Supporting Information

Ionothermal synthesis of cobalt iron layered double hydroxide (LDH) with expanded interlayer spacing: formation mechanism and enhanced electrochemical performance

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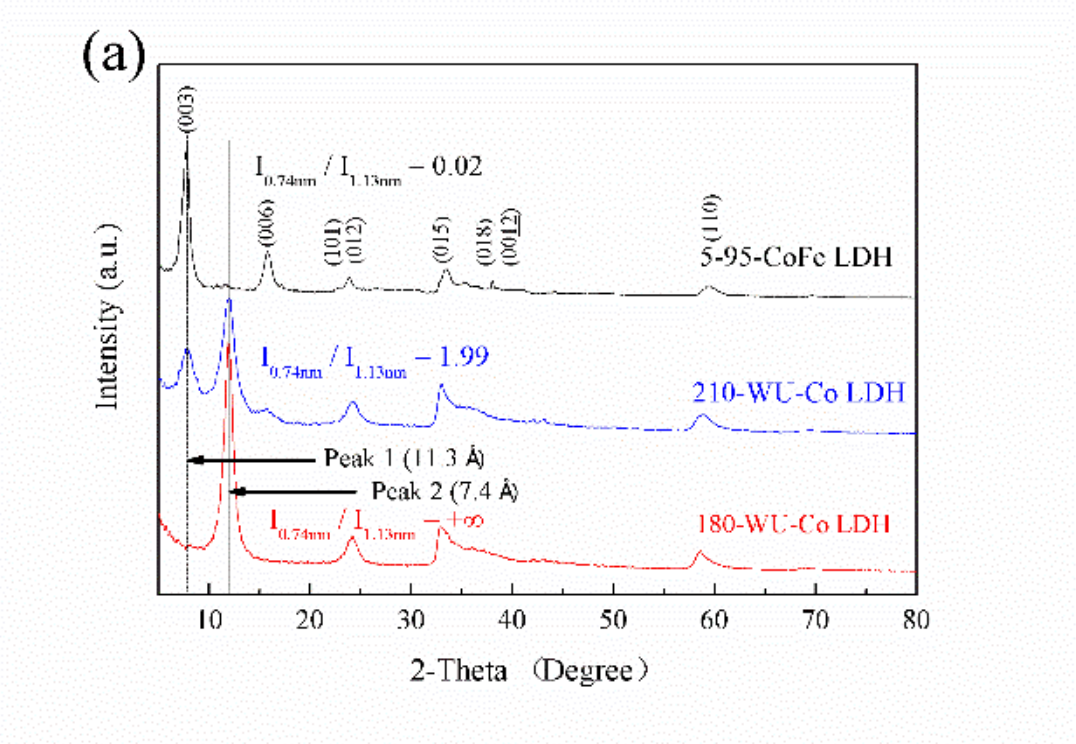
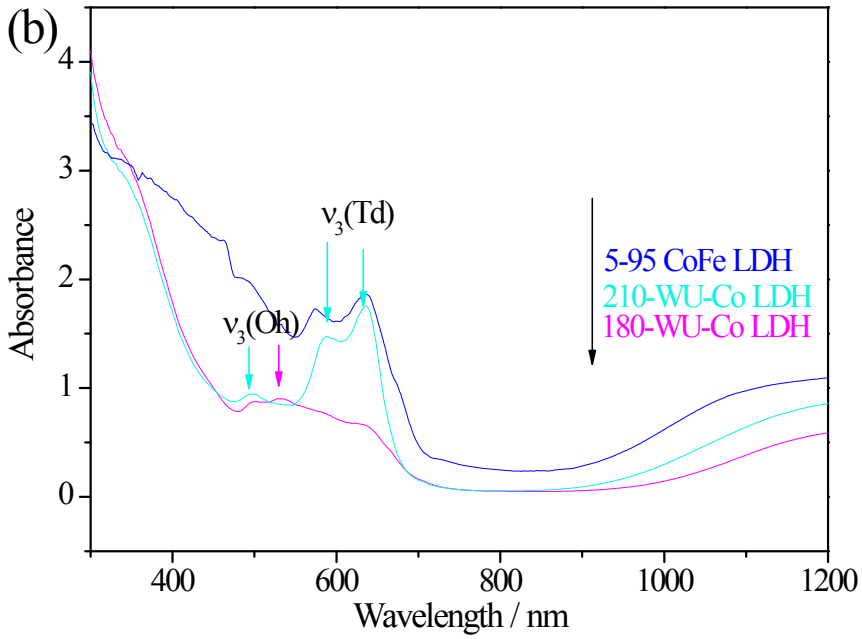
To confirm the tetrahedral coordination model for 5-95 CoFe LDH. we prepared two α-$Co(OH)_2$ samples with different lattice space in (003) as reference group. As seen from the XRD pattern (**Figure S1a**), the feature of the 180-WU Co LDH sample is that it contains only α-$Co(OH)_2$ with 7.4 Å in its (003) plane. 210-WU-Co LDH contains both α-$Co(OH)_2$ with 7.4 Å and 11.3 Å in its (003) plane, with a $I_{7.4} / I_{11.3}$ value of 1.99 (**Figure S1a**).

Comparing the UV-Vis spectra of the samples in **Figure S1b**, it's clear that the occurance of ν_3(Td) at 580 and 630 nm is related to the existance of 11.3 Å (003) planes (See XRD patterns in **Figure S1a**). A simplified Structural model for 7.4 Å layered double hydroxide is provided in **Figure S1c**. The cobalt atoms are octahedrally coordinated.





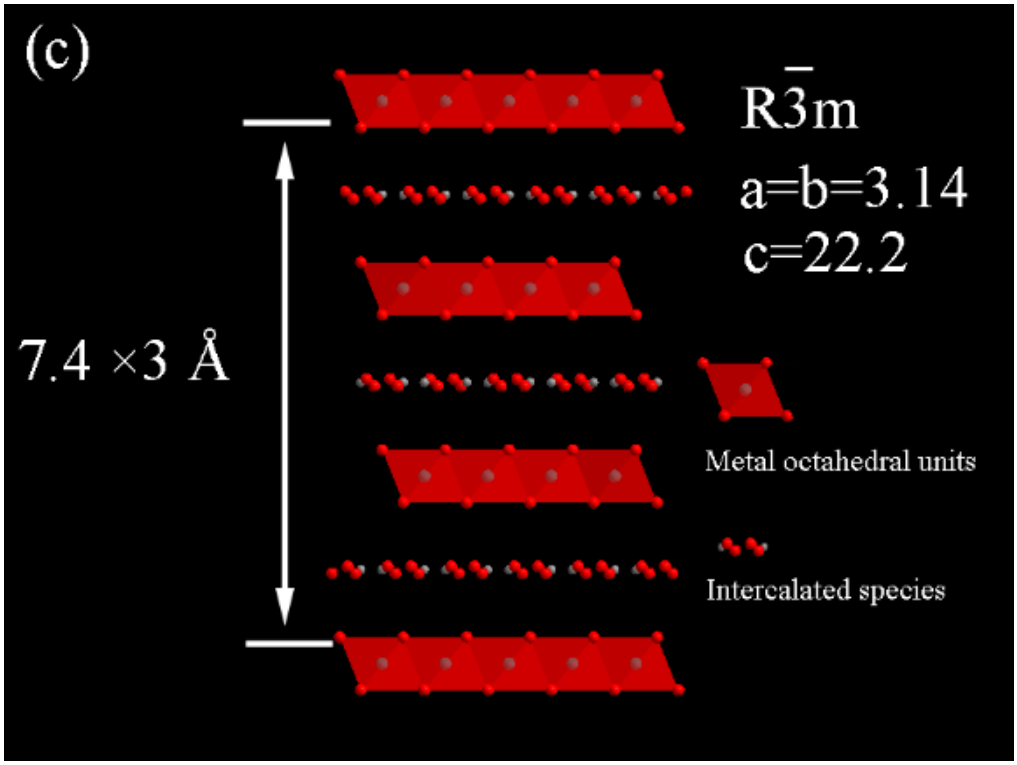


Figure S1 (a) XRD patterns and (b) UV-Vis spectra of 180-WU Co LDH, 210-WU Co LDH and 5-95 CoFe LDH. (c) Structral model of

α-$Co(OH)_2$ with 7.4Å in (003) plane.

Elemental stoichiometry of 5-95-CoFe LDH and the two reference samples are analysed by ICP-AES, IC and CNH elemental analyser. Given amount of samples (See **Table S1**) are used to obtain a H_2SO_4 solution. For IC and ICP-AES experiments, the above solution are diluted to 1/10 and 1/100, respectively. The original data are provide in **Table S1-S5**. The chemical formula for 180-WU Co LDH, 210-WU Co LDH and 5-95 CoFe LDH are determined to be $\mathbf{CoC_{1.008}O_{5.549}N_{0.733}H_{2.643}Cl_{0.032}}$, $\mathbf{CoC_{1.332}O_{4.923}N_{1.194}H_{3.243}Cl_{0.024}}$, and $\mathbf{Co_{0.901}Fe_{0.099}C_{1.398}O_{6.857}N_{0.925}H_{3.375}Cl_{0.018}}$, respectively.

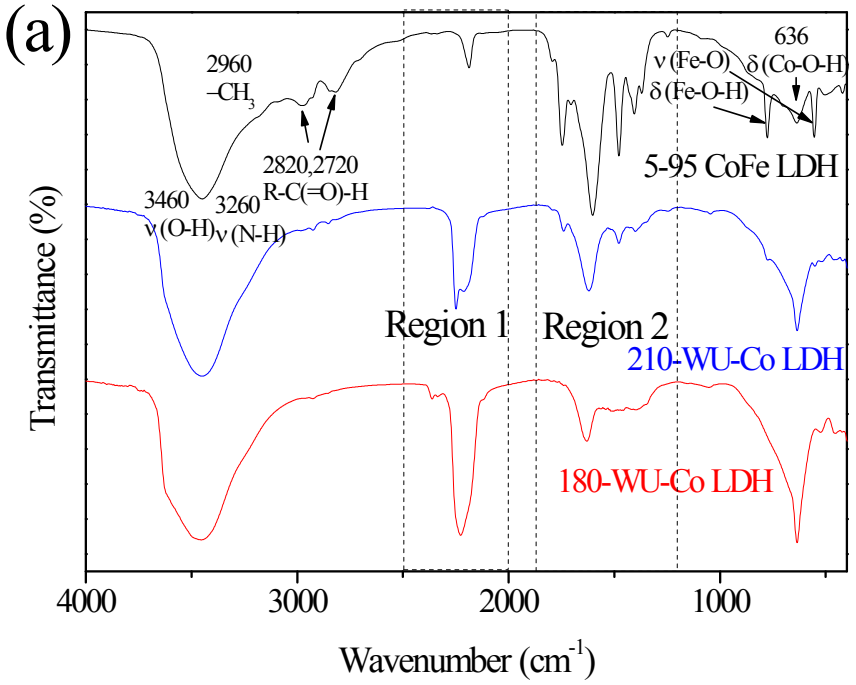
FTIR peaks are indexed in **Figure S2a** based on rational analysis. The most obvious feature is that LDH with larger interlayer spacing is correlated with weaker peaks in Region 1 (2500-2000 cm^{-1}) and stronger peaks in Region 2 (1900-1300 cm^{-1}). This trend is not influenced by iron element in 5-95 CoFe LDH because 210-WU-Co LDH also follow this rule. For 180-WU-Co LDH and 5-95 CoFe LDH, we provide in **Figure S2b and S2c** with their magnified spectra in Region 1 and Region 2, respectively. For 5-95 CoFe LDH, more functional groups including -NH_2, R-C(=O)-H, C-N, and -(C=O)-N are detected and less –N=C=O, -C≡N, -N=C=N- are detected in FTIR.

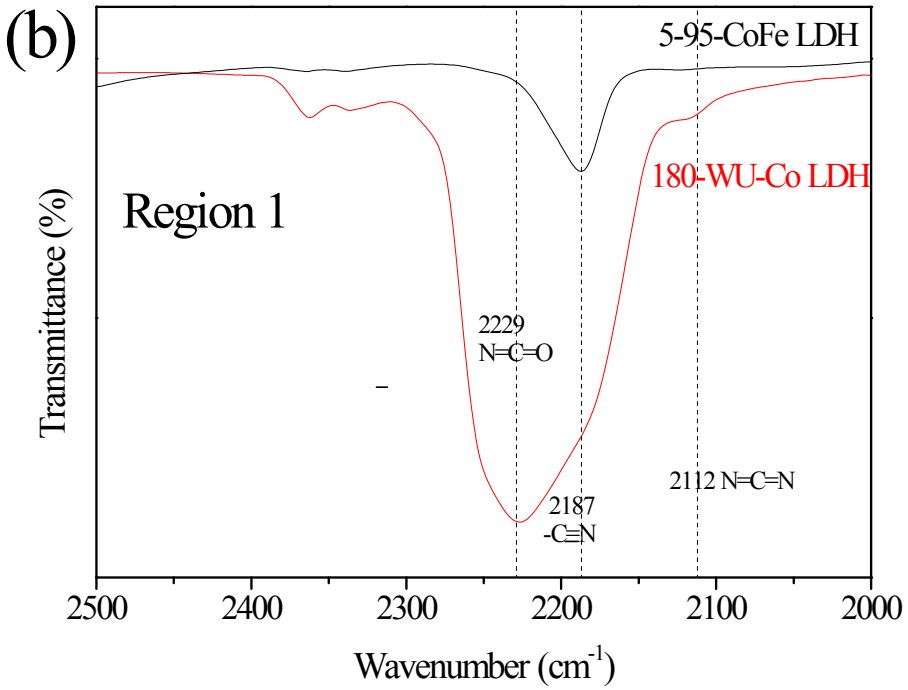
During heating, the decomposition of urea and choline chloride is a very complex process and it's strongly related to the experimental condition. The decomposition products reported in the literatures are collected in **Figure S2d**.[1-5] Combining all the above information, the formation of **LDH with larger interlayer space is accompanied with the following structural changes**:

1: tetrahedrally coordinated cobalt occurs.

2: more functional groups including -NH_2, R-C(=O)-H, C-N, and -(C=O)-N are detected and less –N=C=O, -C≡N, -N=C=N- are detected in FTIR. Considering the possible thermo decomposition process of urea and choline chloride component in CU (Figure S2d), acetaldehyde, ethenol and biuret intercalated (drawn in blue) and less cyanate or isocyanate (drawn in red) species are intercalated into LDH with larger interlayer spacing. This also causes an increase in C, N, H content for 210-WU-Co LDH and 5-95 CoFe LDH. In addition, more CO_3^{2-} are also detected.

3: less Cl- are intercalated.


(a)
2960
–CH3
2820,2720
R-C(=O)-H
3460
ν (O-H)
3260
ν (N-H)
636
ν (Fe-O)
δ (Co-O-H)
δ (Fe-O-H)
5-95 CoFe LDH
Region 1
Region 2
210-WU-Co LDH
180-WU-Co LDH
Transmittance (%)
4000
3000
2000
1000
Wavenumber (cm-1)


(b)
5-95-CoFe LDH
180-WU-Co LDH
Region 1
2229
N=C=O
2187
-C≡N
2112 N=C=N
Transmittance (%)
2500
2400
2300
2200
2100
2000
Wavenumber (cm-1)

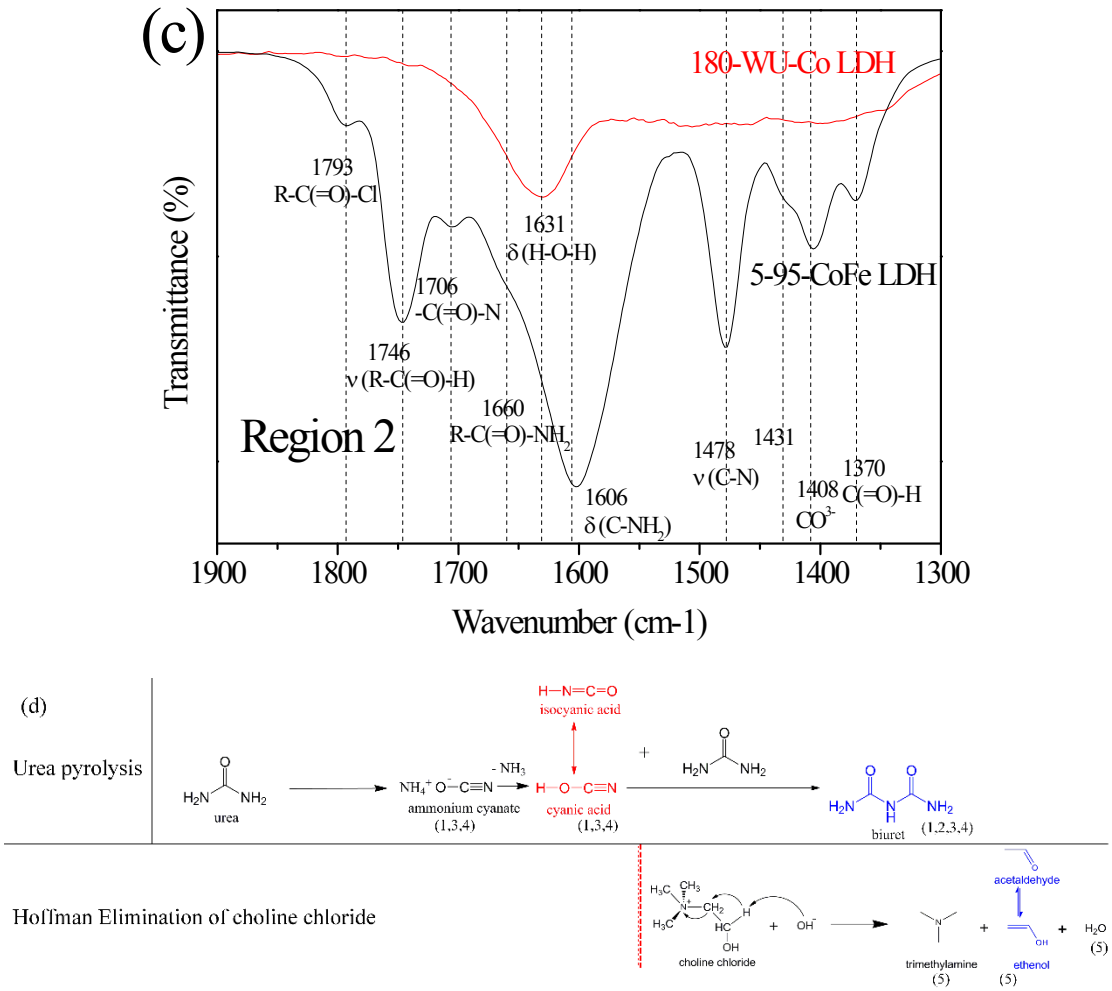


Figure S2 (a) FTIR full spectra of 180-WU-Co LDH, 210-WU-Co LDH and 5-95 CoFe LDH. (b,c) Magnified FTIR images from 2500-2000 cm^{-1} and 1900-1300 cm^{-1}, respectively. (d) Possible pyrolysis route of CU, the numbers in brackets under each decomposition product indicates the related literatures

Table S1 Mass of samples dissolved for IC and ICP-AES analysis

	Mass / mg	solution
180-WU-Co LDH	**5.14**	2.5 mL 0.4% H_2SO_4
210-WU-Co LDH	**5.03**	
5-95-CoFe LDH	**4.92**	

Table S2 C,N,H elemental analysis results

	N %	C %	H %
180-WU-Co LDH	5.90	6.97	1.52
210-WU-Co LDH	9.59	9.17	1.86
5-95-CoFe LDH	6.41	8.30	1.67

Table S3 IC analysis, the samples in Table S1 are diluted by 10 times

	Cl^- (mg L^{-1})	NO_3^- (mg L^{-1})	**Original Cl^- mass ration**
180-WU-Co LDH	1.346	/	**0.65 %**
210-WU-Co LDH	1.003	/	**0.49 %**
5-95 CoFe LDH	0.627	/	**0.32 %**

Table S4 ICP-AES analysis, the samples in Tables S1 are diluted by 100 times.

	Co (mg L^{-1})	Fe (mg L^{-1})	**Mass ratio in the sample (Co)**	**Mass ratio in the sample (Fe)**
180-WU-Co LDH	6.97	\	**33.90 %**	\
210-WU-Co LDH	6.80	\	**33.80 %**	\
5-95-CoFe LDH	5.17	0.54	**26.27 %**	**2.74%**

Table S5 elemental stoichiometry

	Atomic weight ratio	Atomic molar ratio
180-WU-Co LDH	$Co_{0.3390}C_{0.0696}O_{0.5107}N_{0.0590}H_{0.0152}Cl_{0.0065}$	$CoC_{1.008}O_{5.549}N_{0.733}H_{2.643}Cl_{0.032}$
210-WU-Co LDH	$Co_{0.3380}C_{0.0917}O_{0.4518}N_{0.0959}H_{0.0186}Cl_{0.0049}$	$CoC_{1.332}O_{4.923}N_{1.194}H_{3.243}Cl_{0.024}$
5-95 CoFe LDH	$Co_{0.2627}Fe_{0.0274}C_{0.0830}O_{0.5429}N_{0.0641}H_{0.0167}Cl_{0.0032}$	$Co_{0.901}Fe_{0.099}C_{1.398}O_{6.857}N_{0.925}H_{3.375}Cl_{0.018}$

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5. K. Haerens, E. Matthijs, K. Binnemans and B. Van der Bruggen, *Green Chemistry*, 2009, **11**, 1357-1365.