catalysts

Supplementary Materials

3D Co-Ni-C Network from Milk as Competitive Bifunctional Catalysts for Methanol and Urea Electrochemical Oxidation

Dana Ao, Yue Shi, Shuyuan Li, Ying Chang, Aiju Xu, Jingchun Jia * and Meilin Jia

Inner Mongolia Key Laboratory of Green Catalysis and Inner Mongolia Collaborative Innovation Center for Water Environment Safety, College of Chemistry and Environmental Science, Inner Mongolia Normal University, Hohhot 010022, China; aodn@mails.imnu.edu.cn (D.A.); shiy@mails.imnu.edu.cn (Y.S.); lisy@mails.imnu.edu.cn (S.L.); changying@imnu.edu.cn (Y.C.); xuaj@imnu.edu.cn (A.X.); jml@imnu.edu.cn (M.J.)

* Correspondence: jjc@imnu.edu.cn; Tel.: +86-471-4392124

S1 Experimental

S1.1 Experimental Materials

NaCl (AR), $CoCl_2·6H_2O$ (AR), $NiCl_2·6H_2O$ (AR), urea (AR) and CH_3OH (AR) was purchased from Sinopharm Chemical Reagents Co., Ltd (Shanghai, China). Nafion (5 wt%) was given the Sigma-Aldrich Chemical Reagent Co. (Shanghai, China). The milk (cow) is contain protein (3.34 g/100 g), fat (3.38 g/100 g), and lactose (4.87 g/100 g).

The preparation method of samples with different milk (camel milk, and goat milk), and individual components of milk (fat, and protein) are the same as 3D-C-CoNi (1:1). These material mater form fat, protein, camel milk, and goat milk are from the market.

S1.2 Electrochemical Measurements

During the test, all potential values were compared with RHE (*vs.* RHE), and iR correction was not performed. In the 1 M KOH/0.5 M MeOH and 1 M KOH/0.5 M Urea solution, E (RHE) = E (Hg/HgO) + 0.90167 V. The cyclic voltammetric (CV) tests were in the range of 0.2 to 0.8 V *vs.* RHE for MOR and UOR with scanning speed of 50 mV s^{-1}. Linear sweep voltammetry (LSV) tests were between 0.2 and 0.8 V *vs.* RHE for MOR and UOR at scan rate of 5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) data were measured at a potential of 0.5 V *vs.* RHE and the frequency range between 0.01 Hz and 100 KHz for MOR and UOR. Chronoamperometry (CA) test was performed at 0.6 V *vs.* RHE for 4000 s in 1 M KOH/0.5 M MeOH and 1 M KOH/0.5 M Urea solution. All tests were analyzed at room temperature.

Figures

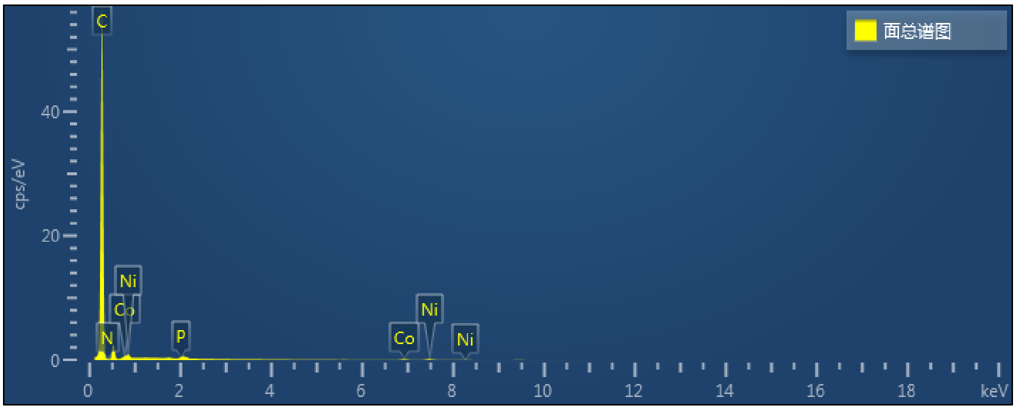

Figure S1. EDS of 3D-C-NiCo (1:1).

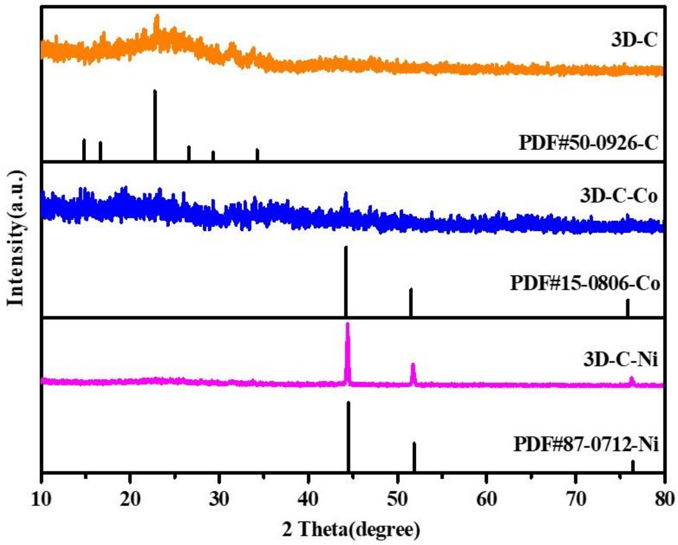

Figure S2. XRD pattern of different catalysts.

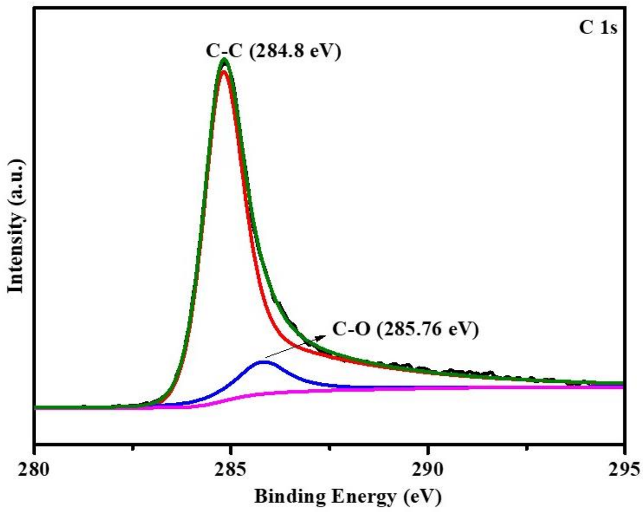

Figure S3. C1s spectrum of 3D-C-NiCo (1:1).

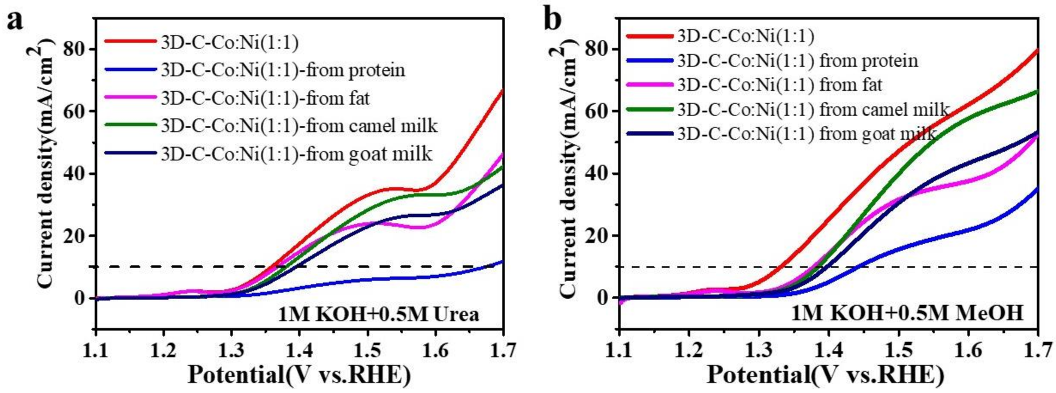

Figure S4. LSV profiles for different catalysts (3D-C-NiCo (1:1), 3D-C-NiCo (1:1)-from protein, 3D-C-NiCo (1:1)-from fat, 3D-C-NiCo (1:1)-from camel milk, and 3D-C-NiCo (1:1)-from goat milk) with 1 M KOH/ 0.5 M Urea (**a**), and 1 M KOH/ 0.5 M MeOH (**b**).

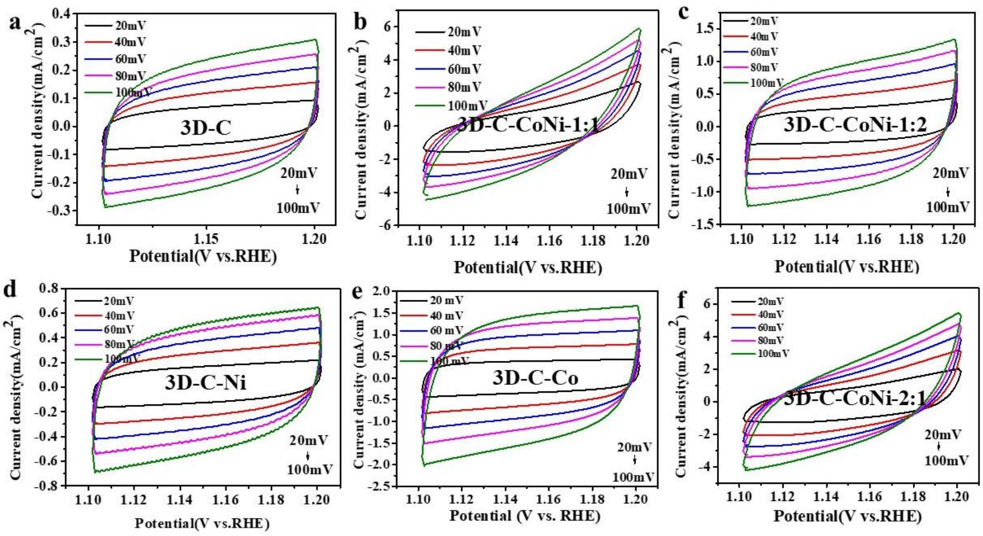

Figure S5. Double-layer capacitance for (**a**) 3D-C, (**b**) 3D-C-Ni:Co(1:1), (**c**) 3D-C-Ni:Co(1:2), (**d**) 3D-C-Ni, (**e**) 3D-C-Co, and (**f**) 3D-C-Ni in 1 M KOH.

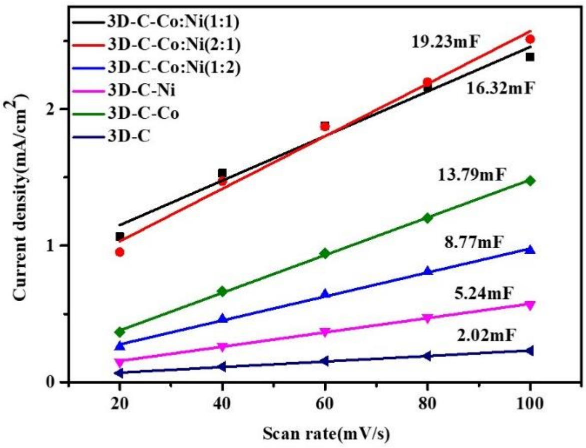

Figure S6. Determination of double-layer capacitance over a range of scan rates.

Table S1. The MOR performance.

Catalyst	**Electrolyte**	**Methanol concentration (M)**	**Potential**	**Current density (Corresponding potential)**	**Ref.**
Co/N-C-1-500	1 M KOH	1	0.8 V (vs. SCE)	231 mA cm^{-2}	[1]
Ni/N–C@500 e	1 M KOH	1	1.66 V (vs. RHE)	147 mA cm^{-2}	[2]
Ni/C-30	0.5 M KOH	0.4	0.86 V (vs.Hg/Hg_2SO_4)	30 mA cm^{-2}	[3]
GC/Ni–Co	0.1 M KOH	0.1	0.6 V (vs. Ag/AgCl)	2.3 mA cm^{-2}	[4]
NiCo/NiO-CoO/NPCC/GCE	0.5 M NaOH	0.5	0.61 V (vs. SCE)	178 mA cm^{-2}	[5]
CNFs–Ni	1 M KOH	0.5	0.526 V (vs. Hg/HgO)	400 mA mg^{-1}	[6]
3D-C-CoNi (1:1)	1M KOH	0.5 M	1.33 V vs. RHE	10 mA cm^{-2}	**This work**

Table S2. The UOR performance.

Catalyst	Electrolyte	Urea concentration (M)	Current density	Potential (Corresponding potential)	Ref.
CoGC	1M KOH	0.3	-	0.1 V (vs. Ag/AgCl)	[7]
Ni-MOF	1M KOH	0.33	10 mA cm^{-2}	1.36V (vs. RHE)	[8]
Ni/C	1M KOH	0.33	-	1.33V (vs. RHE)	[9]
Ni-Co alloys NC600/Ti	1M KOH	0.33	-	0.372 V (vs. Hg/HgO)	[10]
NiCo 25/MWCNT	1M KOH	1	-	0.302 V (vs. Ag/AgCl)	[11]
Ni-Co alloys	1M KOH	0.33	-	0.39 V (vs. Hg/HgO)	[12]
3D-C-CoNi (1:1)	1M KOH	0.5 M	10 mA cm^{-2}	1.35 V vs. RHE	**This work**

Table S3. Content of different element in 3D-C- NiCo (1:1).

	Wt %	Wt % Sigma	Atom %
C	91.59	0.52	95.79
Co	1.83	0.10	0.39
Ni	2.91	0.13	0.62
N	3.48	0.52	3.12
P	0.19	0.03	0.08
Total	100.00		100.00

References

1. Zhai, M.; Chen, F.; Wu, N.; Guo, R.; Zhang, X.; Hu, T.; Ma, M. Porous layered cobalt nanocrystal/nitrogen-doped carbon composites as efficient and CO-resistant electrocatalysts for methanol oxidation reaction. *Appl. Surf. Sci.* **2021**, *545*, 149016.
2. Wu, N.; Zhai, M.; Chen, F.; Zhang, X.; Guo, R.; Hu, T.; Ma, M. Nickel nanocrystal/nitrogen-doped carbon composites as efficient and carbon monoxide-resistant electrocatalysts for methanol oxidation reactions. *Nanoscale* **2020**, *12*, 21687–21694.
3. Hameed, R.M.A.; El-Sherif, R.M. Microwave irradiated nickel nanoparticles on Vulcan XC-72R carbon black for methanol oxidation reaction in KOH solution. *Appl. Catal. Environ.* **2015**, *162*, 217–226.
4. Asgari, M.; Maragheh, M.G.; Davarkhah, R.; Lohrasbi, E.; Golikand, A.N. Electrocatalytic oxidation of methanol on the nickel–cobalt modified glassy carbon electrode in alkaline medium. *Electrochim. Acta.* **2012**, *59*, 284–289.
5. Rezaee, S.; Shahrokhian, S. Facile synthesis of petal-like NiCo/NiO-CoO/nanoporous carbon composite based on mixed-metallic MOFs and their application for electrocatalytic oxidation of methanol. *Appl. Catal. Environ.* **2019**, *244*, 802–813.
6. Wang, J.; Zhao, Q.; Hou, H.; Wu, Y.; Yu, W.; Ji, X.; Shao, L. Nickel nanoparticles supported on nitrogen-doped honeycomb-like carbon frameworks for effective methanol oxidation. *RSC Adv.* **2017**, *7*, 14152–14158.
7. Alotaibi, N.; Hammud, H.H.; al Otaibi, N.; Prakasam, T. Electrocatalytic Properties of 3D Hierarchical Graphitic Carbon–Cobalt Nanoparticles for Urea Oxidation. *ACS Omega* **2020**, *5*, 26038–26048.
8. Zhu, D.; Guo, C.; Liu, J.; Wang, L.; Du, Y.; Qiao, S.Z. Two-dimensional metal-organic frameworks with high oxidation states for efficient electrocatalytic urea oxidation. *Chem. Commun.* **2017**, *53*, 10906–10909.
9. Wang, L.; Ren, L.; Wang, X.; Feng, X.; Zhou, J.; Wang, B. Multivariate MOF-Templated Pomegranate-Like Ni/C as Efficient Bifunctional Electrocatalyst for Hydrogen Evolution and Urea Oxidation. *ACS Appl. Mater. Interfaces* **2018**, *10*, 4750–4756.
10. Gao, X.; Wang, Y.; Li, W.; Li, F.; Arandiyan, H.; Sun, H.; Chen, Y. Free-standing Ni-Co alloy nanowire arrays: Efficient and robust catalysts toward urea electro-oxidation. *Electrochim. Acta* **2018**, *283*, 1277–1283.
11. Tesfaye, R.M.; Das, G.; Park, B.J.; Kim, J.; Yoon, H.H. Ni-Co bimetal decorated carbon nanotube aerogel as an efficient anode catalyst in urea fuel cells. *Sci. Rep.* **2019**, *9*, 479.
12. Yan, W.; Wang, D.; Botte, G.G. Template-assisted synthesis of Ni–Co bimetallic nanowires for urea electrocatalytic oxidation. *J. Appl. Electrochem.* **2015**, *45*, 1217–1222.