

Nanoscale hierarchically porous metal-organic frameworks: Reverse microemulsion synthesis and enhanced iodine capture

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Abstract: Radioactive iodine constitutes a critical and persistent contaminant in nuclear waste management and environmental remediation. Nanoscale hierarchically porous metal-organic frameworks (NH-MOFs) exhibit considerable potential for iodine removal. However, the synthesis of NH-MOFs with tunable porosity and high stability remains an immense challenge. In this study, bimetallic nanoscale hierarchically porous Zn/Co-MOFs were synthesized via a reverse microemulsion method. The resulting nanoscale hierarchically porous Zn/Co-MOFs were characterized using a complementary combination of X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption-desorption isotherms, and thermogravimetric analysis (TGA). These characterization results confirmed that the crystal size, pore size, and number of unsaturated metal sites in the nanoscale hierarchically porous Zn/Co-MOFs (Zn/Co-MOF_An) could be easily tuned by controlling the microemulsion parameters (e.g., the aqueous-to-oil ratio and surfactant concentration). The as-synthesized Zn/Co-MOF_An exhibited excellent iodine adsorption capacities (iodine vapor: 6.55 g/g; liquid-phase iodine: 585 mg/g) owing to the combined effects of shortened diffusion distances and hierarchical porosity. This work highlights the potential of Zn/Co-MOFs as high-performance and scalable adsorbents for radioactive iodine remediation.

Key words: Metal-organic frameworks; Nanoscale crystals; Hierarchically porous structure; Iodine adsorption performance.

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1. Introduction

Iodine, the 53rd element in the periodic table and a member of the halogen group, is a dark purple crystalline solid. Iodine plays a critical role in medical disinfection, chemical synthesis, and nutritional supplementation^[1]. Notably, nuclear fission of uranium-235 produces radioactive iodine isotopes such as ¹²⁹I, which, with a very long half-life of 1.57×10^7 years, is a lasting threat to environmental safety. Therefore, the efficient capture of radioactive iodine has become a key challenge in nuclear waste management^[2, 3]. Iodine capture techniques fall into two main types: wet and dry methods. Wet processes often use solvent-based capture, frequently use alkaline scrubbing solutions^[4]. On the other hand, dry methods derive their advantages from the use of solid adsorbents, which provide lower running cost, produce minimal secondary waste, and easy handling and transport^[5]. To date, researchers have developed many advanced materials to improve iodine uptake capac-

ity by designing pores and surface functionalization^[6]. This suggests an improvement over traditional materials such as activated carbon, one of the first used for iodine adsorption but has several limitations^[7]. For example, pure carbon powder has a low adsorption capacity for gaseous iodine (~0.79 g/g) and poor stability^[8]. Furthermore, the removal efficiency for radioactive methyl iodide decreases to < 60% after ageing^[9].

Recently, advanced porous materials, especially metal-organic frameworks (MOFs) and covalent organic frameworks (COFs)^[10, 11], have shown great potential for gas storage, environmental remediation, and industrial separation applications. MOFs, porous crystalline materials formed through coordination-driven self-assembly between metal ions and organic ligands, show considerable potential for adsorption and separation because of their distinctive features^[12], including high surface areas (typically 500-7,000 m²/g), tunable pore dimensions (0.5-10 nm), and the ability to modify their chemistry^[13]. These characteristics allow precise control over porosity and applying surface functionalization, which helps efficiently capture of target molecules by combining physical adsorption (e.g., van der Waals forces, capillary condensation) and chemical adsorption mechanisms (e.g., coordination interactions, hydrogen bonding, π - π stacking). Consequently, MOFs are regarded as highly promising materials for the capture of radioactive iodine. Researchers are now focusing on boosting

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the iodine capture performance of MOFs through the precise modulation of their pore structures and binding sites for better adsorption. For example, Han et al.^[14] designed isostructural ALP-MOF-1 and ALP-MOF-2 to understand distinct iodine adsorption pathways: the first MOF holds iodine molecules in its three-dimensional cross-linked channels, forming a unique network structure with an uptake of ~ 1.79 g/g. The latter utilizes redox-active Co sites to convert iodine into polyiodide species by reactive adsorption, with a capacity of ~ 1.50 g/g. Moreover, Zhang et al.^[15] reported a pyrazole-based MOFs that exploits the synergistic effects between open Zn^{2+} sites and free nitrogen atoms on organic ligands to adsorb iodine quickly and efficiently from aqueous solution.

Although the promising potential of MOFs for iodine capture, translation research findings into practical applications still suffers from substantial challenges. For instance, Xu et al.^[16] fabricated expanded graphite (EG) composites incorporating MIL-101(Cr), with a thermal conductivity of $2.76 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (a 22-fold enhancement). However, excessive EG loading was found to block accessible adsorption sites, which reduced the saturated adsorption capacity. In addition, Shu et al.^[17] reported that the heterogeneous bimetallic MUV-102(Cu–Ti) suffers from potential metal–ligand bond cleavage during ammonia adsorption–desorption cycling, which leads to structural instability. These studies emphasize that the chemical stability of MOFs remains a key limitation for practical applications when exposed to strongly coordinating guest molecules. Overall, two major challenge limit the application of MOFs for iodine capture: (i) micropore-dominated structures combined with large crystal dimensions slow down adsorption kinetics, which limits the rate and uptake^[18]; (ii) poor long term stability of MOF frameworks in harsh operating conditions (e.g., high temperature and humidity) restricts their durability^[19]. Owing to the advances in synthesis strategies, nanoscale hierarchically porous MOFs (NH-MOFs) have become promising options. By integrating nanoscale diffusion pathways with hierarchically porous structures, NH-MOFs not only enhance mass transfer efficiency but also improve accessibility to active sites^[20]. Their high specific surface area, tunable pore configurations, and high stability make them suitable for demanding adsorption environments such as gas storage, separation, and drug delivery^[21]. With continued progress of synthesis technique, the potential of NH-MOFs to operate is gradually expanding under challenging conditions.

This study addresses these limitations by improving mass transfer, pore accessibility, framework stability, and active site utilization. A reverse microemulsion method was used to synthesize nanoscale hierarchically porous Zn/Co-MOFs, which achieved an increased density of unsaturated metal sites and enhanced pore volumes of 0.80 and $1.08 \text{ cm}^3\cdot\text{g}^{-1}$ substantially higher than those of conventional aqueous-synthesized analogues. The introduction of hierarchical porosity facilitates molecular diffusion and increases access to active sites, which improves adsorption kinetics and capacity. In addition, the synergistic Zn/Co coordination within the same framework significantly enhances hydrolytic stability under humid conditions. Furthermore, the microemulsion technique allows the formation of monodisperse particles with narrow size distribution, which ensure reproducibility and scalability. Overall, these

advancements set a foundation for the development of high-performance MOFs as next-generation adsorbent materials for nuclear waste treatment.

2. Experimental

2.1. Synthesis of Zn/Co-MOFs

In a typical synthesis, 0.5 mmol of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 0.5 mmol of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ were dissolved in 10 mL of deionized water and stirred for 10 min to form solution I. Subsequently, 0.226 g of 2-methylimidazole (2-MeIm) and 0.278 g of N,N,N',N'-tetramethylethylenediamine (TMEDA) were dissolved in 10 mL of deionized water and stirred for 10 min to prepare solution II. Then, 0.9 mL of solution I and 0.9 mL of solution II were sequentially added into a 50 mL reverse microemulsion containing 0.05 mol/L cetyltrimethylammonium bromide (CTAB) and 0.5 mol/L *n*-hexanol in *n*-heptane. The resulting microemulsions were vigorously stirred at room temperature for 30 min . Following this, the two microemulsions were combined in a 250 mL beaker and mixed for an hour. After mixing, the product was centrifuged at 8000 rpm for 10 min , and then the solid product was collected via filtration. The solid product was subsequently activated in an acetone environment at 60°C for 24 h . Finally, the product was dried under vacuum at 90°C for 12 h . The final obtained solid product was labeled as Zn/Co-MOF-*An* (where *n* represents the solution volume *V*, *V* = $50, 45, 40, 30, 20 \text{ mL}$, assigned to *n* = $1, 2, 3, 4, 5$, respectively).

After centrifugation, the secondary reverse microemulsion was collected, and 0.9 mL of solution I and 0.9 mL of solution II were separately added to 50 mL of reverse microemulsion. The reaction was carried out according to the procedure above. The resulting product was dried and activated under identical conditions, and labeled as Zn/Co-MOF-T. Moreover, ZIF-8 and ZIF-67 were synthesized following previously reported literature methods^[22]. For comparison, a Zn/Co-MOF sample was also synthesized in water via a reported method^[23], and denoted as Zn/Co-MOF-W.

2.2. Iodine adsorption experiment

To evaluate the iodine adsorption performance of Zn/Co-MOF-A1, the iodine adsorption capacity of the samples was determined by batch experiments. In this work, the ultraviolet-visible spectroscopy (UV-Vis) was used for full-spectrum scans of diluted iodine solutions within the wavelength range of $200\text{--}800 \text{ nm}$. The concentration of iodine in the supernatant was quantified by measuring the characteristic absorption peak of iodine at about 522 nm . For this purpose, a pre-established calibration curve relating absorbance to iodine concentration was used (Figure S1). The correlation coefficient (*R*²) obtained by linear fitting in Origin is 99.82% , which provided a reliable basis for subsequent experimental tests. In the liquid-phase adsorption experiment, 5 mL of iodine solution with an initial concentration of $1 \text{ g}\cdot\text{L}^{-1}$ was added to a 15 mL glass vial, followed by the addition of 5 mg of adsorbent. The mixture was equilibrated at room temperature for 48 h to ensure complete adsorption. Subsequently, 1 mL of the post-reaction solution was taken out and diluted to 5 mL for analysis.

2.3. Characterization

The morphologies and microstructures of samples were investi-

gated using X-ray diffraction (XRD) patterns (Bruker D8 Advanced X-ray diffractometer), Fourier transform infrared (FTIR) spectra (Vector 33, Bruker Corporation), scanning electron microscopy (SEM, ZEISS Ultra 55 and Carl Zeiss), transmission electron microscopy (TEM, JEM-2100F) and Thermal gravimetric analyzer (TGA, TG 209, Netzsch). Chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB250XI X-ray photoelectron spectrometer.

3. Result and discussion

3.1. Characterization

Figure 1a presents the XRD patterns of ZIF-8, ZIF-67, and Zn/Co-MOF_A1 samples. A high consistency was observed between the experimental and simulated diffraction profiles of ZIF-8 and ZIF-67, which confirms their well-defined crystalline structures. Similarly, the XRD peaks of Zn/Co-MOF_A1 match those of ZIF-8 and ZIF-67, which suggests an analogous crystalline structure^[24]. However, the relatively broader peaks of Zn/Co-MOF_A1 are interpreted as indicative of smaller crystallite sizes or the presence of crystal defects, likely due to the incorporation of both Zn and Co, which can disturb crystal growth^[25, 26]. The crystal structure of Zn/Co-MOF_An and Zn/Co-MOF_T were also analyzed by FTIR, as shown in Figure 1b. The absorption band at 421 cm^{-1} could be attributed to metal–nitrogen (M–N) coordination bonds between organic ligands and metal centers, consistent with previous reports^[27]. Other spectral features also match those in prior studies^[28, 29], which further supports the successful formation of nanoscale hierarchically porous Zn/Co-MOFs crystals. More-

over, the closely matched diffraction pattern of Zn/Co-MOF_T, which was prepared using the centrifugally recovered secondary microemulsion, highlights the feasibility of recycling the microemulsion system. This observation provides critical evidence for developing a more sustainable synthesis strategy by reducing production costs and minimizing chemical waste. In addition, the crystallite size (30–50 nm) and porosity of nanoscale hierarchically porous Zn/Co-MOFs were adjusted by adjusting the water-to-oil ratio in the reverse microemulsion system. Analysis of Zn/Co-MOF_An showed no structural deviations across the tested compositions, as evidenced by consistent XRD peak positions, underscoring the structural robustness of the framework under varying phase conditions (Figure S2). With higher water-to-oil ratios, the XRD peak intensity increased. This is likely due to the expanded aqueous cores in the reverse microemulsion, which improved the nucleation and crystallite growth of Zn/Co-MOF_An^[30]. These results highlight the critical role of the water-to-oil ratio in directing crystallization kinetics and enhancing crystallinity.

The N_2 adsorption-desorption isotherms and pore size distributions of Zn/Co-MOF_A1 and Zn/Co-MOF_T samples are shown in Figure 2. As reported in literature^[31], traditional ZIF-8 and ZIF-67 exhibit characteristic type-I isotherms, which indicates the exclusive microporous structures. In contrast, Zn/Co-MOF_A1 and Zn/Co-MOF_T samples display a combination of type I/IV isotherms (Figure 2a), with pronounced hysteresis loops, which confirms the presence of both micropores and mesopores. The pore size distribution shown in Figure 2b indicates the dominate presence of mesopores around 18 nm for Zn/Co-MOF_A1. In comparison, Zn/Co-MOF_T, synthesized via secondary reverse microemulsion, has larger crystals with an

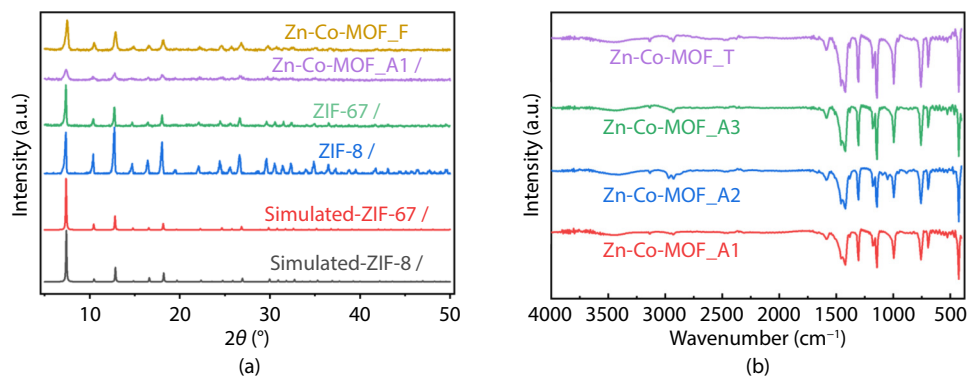


Fig. 1. (a) XRD patterns and (b) FTIR spectra of ZIF-8, ZIF-67, Zn/Co-MOF_An and Zn/Co-MOF_T.

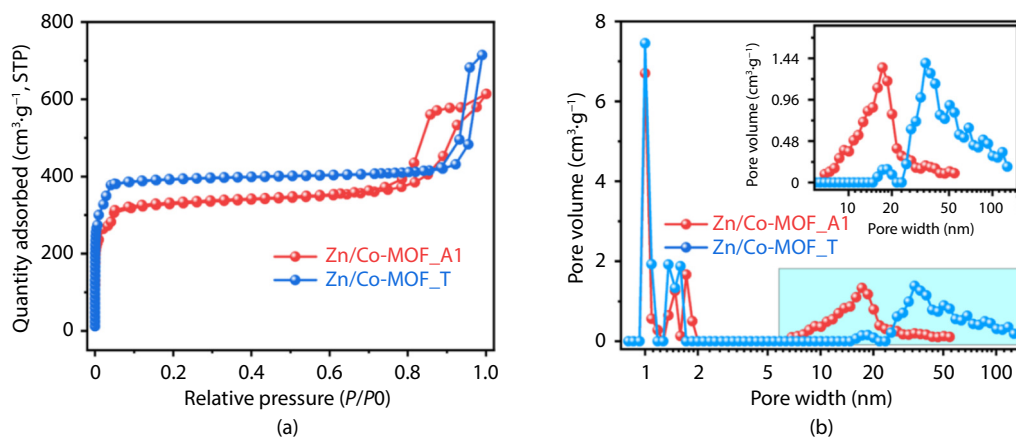


Fig. 2. (a) N_2 adsorption-desorption curves and (b) pore size distribution curves of Zn/Co-MOF_A1 and Zn/Co-MOF_T.

average mesopore size centered at about 30 nm. These results establish reverse microemulsion synthesis as a robust strategy for tailoring hierarchical porosity in Zn/Co-MOF_A_n by controlling template dimensions through water-to-surfactant modulation.

The CTAB-based reverse microemulsion system was key to achieving the nanoscale morphology of Zn/Co-MOF_A1, as shown in SEM and TEM images (Figure S3). Unlike conventional hydrothermal synthesis^[29], this method confines nucleation within aqueous microdroplets, which lead to the formation of nearly spherical nanoparticles (~50 nm) that pack densely to form interparticle channels (Figure S3a). The uniform size of these crystallites matches broadened XRD peaks, which enhances material homogeneity. This homogeneity is also confirmed by the uniform spatial distribution of all elements and a surface Zn/Co ratio of 1:1 (Figure 3), which verifies the successful incorporation of metal ions into a stable, homogeneous framework. Furthermore, elemental mapping analysis demonstrates a homogeneous spatial distribution of C, Zn, O, and Co across the entire material architecture. Quantitative EDS analysis shows a Zn/Co atomic ratio of about 1:1 on the Zn/Co-MOF_A1 surface, matching the 1:1 molar ratio of Zn/Co salt precursors used in synthesis (Figure S4). Overall,

these results confirm the accuracy of the experimental design and confirm that Zn²⁺/Co²⁺ ions are incorporated into the ligand and matrix at the targeted ratio, which results in a stabilized and homogeneous topological framework within Zn/Co-MOF_A1.

The textural properties of Zn/Co-MOFs synthesized via different routes are compared in Table 1. Comparative analysis reveals that Zn/Co-MOF_A1 prepared via reverse microemulsion, has a significantly larger specific surface area of 1287 m²·g⁻¹, much higher than the 181 m²·g⁻¹ observed for the Zn/Co-MOF_W sample synthesized using an aqueous method. The Zn/Co-MOF_T synthesized through secondary reverse microemulsion demonstrates an even greater specific surface area of 1679 m²·g⁻¹. This suggests that adjusting the water/oil ratio in the reverse microemulsion can modify the porosity and specific surface area of Zn/Co-MOFs. During the synthesis of Zn/Co-MOF_A1 and Zn/Co-MOF_T, the organic amines added as templating agents help the deprotonation of organic ligands. As a result, two MOFs have higher pore volumes of 0.80 cm³·g⁻¹ and 1.08 cm³·g⁻¹, respectively, along with enhanced specific surface areas compared to Zn/Co-MOF_W.

TGA was performed under a N₂ atmosphere to assess the

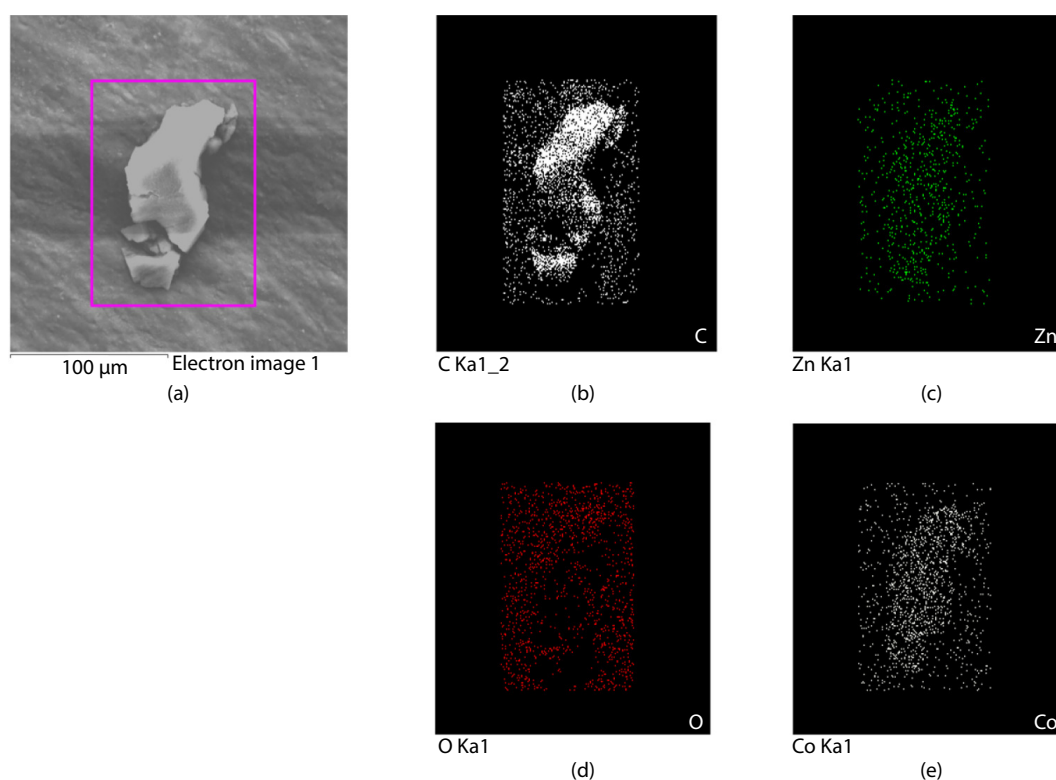


Fig. 3. Structural and compositional characterization of Zn/Co-MOF_A1: (a) SEM image; (b) C, (c) Zn, (d) O and (e) Co elemental distribution maps obtained from EDS mapping.

Table 1. Porosity properties of Zn/Co-MOFs samples.

Sample	αS_{BET} [m ² ·g ⁻¹]	βS_{micro} [m ² ·g ⁻¹]	$\epsilon S_{\text{meso}}/S_{\text{micro}}$	dV_{t} [cm ³ ·g ⁻¹]	ϵV_{meso} [cm ³ ·g ⁻¹]	$\epsilon V_{\text{micro}}$ [cm ³ ·g ⁻¹]
Zn/Co-MOF_A1	1287	1102	0.16	0.80	0.38	0.42
Zn/Co-MOF_T	1679	1559	0.07	1.08	0.53	0.55
Zn/Co-MOF_W	181	124	0.45	0.29	0.24	0.04

αS_{BET} : Brunauer-Emmett-Teller (BET) surface area; βS_{micro} : micropore surface area; ϵS_{meso} : mesopore surface area;

dV_{t} : total pore volume; ϵV_{meso} : mesopore volume; $\epsilon V_{\text{micro}}$: micropore volume.

thermal stability of Zn/Co-MOF_A_n. The as-synthesized Zn/Co-MOF_A_n ($n = 1, 2$) displayed decomposition step patterns comparable to those of ZIF-8 and ZIF-67 (Figure S5). The initial mass loss between 50 and 350°C is due to the desorption of co-adsorbed species, such as H₂O and residual solvents from the porous framework. A secondary decomposition step occurred at about 500°C, which corresponds to the structural collapse of the Zn/Co-MOF_A_n through pyrolysis of organic linkers and metal centers, which leads to the formation of metallic CO, CO₂, and metal oxides, including ZnO and CoO. Importantly, the thermal decomposition temperature of Zn/Co-MOF_A_n, at about 500°C, is between those of Co-MOF and ZIF-8, which undergo framework collapse at roughly 450 and 600°C, as expected. Figure S6 presents the XRD patterns of the Zn/Co-MOF samples after 24-hour immersion in aqueous solution. These patterns show that the sample prepared via

reverse microemulsion maintains its crystallinity, in contrast to the completely collapsed framework of the aqueous-phase synthesized Zn/Co-MOF_W. These results indicate that Zn/Co-MOF_A_n provides distinct morphological and structural advantages, including effective thermal stability modulation and superior water stability.

High-resolution XPS spectra were recorded to determine the chemical states of the constituent elements. As shown in Figure 4a, the Zn 2p region exhibited two peaks at 1021.70 eV (2p_{3/2}) and 1044.69 eV (2p_{1/2})^[32]. Similarly, the Co 2p spectrum in Figure 4b showed characteristic peaks at 780.75 and 796.69 eV, assigned to Co 2p_{3/2} and Co 2p_{1/2}, respectively^[33]. Gauss–Lorentz fitting confirmed that Co²⁺ was the dominant oxidation state^[34]. Figure 4c shows the C 1s spectrum, which was deconvoluted into two components at 284.66 eV (C–C), 285.36 eV (C–O)^[35]. In Figure 4d, the N 1s spectrum showed

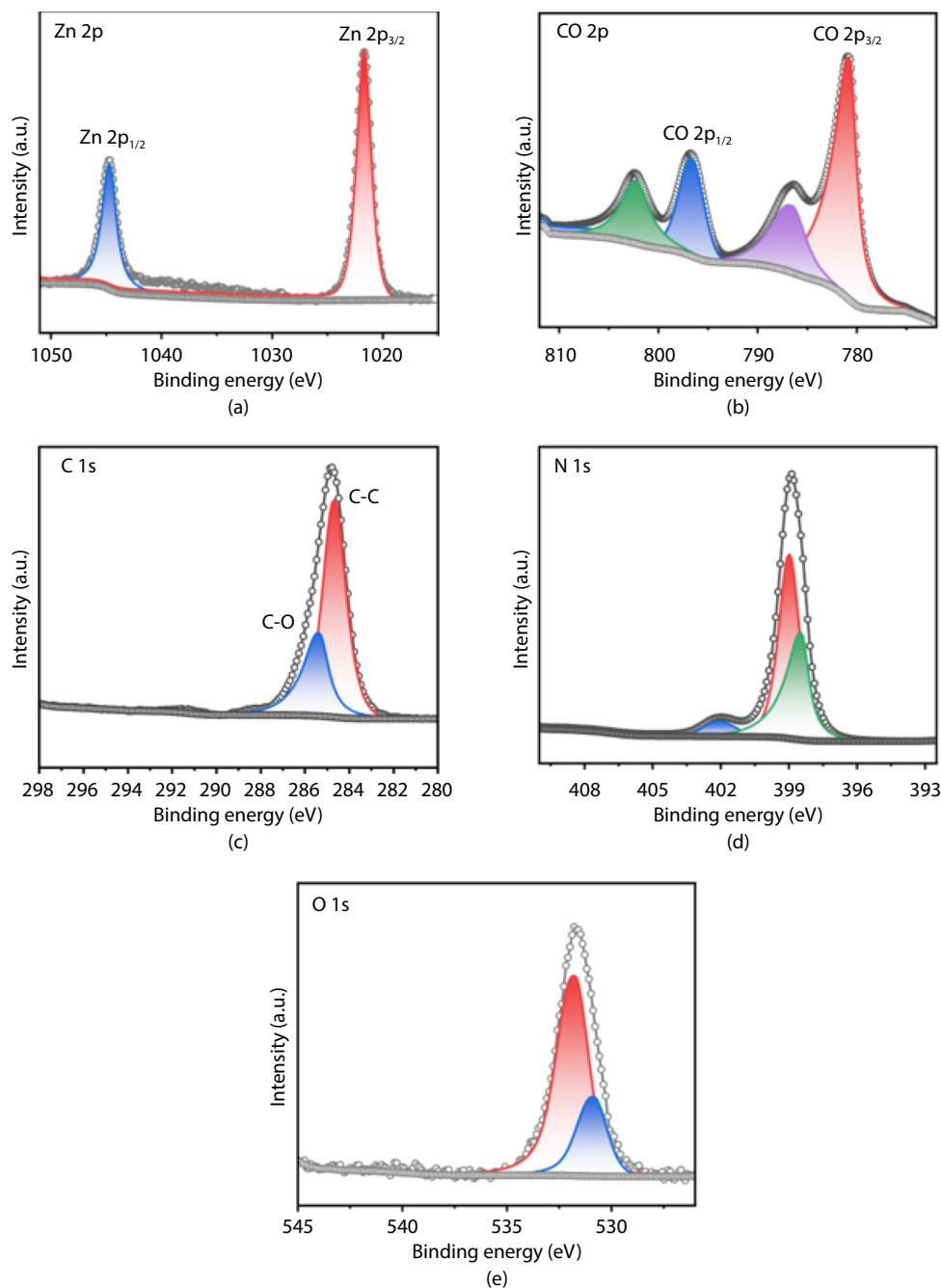


Fig. 4. XPS analysis of Zn/Co-MOF_A1: (a) Zn 2p, (b) Co 2p, (c) C 1s, (d) N 1s, and (e) O 1s regions.

two peaks at 399.2 and 400.5 eV, which correspond to pyridinic N and pyrrolic N species, respectively^[36]. The O 1s spectrum in Figure 4e displayed peaks at 530.87 and 531.75 eV, assigned to metal–oxygen bonds and hydroxyl species, respectively. These findings show that the elemental valence states in Zn/Co-MOF_A1 remained consistent throughout the synthesis, in agreement with literature reports^[37].

To understand the synthesis mechanism of Zn/Co-MOFs via reverse microemulsion, Gaussian software was used to simulate the template agents used in the experiments, as illustrated in Figure S8. The negative charge region of TMEDA is mostly concentrated around the nitrogen atoms (Red area), which suggests that these N atoms are susceptible to electrophilic attack. The rapid synthesis mechanism of Zn/Co-MOFs in reverse microemulsion is shown in Figure 5. Initially, Zn and Co metal precursors coordinate with organic ligands within the microemulsion to form transient coordination polymers. These polymers then aggregate and nucleate at the oil–water interface, gradually growing into nanoscale crystals. After the reaction, centrifugation breaks the emulsion, which releases the Zn/Co-MOFs encapsulated within the aqueous core. The Zn/Co-MOFs form a hierarchical porous structure with micropores, mesopores, and macropores through random stacking. Finally, Zn/Co-MOFs were obtained by acetone activation of the material to remove organic solvents and surfactants from the pores. During synthesis in reverse microemulsion, the surfactant CTAB in the oil phase and the solvent in the aqueous phase form a stable interface, which provides an optimal environment for the formation of Zn/Co-MOFs. The addition of the template agent TMEDA influences the growth rate and morphology of Zn/Co-MOFs crystals, and regulates their pore structure and crystal size. Reverse microemulsion synthesis is characterized by mild reaction conditions and simple operation, which offers a promising approach for the synthesis of NH-MOFs.

3.2. Influencing factors

As described in the literature, Zn/Co-MOF_W was synthesized hydrothermally in aqueous media as a control sample. It was designed to evaluate the effectiveness of the reverse microemulsion method to create hierarchical porosity by com-

paring it with the nanoscale hierarchically porous Zn/Co-MOF_An. As shown in Figure S9, the N₂ sorption isotherm displays significant adsorption-desorption hysteresis, and pore size distribution analysis indicates the presence of hierarchical porosity. These results suggest that organic amine additives play a role in the development of multiscale pore structures within Zn/Co-MOF_An. In contrast, Zn/Co-MOF_W prepared in water has a lower specific surface area and pore volume than the nanoscale hierarchically porous Zn/Co-MOF_An prepared by the reverse microemulsion method. This reduction is due to heterogeneous particle size distribution, crystallographic imperfections, and impurity inclusions associated with aqueous-phase synthesis methods.

In addition to preparing Zn/Co-MOF_An using reverse microemulsion directly, this study also investigated the influence of reverse microemulsion recycling on sample structure. As shown in Figures S10a–b, Zn/Co-MOF_T crystals prepared in the secondary reverse microemulsion are below 200 nm in size. However, due to small particle size and incomplete removal of impurities, many particles aggregate. A similar phenomenon is seen in the synthesis of Zn/Co-MOF_A1, as illustrated in Figures S10c–d. This aggregation seems to come from residual surfactants and organic solvents remaining in the microemulsion system. According to literature^[38], the prepared Zn/Co-MOF_T was immersed in acetone to remove residual organic solvents and other impurities. Figures S10e–f display the morphology of Zn/Co-MOF_T after acetone activation. Activation significantly reduces the aggregation of MOFs, which leads to a larger specific surface area and improves performance in practical applications. Additionally, crystal defects appear in Zn/Co-MOF_T after activation, which match the broader diffraction peaks (Figure 1a). Compared with Zn/Co-MOF_A1, synthesized in a single emulsion (Figures S10g–h), Zn/Co-MOF_T exhibits a wider range of crystal sizes. This suggests that adjusting the water-to-oil phase ratio in the reverse microemulsion can control the crystal size of nanoscale hierarchically porous Zn/Co-MOF_An.

3.3. Adsorption performance of Zn/Co-MOF_A1

In this study, non-radioactive molecular iodine (I₂) was used as a safe and practical chemical surrogate for radioactive iodine

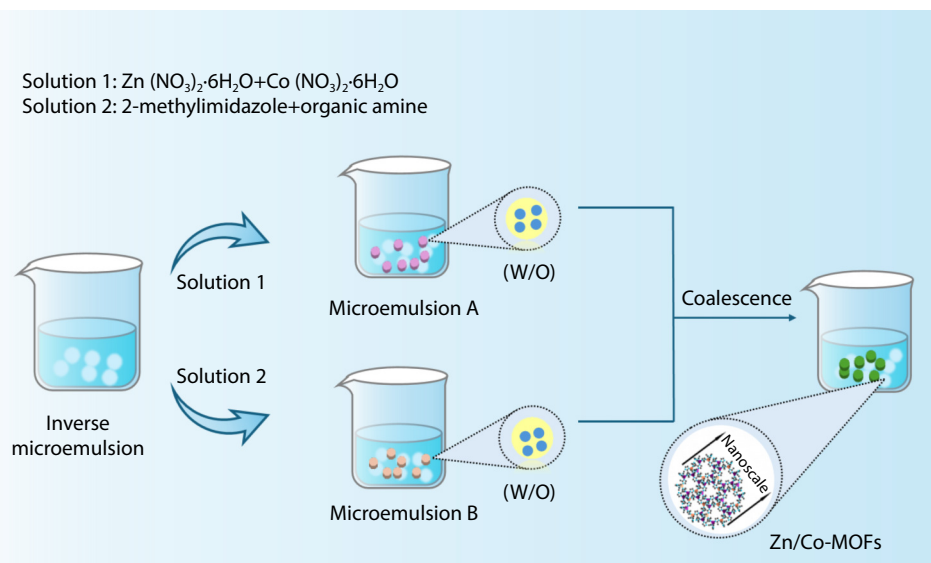


Fig. 5. Mechanism diagram of nanoscale hierarchically porous Zn/Co-MOFs synthesis.

isotopes (e.g., ^{129}I) to evaluate the performance of Zn/Co-MOF_A1 adsorbent for iodine vapor removal in both solution and vapor phases. As shown in Figure 6b, in cyclohexane solution, the Zn/Co-MOF_A1 achieved an iodine adsorption capacity of 585 mg/g, with a removal rate of 58.5%. The comparative data in Table S1 highlight the superior performance of our adsorbent, where it leads other high-capacity materials under comparable testing conditions. The liquid-phase iodine adsorption capacity of our Zn/Co-MOF reaches 585 mg/g. This performance is better than other reported materials: it is much higher than that of KQ-1 and Ag@Cu-Cu, exceeds that of FV-1, and nearly doubles the capacity of Th-HQCA (295 mg/g). For vapor-phase capture, the adsorbent was heated with excess solid iodine at 75°C for 100 h in a sealed system, as shown in Figure 6c, which resulted in a high adsorption capacity of 6.55 g/g. This value exceeds conventional adsorbents^[39]. As summa-

rized in Table 2, it significantly outperforms several high-performance benchmark materials reported under comparable conditions. For instance, it shows a notable improvement over MOF-808 (2.18 g/g at 80°C) and Th-BPYDC (2.23 g/g at 75°C), and even exceeds the high capacity of SCNU-Z7 (2.7 g/g at 80°C). Furthermore, the material performs even better than other well-regarded frameworks, such as DUT-68 (1.08 g/g) and CZJ-3 (1.15 g/g), which is more than three times higher. These results collectively demonstrate that Zn/Co-MOFs are among the most effective MOF-based adsorbents for iodine capture, which highlights their potential for practical application in radioactive waste management.

The electrostatic potential (ESP) analysis shows the origin of the bimetallic synergistic enhancement at the electronic structure level. As shown in Figure 7, the ESP distribution around the metal nodes in the pure Co model exhibits nearly

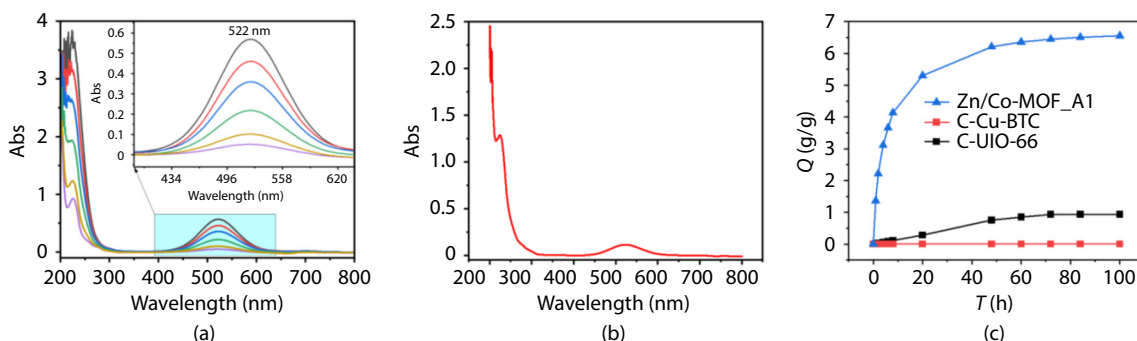


Fig. 6. (a) UV full spectrum of iodine; (b) UV spectrum of Zn/Co-MOF_A1 for the adsorption of liquid-phase iodine and (c) adsorption curve of Zn/Co-MOF_A1, C-Cu-BTC, C-UIO-66 for iodine vapor.

Table 2. The adsorption capacity of various adsorbents for vapor iodine.

Sample	Loading capacity (g/g)	Temperature (°C)	Ref
Th-BPYDC	2.23	75	[40]
MOF-808	2.18	80	[41]
UIO-67	0.53	80	[41]
NH2-MIL-101-0n-NH2-UIO-66	1.93	80	[42]
DUT-68	1.08	80	[43]
DUT-67	0.84	80	[43]
CZ-3	1.15	75	[8]
SCNU-Z7	2.7	80	[44]
CO-IPT-IBA	2.88	75	[45]
MOF-808@PVDF	1.42	80	[46]
Zn/Co-MOF	6.55	75	this work

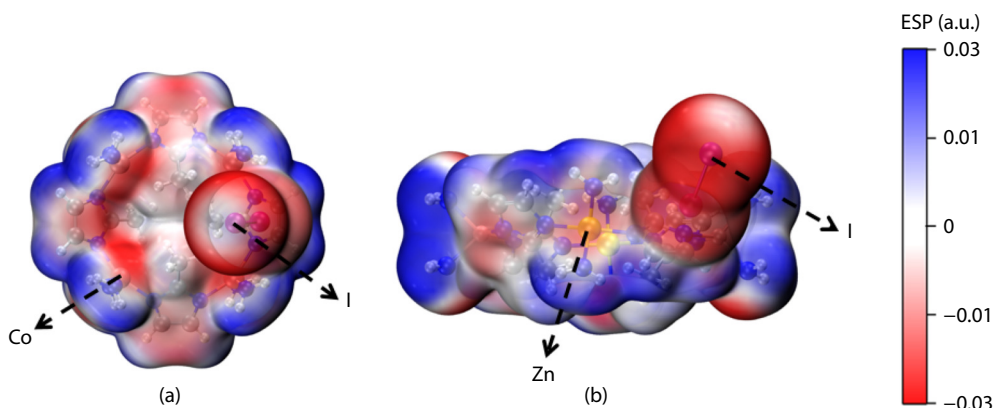


Fig. 7. Calculated electrostatic potential (ESP) mapped on molecular surfaces: (a) Reference model of pure ZIF-67 (b) Zn/Co-MOF model.

neutral characteristics, which indicates its weak Lewis acidity. In contrast, a qualitative shift occurs in ESP around the Zn/Co-MOF model, with a distinct and significantly enhanced positive electrostatic potential region. This change demonstrates that the introduction of Zn modulates the local electron density, which creates an active site with significantly enhanced Lewis acidity alongside the Co center. In addition, DFT calculations showed iodine adsorption energies of about -0.87 and -0.82 eV for the Zn-Co dual-metal site and the pure Co site, respectively. The more negative value indicates the enhanced adsorption strength at the bimetallic site. These strong positive potential sites have stronger electrostatic attraction towards the electron-rich I_2 and can further promote charge transfer, which substantially increases the strength of chemisorption. Atomistic calculations reveal that bimetallic synergy creates strong Lewis acid sites. This mechanism provides a strong theoretical basis for the exceptionally high iodine vapor adsorption capacity (6.55 g/g) achieved by Zn/Co-MOF_A1 in this work, and demonstrates the effectiveness of the bimetallic engineering strategy for optimizing MOF adsorption performance.

4. Conclusions

In summary, nanoscale hierarchically porous Zn/Co-MOF_An were synthesized via the reverse microemulsion method using TMEDA as a functionalizing agent. The resulting nanoscale hierarchically porous Zn/Co-MOF_An exhibit hierarchical porous structures comprising micropores, mesopores and macropores, along with excellent thermal stability. Importantly, this study shed light on the formation mechanism and defect structures of NH-MOFs. The hierarchical porosity and crystal size of Zn/Co-MOF_An can be tuned by varying the solvent type and the water-to-oil ratio in the reverse microemulsion, without compromising their thermal stability. The as-synthesized Zn/Co-MOF_An exhibited excellent performance for iodine capture, with an adsorption capacity of 585 mg/g and a removal efficiency of 58.5% in the liquid phase, as well as a maximum adsorption capacity of 6.55 g/g for iodine vapor. DFT calculations link the exceptional iodine vapor adsorption capacity to a distinct bimetallic synergistic effect. Electrostatic potential (ESP) analysis shows that the Zn-Co dual-metal sites show enhanced positive potential, which confirms their role as strong Lewis acid sites. These sites have strong electrostatic attraction and promote charge transfer to iodine molecules, which enhancing chemisorption. These results highlight the potential of Zn/Co-MOFs as highly effective materials for iodine removal and recovery, which offers a promising route for scalable applications in radioactive iodine remediation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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