A REVIEW OF RECENT WORK ON USING METAL–ORGANIC FRAMEWORKS TO GROW CARBON NANOTUBES

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Abstract. Carbon nanotubes (CNTs) have long been known as a class of one-dimensional carbon nanomaterials with sp^2-hybridized structures that can be constructed with a very large length-to-diameter ratio, which is significantly larger than that of any other carbon nanomaterials. It is well known that CNTs exhibit many excellent properties in mechanics, electricity, chemistry, optics, etc., and are widely used in various fields, thus attracting scientists' attention. In this context, the development of new strategies for optimizing and synthesizing CNTs has far-reaching significance and demand. On the other hand, most metal–organic frameworks (MOFs) are microporous crystals constructed from ordered and uniform metal ions/clusters and organic linkers to obtain crystalline solids with potential porosity. Using MOF materials as precursors, hierarchical CNT-based composite materials, which are difficult to synthesize through the traditional catalyst-assisted chemical vapor deposition method, can be conveniently synthesized by thermal treatment at high temperature. In the process of converting MOFs into CNTs, MOF crystals are used as both catalysts and carbon sources, which are necessary for the growth of CNTs, and they are also used as templates and/or carriers for additional catalysts. Therefore, there are various possibilities for the thermal conversion of MOFs into CNT-based composite materials. In this review, we mainly summarize the two aspects of catalysts and synthetic strategies for MOF-derived CNT-based composite materials. Despite the rapid development in this area, there is still much space for exploration. In order to accurately control the synthesis of CNTs, we should deeply explore the thermal conversion process and mechanism for the conversion of MOFs into CNTs.

Background. Carbon nanotubes (CNTs) have long been known in the form of multi-wall carbon nanotubes (MWCNTs) based on nested single-wall carbon nanotubes (SWCNTs), which are a class of one-dimensional nanomaterials with a radial dimension of nanometers and an axial dimension of micrometers.[1] Such tube-based structures were first observed by Radushkevich and Lukyanovich in 1952.[2] Subsequently, a Japanese scientist, Dr Iijima of the NEC Corporation, described CNTs in detail in Nature in 1991,[3] which ignited extensive research by scientists.[4] It is well known that the carbon element in CNTs exhibits sp^2 hybridization,[5] and CNTs are endowed with many excellent mechanical,[6,7] electrical,[8,9] chemical,[10] optical[11,12] and thermal properties.[13] In this context, CNT-based composites made from two or more constituent materials, which have significantly different physicochemical properties when combined with CNTs, can be widely used in various applications, such as electrocatalysis,[14,15] nanoelectronic devices,[16,17] thermally conductive films,[18] structural materials for aviation,[19]etc. Among the facile synthetic methods,[4] catalyst-assisted chemical vapor deposition (CCVD)[20] can efficiently control the growth of various desired SWCNTs as well as MWCNTs and is utilized on a large scale. To date, optimizing and developing new strategies for growing CNTs still has far-reaching significance and necessity.[21]On the other hand, metal–organic frameworks (MOFs) are ordered and porous crystalline materials built from metal ions/clusters and organic ligands through versatile coordination bonds.[22] According to reported research, the combination of MOFs and CNTs could enhance the electrochemical energy storage and conversion[23,24] and catalytic performance[25] of their composite materials. Therefore, researchers have considered the in situ conversion of MOFs into MOF-derived CNT-based composites,[26] which is a convenient strategy for improving the properties of these derived materials.[27,28] In recent years, due to MOFs' unique pore structures and controllable morphology, and the combination of metal components and carbon sources, people have been keen to use MOF precursors for designing and synthesizing various metal-based and carbon-based nanocomposite materials by pyrolysis at high temperature. Many previous studies have shown that by adjusting the pyrolytic conditions and the combination of ligands and metal species in the MOF materials, the structure and morphology of the derived carbon materials can be controlled and tuned,[1] thereby preparing a variety of carbon materials, such as graphitized carbon nanosheets, carbon nanotubes, porous carbon.At present, due to technical reasons, there are no literature reports on MOF-derived SWCNTs, which need to be explored in the future, so we only discuss MOF-derived MWCNTs in the following. In 2013, Yang et al. doped ZIF-8 with iron ions and pyrolyzed a mixture of the resulting Zn-Fe-ZIF crystals and dicyandiamide under a nitrogen atmosphere, so that N-doped CNT-based composites (NCNTs) were first obtained from a MOF template, which has drawn people's attention to the strategy of converting MOFs into CNTs.

In the transformation process, MOFs can simultaneously act as both catalysts and carbon sources, which are vital for the growth of CNTs, as well as templates and carriers for additional catalysts and carbon sources, providing unlimited possibilities for achieving the thermal conversion of crystalline MOFs to synthesize CNT-based nanocomposite materials. In addition, due to the spatial confinement effect and the energy released during the breakage of coordination bonds, the pyrolysis of MOF materials helps to activate metal-based catalyst nanoparticles (NPs) and organic components and provides favorable conditions for the reorganization of carbon species to form CNTs.–Furthermore, the morphologies of MOFs are diverse and easy to control, and this can be exploited to prepare the expected hierarchical CNT-based structures and composites which are difficult to obtain through traditional CCVD methods. With the emerging prospects of MOF-derived CNT-based nanomaterials in energy-related applications, herein we mainly summarize MOF-derived CNT-based composite materials from the perspective of catalysts and synthetic strategies as listed in Table 1. Finally, recent challenges will be discussed and future perspectives will be proposed for designing and preparing more promising MOF-derived CNT-based nanomaterials for wide ranging applications in various fields.

Catalysts for CNT growth. Generally speaking, high catalytic activity catalysts play a key role in the growth of CNTs.[52,53] Although CNTs can grow without the presence of catalysts,[54] the efficient growth of CNTs heavily relies on the participation of catalysts.[55] Traditionally, according to vapor–liquid–solid theory,[56] iron group transition metal NPs such as iron,[57] cobalt,[58] and nickel[59] are widely used to catalyze the formation of CNTs. Among them, polymetallic alloys like FeNi,[60] CoNi,[61] FeNiCo,[62]etc. also exhibit highly efficient catalytic activity to construct CNTs. Different metals have different interactions with carbon and show different carbon solubility, so the carbon layer is etched by dissolving carbon or by catalytic carbon hydrogenation at a high temperature. Fe, Co, etc. have a large carbon solubility, while Au, Cu, etc. have a low carbon solubility.[63] The dissolution and precipitation of carbon by metal particles may lead to reorganization of the carbon structure and the formation of defective carbon, core–shell structures of carbon-encapsulated metal particles, etc.[64] Besides, some literature has reported that metallic compounds such as ZrO_2/HfO_2[65] and TiO_2[66] can also catalyze CNT growth, which confirms that catalysts with only nanoscale curvature and carbon adsorption sites can also diffuse carbon segments on the crystal planes,[67] so that CNTs can efficiently grow along the specific crystal lattice.[52] Using particulate catalysts, the CCVD growth method is popular for the preparation of CNT materials, as it yields high-quality nanotubes and exhibits a degree of control over diameter, length, and morphology, but achieving repeatability is a major problem.[21] In this context, porous coordination polymers are structurally composed of metal and carbon species, thus pristine MOF materials can be intrinsically and steadily self-catalyzed by MOF-derived metal-based catalysts to construct CNTs according to the previously reported literature.[68] Furthermore, introducing external catalysts into the large pores and channels of MOFs and replacing the original coordinating nodes through transmetallation and impregnation are two common and reliable approaches for the uniform distribution of introduced metal atoms in MOF structures (Fig. 1). We can choose to introduce[46] or not introduce additional catalysts[69] into the MOF precursors which will be decomposed and reduced to form different types of metal-based particulate catalysts (single metals, polymetallic alloys, metallic compounds, etc.) under the high-temperature pyrolysis conditions. In summary, in the pyrolysis process, there are three different types of catalysts which can efficiently catalyze and grow CNTs. In this section, we are going to divide the MOF-derived catalysts for CNT growth into the following types for discussion: (1) single metal catalysts, (2) polymetallic alloy catalysts, and (3) metallic compound catalysts. They grow CNTs through two different catalytic mechanisms. Single metals, polymetallic alloys, and metal carbides with carbon solubility grow CNTs according to the vapor–liquid–solid theory.[70] Metallic compounds composed of metals and nonmetals (excluding metal carbides) provide only nanoscale curvature and carbon adsorption sites for diffusing carbon segments on the crystal planes so that CNTs can efficiently grow along the specific crystal lattice.[65]

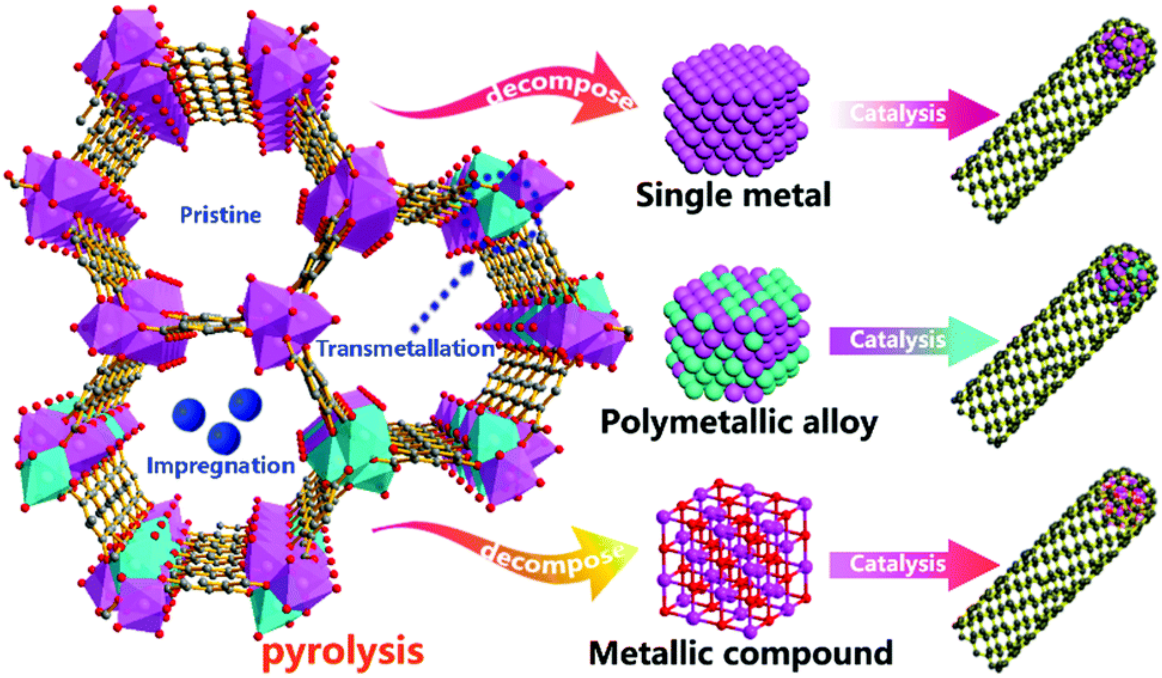

Fig. 1 Schematic diagram of the formation of MOF-derived CNTs catalyzed by three types of catalysts, namely single metals, polymetallic alloys, and metallic compounds.

SINGLE METAL CATALYSTS.

As always, metal elements have been considered to be the best catalysts and many researchers have found that single metal NPs (like Fe,[71] Co,[72] Ni[73]) can efficiently catalyze the formation of CNTs through calcination of the corresponding MOFs. In 2017, Mai's group developed a simple, versatile, and efficient strategy to pyrolyze

MOF crystals in which a single MOF precursor with its own nanocatalyst and carbon sources is decomposed in situ to form a CNT composite with the same morphology by pyrolysis at 435 °C under argon.[47] A schematic diagram of the transformation of a ZIF-67 crystal into a hollow CNT-assembled dodecahedron is shown in Fig. 2a, where the ZIF-67 dodecahedron is pyrolyzed under the protection of Ar at a low temperature. The coordination bond between the metal ion and the organic ligand in ZIF-67 is first broken and the overall structure is gradually decomposed, while the metal ions/clusters are further reduced to nanocatalysts by the generated reductive gas, and these in situ formed nanocatalysts catalyze the formation of N-doped CNTs (N-CNTs) from the residual organic ligands. Since metal nanocrystals preferentially form on the surface, the outer layer is first converted into N-CNTs, and the growth direction is from outside to inside, resulting in internal voids. In Fig. 2b, the thin multi-walled N-CNTs are abundant (10–20 nm outer diameter and 5 nm inner diameter), and the cobalt NP (5 nm diameter) catalysts are encapsulated at the tips of the CNTs. On the one hand, it is found that nanocatalysts derived from iron group based MOFs exhibit high catalytic activity for the in situ formation of CNTs. Secondly, organic ligands with abundant hexatomic or N-heterocyclic carbon rings can lower the cyclization energy barrier and promote the formation of CNTs. Moreover, the decomposed coordination bonds in highly ordered MOFs release more energy to activate the remaining metal ions/clusters as well as organic linkers, thereby facilitating the formation of nanocatalysts and the following growth of CNTs. On the other hand, the particle size of the catalyst has a huge influence on the growth process of CNTs, and a smaller catalyst is more beneficial to the growth of CNTs. Therefore, it is vital to control the pyrolytic conditions to obtain abundant nanocatalysts. Additionally, this method can be successfully extended to other iron group based MOFs, including Ni-ZIF, Ni-BTC, Co-BTC, Co-MOF, etc., to obtain the corresponding MOF-derived CNT assembly architectures (Fig. 2c–f). Zhu et al. also reported for the first time that a new N-molecule-assisted autocatalytic carbonization process converts iron-based MIL-88B-NH_2 into conductive CNTs and micro/mesoporous carbon composites (MIL/CNT-Fe).[74] During the calcination process, the volatile ammonia gas reduces the Fe element in the Fe-MOF to iron nanocrystals, which catalyze the formation of Fe,N-doped CNTs, while the remaining framework is etched by ammonia gas to obtain a type of micro/mesoporous carbon structure (Fig. 2g). In general, by selecting single metal catalysts with high carbon solubility, especially iron group metals, CNT-based composites can be easily synthesized from the corresponding MOFs. We believe that by controlling the pyrolytic conditions, this single metal catalyst strategy can be further extended to other metals (Cu,[79] Au,[80] W,[81] Mo,[82]etc.), which are considered to have low carbon solubility, for the in situ growth of MOF-derived CNT composites with adjustable components and morphology.

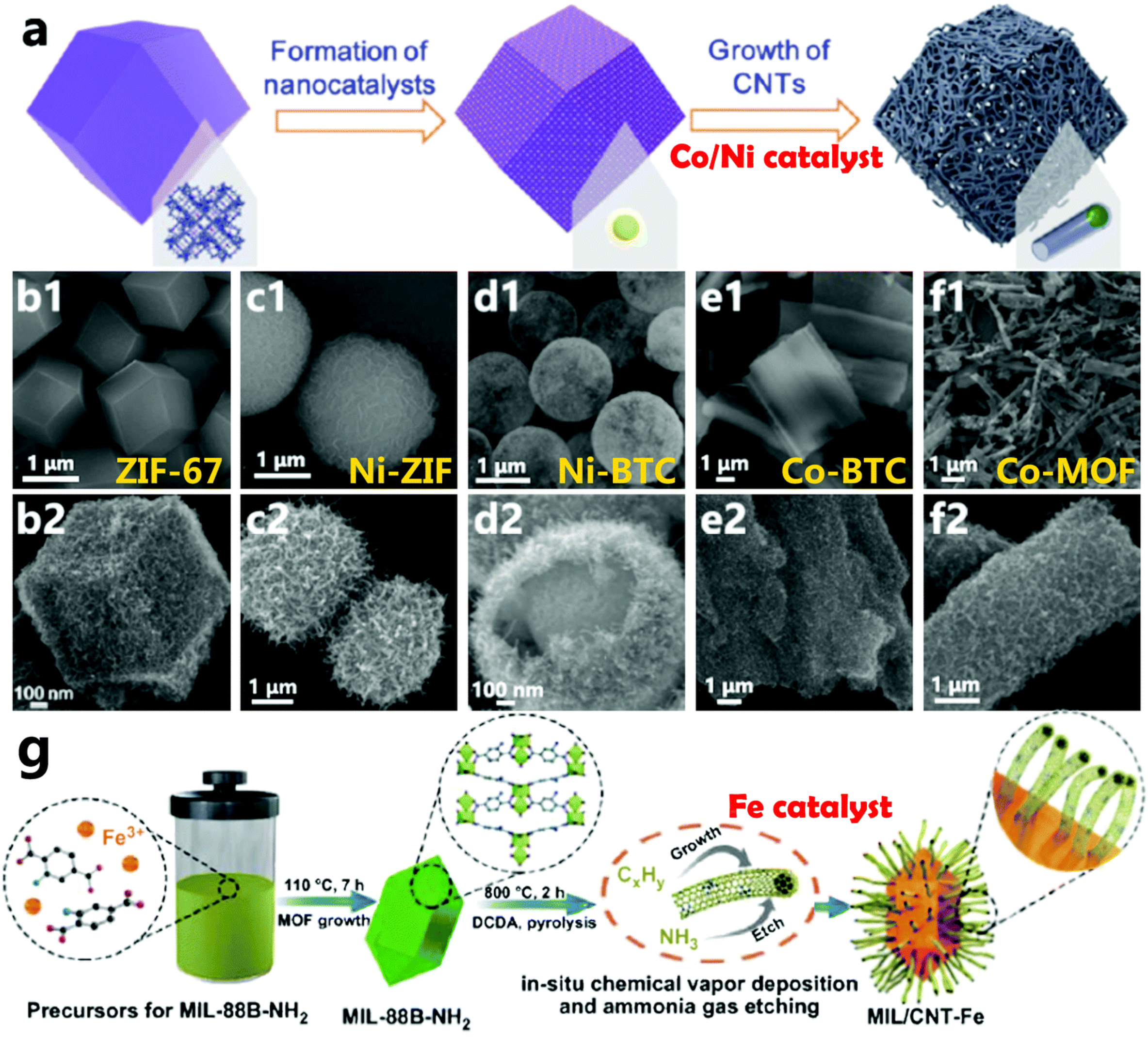

Fig. 2 (a) Schematic of the formation process of N-CNTs from ZIF-67, finally obtaining an N-CNT-assembled hollow dodecahedron. (b1 and b2) SEM images of the ZIF-67 precursor and the derived N-CNT-assembled hollow dodecahedron; (c1 and c2) SEM images of the Ni-ZIF precursor and the derived N-CNT-assembled microspheres; (d1 and d2) SEM images of the Ni-BTC precursor and the derived CNT-assembled hollow microspheres; (e1 and e2) SEM images of the Co-BTC precursor and the derived CNT-assembled microsheets; (f1 and f2) SEM images of the Co-MOF precursor and the derived CNT-assembled nanorods. Reprinted with permission from ref. 47. Copyright (2017) American Chemical Society. (g) Illustrative procedure for the iron(III)-2-aminoterephthalic framework (MIL-88B-NH_2, MIL = Materials from the Lavoisier Institute) and the resultant CNT and Fe-decorated carbon hybrids (MIL/CNT-Fe). Reprinted with permission from ref. 74. Copyright (2019) Springer Nature.

2.2 POLYMETALLIC ALLOY CATALYSTS

In principle, metal alloys can also catalyze the assembly of carbon sources into

CNTs.[83] Arne Thomas et al. reported the preparation of bifunctional catalysts (FeNi catalysts) via one-step pyrolysis of a mixture of bimetallic MIL-88-Fe/Ni and dicyandiamide (DCDA) to obtain MOF-derived N-doped carbon materials (Fe–Ni@NC-CNTs).[75] First, by a solvothermal method, terephthalic acid, $FeCl_3$ salt, and $Ni(NO_3)_2$ salt were assembled into MIL-88-Fe/Ni nanorods. After that, DCDA and the crystalline MOF precursor were physically mixed by mechanical grinding, and pyrolyzed in an inert atmosphere at 800 °C (Fig. 3a). The TEM image of Fe–Ni@NC-CNTs clearly demonstrated that a uniform and porous CNT-anchored network was observed (Fig. 3b), and the nanorod morphology of the precursor could be partially retained. High-resolution TEM showed a particle at the tip of the derived CNT, which was attributed to $FeNi_3$ NPs, which confirmed that the formation of CNTs was conveniently catalyzed by the FeNi alloy (Fig. 3c). In 2018, Wu and colleagues introduced Fe^{3+} cations into a Zn/Co bimetallic organic framework, denoted by Zn_1Co_1-BMOF, and the formed Fe–Co dual sites were annealed at 900 °C in an N_2 atmosphere to catalyze the decomposition of the organic ligands in the bimetallic MOF precursor, thus FeCo alloy NPs embedded in N-doped CNTs [(Fe,Co)/CNT] which were rich in Fe–Co dual sites were successfully constructed (Fig. 3d and e).[76] The Fe and Co atoms were coordinated with N at the atomic scale, which was confirmed by the EEL spectrum (Fig. 3f). And bimetallic NiCo-ZIF is a suitable precursor for the growth of NiCo/NCNTs as shown in Fig. 3g.[77] It is easily reduced into NiCo NPs and almost completely converted into CNTs after being annealed at 700 °C under an H_2/Ar atmosphere. Zhang et al. prepared a bimetallic FeMn3-1 template which was subsequently treated by thermal carbonization with melamine. They successfully obtained a hierarchical carbon structure of Fe_3Mn_1 alloy NPs coated with N-doped CNTs (Fe_3Mn_1/N-CNTs-100) (Fig. 3h),[78] in which Fe may be beneficial to the formation of a carbon layer on the surface of the NPs, and Mn can promote the growth and elongation of CNTs. The synergistic effects of different metals in the polymetallic alloy help to regulate the shape and quality of the obtained carbon materials.[55,84] Thus, we believe that polymetallic alloys consisting of iron group metals (Fe, Co, Ni) and other metals with high carbon solubility are likely to have high catalytic activity for the formation of CNTs,[52] and reconstituted polymetallic alloy catalysts of various types are conducive to the development of different CNT-based nanocomposites for further applications.

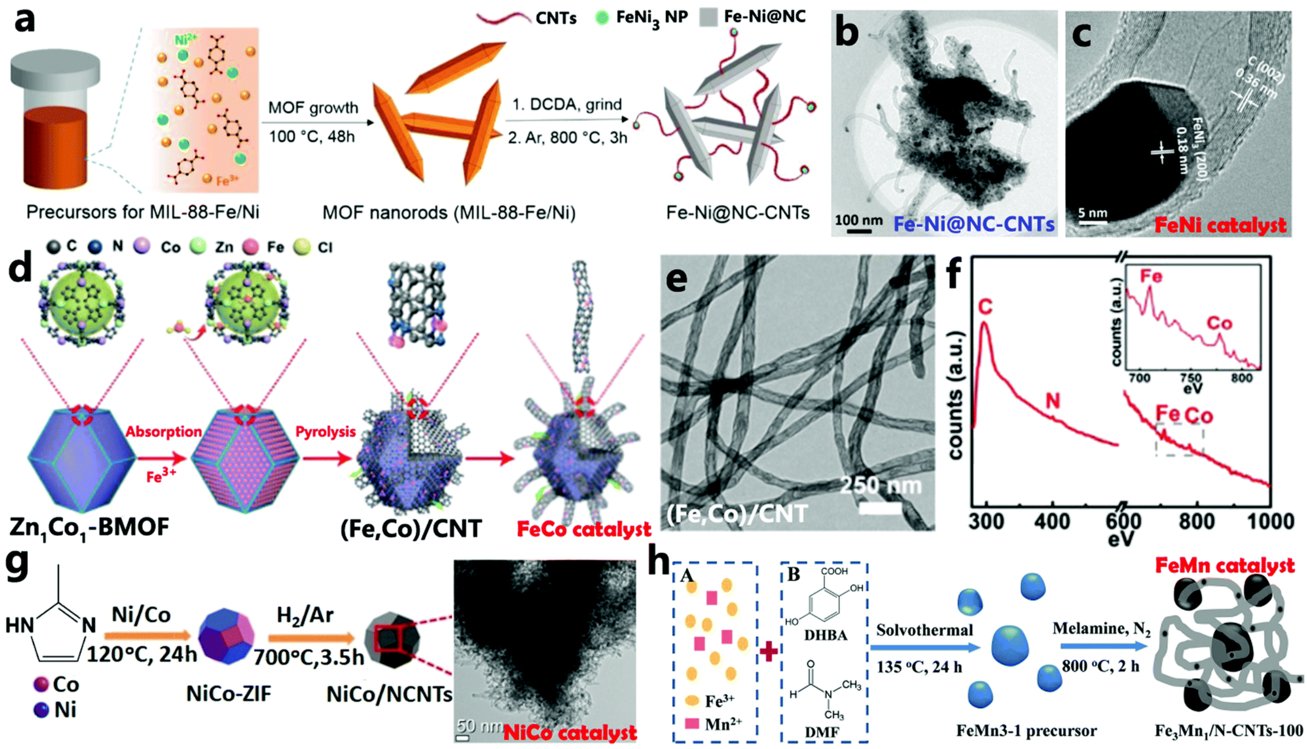

Fig. 3 (a) Synthetic procedure of MIL-88-Fe/Ni and Fe–Ni@NC-CNTs, (b and c) TEM images of Fe–Ni@NC-CNTs. Reprinted with permission from ref. 75. Copyright (2018) Wiley. (d) Schematic image of the preparation of (Fe,Co)/CNT, (e) TEM image, and (f) the EEL spectrum of (Fe,Co)/CNT. Reprinted with permission from ref. 76. Copyright (2018) Royal Society of Chemistry. (g) Scheme of the synthesis of NiCo/NCNTs. Reprinted with permission from ref. 77. Copyright (2020) Elsevier. (h) Illustration of the preparation of the FeMn3-1 precursor and the derived Fe_3Mn_1/N-CNTs-100 catalyst. Reprinted with permission from ref. 78. Copyright (2018) Wiley.

Conclusions and perspectives.

In the past few years, researchers have developed diverse strategies to easily and efficiently prepare unique MOF-derived CNT-based composite materials. Focusing on catalysts and synthetic strategies, we have reviewed the current research results and revealed the conditions and advantages of using MOF precursors to grow CNTs. First, MOF materials are regarded as good self-catalytic precursors containing both metal and carbon sources. Secondly, the abundant and large pore structures in MOFs are able to load external catalysts, and allow spatial confinement during calcination. Finally, the synthesis of MOFs is convenient and controllable, and MOFs can be easily loaded on other substrates or used to form precursors of hierarchical CNT-based composite materials via the self-template method. Despite the recent rapid development of research in this area, there are still many deficiencies and much space to explore. (i) The specific process and mechanism of the catalysis of the formation of carbon components are not clear. (ii) The purity, uniformity, and structure of MOF-derived

CNTs cannot yet be accurately controlled. (iii) The research on the direct growth of CNTs using metallic compounds is still inadequate. (iv) The effect of non-metal elements on the growth of CNTs needs to be deeply researched. (v) The approach of growing CNTs by calcination is too monotonous, thus we need to further develop various energy supply methods. Therefore, in future research work, we will overcome the practical obstacles by designing precise experiments and specific MOF structures, so as to obtain more controllable and diverse MOF-derived CNT-based composite materials for practical applications.

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