**Abstract.** NaN₃, as a kind of rich-nitrogen energetic material, engaged in the synthesis of hierarchical transition metal (Co/Ni) organic framework materials (MOFs) through a facile hydrothermal reaction, during which aqueous N₃⁻ function groups being as an unique ligand in preparation of novel coordination polymer with the existence of Co²⁺ (or Ni²⁺) salts and dicyandiamide. The obtained compounds (Co-eMOF, Ni-eMOF, NiCo-eMOF) were characterized by structure and composition analysis, specific surface area, thermogravimetric analysis (TGA) and crystal X-ray diffraction. The prepared products regardless of the metal cautions (Co, Ni, or coexist Co and Ni), perform a well three-dimensions (3D) nanostructures with spherical shaped monoliths, known as organic framework materials. The as-prepared products with developed porosity demonstrate a high surface area in range of 80~130 m²/g. XRD patterns for these three examples show similar lattice crystalline, which to an extent matches well with the simulated MOF-74 materials, suggesting profound formation of oriented crystal growth. XPS reveals the compounds all equipped with high nitrogen content (54~60 at%), which is largely hinging on the contribution from N₃⁻ function groups, suggesting the superiority of NaN₃ serving as the rich nitrogen precursor. Accounting for extensive application, we will apply this as-prepared (Co/Ni) MOF materials as one kind of nitrogen-rich precursor and conduct them for further calcination treatment for preparation of graphite-based transition metal carbides (TMC), and it is highly anticipated to achieve efficient activity towards electrocatalysis in our follow-up actions.

1. Introduction
Metal–organic frameworks (MOFs), as a kind of crystalline materials with hierarchy surface morphology and adjustable channel structure[1-3], have encouraged a broader range of applications in recent years in bio-detection [4] and electrochemistry[5, 6]. [7-9] MOFs is served as an organic-inorganic hybrid material with pores channel which is self-assembled by coordination bonds between organic ligands and inorganic metal ions or clusters.[10, 11] General methods to obtain classical MOFs are conclusive in stirring, hydrothermal, ionothermal, microwave synthesis.[12] [13]For instance, Yang et al. group prepared a kind of layered structural Co-MOF nanosheets through oil bath in stirring and this products were reported firstly to be applied as an electrode material for super capacitors.[1] Du et al. group fabricated a novel hierarchical porous nickel based metal-organic
framework (Ni-MOF) by a facile hydrothermal process. [14] Works on the rational construction of novel MOFs with appropriate selection of ligands and metal ions are of great significance for the fundamental development of nanomaterials science. [13, 15]

Based on the preceding achievements, it was found that the synthesis of a new MOFs was mainly depends on the control of source of the metal ions, stoichiometry, temperature, the pH value of the solution, from which carbon-based organic polymers were generally applied as the ligand source. [16, 17] In that case, our current interest uncharacteristically focused on the selection of ligand type rather than approach, which we think should be a key research orientation to be taken into account for high quality synthesis of new coordination compounds. In that case, we reported the introduction of NaN3 in this study as a new kind of ligand precursor to prepare coordination polymer, to the best of our knowledge, little has been reported on the nanomaterial synthesis using NaN3 based on the energetic materials filed. NaN3, as a kind of nitrogen rich ionic salt, contains the explosive functional group of N3− and can dissolve in water, making it unique in energetic materials family. That is, the advantage of its simple composition, rich nitrogen and ionicity of NaN3 enable its potential application in chemical synthesis. From the author’s group, researchers were committed to the synthesis of nano energetic materials and repaying to the progress of advanced materials by using energetic materials, that’s what called, EM (energy materials) to AM (advanced materials) strategy, aiming at achieving the novel synthesis and modification of advanced nanomaterials by applying the high density energy of energetic materials. [16] This strategy conducted in our team has proven tremendous possibilities in synthesis of functional nanocarbon-based materials under a controllable operation, it also enables oriented nanostructure shape and profitable element doping through energetic materials, from which the modified materials in our work have already demonstrated significant application towards catalysis field.

In that case, taking NaN3 priority for shaping nanomaterials matches well with our background, it is also a reasonable and ambitious option combined with our preceding effectual attempts. [16, 18, 19] In general, we applied NaN3 in nanomaterials brunch by exploiting its micro-blast effect from deflagration under a certain temperature, such as the highly decomposed Na clusters have strong reductivity in chemical reaction, or taking advantage of high-speed nitrogen radicals as dopant source if things can enable a high nitrogen doping as we expected. Disappointingly, it remains a great challenge to capture those nitrogen species as for their high mobility, as we know most of the nitrogen species split out with the gas flow from the reaction region and just leave tiny amounts in final state. That’s tremendously wasteful as counting on its rich nitrogen condition. In this study, we first applied NaN3 in aqueous solution for the construction of MOFs through hydrothermal process on condition that the technique was comparatively mature and employed extensively. Such relative low temperature condition enables slower thermal decomposition of NaN3 rather than instantaneously lose the nitrogen in form of radicals in an open environment, thus make the in situ generated N3− ligands cross linking to the reactants (nickel (cobalt) ions and dicyandiamide) sufficiently. Creating the aqueous solution for NaN3 helps reserve the composed nitrogen element in maximum, it’s indeed satisfied that we achieved high content of nitrogen dopants in the target products of hierarchical transition-based (Co/Ni) metal-organic framework from XPS results. In terms of application of this kind of prepared coordination compound, we implemented a facile calcination for this kind of polymer to obtain the highly efficient Co/Ni carbon-based electrocatalyst towards oxygen reduction reaction (ORR), which would be demonstrated in details in our next work. However, large-scale application of NaN3 in synthesis of nanomaterials may be limited on account of the toxicity, besides, the N3− reaction mechanism still remains unclear on a microscope level, further investigation on this potential system is still in progress.

2. Experimental Section

2.1. Materials

Ni-eMOF: precursor for hydrothermal reaction were dicyandiamide (DCD), nickel salt (NiCl2) and sodium azide (NaN3). In a typical process, 1 g NaN3 and 1 g DCD were mixed uniformly in a 100 ml
beaker, then 80 ml DI water was added and stirred for 10 minutes. After complete dissolution, 0.5 g NiCl₂ was put into the mixture and continuously stirred for 30 minutes. Subsequently, the aqueous solution of NaN₃, DCD and NiCl₂ was placed in a 100 ml sealed high-pressure reactor and heated at 130°C for 16 hours. The resulting purple precipitates were separated and washed with distilled water for three times, then the as-prepared products (Ni-eMOF) were dried at 60°C for 12 hours. (the letter ‘e’ in label of “Ni-eMOF” represents the introduction of energetic material)

Co-eMOF: the preparation procedure was the same with that of Ni-eMOF except for replacing the metal salt with CoCl₂.

NiCo-eMOF: the preparation procedure was the same with that of Ni-eMOF except for replacing the metal salt with mixture of NiCl₂ and CoCl₂ (mole ratio of NiCl₂: CoCl₂ =2: 1), where the total amount of NiCl₂ and CoCl₂ was 0.5 g.

2.2. Characterization
Transmission electron microscopy (TEM) and High resolution TEM (HRTEM) (FEI F30) with an accelerated voltage/current of 200 kV/90 μA are performed to verify the surface morphology. Thermogravimetric analysis (TGA) were conducted by TGA/DSC1/1100 L from room temperature to 800 °C at a heating rate of 10 °C/min in N₂ mixture atmosphere. Brunauer–Emmett–Teller (BET) was applied to show the surface area using tristar3020 (MICROMERITICS INSTRUMENT CORP). X-ray diffraction (XRD) analyzer Bruker D8 ADVANCE Cu-Kα (λ=1.5418 Å) was performed to observe the crystalline formation. X-ray photoelectron spectroscopy (XPS) measurements was achieved by K-Alpha (Thermo Fisher, America) with accelerated voltage of 5 kV and Al Ka as the excitation light source.

3. Results and Discussion
Hierarchical porous transition-based metal (Co,Ni, Ni/Co) organic framework were fabricated by a facile one-step hydrothermal approach using cobalt (nicketle) acetate tetrahydrate as the metal source and a mixture of DCD and NaN₃ as a ligand. The surface morphological investigations of the obtained transition metal MOF were presented in Figure 1, including Co-eMOF, Ni-eMOF and NiCo-eMOF. The SEM images (Figure 1a—Figure 1f) demonstrated that all the samples possess conglomerated spherical morphologies. Thereinto, the SEM view of Co-eMOF in Figure 1a shows the monolith material was consisted of a large number of agglomerated spheres, the inset image in Figure 1a showed the as-synthesized powder in a deep yellow color. Figure 1d of Co-eMOF presented the surface of MOF crystal formed with numerous of two dimensional nanosheets with typical hexagon nanoflakes structure possessing average size of 1 um, revealing the uniform distribution with dimensions in the nano- to micro-size range. The hierarchical porous structure of Co-eMOF was further investigated by high resolution TEM (HRTEM), as shown in Figure 1g, demonstrating the conglomerated multi-layered porous nanostructure was assembled onto spherical shells with the thickness of approximately 50 nm and some thin nanosheets were also observed on the edges as shown in the inset of Figure 1g. The NiCo-eMOF powder mixing with both Ni and Co (mole ratio/Ni:Co=2:1) has deep brown color, as shown in Figure 1b, the nanostructure of which was also formed into a layered structure. Similarly, Figure 1e shows the as-prepared NiCo-eMOF formed an overall three-dimensional (3D) network with uniform distribution of hexagon shape surface like Co-eMOF. [20]Accordingly, a closer observation by HR-TEM of NiCo-eMOF in Figure 1h shows a hierarchical structure of MOF crystals with the dimension sizes varying from 50-100 nm, however, the surface structure presented an irregular hexagon shape compared with that of Co-MOF, besides, the shell of NiCo-eMOF possessed a smaller thickness of roughly 20 nm compared with that of Co-eMOF. These mild differences may be caused by proportion change of Co element. Here, importing Ni element into the NiCo-eMOF system would also make a profound impact on the resulting nanostructure morphology, which was further investigated from Ni-eMOF sample without Co element. As shown in Figure 1c of Ni-eMOF, it also shows conglomerated spheres with similar average sizes like another two samples. However, the surface shape showed a smooth surface packed with fuzzy strips instead of
hexagon nanoflakes (Figure 1f). Otherwise, the HRTEM (Figure 1i) of Ni-eMOF shows the MOF crystal was solid sphere with rough surface, which suggested a different structure accounting from the hollow spheres of Co-eMOF. The NiCo-eMOF basically possessed the nanostructure combining the features from both Co-eMOF and Ni-eMOF, leading to the formation irregular hexagon nanosheets. These results indicated these transition-based MOF (Ni/Co) samples forming into hierarchical structure can be equipped with distinctive nanostructures by adjusting the element and proportion appropriately.[14]

Additionally, we measured N\textsubscript{2} adsorption–desorption isotherms to observe the surface area and hierarchical pore structures. [21] As shown in Figure 2a, all samples presented type-IV isotherms, suggesting a well-ordered mesoporous structure, with corresponding pore size distribution curves for all the samples shown in Figure 2b. Texture parameters of the as-prepared samples were summarized in Table 1, it displayed that the specific surface areas of Ni-eMOF, Co-eMOF, and NiCo-eMOF hybrid are evaluated to be 129.4, 41.8, and 84 m\textsuperscript{2} g\textsuperscript{-1}, respectively, and the corresponding pore size was consistent with the specific surface areas. The Co-eMOF and NiCo-eMOF samples exhibited lower surface area than that of Ni-eMOF, combined with the morphological investigations from Figure 1, which can be deduced that the coated structures of Co-eMOF and NiCo-eMOF formed larger crystals demonstrating lower adsorbability for gas capture, compared to the more exposed surface region in Ni-eMOF. however, the decreased surface area was still significant in a comparable mesoporous nanostructure. Overall, the prepared monolith MOF samples presented demanded surface area and pore volume nanostructured configuration.
Figure 2. N\textsubscript{2} adsorption/desorption isotherms of (a) Co-eMOF, Ni-eMOF, NiCo-MOF. (b) corresponding pore size distribution curves.

Table 1. Texture parameters and of the as-synthesized materials.

|                 | Surface area (m\textsuperscript{2}g\textsuperscript{-1}) | Pore Volume (m\textsuperscript{3}g\textsuperscript{-1}) | Pore size (nm) |
|----------------|----------------------------------|------------------|----------------|
| Ni-eMOF        | 129.4                            | 0.18             | 5.08           |
| Co-eMOF        | 41.8                             | 0.07             | 7              |
| NiCo-eMOF      | 84                               | 0.11             | 5.4            |

Thermogravimetric analysis experiments were conducted in N\textsubscript{2} atmosphere for the as-prepared samples and pure NaN\textsubscript{3}. As seen from Figure 3, the TGA of NaN\textsubscript{3} shows dramatic weight loss at 385 °C, which is consistent with its ignition temperature. It also illustrates a continuous endothermic reaction for the studied samples was observed in the range of 343°C~393°C, which can be due to the pyrolysis reduction. The final weight loss of samples and NaN\textsubscript{3} were found to be around 66% to 71%, which presented the close value. [22]

Figure 3. Thermogravimetric analysis of Co-eMOF, Ni-eMOF and NiCo-MOF.

XRD was performed to characterize the crystal structure of all the as-prepared samples. Figure 4 compares the XRD patterns of Ni-eMOF, Co-eMOF, and NiCo-eMOF coordination hybrids, it was found that for these three kind of samples were almost equal to each other except for the NiCo-eMOF showed a shark peak at 2theta of 10°. Notably, we observed the typical peaks of the samples displaying diffraction peaks similar to those of the simulated MOF-74 pattern[3, 23], confirming the
formation of crystalline structure of as-prepared MOFs monoliths, demonstrating that this kind of nickel (or cobalt)-based metal–organic frameworks can be synthesized successfully by using a method with a simple hygrothermal method with addition of NaN₃.

![XRD pattern of Co-eMOF, Ni-eMOF and NiCo-MOF.](image)

Figure 4. XRD pattern of Co-eMOF, Ni-eMOF and NiCo-MOF.

![XPS spectra of Co-eMOF.](image)

Figure 5. XPS spectra of Co-eMOF. (a) full spectra, (b) C 1s, (c) N 1s, (d) Co 2p.

Photoelectron spectroscopy (XPS) exhibited the chemical composition and MOFs samples, the elemental content (at%) of all samples were summarized in Table 2. It was found that the samples were mostly composed by C, N, O and Co (or Ni, or Ni/Co) element, elements of carbon and nitrogen in each sample displayed similar content, while the content of Ni in Ni-eMOF, Co in Co-eMOF, and coexisted Ni/Co in NiCo-eMOF stayed within a range of 7 %-8 %, suggesting the metal elements were configured into the carbon framework at a high level. Note that all the samples possessed high nitrogen content, which can be contributed from the addition of NaN₃, which can be regarded as a nitrogen-rich precursor. As for the bond state information, take Co-eMOF as an example shown in Figure 5. The C 1s XPS spectrum of Co-eMOF given in Fig. 5b detected four species at 284.6 eV,
286.1 eV, 284.8 eV and 285.6 eV, which were assigned to C=C, sp²C-N, sp³C-N, and C-O species respectively. [24] The N 1s spectrum is shown in Fig. 5c, which can be deconvoluted into three species at pyridinic N (∼398.8 eV), pyrrolic N (∼400.5 eV) and graphite N (∼402.2 eV), respectively. [25-27] The Co 2p in Figure 4d confirmed two characteristic peaks of Co 2p³/2 and Co 2p¹/2 with a binding energy of ∼782.2 and ∼798.4 eV and their corresponding satellite peaks. [28, 29] It displays that three components of Co²⁺, Co³⁺ and Co single crystal in the Co 2p signal, confirming various functional groups of Co-based MOFs. The XPS survey spectrum reveal a high content of N elements and Co/Ni in final products, to take advantage of the configuration, which MOFs were promising as the unique organic precursors to generate efficient transition-metal carbides catalyst during the subsequent calcination process, which have extensive report in precedent researches. [25, 30-32]

| C (at%) | N(at%) | O(at%) | Ni(at%) | Co(at%) |
|---------|--------|--------|---------|---------|
| Co-eMOF | 26 | 59.65 | 6.78 | / | 7.93 |
| Ni-eMOF | 26.7 | 55.9 | 8.6 | 8.8 | / |
| NiCo-eMOF | 25.9 | 54.6 | 10.7 | 6.74 | 1.667 |

4.Conclusion

In summary, we prepared hierarchical transition metal-based MOF materials with three-dimensions (3D) spherical structures through adding NaN₃ in hydrothermal reaction. NaN₃ as a kind of ionic energetic material, enables rich-nitrogen N₃⁻ anions serving as one of the ligands with the existence of Co²⁺(Ni²⁺) salts and dicyandiamide in synthesis condition, govern the formation of the final coordination compounds (Co-eMOF, Ni-eMOF, NiCo-eMOF). The presence of N₃⁻ can be supported by the composition analysis by measuring the final products configurated with high nitrogen content (54–60 at%) coordinated with transition metal caution (Co or Ni). Crystal structure analysis confirmed the crystalline growth for the obtained polymers was similar to the simulated MOF-74, representing the successful building of metal organic frameworks. TEM images performed the generation of spherical monolith structures regardless of the selection of metal cautions, which were all equipped with high porosity as verified from specific surface area. This kind of high-nitrogen transition metal-based MOF materials show a great potential to achieve the active transition metal carbides towards electrolysis by conducting a simple calcination, which was further studied in our next work. In this study, it is noticeable that NaN₃ gives full play to chemical synthesis for hybrid complexes which was rarely reported, although the fundamental mechanism underlying remains unclear on micro-atomic view, it is certainly instructive to the enrich the synthesis of novel MOFs materials.

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