined over polytopic linkers to form finite SBUs. The different topologies of MOFs can be achieved by varying the arrangement of SBUs.[11]

A number of MOFs with zeolitic architectures have been successfully synthesised as hybrid frameworks. Among them, the advent of zeolitic imidazole frameworks (ZIFs) has recently gained considerable attention. ZIFs are sub-family of MOFs which consist of M-Im-M (where M stands for Zn, Co cation and Im stands for imidazolate linker) formed by a self-assembly approach. The diverse structures of ZIFs are similar to conventional aluminosilicate zeolites, where typically Zn^{2+} ions play the role of silicon and the imidazolate anions form bridges that mimic the role of oxygen in zeolites, with metal-imidazole-metal (namely M-Im-M) angle ~145°.[12, 13] As a result, ZIFs tend to form zeolite-like topologies with structures similar to those observed in zeolites.[14, 15] However, structures that have not been known in traditional zeolites can be also formed in ZIFs.[16] The representative ZIFs with zeolitic structures are shown in Fig. 1.[5] Since these ZIFs simuntaneously possess the characteristics of both MOFs and zeolites, it is not surprising that ZIFs generally display properties that combine the advantages of both zeolites and MOFs, such as ultrahigh surface areas,

unimodal micropores, high crystallinities, abundant functionalities and exceptional thermal and chemical stabilities,[12, 13, 17] which renders ZIFs holding great promise in many application fields including catalysis, separation and sensing. The unique characteristics of ZIFs make them different from conventional zeolites in many aspects, as shown in Table 1.

ANA ZIF-14	DFT ZIF-3	GIS ZIF-6
GME ZIF-68	LTA ZIF-20	MER ZIF-60
POZ ZIF-95	RHO ZIF-11	SOD ZIF-8
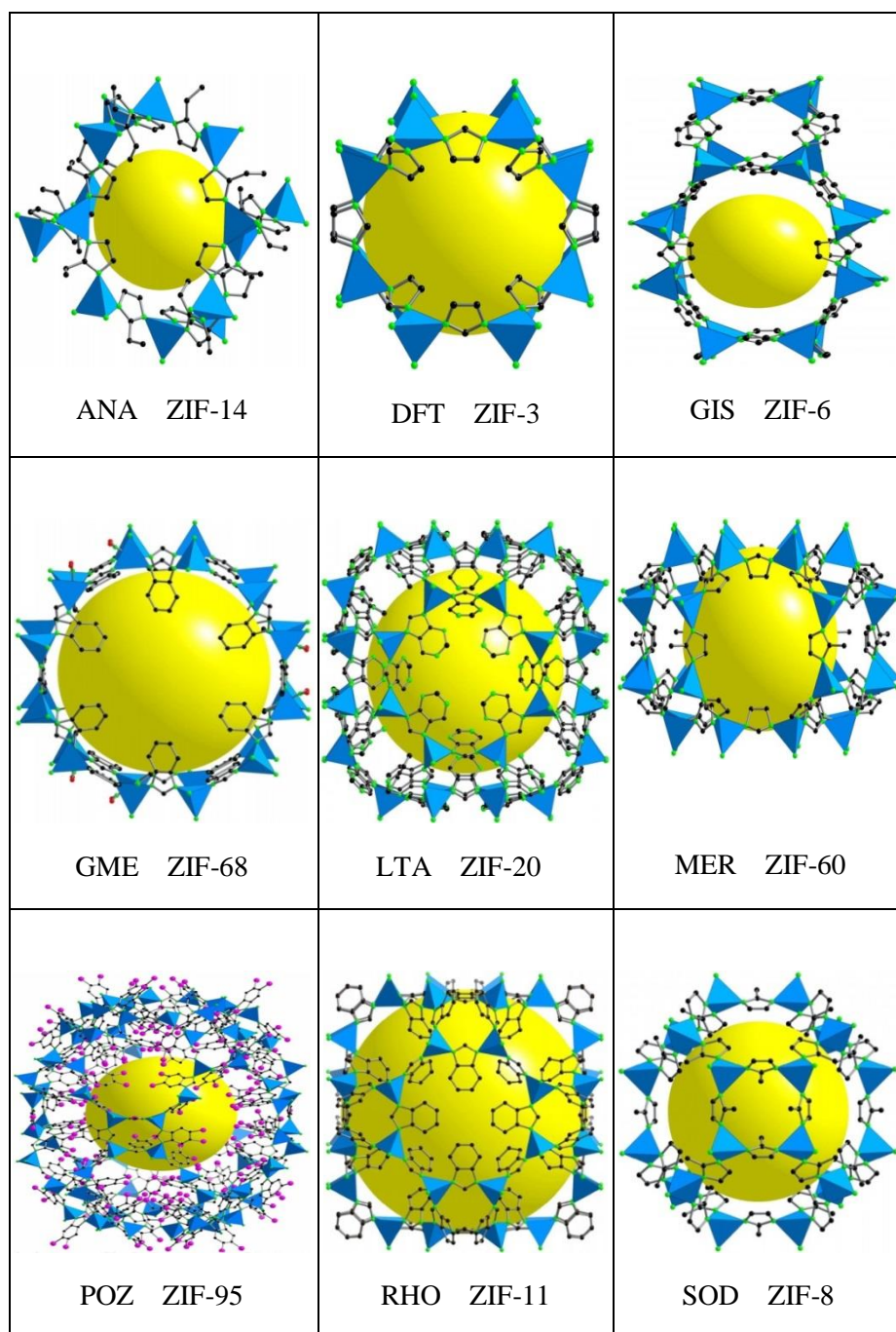
Fig. 1 Representative crystal structures of ZIFs (the first three capital letters under each example stand for the zeolite stucture code). Reprinted with permission from ref. 5. Copyright 2010 American Chemical Society.

Since Yagi's seminar Account on the synthesis and structures of ZIFs published in 2010,[5] the researches in this field have been developed rapidly and attracted increasing attentions in the past 5 years. However, there have been no dedicated reports in the literature ever since to summarise this

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fast developed area on the synthesis and applications of ZIFs although some information of such kind has been dispatched in the reviews on MOFs.[18-24] A dedicated review focused on the state-of-the-art ZIF materials will provide scientists working in the relevant fields the full screen on the new developments of ZIFs, which is highly desirable.

Table 1 Comparison between the zeolites and zeolitic imidazolate frameworks.

Comparison content	Zeolites	Zeolitic imidazolate frameworks
Framework type	Inorganic	Inorganic-organic
Composition	Si; Al; O	Zn; Co; C; N; H and more
Secondary building unites	$[SiO_4]$ and $[AlO_4]$	$M(Im)_2$
Topology	Around 200	Found over 100; the number may increase exponentially
Stability	Depending on the Si/Al ratio, thermal and chemical stability are generally high	Thermal stability up to 500°C and high chemical stability in organic and aqueous media
Compatibility	Poor interaction with polymer	Relatively better compatibility with organic polymer
Functionality	Tuneable Si/Al ratio; generally difficult in functionalisation	Rich chemical functionalities with organic linkers
Development	Over 50 years	Around 10 years
Application prospect	Low-cost; large scale for industry applications	Expensive; potential for industry application

In this review, the recent research developments on the synthesis and applications of ZIF materials are analysed and summarised. It is divided into three sections: we first consider the synthesis strategies available for the generation of powder and membrane based ZIF materials, then summarise their main applications in some important areas, and finally we offer some concluding remarks on the future development of ZIF materials.

2. Synthesis of ZIF materials

ZIF-based materials have been traditionally prepared by hydrothermal or solvothermal synthesis routines in water or organic solvents respectively, with reaction temperatures varying from room temperature up to 200 °C and reaction duration from hours to days.[25] The fast development in this

field has witnessed the emerging of new synthesis strategies of ZIFs in the past years. A variety of preparation methods including both solvent-based routines and solvent-free routines have been developed to generate ZIF-based materials, which were summarised in Fig. 2. Undoubtedly, depending on the status of resulting ZIFs, different synthesis strategies must be adopted in order to generate power or film/ membrane-based ZIF materials.
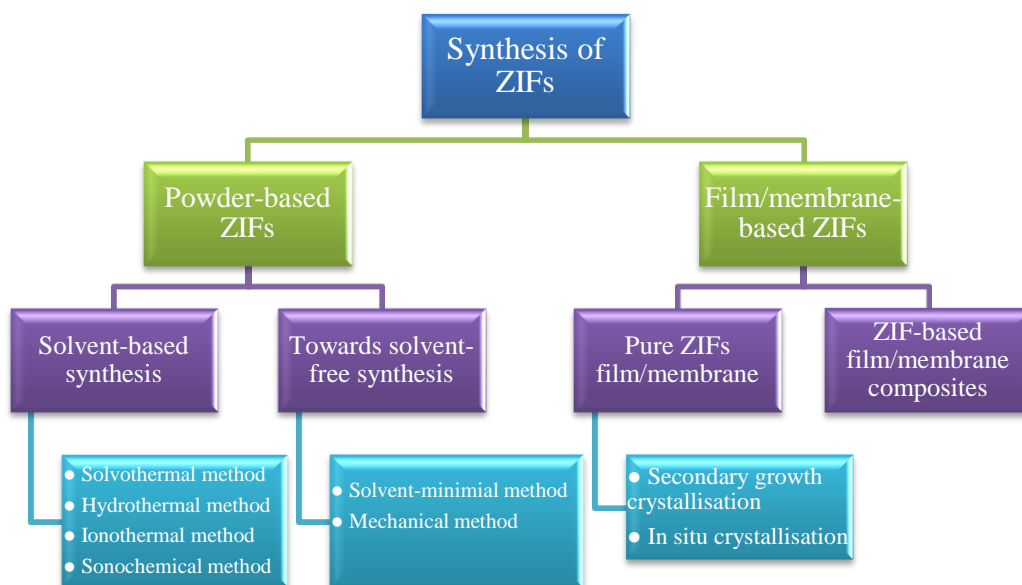

Fig. 2 Summary of different synthesis methods for ZIF-based materials.

2.1. Synthesis of powder-based ZIFs

Most of the ZIF materials, especially at the early research stage of ZIFs, were dominantly existed as power, which were separated from reaction mixture after removal of the solvents or other impurities. So far, both solvent-based and non-solvent-based synthesis approaches have been developed to produce powder-based ZIF materials.

2.1.1. Solvent-based synthesis

2.1.1.1. Solvothermal synthesis

ZIF materials are conventionally prepared through solvothermal method where selected organic solvents acted as reaction medium. In 2006, Yaghi et al pioneered the synthesis of twelve ZIF crystals, termed as ZIF-1 to-12, in organic solvent systems such as N,N-dimethylformamide (DMF), N,N-diethyformamide (DEF) and N-methylpyrrolidine (NMP).[14] The same group also used DMF/DEF/NMP as solvents to synthesise other ZIF materials including ZIF-60 to ZIF-77,[15] ZIF-78 to ZIF-82,[26] ZIF-90,[27] ZIF-95 and ZIF-100.[28] Later on, other researchers synthesised ZIFs using DMF or DEF as well to investigate the formation mechanism and relative properties.[29] Recently, modified recipes from Yaghi's method have been developed. Some organic amines such as pyridine and triethylamine (TEA) were added into the DMF or DEF solvent as the deprotonating agent to

facilitate the materials formation. For instance, micro-sized and hexagonal rod-shaped ZIF-78 crystal was prepared with the assistance of TEA,[30] while ZIF-90 was synthesised with the addition of pyridine in the DMF at room temperature.[31] In addition, NaOH was also applied as a base in the synthesis of ZIF-76 in the mixture of DMF and DEF to achieve the high yield and accelerate the crystal formation.[32]

Methanol was another important organic solvent widely used in the synthesis of ZIFs. In 2006, Chen's group first generated ZIF (it was named as MAF) crystals by using methanol as reaction medium, where 2-methylimidazole or 2-ethylimidazole-containing methanol solution was slowly and carefully layered onto the aqueous ammonia solution containing $Zn(OH)_2$ for one month.[33] Later, using a modified recipe, they obtained ZIF-8 crystals in the mixture of 2-methylimidazole-containing methanol and aqueous ammonia (containing $Zn(NO_3)_2$ or $ZnO/Zn(OH)_2$) after 5 hours stirring at room temperature.[34, 35] In addition, nanoscaled ZIF-8 materials can be prepared in methanol,[36] where the methanol solution containing $Zn(NO_3)_2$ and 2-methylimidazole (MIm) were simply mixed with a Zn^{2+}/MIm molar ratio of 1:8 at room temperature.

The synthesis of ZIFs from methanol-based system was promoted with the utilisation of additives. For examples, Nune et al found that the presence of high molecular weight poly(diallyldimethylammonium chloride) as a stabilizer in methanol can lead to the formation of hexagonally shaped and nanosized ZIF-8.[37] Wiebcke et al improved their previous method[36] to control over the crystal size of ZIF-8 by employing modulating ligands such as sodium formate/1-methylimidazole and n-butylamine in methanol solution.[38] The crystal size of ZIF-8 could be tuneable between 10 and 65 nm for nanocrystals, or about 1 μm for microcrystals. The addition of modulating ligand sodium formate can also lead to a rapid, highly-yielding crystallisation of ZIF-8 in methanol at room temperature.[39] Morevoer, other alcohols such as ethanol[40] and isopropyl alcohol[41] were also successfully used as organic solvents in ZIF synthesis.

2.1.1.2 Hydrothermal synthesis

Although solvothermal synthesis method has been dominated in the early stage of the ZIF research, undoubtedly, the organic solvents are expensive, flammable and not environmentally friendly. Recently, much effort has been devoted to the fabrication of ZIFs in green and facile ways via using less organic solvents or eventually avoiding the use of organic solvents. Pan et al first realised the generation of ZIF-8 in aqueous system at room temperature via a simple procedure:[42] the zinc nitrate solution mixed with the 2-methylimidazole (MIm) solution and the products were then collected by centrifugation after stirring for about 5 min. However, considering that the stoichiometric molar ratio of zinc ions and MIm in ZIF-8 is Zn^{2+}:MIm=1:2, it is obvious that excess amount of MIm (molar ratio of Zn^{2+}:MIm=1:70) in this method was wasted. Therefore, much effort

has been devoted to synthesising ZIFs from stoichiometric molar ration of metal ions and Im derivatives in aqueous system. In particular, Miyake et al[43] succeeded in preparing pure ZIF-8 crystals in aqueous system at room temperature and the crystalline ZIF-8 could be produced from the molar ratio of Zn^{2+}:MIm=1:20.[44] In addition, Qian's group demonstrated that ZIF-67 nanocrystals could be generated from the molar ratio of Co^{2+}:MIm:H_2O=1:58:1100 in aqueous solutions at room temperature.[45]

Water-based systems for the synthesis of ZIFs were also modified by using additives. Both TEA[46] and ammonium hydroxide[47] were applied as deprotonation agents to reduce the use of ligand MIm and initiate the formation of ZIFs. Gross et al could prepare ZIF-8 and ZIF-67 in aqueous system with the addition of TEA at room temperature without the formation of by-products,[46] where the molar ratio of metal ion:MIm could be reduced to 1:4. Yao et al also reported that ZIF-8 could be prepared in the presence of ammonium hydroxide with the molar ratio of Zn^{2+}:MIm:NH_4^+:H_2O=1:4:16:547.[47] Interestingly, ZIFs could be obtained from stoichiometric metal ions and MIm ratio in the presence of other additives such as triblock copolymers poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO)[47] and polyvinylpyrrodlidone (PVP)[48] in aqueous system. For example, both ZIF-8 and ZIF-67 were prepared from stoichiometric metal ions and MIm in aqueous ammonia system in the presence of the triblock copolymer surfactant containing PEO groups,[47] where it was believed that this surfactant could promote the formation of porous ZIF-8 and ZIF-67 due to the electrostatical attraction to the metal ions. Shieh et al also found that micro-sized ZIF-90 crystals could be generated in aqueous system in the presence of PVP (with molecular weight 40000).[48] PVP was hypothesised to control the morphology of crystals and prevent the aggregation of seed crystals.

Very recently, the synthesis of ZIFs from stoichiometric precursors via aqueous ammonia modulation has been successfully realised by us and other groups.[49, 50] Wang's group demonstrated the generation of ZIF-8 from stoichiometric precursors (Zn^{2+}:MIm =1:2) in concentrated ammonium hydroxide aqueous solutions at room temperature.[50] The addition of an appropriate amount of ammonium hydroxide was found to be essential to the formation and growth of ZIF-8 crystal through deprotonation and coordination reactions. Our group also found that ZIF-8 could be readily synthesised from stoichiometric precursors in aqueous ammonia solution without any other additives at room temperature.[49] The structures, particle sizes and textural properties of resulting ZIF-8 materials could be easily tuned by simply controlling over the concentration of aqueous ammonia in the synthesis mixture. Undoubtedly, these cost-effective synthesis strategies of ZIFs will greatly promote the large scale production of ZIFs for practical applications.

2.1.1.3 Ionothermal synthesis

Recently, a new synthesis strategy, ionothermal synthesis,[51-53] has been developed to generate ZIF materials, which involves the use of green solvents such as ionic liquids[54, 55] and eutectic mixture (a special type of ionic liquid)[56] to produce ZIFs. Ionic liquids not only can simultaneously act as both solvents and templates to avoid the competition interactions between the solvent-framework and the template-framework that are presented in hydrothermal preparations,[51] but also have negligible vapour pressure and non-flammability allowing the synthesis to be processed in an open system.[57-59] Moreover, ionic liquids can be recycled for further use.[53] The use of ionic liquid for the synthesis of ZIFs was first realised by Morris and co-workers.[54] They reported that four ZIFs, showing structures that were previously known or unknown, were generated under ionothermal conditions using the ionic liquid 1-ethyl-3-methylimidazolium bis-[(trifluoromethyl)sulfonyl]imide.[54] In addition, it was reported that ZIF-8 could also be synthesised in the presence of ionic liquid 1-butyl-3-methyl-imidazolium tetrafluoroborate[55] or urea-choline eutectic mixture.[56]

2.1.1.4 Sonochemical synthesis

ZIFs can also be produced by sonocrystallisation method. Compared with the conventional oven heating for ZIFs preparations, sonochemical synthesis can not only promote the formation of nucleation, but also help to disperse the nucleation homogeneously.[60] During the sonochemical synthesis, bubbles are formed and collapsed in solutions, known as acoustic cavitation, generating high local temperature, pressure as well as remarkable heating and cooling rates.[61-63] According to Seoane's report, pure ZIF-7, ZIF-8, ZIF-11 and ZIF-20 crystals were obtained under ultrasound radiation, with a power of 110 W and a frequency of 47 kHz, at lower temperature (45-60 °C) and shorter duaration (6-9 h) in respect to the conventional solvothermal synthesis.[64] They also found that the crystals were smaller and had narrower particle size distribution than the conventional synthesised materials. Recently, Cho et al have realised the preparation of a high-yield ZIF-8 using a direct sonochemical route in DMF in the presence of NaOH and TEA.[65] In addition, they have successfully expanded to 1L-scale synthesis of ZIF-8 via this sonochemical method which can be potentially scaled up for industrial applications.

2.1.2 Towards solvent-free synthesis

2.1.2.1 Solvent-minimisation method

Although the synthesis of ZIFs in the aqueous-based system is environmental friendly and cost-effective compared with those in the organic solvents-based system, some problems such as the use of excessive imidazole sources and massive solvent washing still make the aqueous synthesis method inefficient. For this reason, solvent-minimisation methodology has been developed recently.[19, 66] For example, Shi et al succeeded in fabricating porous ZIF-8 and ZIF-67 by steam-assisted conversion method (or dry-gel conversion method).[67] Different from the common hydrothermal synthesis method, the solid phase containing metal salts and excess ligands placed in

a small Teflon cup were surrounded by water vapour (or organic solvent steam such as DMF) under 120 ^{o}C for 24 h, and the small amount of water possibly acted as a structure-directing agent in the synthesis.[68] In addition, ZIF-8 samples were also generated by an vapor-assisted conversion method in nonpolar solvent n-heptane, where the transformation rate from the solid reagents to ZIF-8 was faster than that in methanol or DMF.[69]

Moreover, recent reports have demonstrated that ZIFs can be successfully produced through solvent-free method. For example, Müller-Buschbaum et al has obtained $Co(IM)_2$ via a solvent-free synthesis procedure under heating.[70] Zhang et al has been successfully generated porous ZIF-8 (it was sometimes also called MAF-5) from the oxide/hydroxide-based solvent-free reaction without any by-product.[71] The operating procedure is quite simple: a mixture of ZnO and MIm with molar ratio of 1:2, which had been grinded uniformly, was heated at 180 ^{o}C for 12 hours, and ZIF-8 was then collected. The obtained ZIF-8 sample can be used for adsorptive application without any further treatment. Beobide et al have also realised the preparation of ZIFs with a solvent-free method,[72] in which ZIFs were obtained under the acid-base reaction between $ZnO/CoO/Co(OH)_2$ and imidazolic ligands at temperature of 100-160 ^{o}C in a closed vessel. Moreover, by the addition of small amounts of structure directing agents, it is controllable to generate zinc/cobalt-imidazolates network topology with a high yield (87–97%).

In addition, "accelerated aging" method has also been developed for the preparation of ZIFs. Inspired by the geological biomineralisation and mineral neogenesis, this mild and environmentally friendly novel method exploits the inherent mobility of molecules, which is different from solvent-based or other solvent-free synthesis methods.[73, 74] Friščić et al[73] firstly proposed the "accelerated aging" method and prepared close-packed ZIFs with imidazole, 2-methylimidazole, 2-ethylimidazole and benzimidazole by accelerated aging in a solvent-free and low-energy manner.[75-77] The 'proton-transfer' mechanism was also proposed by Friščić et al[73] where the catalytic salts could induce and accelerate the transformation of a metal oxide into a ZIF material. In detail, a stoichiometric molar ratio of zinc oxide and imidazole ligand were grinded to form a mixture, together with the catalyst ammonium sulfate were placed in an open vial and aged at 45°C and 98% relative humidity for several days, and closed-packed ZIFs were then obtained after washing and drying. In addition, the well-known open framework ZIF-8 can be obtained by the transformation of the closed-packed one under methanol vapours at room temperature. Recently, Friščić et al have further developed the accelerated aging for the one-step synthesis of scalable microporous ZIFs.[74] By changing different salt additives such as $KHSO_4$, $(IM)_2SO_4 \cdot H_2O$ and $(Hcaf)(HSO_4)$ (Hcaf = caffeine), accelerated aging can be optimised for the synthesis of microporous products. They claimed that microporous ZIF-8 and ZIF-67 can be assembled

efficiently from metal oxide and MIm without any further activation, such as microwave and sonochemical treatment.

2.1.2.2 Mechanochemical synthesis

Mechanochemistry has shown significant potential as a green and efficient strategy for the construction of materials.[78] Therefore, the fabrication of ZIFs from mechanochemical synthesis method (via ball milling) has been developed. In 2006, partial formation of the nonporous $Zn(IM)_2$ was first obtained by manual grinding ZnO with large excess amount of imidazole (IM).[79] The same nonporous $Zn(IM)_2$ products were also generated by Adams et al. using a two-step mechanochemical process starting from $ZnCl_2$.[80-82] Realised the limitation of oxide-based precursors for ZIF synthesis via neat grinding, Friščić et al. used modified mechanochemical methods called liquid-assisted grinding (LAG) or ion- and liquid-assisted grinding (ILAG) to produce ZIFs from a stoichiometric molar ratio (1:2) of ZnO and ligand such as imidazole, 2-methylimidazole and 2-ethylimidazole at room temperature.[83] It was found that the addition of a small amount of a liquid phase could enhance the mobility,[84, 85] and salt additives could facilitate the formation of ZIFs.[86] In addition, the topology of synthesised ZIFs could be controlled by choosing different grinding liquids (such as DMF, DEF and ethanol) and salt additives (such as NH_4NO_3, $(NH_4)_2SO_4$ and $NH_4CH_3SO_3$). Furthermore, Friščić et al. could directly monitor the ball milling reaction, the formation of intermediates and the interconversion of ZIF topologies by in situ diffraction of high-energy synchrotron X-rays.[87] Recently, Tanka et al have claimed a truly solventless mechanical dry conversion of ZnO to ZIF-8 without adding any other additives.[88] Nano-sized ZnO powders (average particle size of 24 nm) and MIm were added into a ball mill under a rotation of 100 rpm. They found that the obtained nanoparticles of larger size contained untransformed ZnO, while the smaller nanoparticles had no ZnO. Thus, ZnO crystals were more likely to be converted into ZIF-8 due to the use of nano-sized ZnO particles. The proposed mechanism is shown below in Fig. 3. In details, the nanoparticle agglomerates are firstly broken into small pieces; then the complex is formed through the reaction of ZnO and MIm; the obtained ZIF-8 is agglomerated into nanoparticles which cover over ZnO. Apart from the crystalline ZIFs, Cheetham et al found that the amorphous ZIFs can be synthesised by ball milling too.[41, 89, 90] Various amorphous products including ZIF-1,[89] ZIF-3,[89] ZIF-4,[89] ZIF-8[89, 90] and ZIF-69 [41] can be obtained under grinding.
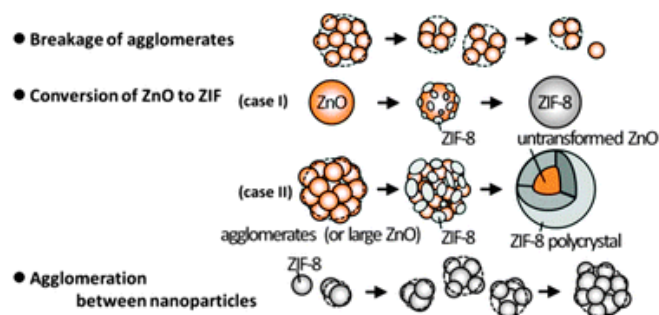
Fig. 3 Proposed mechanism of mechanochemical synthesis dry conversion of ZnO to ZIF-8. The three main processes take place at the same time. Reprinted with permission from ref. 88. Copyright 2013 Royal Society of Chemistry.

2.2 Synthesis of ZIF-based films and membranes

Shortly after the synthesis of powder ZIF crystals, it is recognised that the formation of ZIFs film/membrane is very important in many applications such as gas separation and chemical sensors, due to their intrinsic properties especially the molecule-sized porosity and easy handling.

2.2.1 Pure ZIFs film

So far, diverse synthesis strategies on the fabrication of ZIF films and membraes have been explored. Generally, the preparation of ZIF membranes can be classified into two basic categories: secondary growth crystallisation and in situ crystallisation.

2.2.1.1 Secondary growth crystallisation

The preparation of membrane via the secondary growth crystallisation usually can be realised via two different routes: (1) Depositing the crystal seeds via rubbing, dip-coating, thermal seeding or by repeated growth; (2) Pre-treating the support by using reactive seeding or organic functional groups. Internal gaps among seeds can be closed-up by the growth of seeds, and finally a continuous membrane is formed. The notable advantage of the seeded growth method is that the membrane orientation can be systematically controlled. Other membrane properties such as membrane thickness and grain boundary structure can also be modulated by this method, which can lead to better membrane performance.[91] For example, Carreon et al prepared ZIF-8 membrane by secondary growth crystallisation method,[92] where an alumina support was seeded with ZIF-8 crystals by rubbing, followed by secondary growth to form a ZIF-8 layer on the support. ZIF-8 thin layer was also prepared on the seed rubbed vertically-aligned carbon nanotube.[93] Moreover, high optical quality ZIF-8 films were prepared by dip-coating a colloidal solution of ZIF-8 nanoparticles on a polished silicon wafer,[94] while ZIF-69 membrane was fabricated by dip-coating a colloidal solution on a porous α-alumina substrate.[91] In addition, ZIF-8 membrane was prepared by secondary growth methods in an aqueous system at near room temperature.[95-97] Particularly, hollow

fiber supported and continuous ZIF-8 membranes were generated from a diluted aqueous solutions.[98]

For secondary growth crystallisation method, seeding on the support is regarded as the key factor to obtain high quality ZIF membranes. Thus, it is important to enthance the interaction between ZIF crystals and the support. Apart from the traditional seeding approaches such as dip-coating, slip-coating and rubbing seeding, many advanced seeding approaches including reactive seeding,[99-101] pre-coating polymer or organosilane binder,[102-107] infiltrating precursors[108] and microwave-assisted seeding[109] have been explored. These advanced seeding approaches are addressed as follows one by one.

Reactive seeding was proposed to eliminate the cracks and intercrystalline defects.[100] A ZIF-78 membrane was prepared by reactive seeding on a porous zinc oxide support,[100] where ZnO supports were first seeded by hydrothermal synthesis, and secondary seeded growth was then carried out to crystallize a ZIF-78 layer on the support by hydrothermal synthesis.[100] A similar method was utilised to produce a ZIF-71 membrane using reactive seeded ZnO supports by solvothermal synthesis.[99] In addition, Tao et al successfully fabricated a continuous and well-intergrown ZIF-8 membrane on hollow ceramic fibre tube.[101] In this method (as shown in Fig. 4), loosely packed crystals were first deposited on the support by in situ crystallisation, followed by the formation of a compact seed layer by rubbing seeding, and the secondary growth method was then applied to form the continuous and defect free ZIF-8 membrane on the seed loaded hollow ceramic fiber tube.
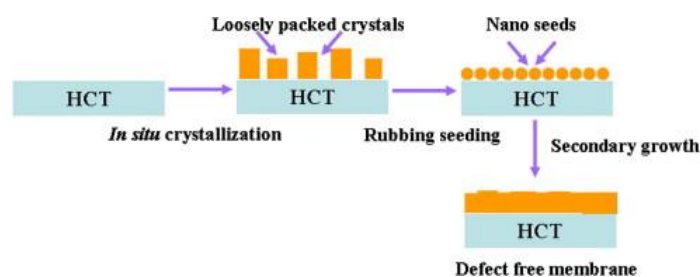

Fig. 4 Schematic representation of ZIF-8 membrane fabrication by reactive seeding (crystallizing-rubbing seeding) approach followed by secondary growth (HCT: hollow ceramic fiber tube). Reprinted with permission from ref. 101. Copyright 2013 Elsevier.

Pre-coating polyethyleneimine (PEI) solution containing ZIF-7 seeds has been successfully used in the preparation of ZIF-7 membranes.[102-104] Although ZIF-7 cannot be dispersed in the aqueous phase due to its hydrophobic property, it can be homogeneously dispersed in an aqueous PEI solution because PEI can coordinate with the zinc ions at the surface of the nanoseeds, thereby making them compatible with the aqueous solution.[110] Moreover, PEI can effectively enhance the linkage between the seeds and the support through hydrogen bonding interactions. For instance, ZIF-8 membranes were prepared by pre-coating PEI solution containing ZIF-8 seeds[105, 106] and

ZIF-8 films were fabricated on the 3-(2-imidazolin-1-yl)propyltriethoxysilane modified substrates at room temperature in aqueous system.[107]

Infiltrating precursors as a seed-and-nutrient layer was explored to produce dense and mechanically stable ZIF-8 membranes on a porous alumina support.[108] In this method, the alumina support was first infiltrated with MIm and zinc nitriate, then the infiltrated alumina discs were dipped into the solution of ZIF precursors, and finally the alumina discs saturated with ZIF precursors were subject to heat treatment at different temperatures.

The microwave-assisted seeding has been reported recently as a new approach to rapidly prepare supports strongly attached to seed crystals by Kwon et al.[109] With the assistance of microwave, the strong absorption of microwave energy by precursor increased the temperature of the supports quickly, resulting in the rapid heterogeneous nucleation and growth of ZIF-8 nanocrystals (as shown in Fig. 5). Thus, the seeded supports with a high packing density were quickly generated in a couple of minutes. Consequently, continuous and well-intergrown ZIF-8 membranes were formed after subsequent secondary growth on the seeded supports.
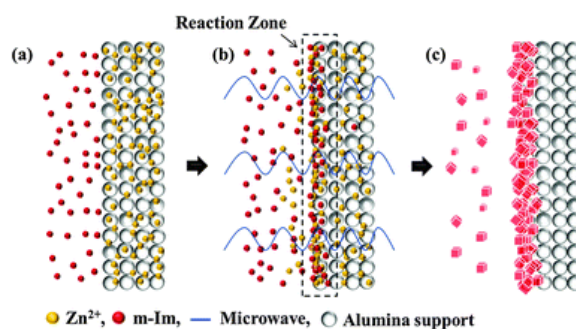

Fig. 5 Scheme of microwave-assisted seeding; (a) a support saturated with a metal solution in a ligand solution, (b) formation of a reaction zone at the interface and microwave irradiation, and (c) heterogeneous nucleation near the support surface. Reprinted with permission from ref. 109. Copyright 2013 Royal Society of Chemistry.

An alternative way to improve the bonding between ZIF crystals and the support is to make use of an appropriate polymeric support because of the high affinity between ZIF and polymer. In this regard, continuous ZIF-90 membrane was fabricated on polymeric hollow fiber which is poly(amide–imide)Torlon.[111] Continuous and dense ZIF-8 thin layer was also synthesised on the porous polyethersulfone (PES) support via secondary seeded growth,[112] in which ZIF-8 has good affinity with the PES support due to the trapping of ZIF-8 crystals into the surface pores of polymer and the favorable interactions between the organic ligands of ZIF-8 and PES.

However, on the other side, secondary growth crystallisation method requires the seeding step ahead of the solvothermal growth step. As a result, potential reproducibility issues may occur due to the increased number of steps in the process.[113] In addition, it is not easy to control the membrane thickness on the submicron scale by this method.[107]

2.2.1.2 In situ crystallisation

ZIF films or membranes can also be prepared by in situ crystallisation method, where the polycrystalline layer is grown on the plain or chemically modified support through a one-step or one-pot solvothermal or hydrothermal synthesis without any seeding growth process.

In situ crystallisation method for the generation of ZIF membranes has been widely explored by many researchers. ZIF-8 membrane was prepared by Bux et al in a microwave assisted solvothermal reaction through in situ crystallisation method.[114][115] In brief, the solution mixture with porous titania support was charged into an autoclave and heated in a microwave oven, then a compact ZIF-8 layer was formed on the porous titania support. Meanwhile, continuous and compact ZIF-8 membrane was produced on the outer surface of porous hollow fibres by in situ crystallisation too.[116] It is worth noting that the direct growth of ZIF-8 membrane from zinc foil was reported by Zhu et al.[117] It is believed that the nucleation of ZIF-8 crystals took place heterogeneously from the grain boundaries at the zinc foil surface, which acted as both the substrate and the reagent. In addition, ZIF-69 membrane was also fabricated on the porous α-alumina discs by solvothermal in situ synthesis.[118]

In order to prepare ZIF films and membranes efficiently via in situ crystallisation method, several advanced approaches, including substrate modification before in situ crystallisation, counter-diffusion-based in situ crystallisation and solvent evaporation-based in situ crystallisation, have been developed.

Substrate modification before the in situ crystallisation process is a widespreaded strategy to obtain continuous ZIF membranes. As shown in Fig. 6A, a simple support modification by heating and fast evaporating before rapid solvothermal in situ synthesis resulted in the preparation of ZIF-7 and ZIF-8 membranes easily.[119]
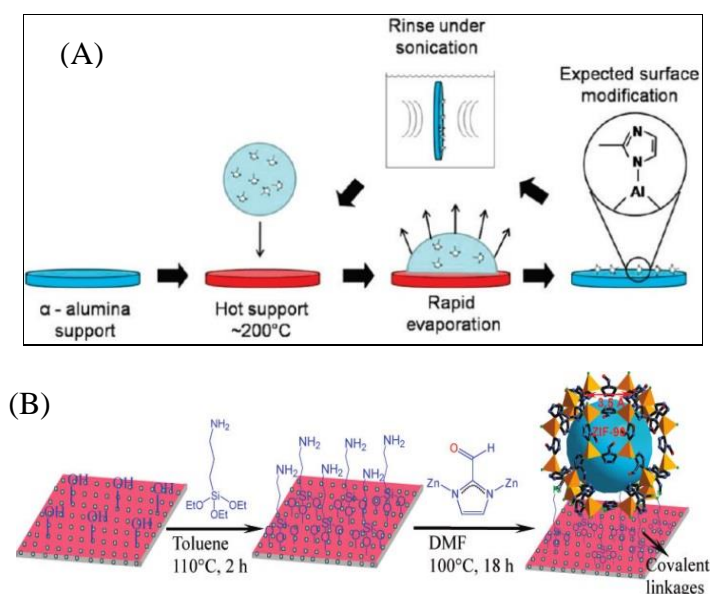
Fig. 6 (A) Illustration of the substrate modification process and (B) the preparation of ZIF-90 membranes using APTES as a covalent linker between membrane and alumina support. Reprinted with permission from ref. 119 and 121. Copyright 2010 American Chemical Society.

On the other hand, 3-aminopropyltriethoxysilane (APTES) was used as covalent linkers to promote the heterogeneous nucleation and membrane growth for in situ crystallisations.[108] A compact layer of ZIF-22, ZIF-90 and ZIF-95 was successfully formed on the APTES-modified support after the solvothermal synthesis.[120-123] The scheme of preparation of ZIF-90 membranes using APTES as a covalent linker is shown in Fig 6B. In addition, a ZIF-9-67 hybrid membrane was prepared on vinyltrimethoxysilane modified α-alumina support by solvothermal synthesis method.[124]

Recently, a one step in situ synthesis of ZIF-8 membranes on unmodified porous α-alumina supports in the presence of sodium formate has been reported by Shah et al,[125] where the sodium formate has been found to enhance the heterogeneous nucleation of ZIF-8 crystals on alumina support as well as to promote the intergrowth of ZIF-8 crystals for the formation of continuous ZIF-8 membranes. Other continuous ZIF membranes such as ZIF-7, ZIF-90, ZIF-61 and SIM-1 can also be prepared using the same one step in situ crystallisation method.

In addition, ZIF membranes can be prepared by counter-diffusion-based in situ crystallisation method where the supports physically separate the metal ions from the ligand molecules. The counter-diffusion concept enables the synthesised membranes to be healed readily without completely disassembling the membrane capacity.[126] This unique feature of the counter-diffusion concept made the poorly intergrown membranes to be healed. Furthermore, the costly precursor solutions can be recycled multiple times for in situ synthesis.[126] Yao's group first reported the preparation of ZIF-8 membrane using counter-diffusion-based (or contra-diffusion) in situ crystallisation synthesis method.[127] Two different synthesis precursor solutions were separated by the nylon membrane, and the ZIF-8 films were then grown on the surface of the nylon membrane (shown in Fig. 7). Recently, they have claimed that ZIF-8 membrane was prepared in aqueous system using a stoichiometric ratio of Zn^{2+} and MIm (1:2) through a similar method.[128] Moreover, Xie et al generated ZIF-8 membrane by contra-diffusion synthesis where two precursor solutions were separately filled inner and outer volume of the APTES-modified tubular support.[129] In addition, Kwon et al successfully prepared continuous and well-intergrown ZIF-7, ZIF-8 and SIM-1 membranes with enhanced microstructure on precursor-soaked alumina support,[126] where the porous alumina support was first saturated with a metal precursor solution, which was then placed in the ligand solution to initiate the reaction, and the ZIF-8 membrane was finally formed by counter-diffusion-based in situ crystallisation method.
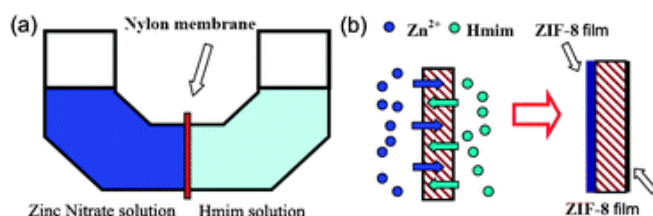
Fig. 7 (a) Diffusion cell for the preparation of ZIF-8 film and (b) the schematic formation of ZIF-8 films on both sides of the nylon support via contra-diffusion of Zn^{2+} and MIm through the pores of the nylon support. Reprinted with permission from ref. 127. Copyright 2011 Royal Society of Chemistry.

Based on the concept of evaporation-induced crystallisation as reported by Ameloot et al,[130] Shah et al came up with the solvent evaporation-based in situ crystallisation (rapid thermal deposition).[131] They successfully prepared well-intergrown ZIF-8 membrane on a α-alumina support. In this rapid thermal deposition approach, the porous supports were soaked with a precursor solution and then subjected to elevated temperature. Rapid solvent evaporation from the supports drived the flow of the precursor solution from inside to outside of the supports, consequently, crystallisation was realised both inside and outside the supports simultaneously to form ZIF-8 membrane (as shown in Fig. 8).
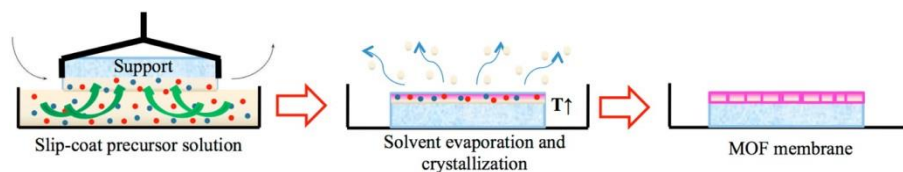

Fig. 8 Scheme of the rapid thermal deposition approach. Reprinted with permission from ref. 131. Copyright 2013 American Chemical Society.

Compared with secondary growth crystallisation method, in situ crystallisation method is relatively simple and, therefore, it is the popular synthesis approach for the preparation of ZIF membranes. However, it is worth noting that in situ crystallisation method has its intrinsic disadvantage that it critically relies on the high rates of heterogeneous nucleation on the support surface to successfully obtain continuous and well-intergrown ZIF layers. Whether a high surface nucleation rate can occur or not depends on various factors, e.g., the surface chemistry of the support material. On the contrary, in the secondary growth crystallisation method, nucleation and crystal growth are decoupled, hence, high nucleation rates and chemical interactions with the support material are less crucial.[105]

2.2.2 ZIF based film/membrane composites

ZIFs have gained great attention as fillers for the generation of ZIF based film/membrane composites, namely, mixed matrix membranes (MMMs), due to their molecular sieving effect, facile synthesis and good compatibility with polymers. A desirable MMM usually consists of

well-dispersed particles as high loading as possible.[132] Although polymers are frequently used in the commercial gas separation, they often confront a significant problem of the compatibility between the polymeric phases and inorganic phases for optimum dispersion and interfacial contact that leads to moderate loading of inorganic materials.[133, 134] Superior MMM permeability and performance selectivity can be achieved by matching the properties of the polymer and ZIF. Generally, several main issues, such as the tuneable synthesis of the sub-micrometer ZIF nanoparticles, the defect-free interface between the polymers and ZIFs and the controllable dispersion of ZIFs within the polymer, should be considered during the fabrication of ZIF/polymer MMMs.[135]

Traditionally, the supported MMMs are prepared through several steps including solution-blending, dip-coating and solution-casting. Briefly, the polymer and ZIF with specific permeability and performance selectivity are selected, and the amount of ZIF with a desired concentration which is necessary for the preparation of MMM is added to an organic polymer solution of known composition under stirring. The resulting mixture is sonicated or stirred for some time until an apparently homogeneous suspension was obtained. The suspension is cast or coated onto a substrate to form membranes, followed by heating and drying under vacuum. Finally, the membrane is cooled down to room temperature under vacuum (shown in Fig. 9).

Fig. 9 Basic procedures for the preparation of mixed matrix membranes.

The preparation of ZIF-8/polydimethylsiloxane (PDMS) MMMs for solvent resistant nanofiltration was reported by Basu et al.[136] It was found that the introduction of ZIF-8 as filler into PDMS-based MMMs was not successful due to the poor adhesion between PDMS and ZIF-8; however, it was successful after surface modification of ZIF-8 with trimethylsilyl which resulted in a strongly improved adhesion. In addition, ZIF-8/polymethylphenylsiloxane (PMPS) MMMs was also successfully fabricated by incorporating ZIF-8 nanoparticles into silicone rubber (PMPS) membranes.[137] The resulting MMM showed very promising performance in recovering bio-alcohols from dilute aqueous solution and offered significant potential for the construction of a membrane reactor for in situ product recovery applications.[137]

A variety of polyimides have been used in the production of ZIF/polyimide MMMs. So far ZIF-8,-90/Matrimid® polyimide[132, 135, 138-140] ZIF-8,-90/6FDA-DAM polyimide[140, 141] and ZIF-8/6FDA-based polyimide[142] MMMs have been successfully prepared using the conventional ZIF/polyimides fabrication method. In addition, sulfone-based polymer had been used in the generation of ZIF/polymer MMMs. For example, the preparation of ZIF-8/poly(1,4-phenylenether-ether-sulfone)[143] and ZIF-20,-8/polysulfone MMMs[29, 144, 145] were

reported. Moverover, polybenzimidazole (PBI) is another major polymer that has been widely used in the fabrication of ZIF/polymer MMMs, and PBI has remarkable resistance to high temperatures (up to 500 ^{o}C)[146] with superior compression strength.[147] The preparation of ZIF-7/PBI nano-composite membranes was reported by Yang et al.[148] ZIF-8,-90/PBI MMMs were also prepared by the dip-coating or solution-casting method.[31, 149-151] Besides, other MMMs such as ZIF-90/P84,[152] ZIF-8/PIM-1,[153] ZIF-7/poly (amide-b-ethylene oxide) (Pebaxs1657)[154] and ZIF-7/chitosan[155] MMMs have been prepared too.

Apart from the traditional method used for the preparation of MMMs, recently advanced MMMs fabrication approaches have been developed.[156-158] The first successful production of mixed matrix asymmetric hollow fibre membranes containing ZIF-8 fillers was reported by Dai et al.[156] They incorporated ZIF-8 into a polyetherimide matrix and produced dual layer asymmetric hollow fibre membranes via the dry jet-wet quench method. SEM images of pure polyetherimide and ZIF-8/polyetherimide mixed matrix hollow fibre membranes are displayed in Fig. 10. The dual-layer fibres incorporating the ZIF-8 show a noticeable interface indicating good adhesion between the two layers.
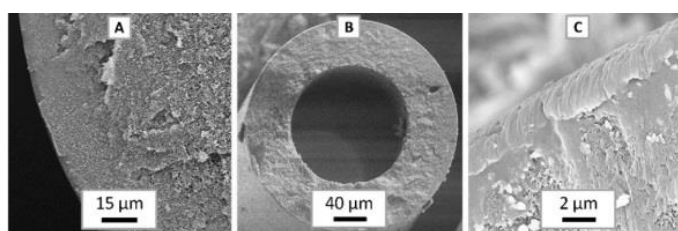

Fig. 10 SEM images of pure polyetherimide (A) and ZIF-8/polyetherimide mixed matrix hollow fiber membranes (B and C). Reprinted with permission from ref. 156. Copyright 2012 Elsevier.

Liu et al successfully prepared a homogeneous ZIF-8/silicone rubber (PMPS) nanocomposite membrane with high particle loading and excellent stability on a hierarchically ordered stainless-steel-mesh (HOSSM) via a novel ''plugging–filling'' method.[158] In this synthesis strategy, the use of HOSSM can effectively avoid the problems such as the poor dispersion of the ZIF-8 nanoparticles at high particle loading and the deterioration of membrane performance during long-term operation, therefore remarkably improve the separation index and selectivity of ZIF-8. As shown in Fig. 11, the holes were plugged in the top layer of the HOSSM with ZIF-8 nanoparticles, and silicone rubber was then filled the spaces between the ZIF-8 nanoparticles and the mesh wires. A homogeneous ZIF-8/silicone rubber (PMPS) membrane was finally obtained after repeated dip-coating and evaporation.
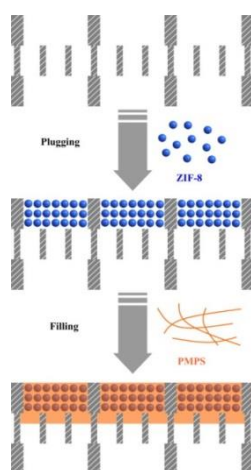
Fig. 11 Schematic illustration of the fabrication procedure of the HOSSM-ZIF-8/silicon rubber membrane by the ''plugging–filling'' method. Reprinted with permission from ref. 158. Copyright 2013 Elsevier.

Although numerous research groups have studied ZIF/polymer MMMs, only a few reports on cross-linked MMMs have been published. Recently, Wijenayake et al[157] have reported the cross-linked ZIF-8/6FDA-durene. The surfaces of the synthesised MMMs were cross-linked by reacting with the ethylenediamine (EDA) vapour to improve gas selectivity. In brief, annealed ZIF-8/6FDA-durene MMM was first suspended in the chamber containing EDA vapour; the MMM was then reacted with EDA vapour inside the chamber for 40 min at about 35 °C, the cross-linked MMM was finally obtained after washing and drying. The chemical reaction taking place is the ring-opening reaction of the imide group in the 6FDA-durene to an amide group followed by cross-linking during EDA vapour reaction.[157]

2.3 Summary

In summary, undoubtedly there are a variety of synthesis methods available for the generation of ZIFs and ZIF-based composites. For the powder-based ZIF materials, the conventional synthesis methods such as solvothermal and hydrothermal method, have been widely applied and developed with modifications (such as ionothermal method and sonothermal method). Meanwhile, other synthesis methods like solvent-free synthesis and mechanical method have been developed quickly too. In particular, solvent-free synthesis method holds great economic and environmental perspectives since it can not only avoid the use of solvents and salts, but also reduce contamination and impurity incorporated into the crystals. While for the film/membrane-based ZIF materials, apart from the conventional secondary growth and in-situ method, novel ZIF membrane fabrication method such as electrospray deposition technique has recently been developed.[159, 160] The remaining challenge in the field is to produce ZIFs in large scales to meet the potential commercial application needs. Nevertheless, there is no doubt that novel synthesis approaches for ZIF materials which can

offer reproducibility, scalability and cost-effectiveness will emerge with the effort of scientists in the future.

3. Applications of ZIF materials

Owing to their high level of porosity, adjustable compositions and controllable structures, applications of ZIF materials are emerging. Both pure ZIFs and ZIF-based films/membranes have been developed as multifunctional materials to show versatile excellent performances beyond the traditional uses as adsorbents and catalysts, and even contribute to the developments in the fields ranging from sensing and electrical device to drug delivery. In this section, the typical and emerging applications of ZIF materials are highlighted and discussed.

3.1 Separation

Gas separation is becoming a more and more important research topic with the increasing of the global issues such as natural gas purification and carbon dioxide capture. Therefore, it is urgent and desirable to develop green and energy-efficient ways to realise gas separations effectively. As a novel class of highly porous materials with similar structures to zeolites, ZIF materials possess tuneable pore sizes, variable structures and multiple chemical functionalities. As a result, they hold great potential in gas separation applications. Both pure ZIFs and ZIF-based polymer mixed matrix membranes (MMMs) have been widely explored in various gas separations, which was summarised Fig. 12.

The pure ZIF membranes have been explored in various gas separations showing very promising separation performance. Some gas separation results on pure ZIF membranes are summarised in Table 2. Obviously, most of the investigations are focused on the hydrogen separation and carbon dioxide separation, due to the great potential in practical applications of ZIF membranes in these
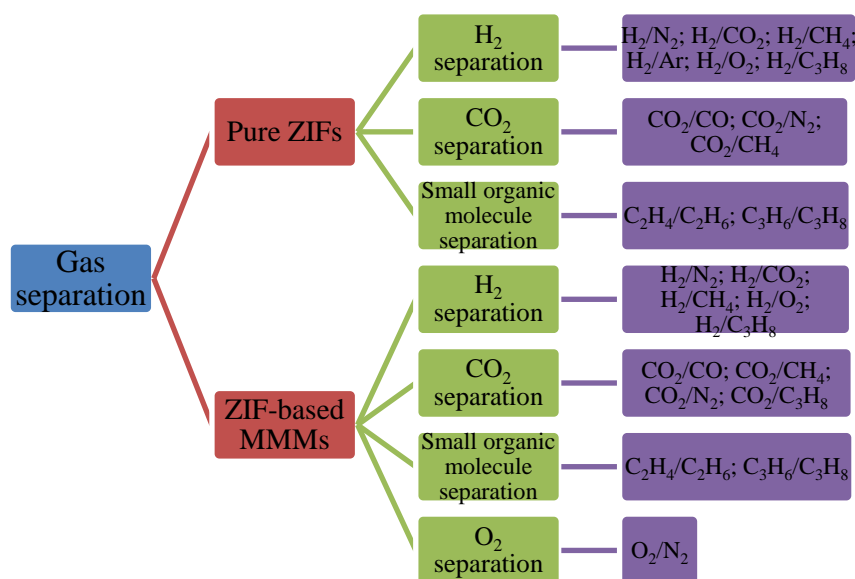

Fig. 12 Summary of gas separation on both pure ZIFs and ZIF-based MMMs.

fields. Moreover, the reported ideal selectivity of pure ZIF membranes is variable and depending on the properties of the gases involved. Generally, the nature and content of the target gas, the ZIF types and the operation conditions such as temperature and pressure, can all affect the separation efficiency.For example, due to the fact that the pore size of ZIF-7 with sodalite (SOD) topology is about 0.3 nm,[14] which is just between the molecule sizes of H_2 (0.29 nm) and CO_2 (0.33 nm), ZIF-7 membrane was applied in the H_2 mixed gas separations, such as H_2/CO_2, H_2/N_2 and H_2/CH_4. ZIF-7 membrane prepared by Li's group exhibited high H_2 permeance.[102, 103] Moreover, the high H_2/CO_2 ideal selectivity and separation factor exceed the Knudsen separation factor and the latest Robeson's "upper-bound" line.[161] ZIF-8 material is another promising porous membrane. Thanks for its pore size (~ 0.34 nm) and hydrophobic nature, ZIF-8 membrane has advantages to separate H_2 from other large gas molecules.[22] For instance, the ZIF-8 membrane prepared by Bux et al showed high H_2/CH_4 separation factor (11.2), which significantly exceeded the Knudsen separation factor for H_2/CH_4 (~ 2.8).[114] ZIF-8 membranes also exhibited excellent separation performance for C_2-C_3 hydrocarbon mixtures. The high quality ZIF-8 membranes prepared by Pan et al showed that the separation factors for mixtures of ethane/propane, ethylene/propylene and ethylene/propane are 80, 10 and 167, respectively.[95] In addition, ZIF-69 membrane was reported for the CO_2/gas mixtures separation, such as CO_2/CO, CO_2/N_2 and CO_2/CH_4. The continuous ZIF-69 membrane presented high separation factor of CO_2/CO (3.5) with CO_2 permeance of 3.6×10^{-8} mol m^{-2} s^{-1} Pa^{-1} at room temperature.[118]

Table 2 Gas separation performance of pure ZIF membranes

Materials	Gases	Separation performance	Ref.
ZIF-7	H_2/CO_2	Ideal selectivity 6.7; separation factor 6.5	102
ZIF-7	H_2/CO_2; H_2/N_2; H_2/CH_4;	Separation factor 13.6; 18.0; 14.0 (H_2 permeance of 4.5×10^{-8} mol m^{-2} s^{-1} Pa^{-1}; at 220 °C)	103
ZIF-7	H_2/CO_2	Separation factor 9.6 (H_2 permeance of 4.61×10^{-7} mol m^{-2} s^{-1} Pa^{-1}; at 25 °C)	159
ZIF-78	H_2/CO_2	Ideal selectivity 11.0; separation factor 9.5	100
ZIF-8	H_2/CH_4	Separation factor 11.2 (298 K) (1 bar)	114
ZIF-8	H_2/N_2; H_2/CH_4	Ideal selectivity 11.6; 13	119
ZIF-8	H_2/C_3H_8	Separation factor above 300	105
ZIF-8	H_2/CO_2	Ideal selectivity 32.2; (7.1 for a H_2/CO_2 binary mixture (45% H_2))	116

ZIF-8	H_2/N_2; H_2/CO_2	Ideal selectivity 15.4 (H_2 permeance 5.73 x 10^{-5} mol m^{-2} s^{-1} Pa^{-1}); 17.0	[129]
ZIF-8	H_2/N_2	Ideal selectivity 5.7 (H_2 permeance 1.7 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1})	[108]
ZIF-8	H_2/CO_2; H_2/Ar; H_2/O_2; H_2/N_2; H_2/CH_4	Ideal separation factor 4.9; 7.0; 13.6; 15.1 and 9.8.	[162]
ZIF-8	H_2/C_3H_8	Ideal selectivity more than 1000 (H_2 permeance 15×10^{-7} mol m^{-2} s^{-1} Pa^{-1}; room temperature)	[97]
ZIF-8	H_2/Ar; H_2/O_2; H_2/N_2; H_2/CH_4	Ideal separation factor 9.7; 10.8; 9.9; 10.7 (H_2 permeance 4×10^{-7} mol m^{-2} s^{-1} Pa^{-1}; 333K)	[112]
ZIF-8	H_2/CO_2; H_2/N_2; H_2/CH_4	Ideal separation factor 5.2; 7.3; 6.8 (H_2 permeance 1.1 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1})	[101]
ZIF-8	H_2/N_2	Ideal selectivity 4.6	[128]
ZIF-8	H_2/N_2; H_2/CH_4	Ideal selectivity 10.3; 10.4 (H_2 permeance 20.8 x 10^{-8} mol m^{-2} s^{-1} Pa^{-1})	[163]
ZIF-8	H_2/CO_2; H_2/N_2; H_2/CH_4	Ideal selectivity 5.8; 11.1; 12.8 (303 K and 0.1 MPa)	[164]
ZIF-95	H_2/CO_2; H_2/N_2; H_2/CH_4; H_2/C_3H_8	Mixture separation factor 25.7; 10.2; 11.0; 59.7 (325 °C; 1 bar) (H_2 permeance 1.9 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1})	[123]
ZIF-9 and ZIF-67 hybrid	H_2/CO_2	Ideal separation factor 8.89 (room temperature).	[124]
ZIF-69	CO_2/CO	Permselectivity 3.5 (3.6 x 10^{-8} mol m^{-2} s^{-1} Pa^{-1}; at room temperature)	[118]
ZIF-69	CO_2/N_2; CO_2/CO; CO_2/CH_4	Separation factor 6.3; 5.0; 4.6. (1 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1}; at room temperature; 1 atm)	[91]
ZIF-7	CO_2/CH_4	Selectivity 12.22 (298K)	[165]
ZIF-8	C_2H_6/C_3H_8; C_2H_4/C_3H_6; C_2H_4/C_3H_8	Separation factors 80; 10 and 167	[95]
ZIF-8	C_3H_6/C_3H_8	Separation factor up to 50	[96]
ZIF-8	C_2H_4/C_2H_6	Selectivity 2.8 (1 bar); 2.4 (6 bar)	[93]
ZIF-8	H_2/C_3H_8;	The ideal separation factors 2000 and 59	[166]

	C_3H_6/C_3H_8	(298K)	
ZIF-8	C_3H_6/C_3H_8	Selectivity about 30 (C_3H_6 permeance 1.1 x 10^{-8} mol m^{-2} s^{-1} Pa^{-1})	167

In addition, the presence of organic linkers in ZIFs offers better compatibility with organic polymers compared with other additives. Therefore, there has been growing interest in MMMs containing ZIF fillers, and a number of ZIF-polymer MMMs have been developed. Polymers that have been frequently explored include polysulfones, polyimides, polyetherimide, poly(1,4-phenylen ether-ether-sulfone) and polybenzimidazole. The MMMs can not only potentially extend the separation performance of traditional polymers, but also maintain the processing convenience of polymers. Generally, the permeability and diffusion properties of gases increase with the increase of ZIF loading. For this reason, a desirable MMM consists of well-dispersed ZIF particles with loadings as high as possible. For instance, polyimides and polyimides were frequently applied with the combination of ZIFs for gas separations due to their high gas selectivity and high stability. With the increased amount of ZIF-8, ZIF-8/Matrimid® MMMs exhibited increasing gas selectivity of CO_2/CH_4, as evidenced by the reported ideal selectivity of CO_2/CH_4 to be around 124.89 (~ 50% ZIF-8),[132] 35.8 (~ 20% ZIF-8)[135] and 39 (~ 25% ZIF-8)[139] respectively. Other polyimides, such as 6FDA-based polyimides, 6FDA-durene and 6FDA-durene/DABA,[142] and 6FDA-DAM,[140, 141] were used in MMMs for gas separation. The ideal selectivity for C_3H_6/C_3H_8 was 27.38 by using 6FDA-durene/DABA (9/1), which increased up to 31 by using 6FDA-DMA. In addition, polybenzimidazole (PBI) was also applied in the incorporation of ZIF particles. Yang et al put ZIF-7 into PBI as ZIF-7/PBI MMMs, which exhibited high ideal H_2/CO_2 selectivity up to 12.3.[148, 168] ZIF-8/PBI MMMs also demonstrated good separation property, where the ideal selectivity of H_2/CO_2 was 12.3 at 230 °C,[151] and the separation factor of CO_2/CH_4 was 32.[168]

Apart from the gas separation, recent experimental and computational researches have demonstrated that ZIF materials can be good candidates in the vapor separation, especially in biofuel recovery.[169-176] Julien et al found that biobutanol can be efficiently separated from aqueous solution in the presence of other contaminants by using ZIF-8 membranes.[175] Moreover, Ke et al evaluated the vapor-phase sorption and permselectivity of ethanol solutions in water to measure ethanol/water separation properties using ZIF-8 membranes.[173] The adsorption of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol from water vapor, revealed ZIF-8, ZIF-71 and ZIF-90 have potential for biofuel recovery.[174] In addition, several advanced MMMs have already been made recently for vapor separation.[177, 178] For example, Li et al [177] prepared MMMs based on polymethylphenylsiloxane (PDMS) and ZIF-71(PDMS : ZIF-71 = 10 : 2) exhibiting double pervaporation separation factors for alcohols comparing with those of the pure PDMS membranes.

Moreover, Fan et al fabricated well-dispersed ZIF-8-PDMS nanohybrid membranes with high pervaporation performance in biobutanol recovery from aqueous solutions. In the recovery of n-butanol from aqueous solution (1.0 wt%; 80 $^{\circ}$C), the separation factor can be as high as 81.6 when the ZIF-8 loading was increased to 40 wt%.

It is worth noting that the flexibility of ZIFs under certain condition has recently been reported.[106, 172, 179, 180] This phenomenon including gate opening[106] and pore size increase,[172, 179, 180] may cause more complexity to the ZIFs or ZIF-based membranes in the separation field.

3.2 Catalyst

Since ZIFs are analogous to another typical kind of porous materials aluminosilicate zeolites, one of the most important and commercially available catalytic materials,[181] ZIFs and ZIF-based materials have been considered as efficient catalysts for a number of reactions, although much development is still required. Generally, pure ZIF materials can be active catalysts for many reactions including transesterification,[182] the Knoevenagel reaction,[183, 184] the Friedel-Crafts acylation,[185] the monoglyceride synthesis,[186] the synthesis of carbonates,[187-189] oxidation and epoxidation,[190-192] and the hydrogen production.[193, 194]

ZIFs including ZIF-8,[183] ZIF-9 and ZIF-10 [184] have been demonstrated as efficient heterogeneous catalysts for the Knoevenagel reaction between the condensation of benzaldehyde and malononitrile to form benzylidene malononitrile. In addition, it has been reported that ZIF catalysts can be facilely separated from the reaction mixture and re-used without significant degradation in catalytic activity.[183, 184]

ZIF-8 was reported as an effective heterogeneous catalyst not only for transesterification reaction of vegetable oil with significant reactivity,[182] but also for Friedel-Crafts acylation reaction between benzoyl chloride and anisole without the requirement of an inert atmosphere, where high reaction conversion was achieved with small amount of ZIF-8 (2-6 mol%).[185] Moreover, hierarchical nanosized ZIF-8 was explored as a re-usable catalyst for monoglyceride synthesis by Wee et al.[186] They found that the hierarchical ZIF-8 with mesopores which was transformed from the ZIF-8 nanoparticles through reaction with fatty acid, was a promising heterogeneous catalyst for selective monoglyceride formation through esterification of oleic acid with glycerol under mild reaction conditions. Furthermore, ZIF-8 was demonstrated as an active catalyst for the formation of carbonates. For example, ZIF-8 preformed as an efficient and reusable heterogeneous catalyst for the synthesis of ethyl methyl carbonate from the dimethyl carbonate and diethyl carbonate.[187] Carreon et al[188] found that ZIF-8 and amine-functionalised ZIF-8 exhibited high epoxide conversions and moderate to high selectivities at reaction temperature as low as 70 $^{\circ}$C in the synthesis of chloropropene carbonate from carbon dioxide and epichlorohydrin. In addition, They also reported the catalytic performance of ZIF-8 in the reaction between carbon dioxide and styrene

oxide.[189] The reusable ZIF-8 catalyst showed significant catalytic activity at temperature as low as 50 °C. It is believed that Lewis acid Zn^{2+} sites and the nitrogen basic moieties from the imidazole linker in the frameworks of ZIF-8 can promote the adsorption of carbon dioxide, which can boost the further conversion to the carbonates.

Moreover, ZIFs have also exhibited catalytic activity in both oxidation and epoxidation reactions. For instance, ZIF-9 has been successfully used for the aerobic oxidation of tetralin with good reusability.[190] Meanwhile, ZIF-9 catalyst has also demonstrated catalytic activity in the oxidation of small aromatic molecules including phthalan, vanillyl alcohol, guaiacol, syringol, veratryl alcohol, and cinnamyl alcohol in the presence of molecular oxygen.[191] It has been reported that ZIF is catalytic active in the aerobic epoxidation of olefins by using isobutyraldehyde under facile conditions.[192]

In addition, ZIFs have been demonstrated as catalysts for the hydrogen production. Fischer et al [193] reported the heterogeneous ZIF-8 catalyst for the dehydrogenation of dimethylamine borane (DMAB) shown in Fig. 13. The reaction could be carried out at room temperature due to the strong caging effect, probably combined with the polar and Lewis acid/base properties of the framework. In addition, ZIF-9 was also reported to be an efficient catalyst for $NaBH_4$ hydrolysis with relatively high stability.[194]
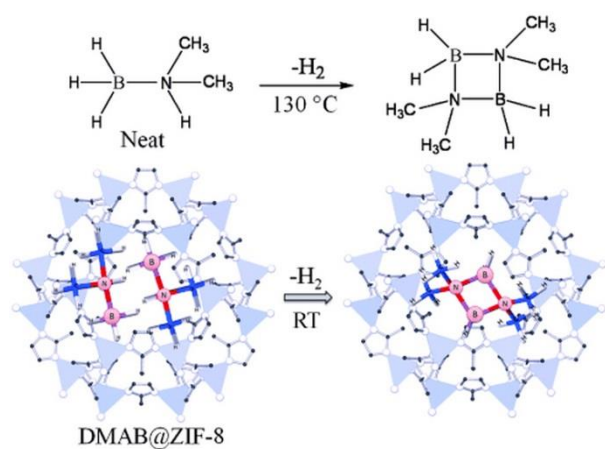

Fig. 13 Conceptual representation of the catalytic dehydrogenation and cyclisation of DMAB inside ZIF-8. Reprinted with permission from ref. 193. Copyright 2011 Wiley-VCH.

Apart from the pure ZIFs being active catalysts for a number of reactions, due to the large surface area and tuneable pore size, ZIFs can also act as promising supports for the incorporation of various metal or oxide nanoparticles to form novel catalysts with novel physical and chemical properties. Some typical catalytic applications of metal or metal oxide particles supported on ZIF materials are summarised in Table 3.

Table 3 Summary of the catalytic applications of metal or metal oxide particles supported on ZIF materials

ZIF material	Additional materials	Reaction(s) catalysed	Ref.
ZIF-8	Au nanoparticles	Oxidation of CO	195
ZIF-8 ZIF-90	Au nanoparticles	Oxidation of the aldehyde groups	196
ZIF-8	Au@Ag core-shell nanoparticles	Reduction of 4-nitrophenol	197
ZIF-8	Au, Ag and Pt nanoparticles	Oxidation of CO, hydrogen of n-hexene	198
ZIF-8	Pt nanoparticles	Hydrogen of alkene	199
ZIF-8	Pt and TiO_2 nanotubes	Degradation of phenol	200
ZIF-8	Pd nanoparticles	Amincarbonylation	201
ZIF-8	Ir nanoparticles	Hydrogenation of cyclohexene and phenylacetylene	202
ZIF-8	Ru nanoparticles	Asymmetric hydrogenation of acetphenone	203
ZIF-8	Fe_3O_4 micropheres	Knovenenagel condensation	204
ZIF-8	Zn_2GeO_4 nanorods	Conversion of CO_2	205
ZIF-65	Molybdenum oxide	Degradation of methyl orange and orange II dyes	206

Recently, the immobilisation of noble metal nanoparticles on the surface of ZIF materials as catalytically active catalysts has been widely explored. For instance, Au nanoparticles have been introduced into ZIF-8 to form nanocomposite which was applied as an active catalyst in the gas phase CO oxidation.[195] In another example, the encapsulation of Au nanoparticles into the ZIF-8 and ZIF-90 matrixes results in the formation of Au@ZIF-8 and Au@ZIF-90 nanocomposites respectively, which exhibited high catalytic activity in the aerobic oxidation of benzyl alcohol in methanol and benzene. It is claimed that the functional groups of ZIF-90 can promote the stabilisation and monodispersion of those size-matched Au nanoparticles.[196] Various nanoparticles including Au, Ag and Pt have been incorporated into ZIF-8 via an encapsulation strategy by Guang et al,[198] and the resulting supported catalysts have demonstrated good catalytic activity in CO oxidation and excellent selectivity for catalytic hydrogen of n-hexene versus cis-cyclooctene. Other

noble metal nanoparticles such as Ir,[202] Pd,[201] Ru [203] and Pt [199], were also incorporated into ZIF-8 as efficient catalysts.

Moreover, it has also been reported that the core-shell structured bimetallic Au@Ag nanoparticles can be stabilised on ZIF-8, synergistically improve the catalytic reduction reaction activity compared with the monometallic and alloy metal nanoparticles.[197] In particular, yolk-shell nanocrystal/ZIF-8 nanocomposites were produced using Cu_2O as a sacrificial template and the resulting yolk-shell nanostructures showed high activity and selectivity for gas-phase hydrogenations catalysis, where the measured activation energy of the yolk−shell nanostructure was different from that of the core−shell nanostructure, demonstrating the influence of the cavity structure on catalytic performance.[207] Additionally, core-shell magnetic microspheres Fe_3O_4/ZIF-8 were successfully prepared and exhibited excellent catalytic activity for Knoevenagel condensation reaction of benzaldehyde and ethyl cyanoacetate.[204]

In addition, other nanostructured materials such as nanotubes[200] and nanorods[205] have also been incorporated into ZIFs for photocatalytic activities. For example, Tayirjan et al loaded TiO_2 nanotubes with Pt/ZIF-8 and found that Pt/ZIF-8-TiO_2 nanotubes had remarkably improved the performance in the photodegradation of phenol,[200] which could be served as a potential photocatalyst for water purification. Moreover, ZIF-8/Zn_2GeO_4 nanorods composite exhibited enhanced photocatalytic conversion of CO_2 into liquid CH_3OH fuel,[205] and Molybdenum oxide incorporated into ZIF-65 deomonstrated the photocatalytic property of degradation methyl orange and orange II dye under visible light.[206]

3.3 Sensing and Electronic devices

The intrinsic properties of ZIF materials such as high textural properties, tuneable pore diameters and easy functionalisation enable them to be used in sensors and electronic devices. Particularly, the excellent selective adsorption properties of ZIFs render them good candidates for chemical sensing while the large microporosity and hydrophobicity of ZIFs are attractive for low dielectric constant applications.

Hupp and co-workers first demonstrated the using of ZIF-8 as a sensing material by constructing ZIF-8-based Fabry−Pérot device as a selective sensor for chemical vapors and gases.[208] The ZIF-8 sensor exhibited some chemical selectivity when it was exposed to the vapor of ethanol-water mixtures with varied ethanol contents, and the sensor could also showed ethanol-concentration-dependence responses.

In addition, due to the excellent properties, ZIFs are attractive matrices for the biosensor constructions. For instance, ZIFs based electrochemical biosensors for in vivo electrochemical measurement such as glucose have been successfully prepared.[209] ZIF materials including ZIF-7, ZIF-8, ZIF-67, ZIF-68 and ZIF-70 were served as a matrix respectively for co-immobilising

electrocatalysts methylene green and dehydrogenases glucose dehydrogenase on the electrode surface, and the as-fabricated ZIF-based biosensors demonstrated a high selectivity and sensitivity to the glucose in the cerebral system.

Based on the luminescence intensity, ZIF-8 has been studied as luminescent probes with multi-function sensitivity to detect metal ions and small molecules.[210] The luminescence intensity of ZIF-8 is highly sensitive to Cu^{2+} and Cd^{2+} ions and small molecules such as acetone due to the imidazole nitrogen site within the porous frameworks. Meanwhile, ZIF-8 nanoparticles can be used as sensing platform for fluorescence-enhanced detection of nucleic acids with a high selectivity down to single-base mismatch.[211] The DNA detection is shown in Fig. 14. In detail, the ZIF-8 nanoparticles combine closely with dye-labeled ssDNA after quenching the dye fluorescence; dsDNA, which detaches from the ZIF-8 nanoparticles, is formed from the fluorescence recovery of the ZIF-8/ssDNA complex with target. In addition, another ZIF material, $Zn_2(IM)_4 \cdot (DMF)$, where IM represents imidazolate and DMF stands for dimethyl formamide, exhibits broad range near-UV excitation and broadened photoluminescence emission, which makes this material potentially useful in sensing near-UV or UV white light.[212]
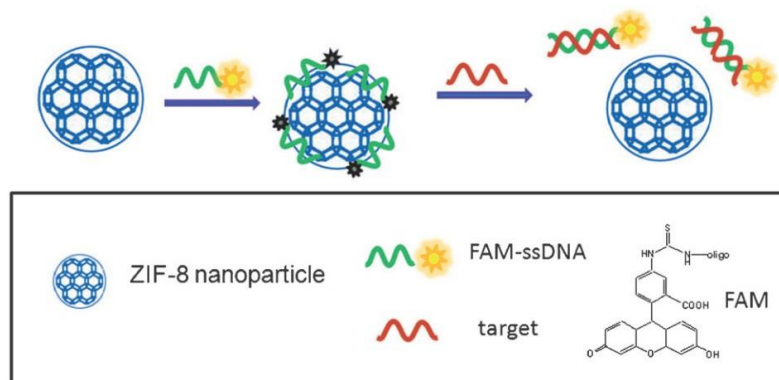

Fig. 14 A schematic illustration of fluorescence-enhanced nucleic acid detection using ZIF-8 nanoparticles as a sensing platform. Reprinted with permission from ref. 211. Copyright 2012 Wiley-VCH.

Recently, branched polyethylenimine-capped carbon quantum dots (BPEI-CQDs)/ZIF-8 nanocomposites have been successfully developed for the detection of Cu^{2+} ions in environmental water, and the results showed that it can be used as an ultrasensitive and highly selective sensor for Cu^{2+} ion.[213] It is also recognised that BPEI-CQDs/ZIF-8 composites not only exhibit excellent fluorescent activity and sensing selectivity due to the addition of CQD, but also show strongly and selectively accumulate target analytes because of the adsorption property of ZIF-8.[213]

ZIF materials have been used in electronic devices as well.[214, 215] For example, ZIF-8 was claimed to be a promising candidate to substitute future low-κ dielectrics in microelectronics by Salvador et al who found that the ZIF-8 films that were deposited on silicon wafers, had the effective κ value necessary for the chip devices and good mechanical properties too.[214] On the other

hand, ZnO@ZIF-8 heterostructures have shown great potential in electronic devices such as sensors. In particular, Zhang et al developed ZnO@ZIF-8 core-shell heterostructures which exhibited selective photoelectrochemistry responses to various hole scavengers because of ZIF-8 could successfully detect H_2O_2 in the presence of series buffer solutions (shown in Fig. 15).[215] In addition, the ZnO@ZIF-8 core-shell heterostructures, where ZnO forms the core and ZIF-8 forms the shell, have exhibited not only excellent semiconducting properties because of the addition of ZnO,[216, 217] but also molecule-size-selective abilities due to the adsorption property of ZIF-8.
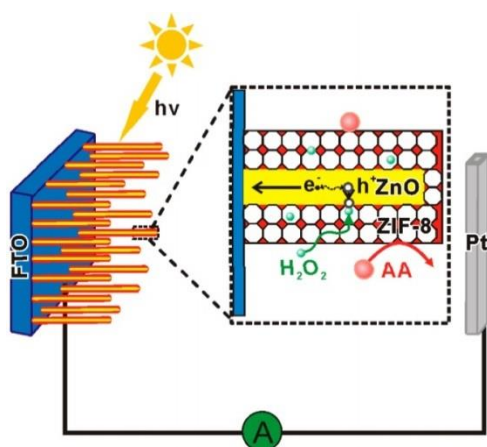

Fig. 15 Scheme of the photoelectrochemistry sensor with selectivity to H_2O_2 (where AA is ascorbic acid, FTO is fluorine-doped tin oxide). Reprinted with permission from ref. 215. Copyright 2013 American Chemical Society.

3.4 Drug delivery

Thanks to the excellent porous structures, exceptional thermal and chemical stabilities, tuneable multifunctionalities in the frameworks and pH-sensitive release properties, ZIF materials are emerging as a powerful platform for drug deliveries and/or controlled release of drug molecules.[218]

ZIF-8 has been treated as a valuable candidate for the delivery of anticancer agents. Inspired by the fact that ZIF-8 is stable in water and sodium hydroxide aqueous solution[14] but quickly decomposable in acid solution, Sun et al first found that ZIF-8 could be used as a drug delivery vehicle due to its pH-sensitive property.[219] ZIF-8 has also exhibited a significant loading capacity for the anticancer drug 5-fluorouracil due to its highly porous structures and excellent textural properties. By responding to the physio-pathological pH signals, two different approaches for the release of the encapsulated 5-fluorouracil from ZIF-8 are illustrated as shown in Fig. 16. The anticancer drug doxorubicin (DOX) was readily incorporated into ZIF-8 matrix.[220] The DOX incorporated ZIF-8 not only exhibited a high-loading (0.049 g DOX g^{-1}) and progressive release (66% of the drug released after 30 days), but also demonstrated a higher antitumoral potential and lower cytotoxicity towards the HL-60 and MCF-7 cell lines compared with the pure DOX. Recently, polyacrylic acid@ZIF-8 nanoparticles have been fabricated and employed as pH-dependent drug

delivery vehicles in a facile and simple way.[221] The synthesised polyacrylic acid@ZIF-8 nanoparticles possessed ultrahigh loading capability for drug DOX (1.9 g DOX g^{-1}) with pH-sensitive drug release property and excellent biocompatibility. More recently, carbon nanodots@ZIF-8 nanoparticles with tuneable sizes and fluorescence intensity have been produced as a carrier for simultaneous pH-responsive drug delivery and fluorescence imaging of cancer cells.[222] Release experiments showed that the 5-fluorouracil loaded carbon nanodots@ZIF-8 nanoparticles exhibited a slow release at an early stage while a faster one at later stage.
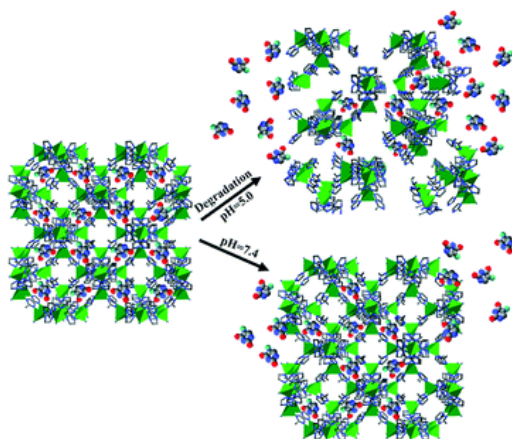

Fig. 16 Schematic illustration of two ways to release the encapsulated 5-fluorouracil from ZIF-8. Reprinted with permission from ref. 219. Copyright 2012 Royal Society of Chemistry.

Moreover, caffeine, an amphiphilic drug with remarkable lipolytic activity, has been encapsulated into the ZIF-8 cages.[223] In this case, ZIF-8 material could not only control the release of caffeine, but also provide thermal protection for the drug molecules in the cages during the high temperature process.

3.5 Summary

The intrinsic nature of ZIFs, such as diverse structures mimicking to convenetional zeolites, adjustable components and functionalities and excellent textural properties, enables ZIF materials a truly versatile class of crystalline porous materials with great potential for numerous applications, ranging from conventional applications including adsorption, gas separation and catalysis to beyond traditional ones like sensing and electronic devices, and drug delivery. Both pure ZIFs and ZIF-based films/membranes or composites have been developed as multifunctional materials with versatile performances in many application fields. The combinations of ZIFs with other nanostructured components to form novel nanocomposites may further facilitate the wide applications due to the advantages of both components. Other novel applications of ZIFs such as in the areas of electrochemical and mechanical applications are to be developed. More exploiting of ZIFs in clean energy and/or environmentally sustainable energy resources will be emerged soon.

4. Conclusions and Outlook

Recent years have witnessed explosive researches and development in ZIFs, from synthesis to characterisation and applications. Their intrinsic porous nature of ZIFs combined with structures analogous to conventional aluminosilicate zeolites render a wide range of synthesis approaches being available for efficient generation of ZIFs. The abundant functionalities in their framework coupled with the high textural properties enable ZIF materials to be a class of versatile crystalline porous materials with great potential in a large number of applications, ranging from conventional adsorption, separation and catalysis to modern electronic devices, sensing and drug delivery, from clean energy to environmental remedy. Although great progress has been made on the synthesis and applications of ZIF-based materials, undoubtedly more new synthesis strategies and utilisation fields of ZIFs will emerge in the future.

To date, conventional synthesis methods including solvothermal and hydrothermal routes have been widely explored to produce powder-based ZIF materials, while ionothermal and sonochemical synthesis routes have been developed quickly in the past years. Moreover, other alternative approaches such as mechanochemical synthesis method, dry-gel or steam assisted conversion methods have also been adapted for the preparation of ZIFs. To fabricate ZIF-based films/membranes, both secondary growth crystallisation and in situ crystallisation methods are readily available for effective synthesis. Generally, the properties of the obtained ZIF materials are variable depending on the synthesis methods used.

The variety of organic linkers and the diversity of link-link interactions offer rich chemistry to be developed and provide huge amounts of possibilities to form ZIFs with wide range of structures and properties, which is a much larger playground compared to conventional zeolites. Nevertheless, the concepts from other research areas, especially from zeolite chemistry, have found their way in ZIF synthesis, but they need to be extended and pursued deeper in detail. Some synthesis strategies such as microwave-assisted syntheses, electrochemical synthesis as well as continuous microfluidic synthesis, have emerged as alternative approaches to yield ZIF materials under milder reaction conditions with tuneable particle sizes and properties. Furthermore, novel synthesis routes such as electrospray deposition technique may be developed to fabricate ZIF membranes.

Apart from the generation of ZIF materials in the form of powder or film/membrane, shaping ZIF powders into pellets or monoliths is vital in some practical applications, which needs further investigations. In addition, developing new synthesis strategies to form hierarchical superstructures will be of importance for some targeted applications of ZIFs. On the other hand, in order to bring ZIFs from laboratory studies to industry applications, it is crucial to develop practically available synthesis method which is cost-effective and reproducible to produce ZIFs in large scales to meet the potential commercial application needs. With the effort from scientists in relevant fields, novel

synthesis approaches for ZIF materials that are low-cost, scalable and reproducible will emerge in the near future.

The potential applications of ZIFs and ZIF-based materials are directly linked to their properties. The diverse structures of ZIFs mimicking to convenetional zeolites form a large amount of permanent porosities in the frameworks, and the rich imidazolate linkers offer abundant components and functionalities for effectively adjusting the porosities and surface chemistry. Therefore the crystalline ZIF materials present great potential in conventional applications of porous materials, such as adsorption, catalysis and separation. ZIF materials have exhibited great adsorption capacities in various energy gases such as CO_2, methane and hydrogen, and ZIF-based membranes have shown very good separation performance in various gas separations. Moreover, ZIF-based materials also have demonstrated promising applications in fields that are beyond traditional applications of porous materials, ranging from sensing and electronic devices to drug delivery. Undoubtedly, more research is needed to explore those fast developing and emerging fields.

Both pure ZIFs and ZIF-based films/membranes or composites have been developed and exhibited as functional materials with versatile performances in many application fields, moreover, the combination of ZIFs with other nanostructured components to form novel multifunctional nanocomposites can further facilitate the wider applications due to the fact that they have the advantages of both components. In addition, novel applications of ZIFs in the fields of electrochemical and mechanical applications will no doubt be developed in the future, and more exploiting of ZIFs in the applications of environmentally sustainable energy resources will emerge soon.

To further develop new synthesis strategies and explore the potential applications of ZIFs, it is vital to take advantages of the knowledge and experiences gained from other research fields such as those in zeolites. Despite of a very short development history, ZIFs have attracted increasing attention and many achievements have been obtained in the past 5 years. Given the strong interest in ZIFs by various research communities, we believe that new concepts and techniques for the synthesis of ZIFs and ZIF-based materials, new applications of the fast-growing unique materials and even more new opportunities for further exploring ZIFs and ZIF-based materials will continue to emerge in the future.

Acknowledgements

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Table of Contents:

Recent progress on the synthesis and applications of zeolitic imidazolate framework materials is presented in this review.