Selective electrooxidation of 5-hydroxymethylfurfural at low working potentials promoted by 3D hierarchical $Cu(OH)_2@Ni_3Co_1$-layered double hydroxide architecture with oxygen vacancies

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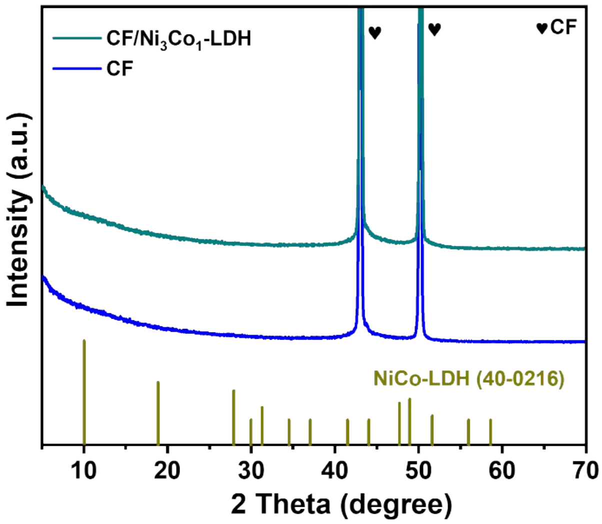

Fig. S1. XRD patterns of CF and CF/Ni_3Co_1-LDH.

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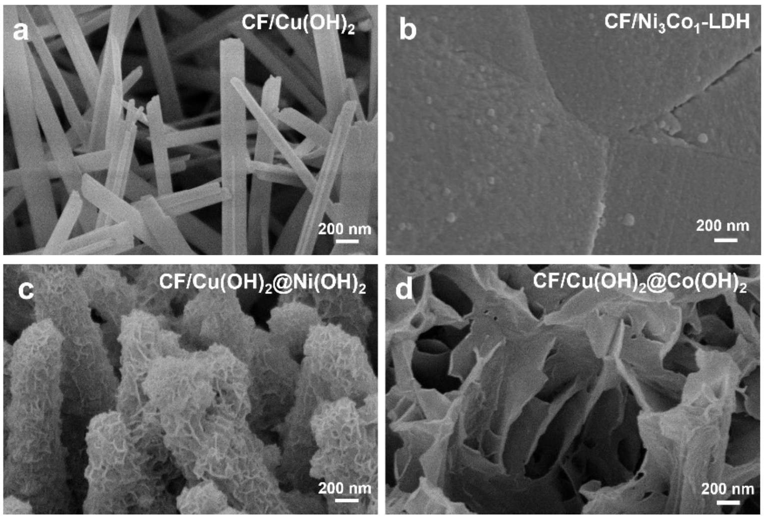

Fig. S2. SEM images of (a) CF/$Cu(OH)_2$, (b) CF/Ni_3Co_1-LDH, (c) CF/$Cu(OH)_2$@$Ni(OH)_2$, and (d) CF/$Cu(OH)_2$@$Co(OH)_2$, respectively.

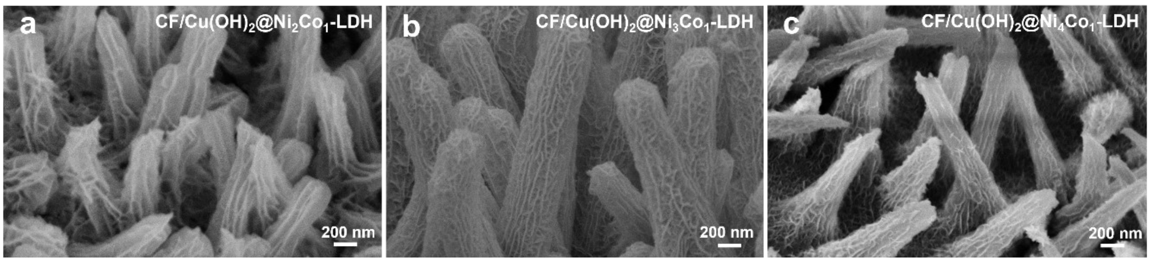

Fig. S3. SEM images of CF/$Cu(OH)_2$@Ni_xCo_y-LDH (x/y = 2/1, 3/1, 4/1).

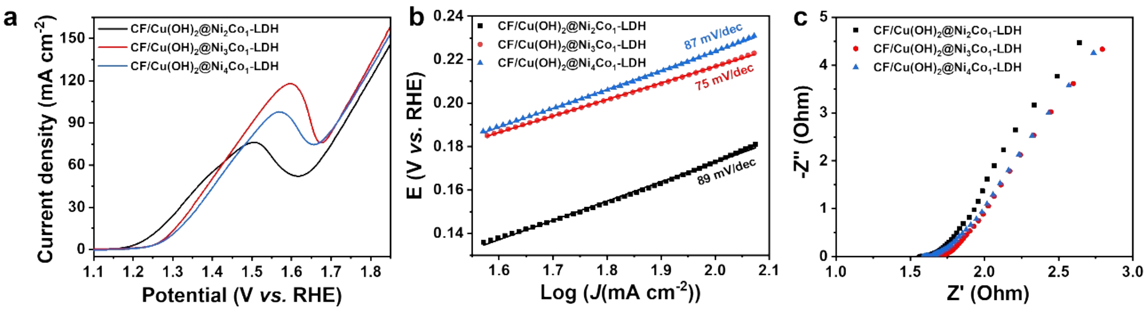

Fig. S4. (a) LSV curves measured a scan rate of 50 mV s^{-1}, (b) Tafel, and (c) EIS spectra of CF/$Cu(OH)_2$@Ni_xCo_y-LDH (x/y = 2/1, 3/1, 4/1) in 1.0 M KOH and 10 mM HMF solution.

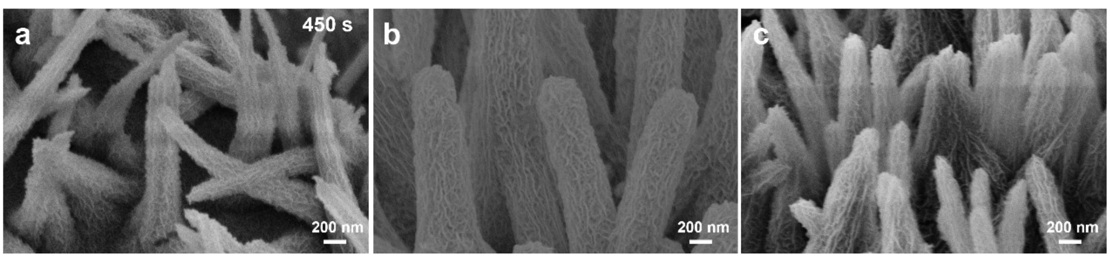

Fig. S5. The SEM images of CF/$Cu(OH)_2$@Ni_3Co_1-LDH fabricated at different deposition time (t = 450, 600, 750 s).

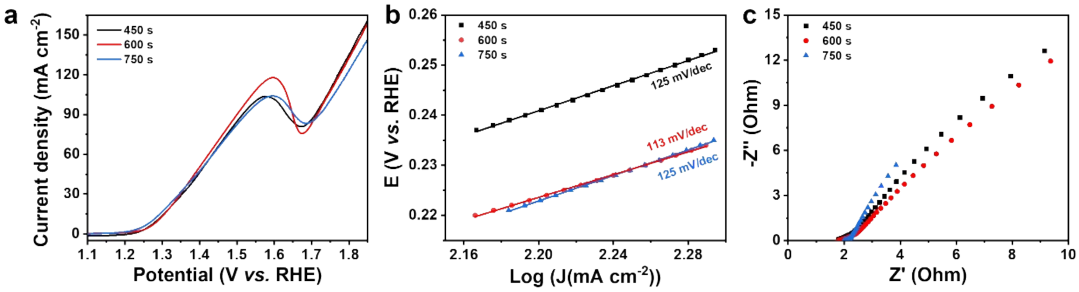

Fig. S6. (a) LSV curves measured at a scan rate of 50 mV s $^{-1}$, (b) Tafel, and (c) EIS spectra of CF/$Cu(OH)_2$@Ni_3Co_1-LDH fabricated at different deposition time (t = 450, 600, 750 s) in 1.0 M KOH and 10 mM HMF solution.

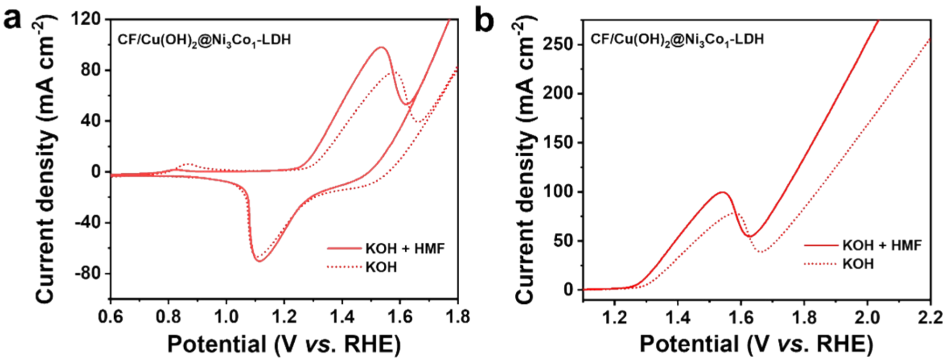

Fig. S7. (a) CV curves and (b) LSV curves of CF/$Cu(OH)_2$@Ni_3Co_1-LDH measured at a scan rate of 50 mV s $^{-1}$ in 1.0 M KOH and 10 mM HMF solution.

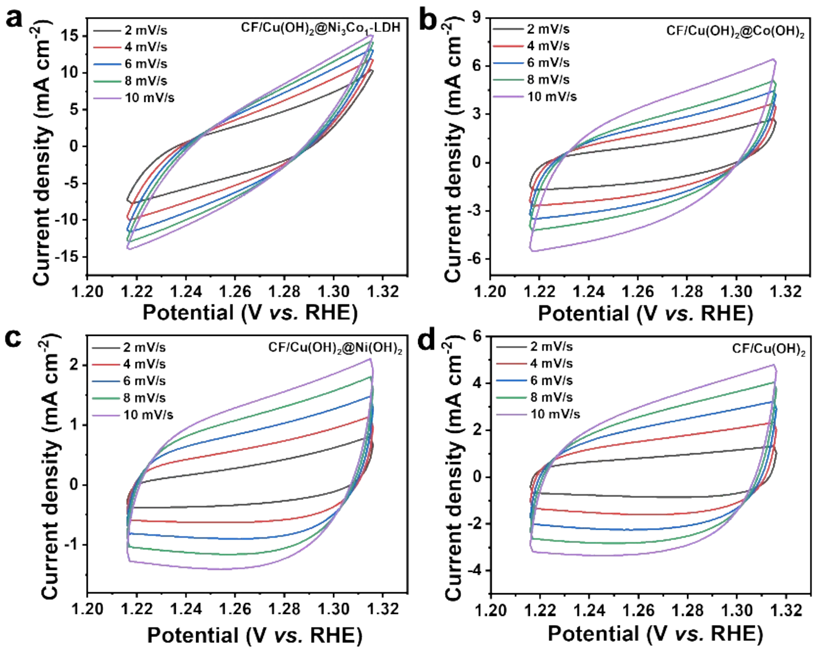

Fig. S8. The CV curves of the (a) CF/$Cu(OH)_2$@Ni_3Co_1-LDH, (b) CF/$Cu(OH)_2$@$Co(OH)_2$, (c) CF/$Cu(OH)_2$@$Ni(OH)_2$ and (d) CF/$Cu(OH)_2$ in 1.0 M KOH and 10 mM HMF solution at sweep rate of 2, 4, 6, 8 and 10 mV·s^{-1}, respectively.

Table S1. Fitting impedance values of $CF/Cu(OH)_2$, $CF/Cu(OH)_2@Ni_3Co_1$-LDH, $CF/Cu(OH)_2@Ni(OH)_2$, and $CF/Cu(OH)_2@Co(OH)_2$, respectively.

Sample	Rs (Ω)	Rct (Ω)
$CF/Cu(OH)_2$	1.54	0.51
$CF/Cu(OH)_2@Ni_3Co_1$-LDH	**1.42**	**0.34**
$CF/Cu(OH)_2@Ni(OH)_2$	1.64	0.48
$CF/Cu(OH)_2@Co(OH)_2$	1.76	0.49

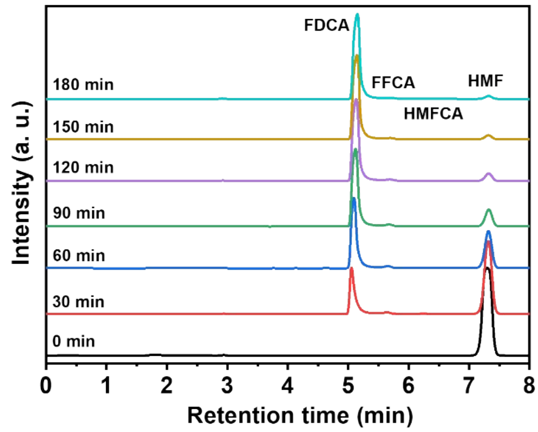

Fig. S9. The procedure of HMF electrooxidation over $CF/Cu(OH)_2@Ni_3Co_1$-LDH from HPLC chromatograms spectra. Reaction conditions: 35 mL of 10 mM HMF, 25°C, onset potential 1.0 V *vs*. RHE, and reaction time 3 h.

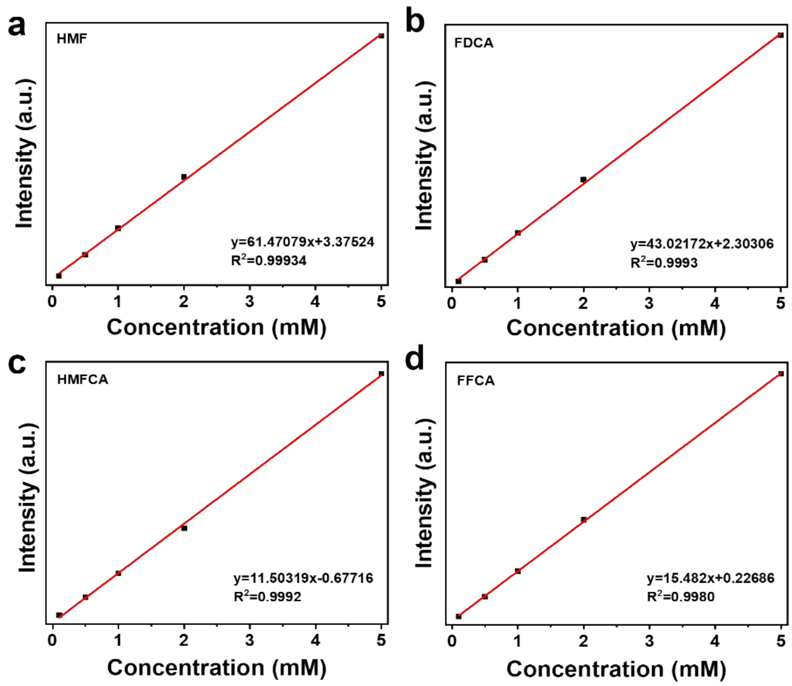

Fig. S10. Calibration curves of HMF, FDCA, HMFCA, and FFCA standard samples.

Table S2. Comparison of electrocatalytic performance and recycled stability of the CF/$Cu(OH)_2$@Ni_3Co_1-LDH with other reported catalysts toward HMF electrocatalytic oxidation in alkaline medium.

Catalyst	Oxidation potential (*vs.* RHE)	Reaction time/Charge Passed	Cycles	FDCA Yield	FDCA FE	Ref.
CF/$Cu(OH)_2$@Ni_3Co_1-LDH	1.0 V (25 °C)	3 h	8	98.64%	86.5%	This work
Cu_xS-NiCo-LDH/CF	1.34 V	10 min/57.6 C	5	~99%	~99%	1
NiCoFe-LDH	1.52 V (60 °C)	1 h/55 °C	10	84.90%	90%	2
NiFe-LDH/CP	1.23 V (60 °C)	1.5 h	10	98%	99.4%	3
NiVCo-LDH	1.376 V	50 min/57.89 C	10	~99%	~92%	4
NiCoMn-LDHs/NF	1.50 V	2.5 h	4	91.7%	65%	5
$NiCo_2O_4$	1.50 V	1 h/34.75 C	3	90.8%	87.5%	6
Ni_xSe_y-NiFe LDH@NF	1.423 V	116 C	6	~97%	~96.7%	7
CoO-$CoSe_2$	1.43 V	1 h	6	99%	97.9%	8
d-NiFe LDH/CP	1.48 V	5 h	10	96.8%	84.47%	9
NiFe-LDH/CoCH/NF	1.58 V	1.5 h	5	98%	98%	10
CoO_xH_y-MA/BH	1.52 V	5 h	/	98%	83%	11
Ni_3S_2-MoS_2/NF	1.61 V	1 h	6	98%	88%	12
$CuCo_2O_4$	1.45 V	62.5 C	6	93.70%	94%	13
NiO-Co_3O_4	1.28 V	60 C	6	98%	96%	14
E-CoAl-LDH-NSA	1.52 V	59.1 C	7	99%	95%	15
Ni_3S_2/NF	1.423 V	58 C	5	98%	94%	16
NiCoBDC-NF	1.55 V	4 h	4	99%	78.8%	17

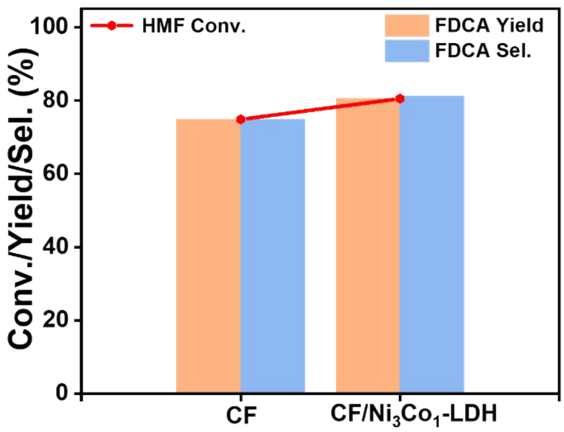

Fig. S11. The HMF conversion, FDCA yield and selectivity over CF and CF/@Ni_3Co_1-LDH. Reaction conditions: 35 mL of 10 mM HMF, 25 °C, onset potential 1.0 V *vs*. RHE, and reaction time 3 h.

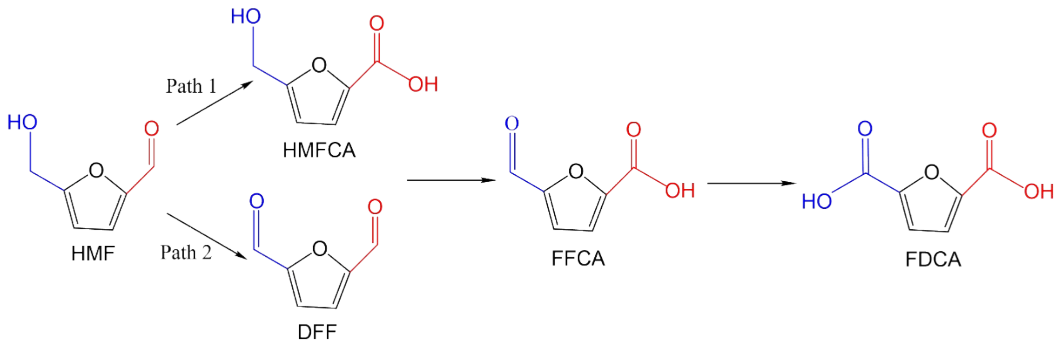

Fig. S12. Two possible oxidation routes from HMF to FDCA.

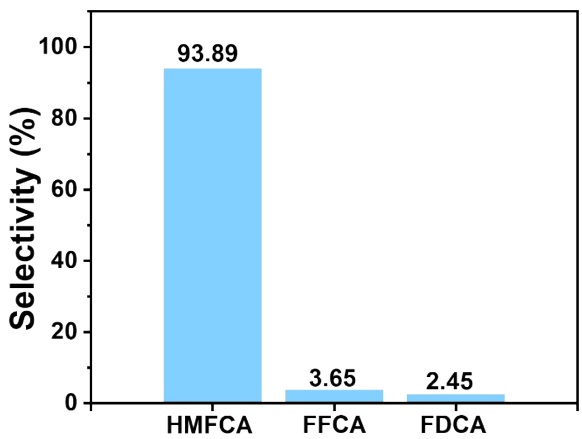

Fig. S13. The selectivity of FDCA, FFCA, and FDCA over CF/$Cu(OH)_2$@Ni_3Co_1-LDH. Reaction conditions: 35 mL of 10 mM HMF, 25 °C, onset potential 0.2 V *vs*. RHE, and reaction time 3 h.

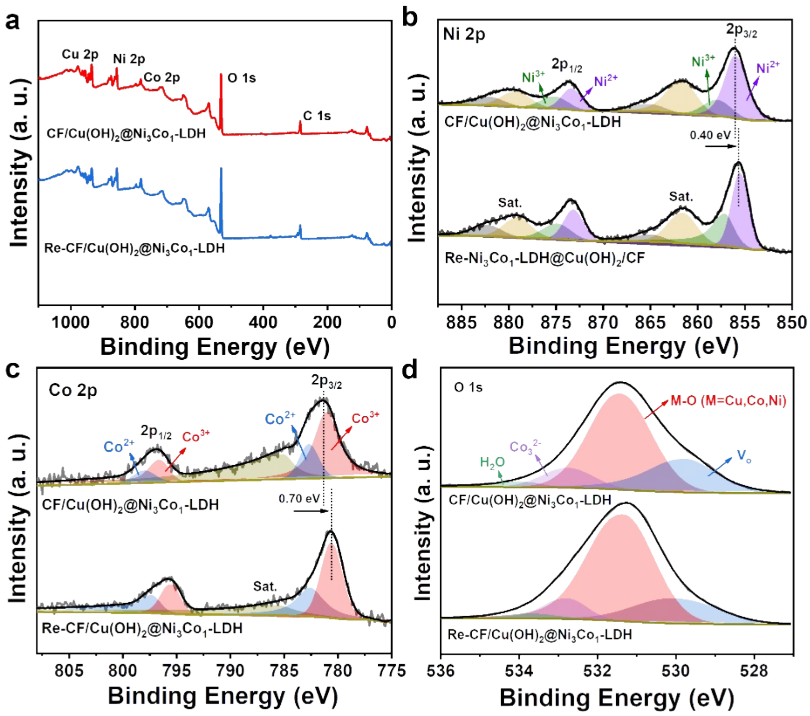

Fig. S14. (a) Survey spectrum, (b) Ni 2p, (c) Co 2p, and (d) O 1s spectra of CF/$Cu(OH)_2$@Ni_3Co_1-LDH and Re-CF/$Cu(OH)_2$@Ni_3Co_1-LDH.

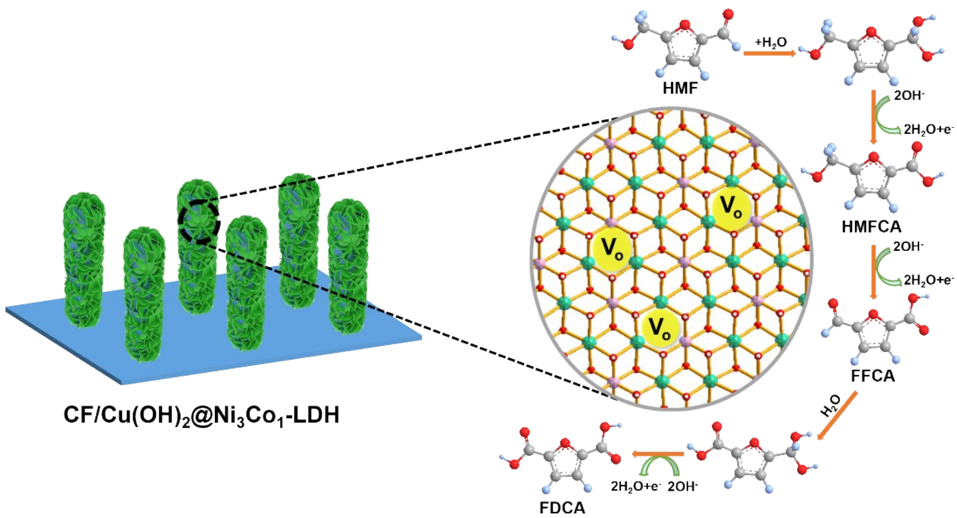

Fig. S15. The possible electrooxidation pathways of HMF to FDCA on CF/$Cu(OH)_2$@Ni_3Co_1-LDH.

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