

Electronic Supplementary Information

A novel route for generation of Co/CoZn/CoNi layered double hydroxides at ambient temperature

Liyong Chen, Huifang Wang, Xiaoshuang Shen, Yingyue Zhang, Dezhi Li, and Chunying Duan**

Experimental Section

Material characterization and synthesis method

All chemical reagents, including cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole (Hmim), and methanol, were purchased from Sinopharm Chemical Reagent Co., Ltd, China and were directly used as received.

The structural and morphological investigation was performed on a Tecnai F30 transmission electron microscope operated at 300 kV and a HITACHI UHR FE-SEM SU8220 scanning electron microscope. The phase of materials was characterized in a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu- $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The measurement of thickness of sheets was carried out on a Park System XE-70 atomic force microscope with non-contact mode. Brunauer-Emmett-Teller (BET) surface area analysis and porosity measurement in the relative pressure range $P/P_0 = 0-1.0$ were performed at 77 K on an automated adsorption analyzer (Autosorb iQ, Quantachrome Corp., US). Raman spectra were collected on by Jobin Yvon LabRAM HR Evolution Raman Spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on Thermo ESCALAB 250Xi with Al- $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). Electrocatalytic studies were conducted with a CHI760E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was measured in a ZAHNER ENNIUM electrochemical workstation.

Preparation of ZIF-67 rhombic dodecahedra (RDs). In a typical synthetic procedure, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.4 mmol, 116.4 mg) and Hmim (0.8 mmol, 65.7 mg) were dissolved into methanol (5 mL), respectively. The methanolic solution of Hmim was slowly poured into the methanolic solution of $\text{Co}(\text{NO}_3)_2$ with vigorously stirring prior to being kept at 25 °C for 24 h without turbulence. The dark violet powder was collected by centrifugation and rinsed twice by methanol. The final product was dried in vacuum at 80 °C for 12 h.

Preparation of Co-LDHs. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6 mmol, 1746.2 mg) and Hmim (12 mmol, 985.2 mg) were dissolved into methanol (5 mL), respectively. The methanolic solution of Hmim was slowly poured into the methanolic solution of $\text{Co}(\text{NO}_3)_2$ with vigorously stirring prior to being kept at 25 °C for 24 h without turbulence. The yellowish brown powder was collected by centrifugation and rinsed twice by methanol. The final product was dried in vacuum at 80 °C for 12 h.

Preparation of hybrids of ZIF-67/Co-LDHs. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4 mmol, 1164.2 mg) and Hmim (8 mmol, 656.8 mg) were dissolved into methanol (5 mL), respectively. The methanolic solution of Hmim was slowly poured into the methanolic solution of $\text{Co}(\text{NO}_3)_2$ with vigorously stirring prior to being kept at 25 °C for 24 h without turbulence. The dark violet powder was collected by centrifugation and rinsed twice by methanol. The final product was dried in vacuum at 80 °C for 12 h.

To further understand the effect of concentration and molar ratio on material phase, the concentrations of $\text{Co}(\text{NO}_3)_2$ and Hmim in methanol were adjusted with the same molar ratio of 1:2 from $\text{Co}(\text{NO}_3)_2$ to Hmim; the molar ratio from $\text{Co}(\text{NO}_3)_2$ to Hmim was adjusted with the fixed amount of $\text{Co}(\text{NO}_3)_2$, such as 0.4 and 4 mmol. The synthetic conditions were summarized in Table S1.

Transformation of ZIF-67 to Co-LDHs. The as-made ZIF-67 RDs (50 mg) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4 mmol, 328.4 mg) were dispersed into methanol (10 mL) to obtain uniform suspension after sonication for 5 min. The resulting mixture was kept at 25 °C for 4 d without turbulence. The yellowish brown powder was collected by centrifugation and rinsed twice by methanol. The final product was dried in vacuum at 80 °C for 12 h.

Transformation of Co-LDHs to ZIF-67. Similarly, the sheets-assembled Co-LDHs (50 mg) and Hmim (4 mmol, 1164.2 mg) were dispersed into methanol (10 mL) to obtain uniform suspension after sonication for 5 min. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave (20 mL) and kept at 80 °C for 4 h. The dark violet powder was collected by centrifugation and rinsed twice by methanol. The final product was dried in vacuum at 80 °C for 12 h.

Preparation of hetero-bimetallic CoZn- and CoNi-ZIFs. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.5 mmol, 1018.6 mg) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 148.7 mg) were dispersed into methanol (5 mL), and a solution containing Hmim (12 mmol, 985.2 mg) and methanol (5 mL) were slowly added with vigorously stirring prior to being kept at 25 °C for 24 h without turbulence. The dark violet powder was collected by centrifugation and rinsed twice by methanol. The final product was dried in vacuum at 80 °C for 12 h.

To prepare CoNi-ZIFs, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.9 mmol, 1135 mg) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 29.1 mg) were used in the synthetic process under the otherwise identical conditions.

Preparation of sheets-assembled CoZn- and CoNi-LDHs. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.5 mmol, 1018.6 mg) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 148.7 mg) were dispersed into methanol (5 mL), and a solution containing Hmim (1 mmol, 82.1 mg) and methanol (5 mL) were slowly added with vigorously stirring prior to being kept at 25 °C for 24 h without turbulence. The pale pink powder was collected by centrifugation and rinsed twice by methanol. The final product was dried in vacuum at 80 °C for 12 h.

To prepare CoNi-LDHs, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.9 mmol, 1135 mg) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 29.1 mg) were used in the synthetic process under the otherwise identical conditions.

Electrochemical Measurements

Preparation of Catalyst Ink: The mixture containing 2 mg of electrocatalysts (Co-LDHs-(0.6:1.2)-25 and CoNi-LDHs), 980 μL of ethanol, and 20 μL of Nafion solution (5 wt%) was sonicated for 20 min to form a well-dispersed suspension.

Preparation of working Electrode: Glassy carbon (GC) electrodes (3 mm in diameter) were polished by using alumina suspension on a Nylon plate, rinsed with deionized water and dried at room temperature in air. The catalyst ink (5 μL) was drop-casted on the polished GC electrode, and dried naturally.

In addition, Ag/AgCl (3.5 M KCl) and polished Pt wire were used as the reference electrode and the counter electrode, respectively.

Electrochemical Measurement: Linear-sweep voltammetry (LSV) were performed at a sweep rate of 5 mV s^{-1} at a potential window of 0 to 0.8 V vs Ag/AgCl after scanning

cyclic voltammetry (CV) between 0 V and 0.6 V for five times. To estimate the double-layer capacitance of Co- and CoNi-LDHs, CV curves were carried out at variable sweep rates of 10, 20, 30, 40, and 50 mV s⁻¹ in the range from 0.207 to 0.307 V vs Ag/AgCl. EIS was measured at overpotential of 300 mV in the frequency range of 0.1 Hz to 100 kHz with oscillation potential amplitudes of 5 mV. All electrochemical measurements were conducted in 1 M KOH solution.

The measured potential vs Ag/AgCl can be converted the potential vs reversible hydrogen electrode (RHE) by using the Nernst equation of $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591\text{pH} + 0.197$.

Table S1. Preparation of ZIF-67, Co-LDHs and their hybrids under different conditions.

entry	Amount (mmol)		Molar ratio	Reaction condition		
	Co(NO ₃) ₂	Hmim	Co ²⁺ /Hmim	Temperature	solvent	Time/h
1a	0.4	0.8	1:2	25 °C	Methanol (10 mL)	24
1b	2	4	1:2			24
1c	3	6	1:2			24
1d	4	8	1:2			1min/1/24/72
1e	5	10	1:2			24
1f	6	12	1:2			24
1g	8	16	1:2			24
1h	0.4	1.2	1:3			24
1i	0.4	0.4	1:1			2/24
1j	0.4	0.2	2:1			24
1k	4	16	1:4			24
1l	4	12	1:3			24
1m	4	4	1:1			24
1n	4	2	2:1			24
2a	0.2	0.4	1:2			80 °C
2b	0.4	0.8	1:2	4		
2c	2	4	1:2	4		
2d	3	6	1:2	4		
2e	4	8	1:2	4		
2f	6	12	1:2	4		
2g	0.4	1.2	1:3	4		
2h	0.4	0.4	1:1	4		
2i	4	16	1:4	4		
2j	4	12	1:3	4		
2k	4	4	1:1	4		

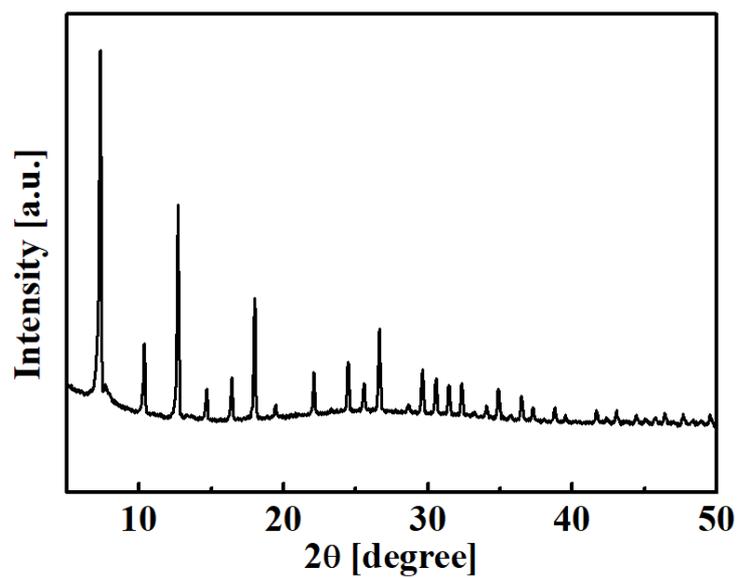


Figure S1. XRD pattern of ZIF-67 RDs prepared by a typical procedure shown as follows: a methanolic solution containing 0.04 M $\text{Co}(\text{NO}_3)_2$ and 0.08 M Hmim at 25 °C within 24 h.

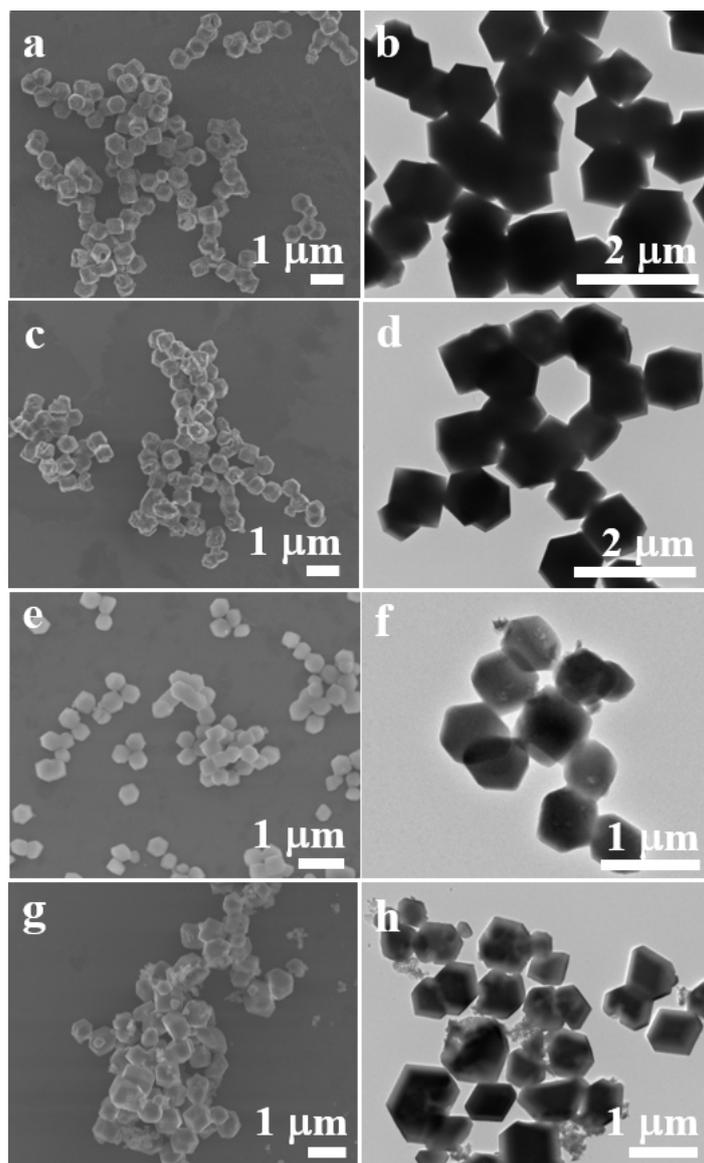


Figure S2. Panoramic SEM (left) and TEM (right) images of samples prepared with different concentrations of Co^{2+} and Hmim at 25 °C: (a,b) 0.04 and 0.08 M, (c,d) 0.2 and 0.4 M, (e,f) 0.3 and 0.6 M, (g,h) 0.4 and 0.8 M.

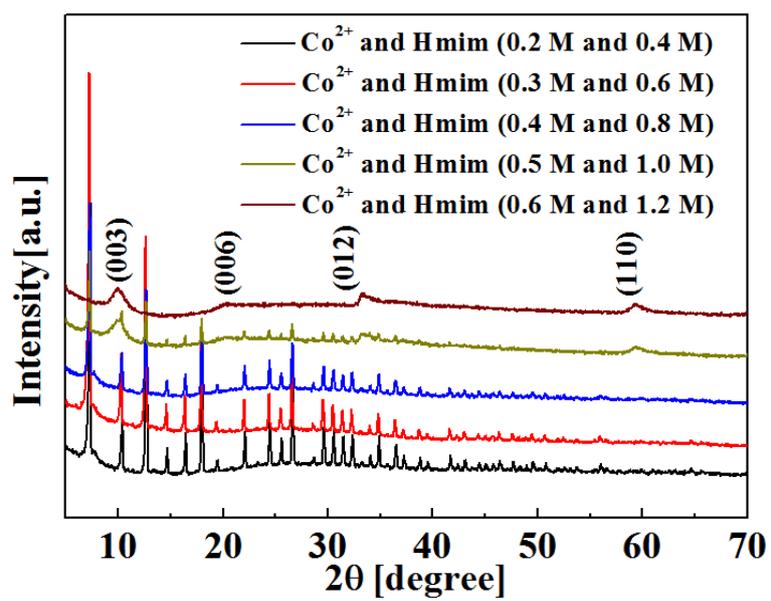


Figure S3. XRD patterns of samples prepared at different concentrations of Co^{2+} and Hmim with their molar ratio of 1:2.

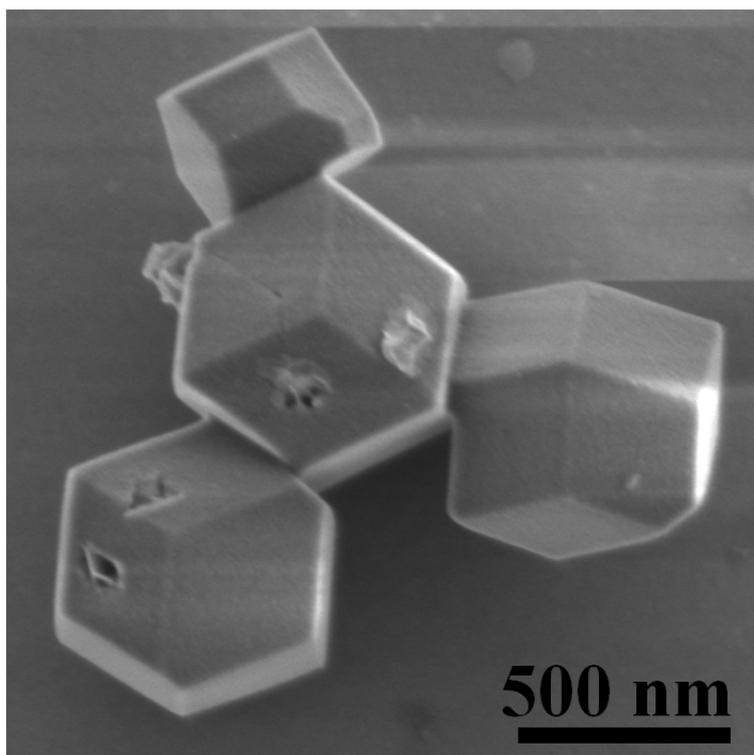


Figure S4. The magnified SEM image of ZIF-67/Co-LDHs-(0.3:0.6) hybrids shown in Figure 2f.

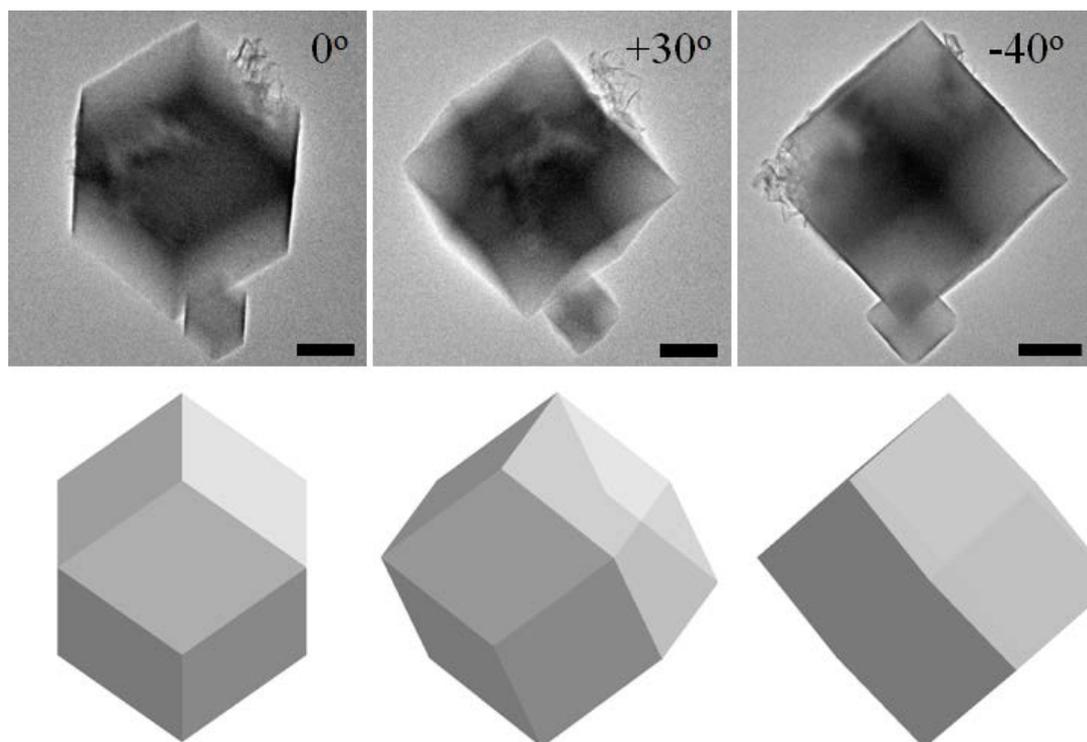


Figure S5. TEM images of ZIF-67/Co-LDHs-(0.3:0.6) hybrids observed from different directions (top); corresponding to schematic illustrations of rhombic dodecahedron (bottom).

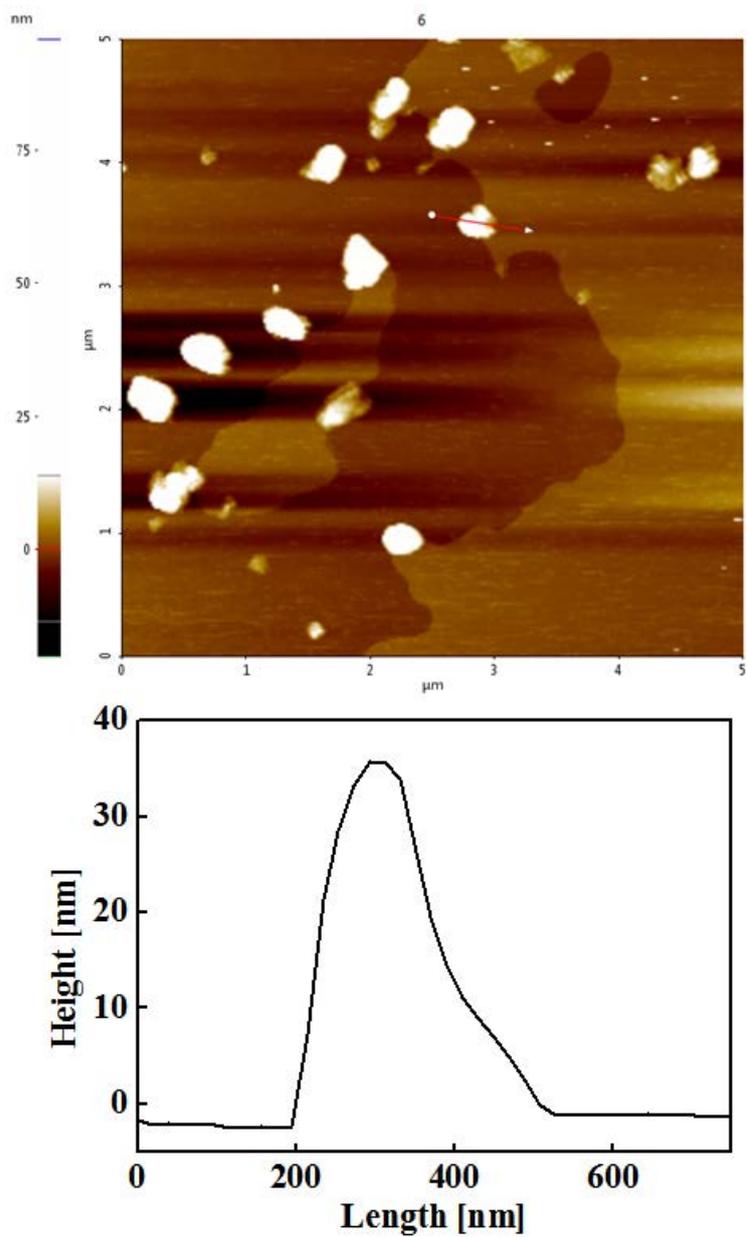


Figure S6. AFM image of Co-LDHs-(0.6:1.2) (top); the thickness of a sheet labeled in the AFM image (bottom).

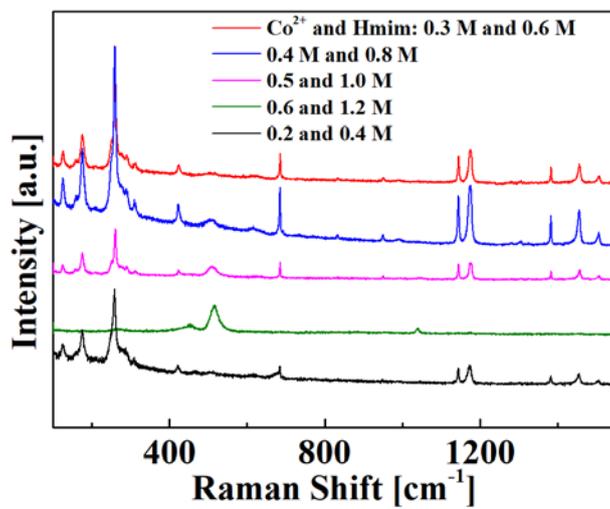


Figure S7. Raman spectra of samples prepared from different concentrations of Co^{2+} and Hmim at 25 °C.

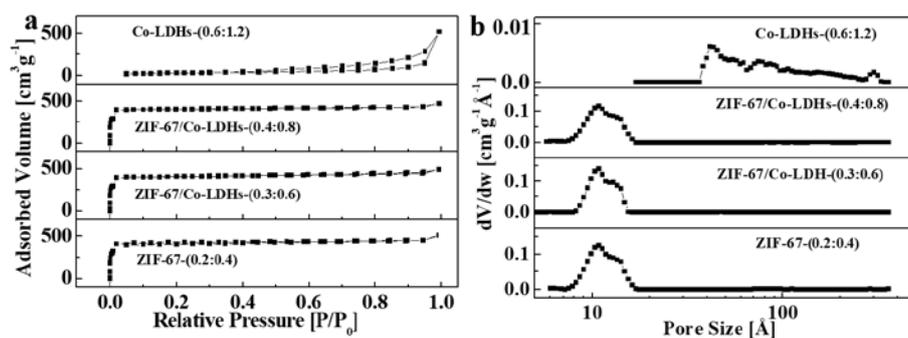


Figure S8. (a) N₂ sorption isotherms at 77 K for samples prepared at different concentrations of Co²⁺ and Hmim at 25 °C; (b) corresponding pore size distribution curves

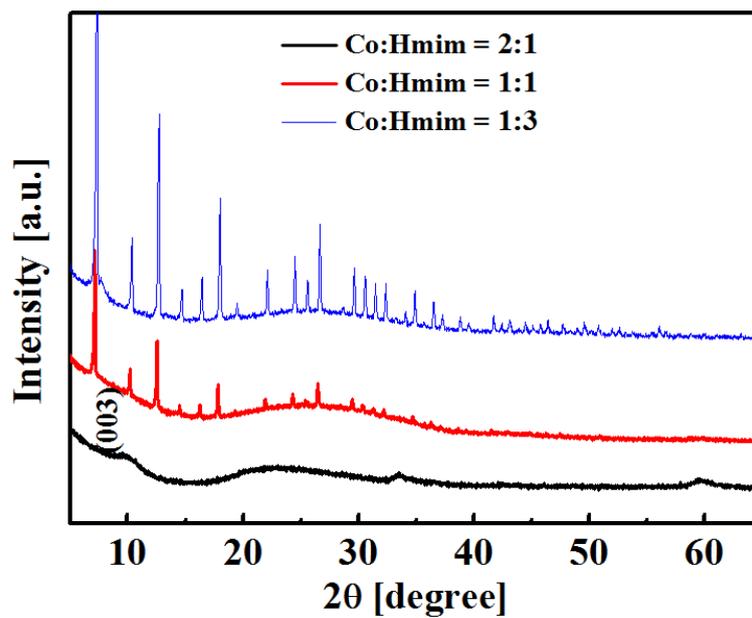


Figure S9. XRD patterns of samples prepared at different molar ratios of Co²⁺ to Hmim with a constant concentration of 0.04 M Co²⁺.

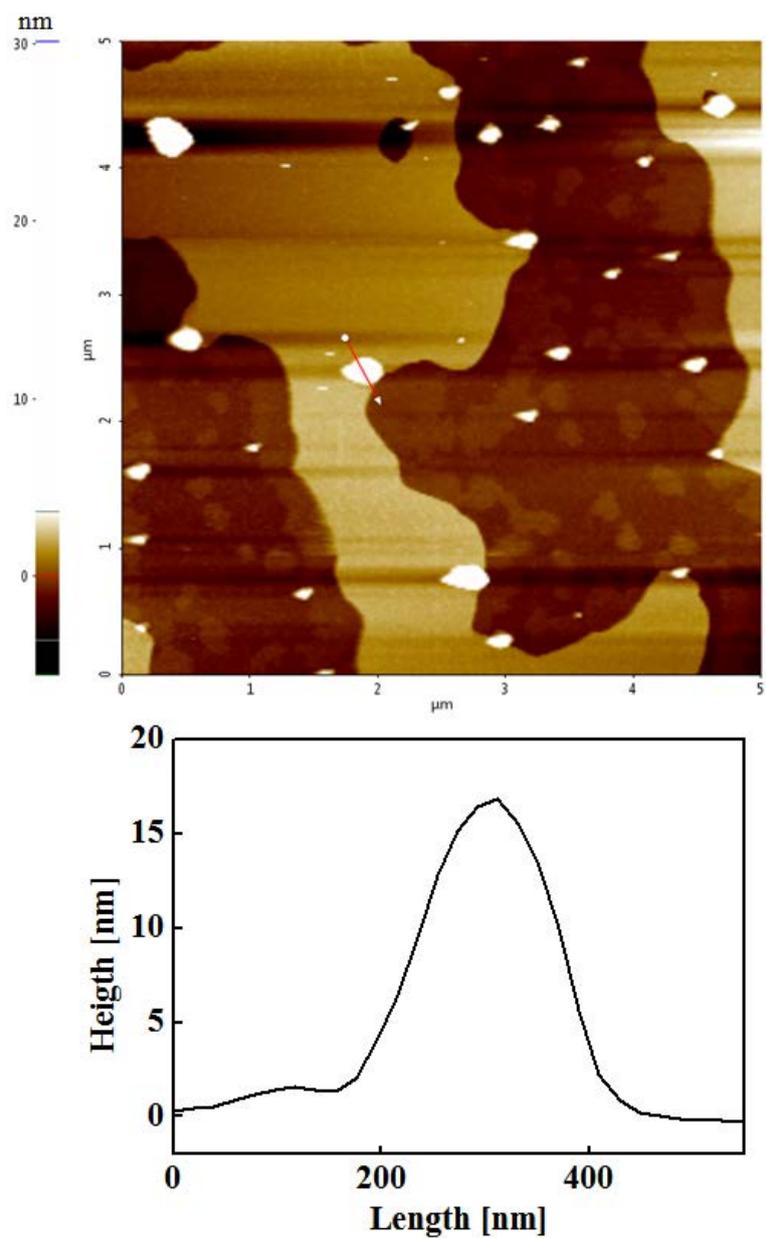


Figure S10. AFM image of Co-LDHs-(0.04:0.02) (top); the thickness of a sheet labeled in the AFM image (bottom).

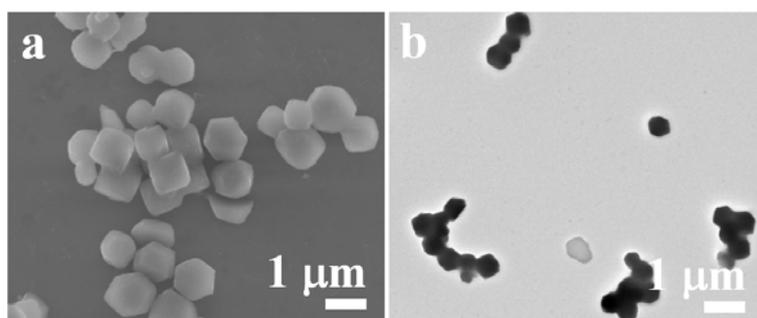


Figure S11. Panoramic SEM (a) and TEM (b) images of samples prepared at $\text{Co}^{2+}/\text{Hmim}$ molar ratio of 1:3.

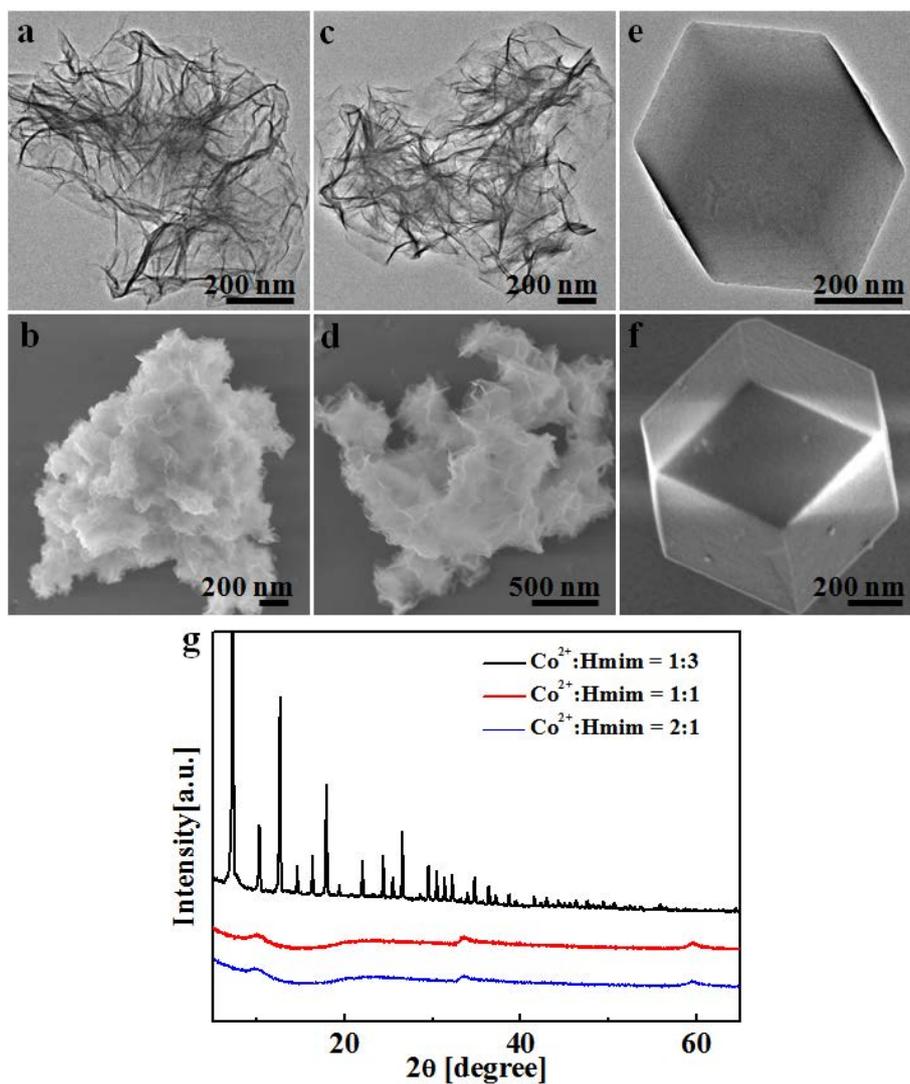


Figure S12. TEM (top) and SEM (middle) images of samples prepared at different molar ratios from Co^{2+} to Hmim with a constant concentration of 0.4 M Co^{2+} : (a, b) 2:1, (c, d) 1:1, and (e, f) 1:3. (g) XRD patterns of these samples.

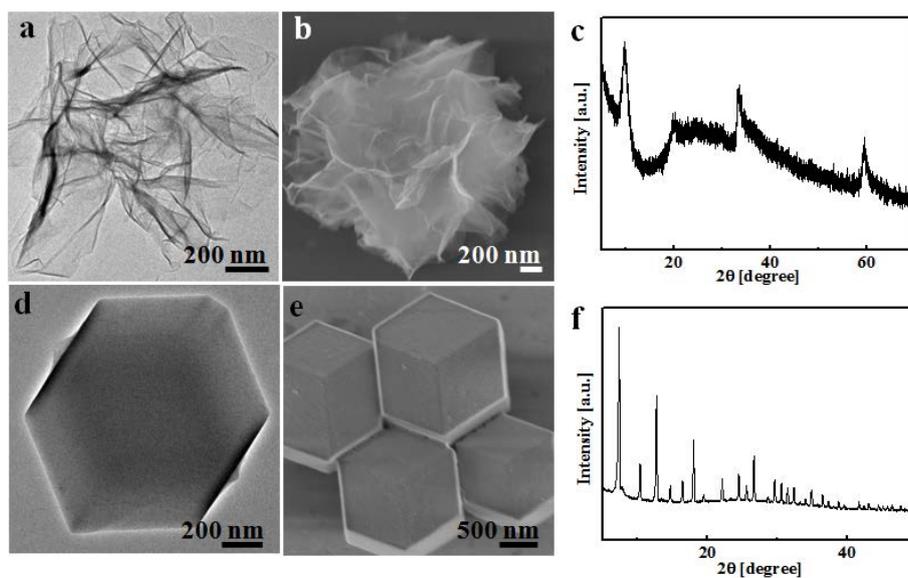


Figure S13. Co-LDHs prepared in methanolic solution of 0.8 M Co^{2+} and 1.6 M Hmim (top) and ZIF-67 obtained in methanolic solution of 0.4 M Co^{2+} and 1.6 M Hmim (bottom) at 25 °C: (a, d) TEM and (b, e) SEM images and (c, f) XRD patterns.

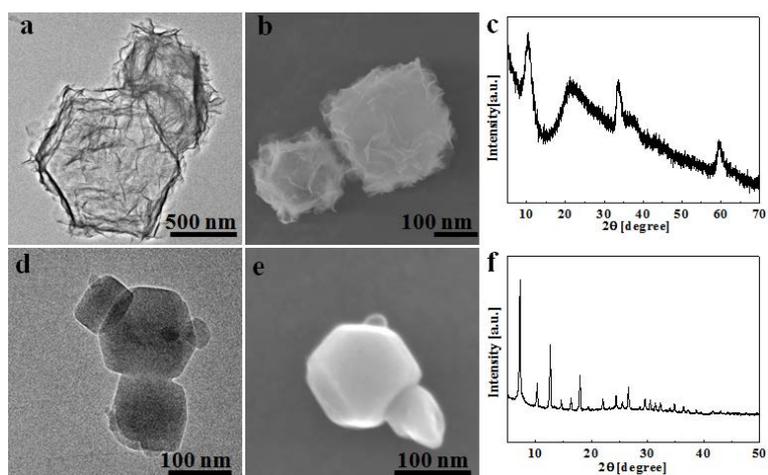


Figure S14. TEM and SEM images and XRD patterns of (a, b, c) cage-like Co-LDHs assembled with sheets by transformation of ZIF-67 RDs at 25 °C after adding Co^{2+} ions and (d, e, f) ZIF-67 nanocrystals by transformation of Co-LDHs sheets at 80 °C after adding Hmim.

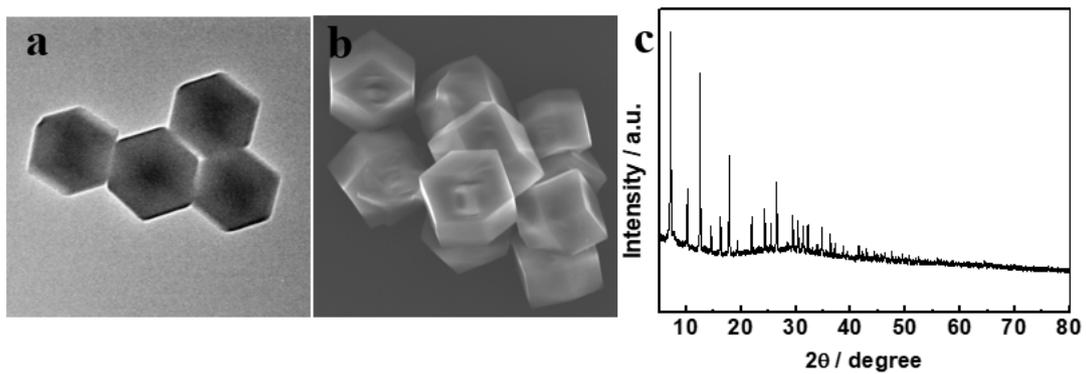


Figure S15. (a) TEM and (b) SEM images and (c) XRD pattern of ZIF-67 nanocrystals at 25 °C for 24 h while adding 0.8 mmol Hmim to the used solvent of methanol (5 mL).

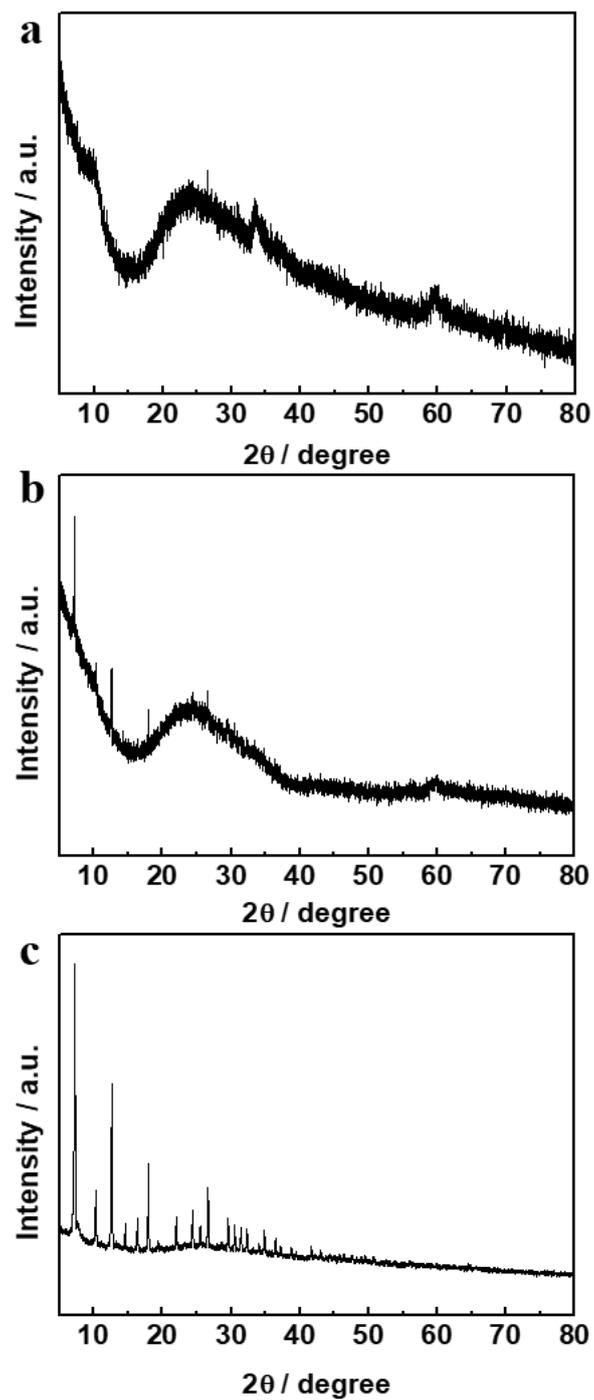


Figure S16. XRD patterns of samples prepared in the used solvent of methanol at different ratios of Co^{2+} to Hmim with a constant concentration of 0.04 M Co^{2+} at 25 °C: (a) 2:1, (b) 1:1, and (c) 1:3.

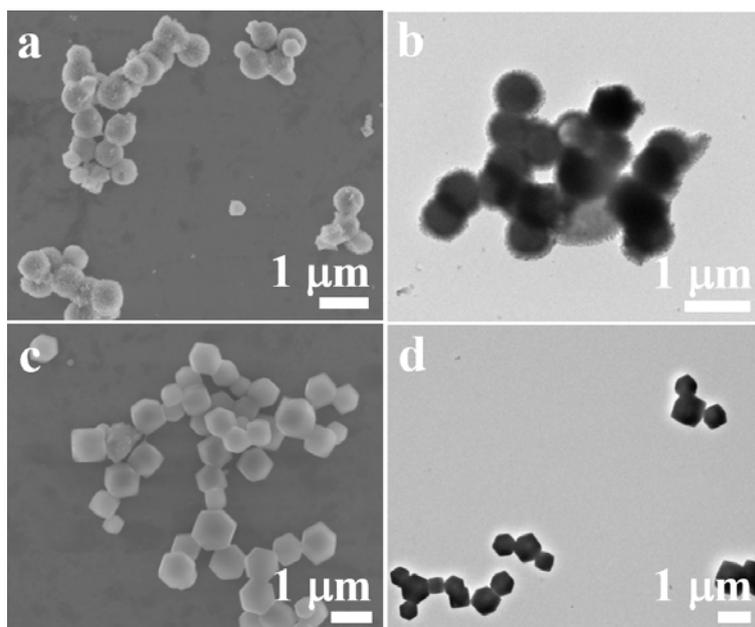


Figure 17. Panoramic SEM (left) and TEM (right) images of samples prepared in the used solvent of methanol at different ratios of Co^{2+} to Hmim with a constant concentration of 0.04 M Co^{2+} at 25 °C: (a, b) 1:1 and (c, d) 1:3.

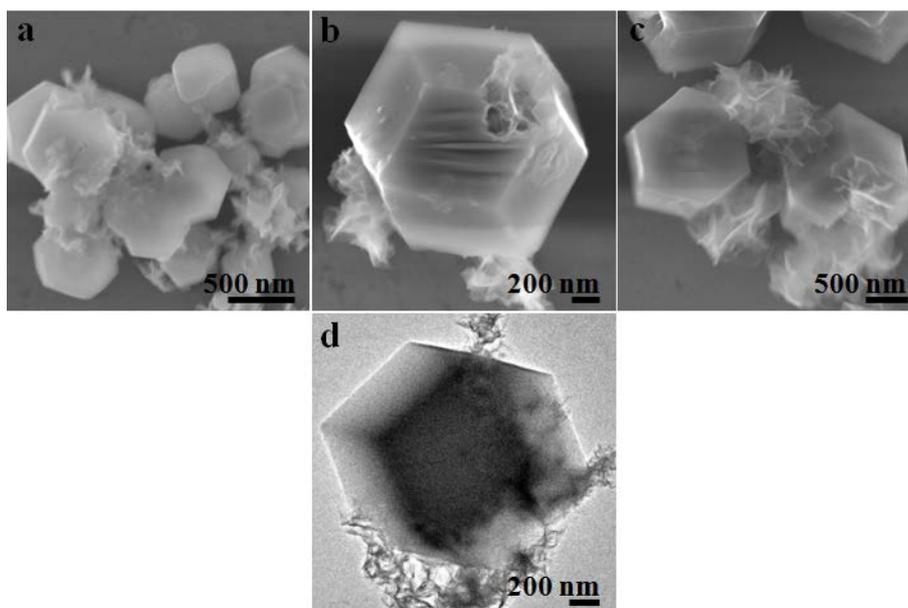


Figure S18. SEM images of intermediates prepared within (a) 1 min, (b) 1 h, and (c) 72 h at room temperature; (d) TEM image of the intermediate prepared within 1 h. The synthetic system is the methanolic solution of Co^{2+} (0.4 M) and Hmim (0.8 M).

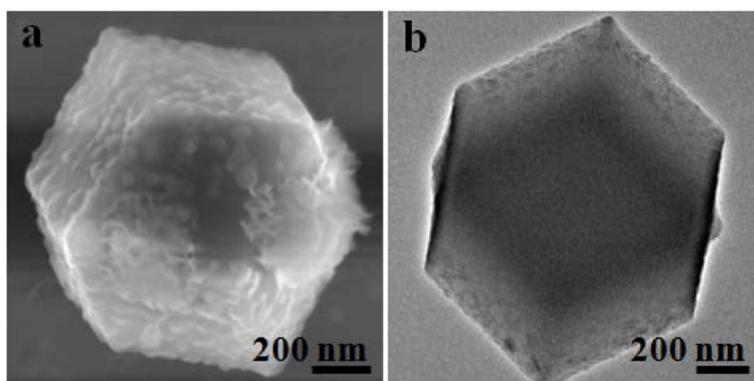


Figure S19. (a) SEM and (b) TEM images of intermediates prepared for 2 h at 25°C. The synthetic system is the methanolic solution of Co^{2+} (0.04 M) and Hmim (0.04 M).

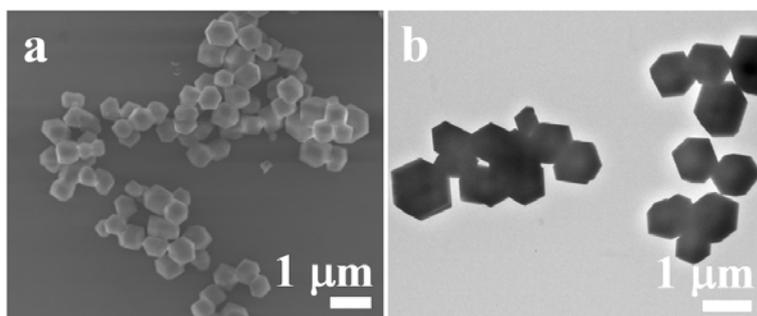


Figure S20. Panoramic SEM (a) and TEM (b) images of CoZn-LDHs.

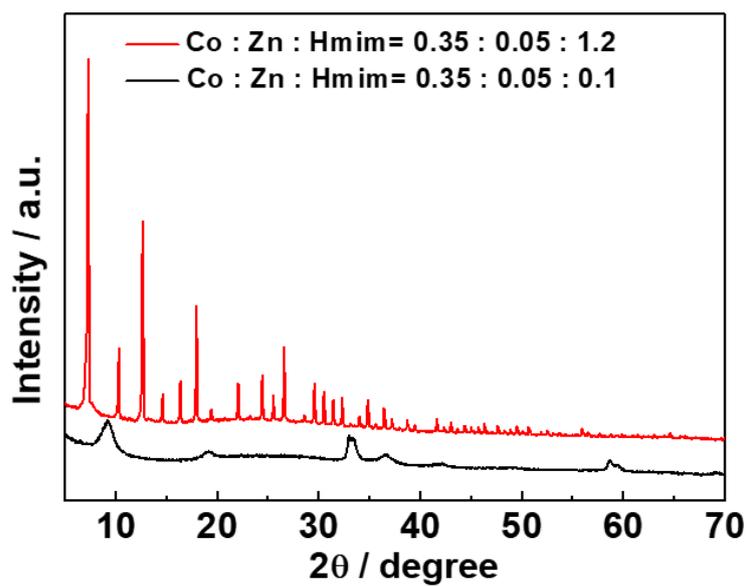


Figure S21. XRD patterns of samples prepared at different ratio of 1:3 and 4:1 from metal ions (Co^{2+} and Zn^{2+}) to Hmim with metal ion concentration of 0.4 M.

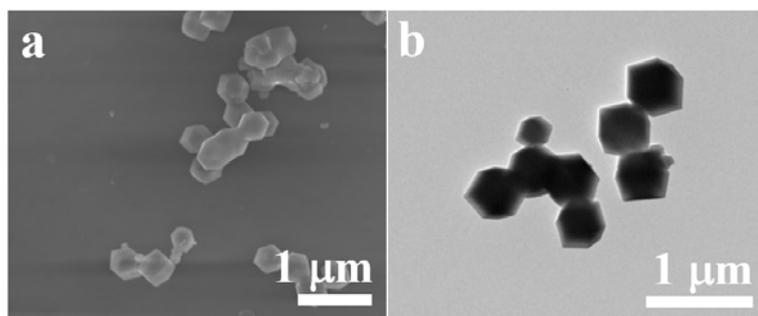


Figure S22. Panoramic SEM (a) and TEM (b) images of CoNi-LDHs.

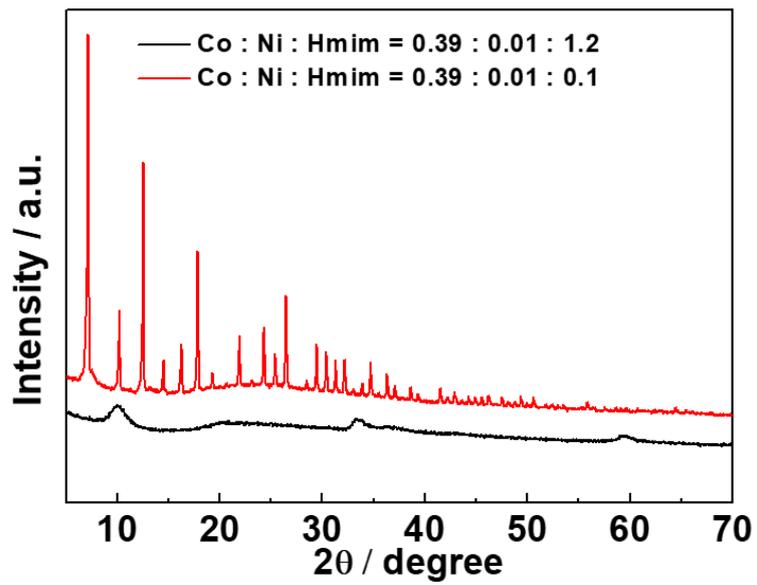


Figure S23. XRD patterns of samples prepared at different ratio of 1:3 and 4:1 from metal ions (Co^{2+} and Ni^{2+}) to Hmim with metal ion concentration of 0.4 M.

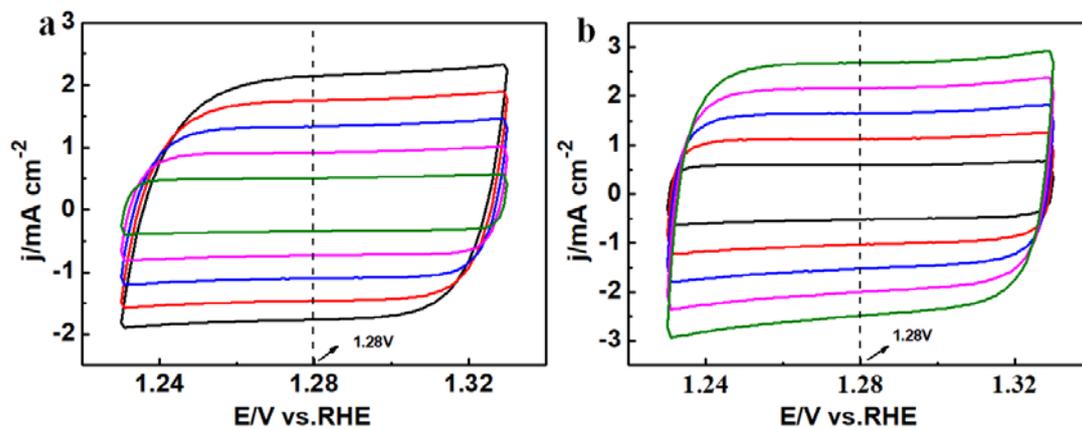


Figure S24. CV curves of (a) Co-LDHs-(0.6:1.2) and (b) CoNi-LDHs with a potential window between 1.23 and 1.33 V vs. RHE at different scan rates of 10, 20, 30, 40 and 50 mV s^{-1} .