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Supplementary Material

Constructing bimetal, alloy, and compound-modified nitrogen-doped biomass-derived carbon from coconut shell as accelerants for boosting methane production in bioenergy system

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Characterization

The morphology, structure, and component of the synthesized hybrid samples (Ni-N-C, Fe-N-C, and Fe/Ni-N-C) were identified by X-ray powder diffraction (XRD, D/Max2200, America), Raman spectroscopy (LabRAM HR Evolution, Horiba, France), Scanning electron microscopy (SEM, JSM-7001F, Japan), Energy dispersive X-ray spectroscopy (EDS), Transmission electron microscopy (TEM, JEM-3010, JEOL, Japan), and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo-Fisher, USA). The drainage method was used to measure biogas production. The composition of methane was measured by gas chromatograph (GC9790, China). COD, TS, and VS are measured by the standard methods of the American Public Health Association (APHA, 2005) [1, 2]. The pH value was measured by an acidometer (PHS-3C, China). Thermogravimetry (TG), differential thermogravimetry (DTG), and differential scanning calorimetry (DSC) were tested by using thermal analyzer (STA449F3, Germany) to evaluate the stability of the digestates. Total nitrogen (TN), total phosphorus (TP), and total potassium (TK) were estimated according to standard methods (NY525-2021).

Mediated electrochemical reduction/oxidation (MER/MEO) were tested on an electrochemical workstation (CHI660E, China) in a typical three-electrode system with Ag/AgCl as the reference electrode, graphite rod as the counter electrode and glassy carbon electrode as the working electrode [3]. MER and MEO were carried out in buffer solutions (0.1 M K_2HPO_4, 0.1 M KCl, pH=7) using dibromide monohydrate (DQ) and 2, 2′-azino-bis (3-ethylbenzothiazolin-6-sulfonic acid) diammonium salts (ABTS) as electronic shuttles, respectively. Electron accepting/donating capacity (EAC/EDC) were calculated by the following formula:

$$EAC = \frac{\int \frac{I_{red}}{F} dt}{m} \tag{1}$$

$$EDC = \frac{\int \frac{I_{ox}}{F} dt}{m} \tag{2}$$

Where I_{red} and I_{ox} are the baseline-corrected currents of EAC and EDC, respectively, F is the Faraday constant (96485 A · s/mol e^-), m is the mass of added accelerants, and the unit of EDC or EAC is μmol e^-/g.

Kinetic analysis of biogas production

The modified Gompertz model was used to fit the biogas production and determine the relevant dynamic parameters [4, 5]. The formula of the modified Gompertz model is as follows in **Eq. (3)**.

$$Q(r) = Q_m * exp\left\{- exp\left[\frac{B_m \times e}{Q_m}(\beta - r) + 1\right]\right\} \tag{3}$$

Where $Q(r)$ is the cumulative biogas production (mL/g VS) at time t; Q_m is the biogas production potential (mL/g VS); B_m is the maximum biogas production rate (mL/g VS/d); β is the lag phase (d); r is the digestion time (d); and e is constant (2.71828).

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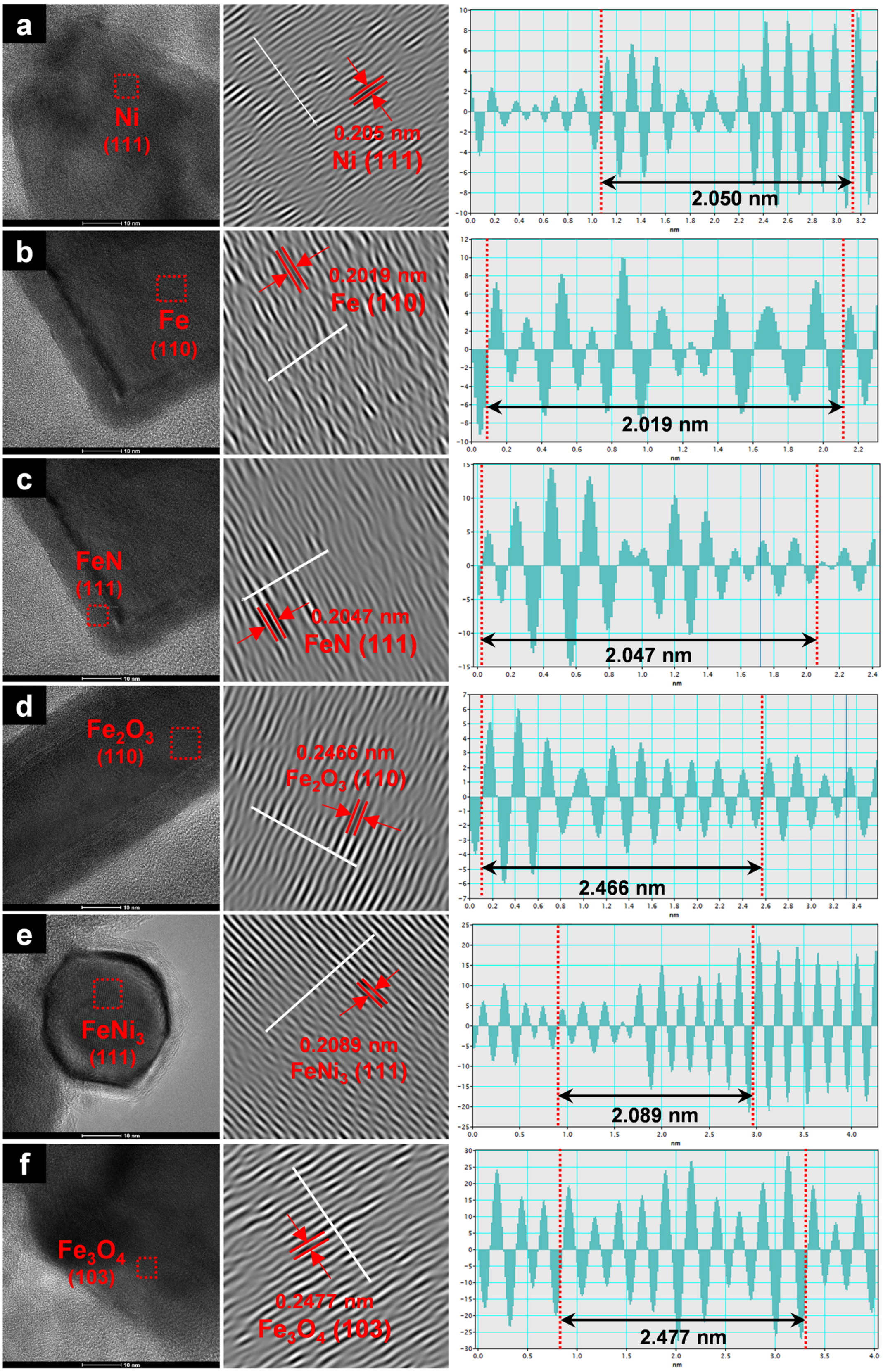

Fig. S1. (a) HRTEM images and IFFT images for the (111) planes of Ni of Ni-N-C. (b-d) HRTEM images and IFFT images for (110), (111), and (110) planes of Fe, FeN, and Fe_2O_3 of Fe-N-C. (e-f) HRTEM images and IFFT images for (111) and (103) planes of $FeNi_3$ and Fe_3O_4 of Fe/Ni-N-C.

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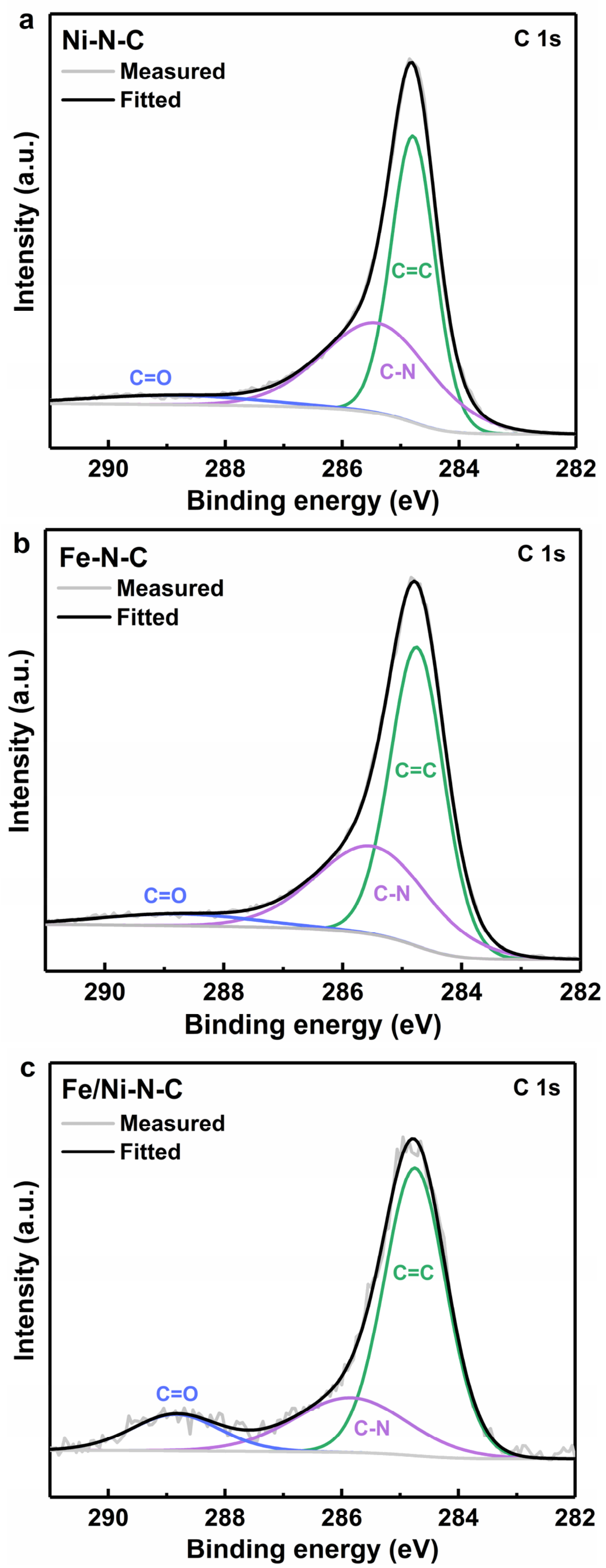

Fig. S2. C 1s XPS spectra of Ni-N-C (a), Fe-N-C (b), and Fe/Ni-N-C (c).

Table S1. Fitting results for N 1s XPS spectra (at.%).

Accelerants	Pyridinic-N	Ni/Fe-N	Pyrrolic-N	Graphitic-N	Oxidized-N
Fe-N-C	18.80	24.06	27.52	7.72	21.91
Ni-N-C	26.89	17.42	21.97	9.89	23.83
Fe/Ni-N-C	11.81	12.79	42.53	10.80	22.07

Table S2. Kinetic parameters related to the cumulative biogas production of different accelerants by the modified Gompertz model.

Groups	Measured cumulative biogas yield (mL/g VS)	Q_m (mL/g VS)	B_m (mL/g VS/d)	β (d)	Predicted cumulative biogas yield (mL/g VS)	R^2
Control	346.32 ± 14.71	372.40 ± 17.46	14.98 ± 0.28	1.42 ± 0.18	347.52 ± 1.18	0.9997
Ni-N-C						
0.875 g/L	402.95 ± 11.70	471.25 ± 17.27	15.75 ± 0.43	1.26 ± 0.29	415.11 ± 11.84	0.9983
1.750 g/L	444.73 ± 19.80	546.87 ± 21.64	17.82 ± 0.45	2.67 ± 0.27	468.23 ± 19.33	0.9983
2.625 g/L	509.92 ± 15.10	562.14 ± 10.46	22.97 ± 0.44	2.52 ± 0.17	522.19 ± 12.11	0.9995
3.500 g/L	470.87 ± 21.10	520.69 ± 12.67	20.35 ± 0.54	1.43 ± 0.17	481.95 ± 10.90	0.9990
Fe-N-C						
0.875 g/L	409.22 ± 37.95	490.90 ± 17.46	16.01 ± 0.37	1.39 ± 0.21	427.54 ± 17.98	0.9995
1.750 g/L	441.84 ± 33.12	485.57 ± 7.29	18.65 ± 0.31	1.37 ± 0.16	447.73 ± 5.78	0.9997
2.625 g/L	510.60 ± 41.21	534.00 ± 4.66	23.60 ± 0.32	1.73 ± 0.12	507.96 ± 2.60	0.9998
3.500 g/L	553.65 ± 26.73	567.45 ± 4.20	26.33 ± 0.33	1.41 ± 0.11	545.58 ± 8.01	0.9999
Fe/Ni-N-C						
0.875 g/L	494.69 ± 37.95	619.46 ± 28.73	19.09 ± 0.46	2.17 ± 0.24	520.70 ± 25.30	0.9987
1.750 g/L	563.35 ± 33.12	666.83 ± 16.94	23.55 ± 0.49	3.39 ± 0.21	585.08 ± 19.87	0.9993
2.625 g/L	587.76 ± 41.21	650.08 ± 10.56	28.17 ± 0.72	2.60 ± 0.25	612.34 ± 23.73	0.9994
3.500 g/L	507.08 ± 26.73	654.75 ± 29.17	18.27 ± 0.46	1.77 ± 0.33	526.14 ± 14.67	0.9991

Table S3. Parameter changes before and after AcoD.

Groups	Initial TS (g/kg)	Final TS (g/kg)	TS degradation (%)	Initial VS (g/kg)	Final VS (g/kg)	VS degradation (%)	Initial COD (mg/L)	Final COD (mg/L)	COD degradation (%)	Initial pH	Final pH
Control	73.60 ± 0.15	50.09 ± 0.14	29.64 ± 0.23	39.01 ± 0.13	21.95 ± 0.15	44.85 ± 0.04	59740.86 ± 258.3	40602.93 ± 302.35	32.03 ± 1.14	7.23 ± 0.04	7.59 ± 0.06
Ni-N-C											
0.875 g/L	73.60 ± 0.15	48.11 ± 0.13	34.64 ± 0.20	39.01 ± 0.13	21.95 ± 0.14	42.51 ± 0.12	59740.86 ± 258.3	35134.95 ± 412.20	41.19 ± 0.52	7.15 ± 0.04	7.56 ± 0.00
1.750 g/L	73.60 ± 0.15	47.39 ± 0.10	34.99 ± 0.19	39.01 ± 0.13	20.55 ± 0.17	46.01 ± 0.05	59740.86 ± 258.3	31229.25 ± 580.12	47.73 ± 0.47	7.16 ± 0.06	7.54 ± 0.01
2.625 g/L	73.60 ± 0.15	44.78 ± 0.15	38.48 ± 0.12	39.01 ± 0.13	19.42 ± 0.21	51.59 ± 0.18	59740.86 ± 258.3	26.932.98 ± 496.47	54.92 ± 0.39	7.21 ± 0.07	7.52 ± 0.01
3.500 g/L	73.60 ± 0.15	46.81 ± 0.11	35.78 ± 0.18	39.01 ± 0.13	19.90 ± 0.06	47.62 ± 0.12	59740.86 ± 258.3	30448.11 ± 328.64	49.03 ± 0.28	7.1 1± 0.02	7.54 ± 0.05
Fe-N-C											
0.875 g/L	73.60 ± 0.15	46.50 ±0.14	38.06 ± 0.23	39.01 ± 0.13	20.31 ± 0.11	49.19 ± 0.15	59740.86 ± 258.3	37478.37 ± 303.74	36.39 ± 0.55	7.30 ± 0.07	7.51 ± 0.10
1.750 g/L	73.60 ± 0.15	45.69 ± 0.11	39.21 ± 0.18	39.01 ± 0.13	19.40 ± 0.09	51.57 ± 0.13	59740.86 ± 258.3	35134.95 ± 285.12	45.48 ± 0.16	7.20 ± 0.06	7.52 ± 0.04
2.625 g/L	73.60 ± 0.15	43.60 ± 0.08	42.14 ± 0.11	39.01 ± 0.13	18.93 ± 0.23	52.81 ± 0.08	59740.86 ± 258.3	28885.83 ± 496.33	51.65 ± 0.62	7.17 ± 0.03	7.52 ± 0.01
3.500 g/L	73.60 ± 0.15	41.14 ±0.13	45.60 ± 0.23	39.01 ± 0.13	17.95 ± 0.19	55.39 ± 0.16	59740.86 ± 258.3	23808.42 ± 214.26	60.15 ± 0.88	7.14 ± 0.02	7.45 ± 0.05
Fe/Ni-N-C											
0.875 g/L	73.60 ± 0.15	43.28 ± 0.13	42.59 ± 0.19	39.01 ± 0.13	19.32 ± 0.10	51.78 ± 0.14	59740.86 ± 258.3	30057.54 ± 205.68	49.69 ± 0.47	7.25 ± 0.00	7.51 ± 0.02
1.750 g/L	73.60 ± 0.15	40.33 ± 0.09	46.74 ± 0.17	39.01 ± 0.13	16.25± 0.13	59.87 ± 0.03	59740.86 ± 258.3	24198.99 ± 132.59	59.49 ± 0.39	7.34 ± 0.04	7.55 ± 0.03
2.625 g/L	73.60 ± 0.15	28.81 ± 0.08	62.92 ± 0.10	39.01 ± 0.13	14.50 ± 0.16	64.47 ± 0.16	59740.86 ± 258.3	20683.86 ± 294.15	65.38 ± 0.74	7.12 ± 0.03	7.57 ± 0.04
3.500 g/L	73.60 ± 0.15	39.70 ± 0.12	47.62 ± 0.22	39.01 ± 0.13	18.31 ± 0.14	54.45 ± 0.07	59740.86 ± 258.3	27323.55 ± 325.28	54.26 ± 0.26	7.24 ± 0.02	7.49 ± 0.02

Table S4. The mass balance of COD in anaerobic digestion process.

Groups	COD (mg/L)			Cumulative biogas yield (mL/g VS)	Required COD (mg/L)
	Initial	Final	Reduction		
Control	59740.86	40602.93	19137.93	346.32	22362.38
Ni-N-C					
0.875 g/L	59740.86	35134.95	24605.91	402.95	26019.06
1.750 g/L	59740.86	31229.25	28511.61	444.73	28716.85
2.625 g/L	59740.86	26932.98	32807.88	509.92	32926.26
3.500 g/L	59740.86	30448.11	29292.75	470.87	30404.75
Fe-N-C					
0.875 g/L	59740.86	37478.37	22262.49	409.22	26423.92
1.750 g/L	59740.86	35134.95	24605.91	441.84	28530.24
2.625 g/L	59740.86	28885.83	30855.03	510.6	32970.17
3.500 g/L	59740.86	23808.42	35932.44	553.65	35749.97
Fe/Ni-N-C					
0.875 g/L	59740.86	30057.54	29683.32	494.69	31942.84
1.750 g/L	59740.86	24198.99	35541.87	563.35	36376.31
2.625 g/L	59740.86	20683.86	39057	587.76	37952.50
3.500 g/L	59740.86	27323.55	32417.31	507.08	32742.88

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Table S5. The co-digestion performance of natural plant and cattle manure with the accelerant fabricated without the coconut shell or with other biomass from our previous work.

Substract	Accelerants	Biogas yield (mL/g VS)	COD removal rate	Ref.
Cow dung	Bio-based carbon derived from corn cob, sawdust, waste carton, and walnut shell	380-502	51.3-67.8%	[6]
Cow dung and aloe peel waste	/	250-300	27.3-61.8%	[1]
Cow dung and acorn slag waste	Aloe peel-derived bio-based carbon and acorn shell derived bio-based carbon	431-580	60.5-79.3%	[7]
Cow dung and aloe peel waste	Vermiculite	295-354	45.5-71.0%	[8]
Cow dung and aloe peel waste	Ti-sphere core–shell structured additives	366-498	53.0-78.3%	[9]
Cow dung and aloe peel waste	Fly-ash	476-588	35.9-52.7%	[10]
Cow dung and aloe peel waste	Dual-heteroatom doped bio-based carbon	385-527	40.6-80.2%	[11]
Cow dung and aloe peel waste	Surface-annealed titanium spheres	435-552	59.8-71.3%	[5]
Cow dung and aloe peel waste	Modified black phosphorus	320-362	47.1-64.4%	[12]
Cow dung and aloe peel waste	Aloe peel-derived carbon quantum dots	522-570	48.8-57.9%	[13]
Cow dung and food waste	/	147-300	48.1-65.1%	[14]
Cow dung and aloe peel waste	Ni-N-C, Fe-N-C, and Fe/Ni-N-C	403-588	36.4-65.4%	This work

Table S6. Comparisons of TS reduction between the Ni-N-C, Fe-N-C, and Fe/Ni-N-C

Contrast		Mean Difference (TS reduction for same concentration (0.875 g/L))	Significance (TS reduction for same concentration (0.875 g/L))	Mean Difference (TS reduction for best concentration)	Significance (TS reduction for best concentration)
bimetallic	**monometallic**				
Fe/Ni-N-C	Ni-N-C	7.95*	<0.01	24.43*	<0.01
Fe/Ni-N-C	Fe-N-C	4.52*	<0.01	17.32*	<0.01

*. The mean difference is significant at the 0.05 level. To more intuitively explain the reason for selecting the bimetallic accelerant as the optimal one, we performed a one-way analysis of variance on the TS reduction of same concentration (0.875 g/L) and best concentration (2.625 g/L for Ni-N-C, 3.500 g/L for Fe-N-C, and 2.625 g/L for Fe/Ni-N-C) of Ni-N-C, Fe-N-C, and Fe/Ni-N-C, respectively. The contrast result of VS reduction is similar.

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