

**Boosting eco-friendly hydrogen generation by urea-assisted water electrolysis using
spinel M_2GeO_4 ($M = Fe, Co$) as an active electrocatalyst**

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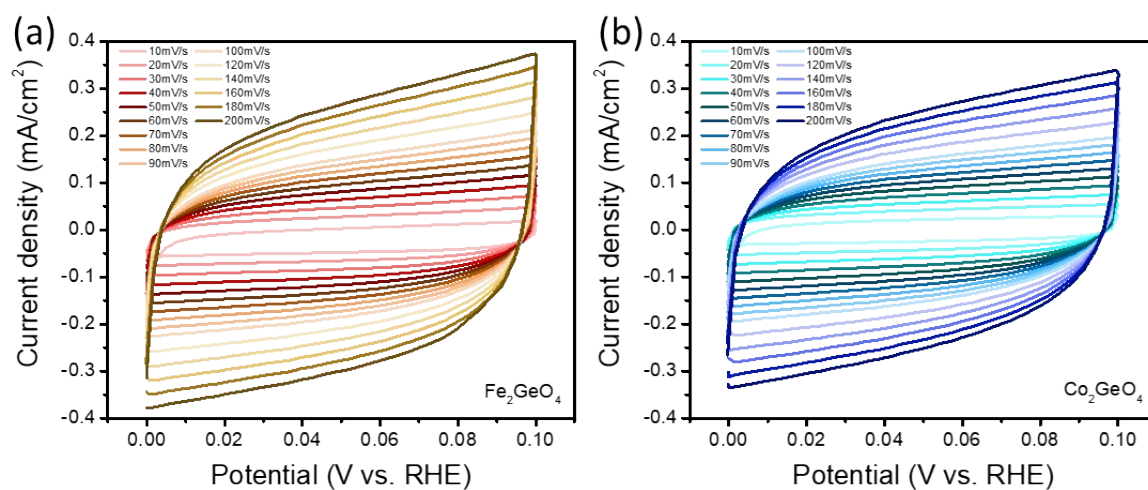


Fig. S1. CV analysis of (a) Fe₂GeO₄ and (b) Co₂GeO₄ at different scan rates for the electrochemical surface area measurement.

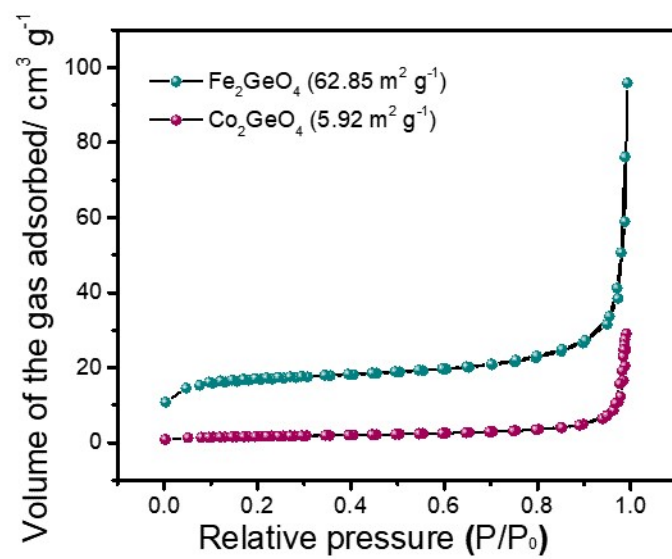


Fig. S2. BET results of prepread Fe_2GeO_4 and Co_2GeO_4 particles showing surface area of electrocatalysts.

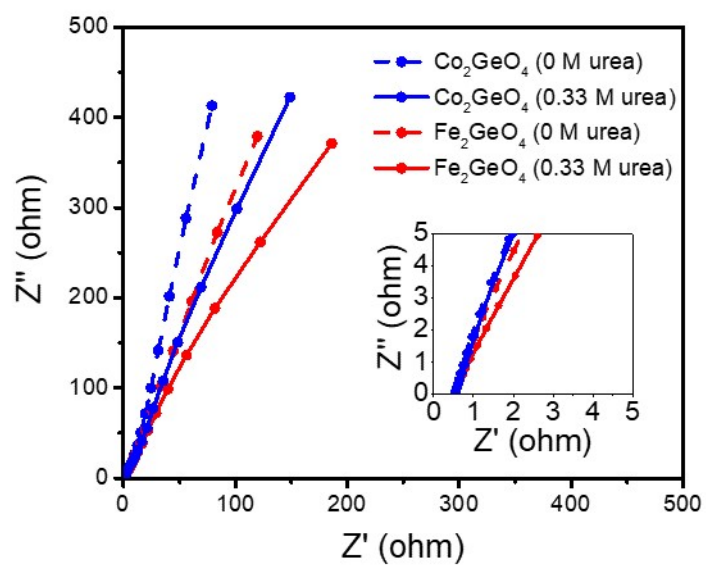


Fig. S3. Electrochemical analysis of the prepared M_2GeO_4 . EIS analysis of Fe_2GeO_4 and Co_2GeO_4 at open-circuit voltage under 1 M KOH with/without 0.33 urea condition.

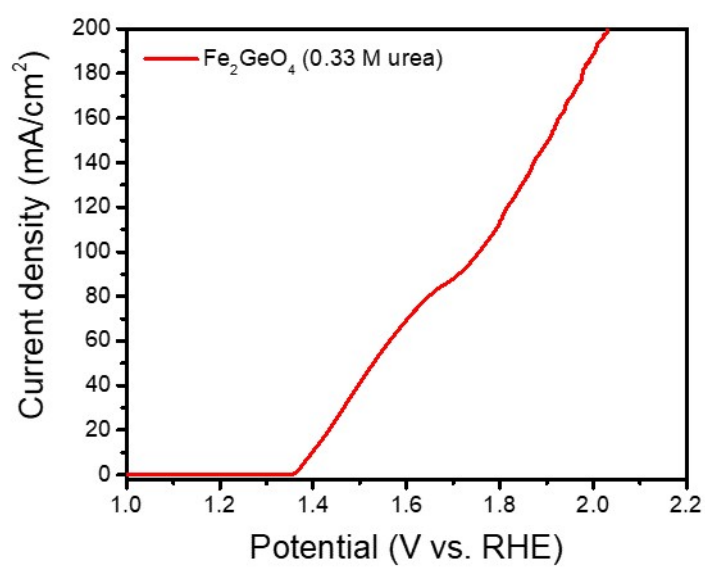


Fig. S4. Linear sweep voltammetry analysis of Fe₂GeO₄ electrocatalyst in 1 M alkaline with 0.33 M urea condition under wide potential window.

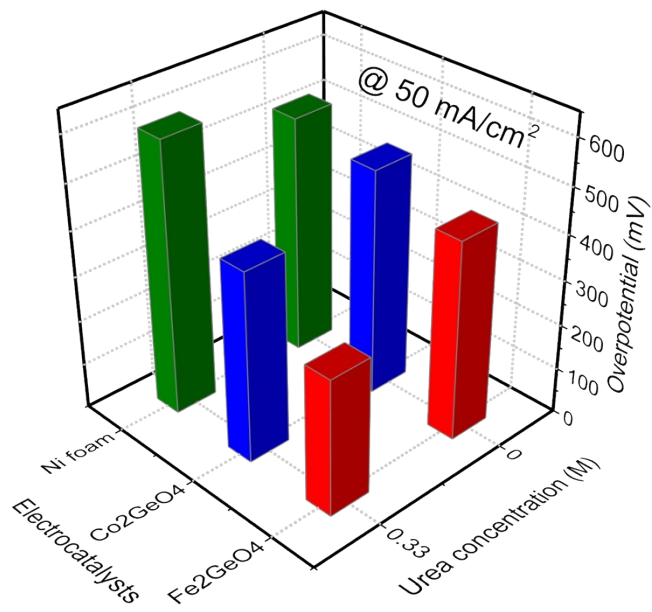


Fig. S5. The overpotential at 50 mA/cm² of prepared electrode under 1.00 M KOH with/without 0.33 M urea.

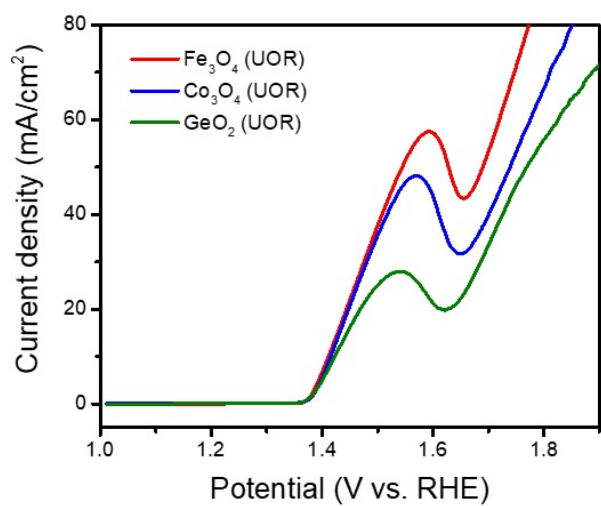


Fig. S6. Linear sweep voltammetry analysis of Fe₃O₄, Co₃O₄, and GeO₂ in 0.1 M alkaline with/without 0.33 M urea condition

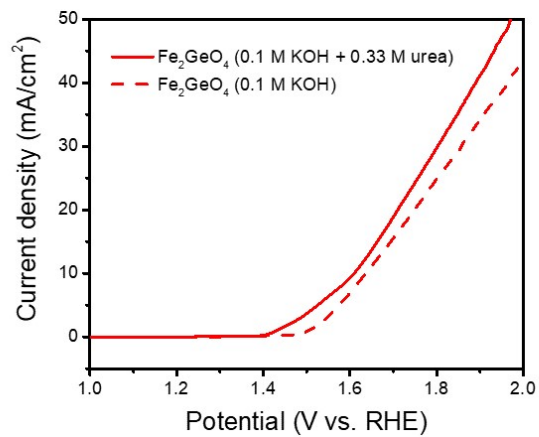


Fig. S7. Linear sweep voltammetry analysis of Fe₂GeO₄ in 0.1 M alkaline with/without 0.33 M urea condition.

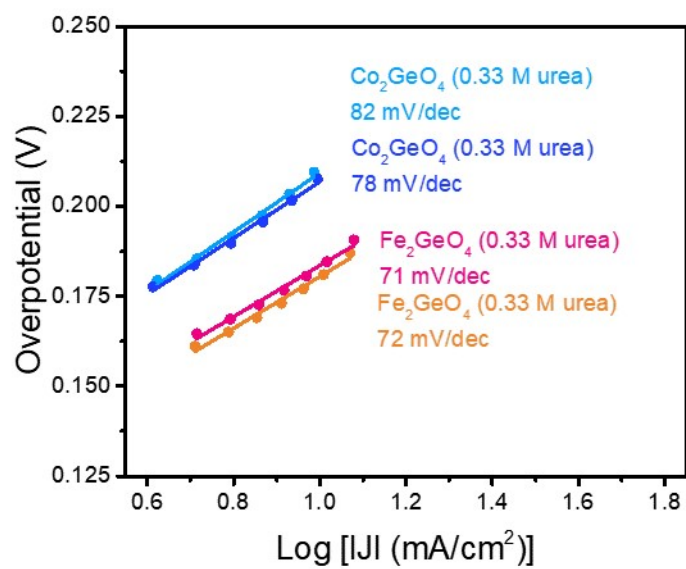


Fig. S8. Tafel slopes of the prepared electrode in alkaline solution with urea.

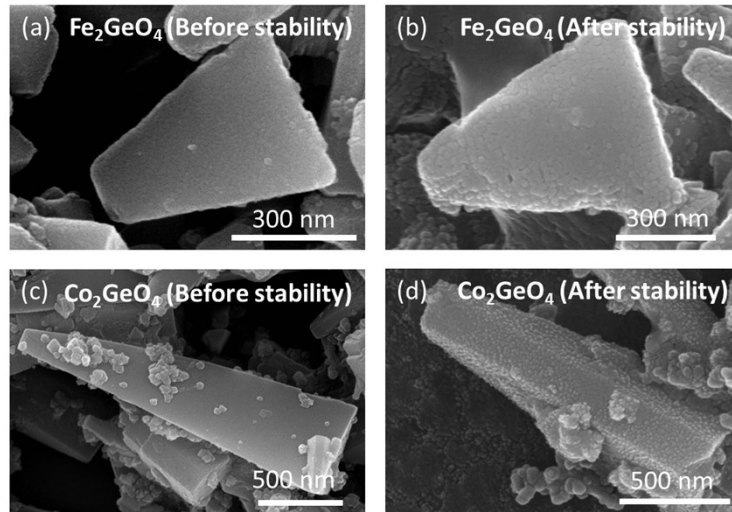


Fig. S9. SEM images of Fe_2GeO_4 on Ni foam before (a) and after (b) stability test, respectively, and Co_2GeO_4 on Ni foam before (c) and after (d) stability test, respectively.

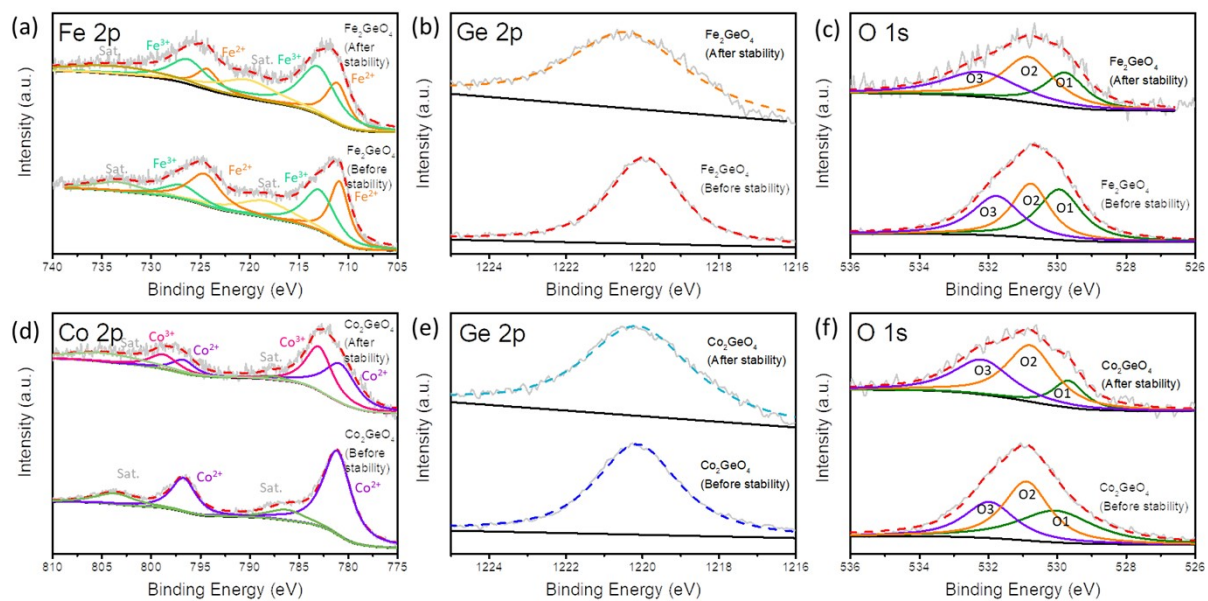


Fig. S10. XPS analysis of Fe_2GeO_4 and Co_2GeO_4 : high-resolution spectra of (a) Fe 2p (b) Ge 2p, and (c) O 1s of Fe_2GeO_4 before and after stability test, (d) Co 2p (e) Ge 2p, and (f) O 1s of Co_2GeO_4 before and after stability test.

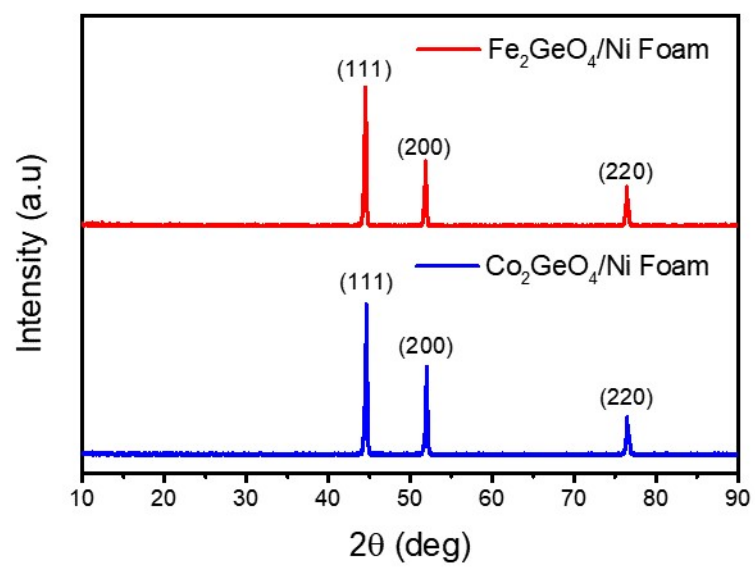


Fig. S11. XRD analysis of Fe₂GeO₄ (red) and Co₂GeO₄ (blue) on Ni foam after stability test.

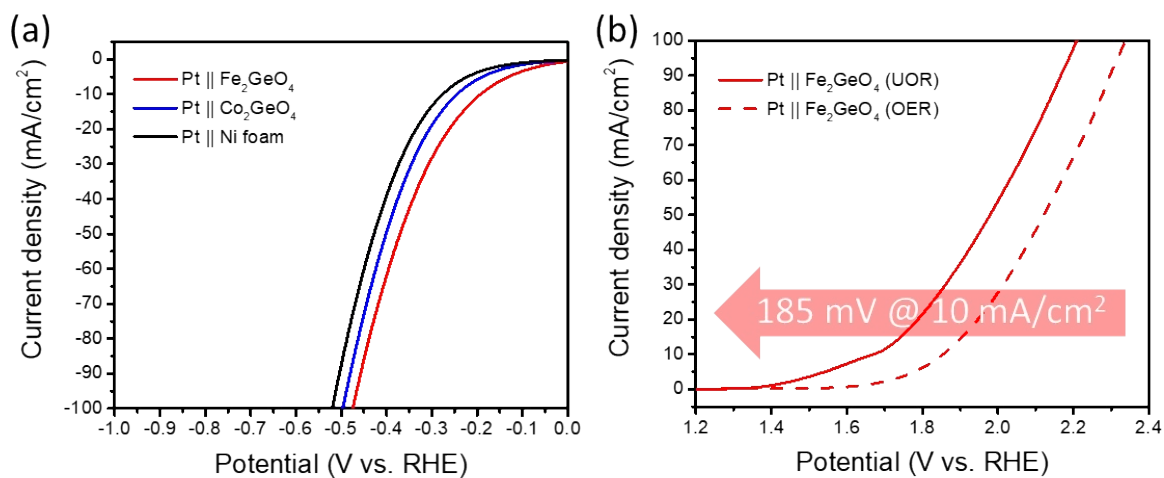


Fig. S12. (a) Hydrogen evolution reaction of Pt coil in prepared electrocatalysts under 1 M KOH, (b) urea oxidation reaction of Pt||Fe₂GeO₄ under 1.00 M KOH with/without 0.33 M urea.

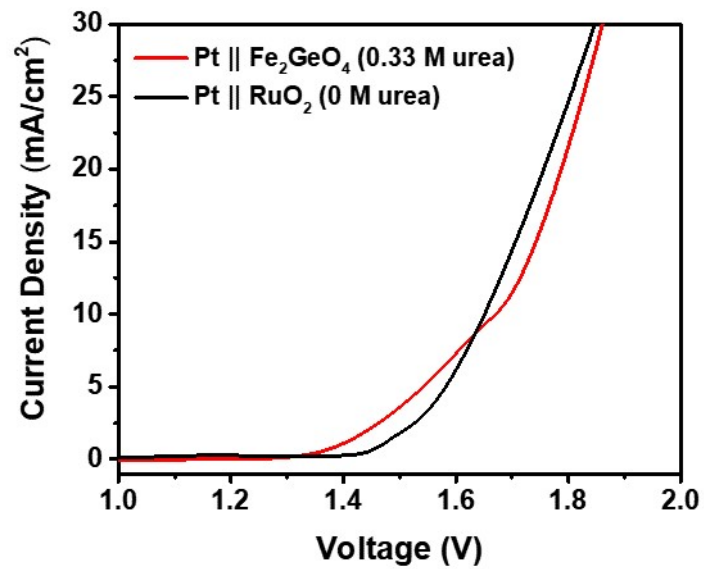


Fig. S13. Linear sweep voltammetry analysis of Pt || Fe₂GeO₄ system in 1 M KOH with 0.33 M urea condition and Pt || RuO₂ system in 1 M KOH.

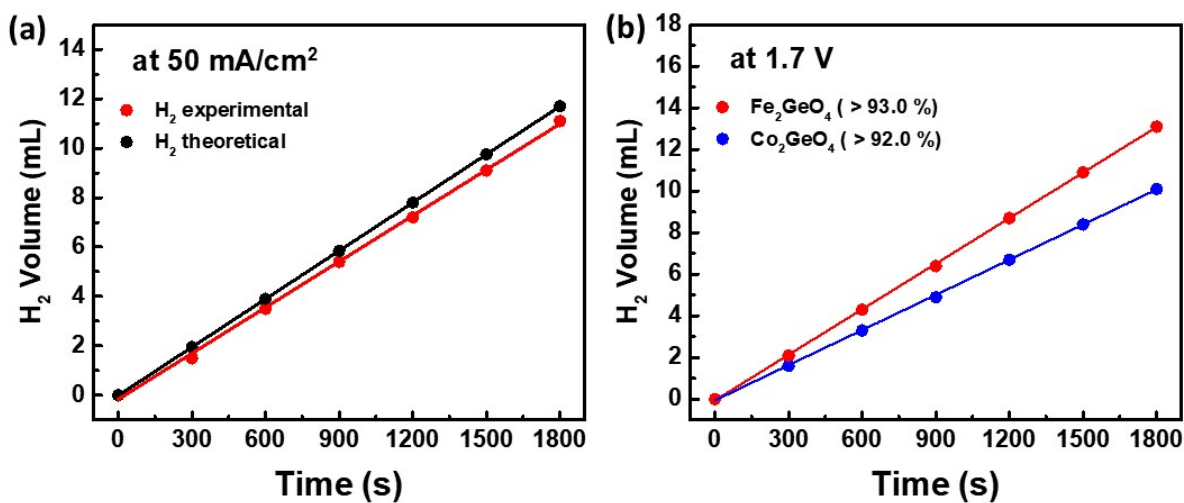


Fig. S14. Faradic efficiency of Fe₂GeO₄ electrocatalyst at constant current (a) and potential (b).

To verify the effectiveness of urea-assisted water electrolysis, Faradaic efficiency (FE) was calculated by the below equation: ¹

$$FE = (\text{experimental } \mu\text{mol of H}_2 \text{ gas} / \text{theoretical } \mu\text{mol of H}_2 \text{ gas}) * 100$$

For the experimental amount of H₂ gas, the number of mol H₂ gas produced in water displacement is calculated from the ideal gas equation :

$$PV = nRT$$

where P [atm] is pressure considering vapor pressure of water Dalton's law of partial pressure equation (0.975 [atm]), V [L] is the volume of experimentally measured H₂ gas, T [K] is the experiment temperature, and R [L * atm / mol * K] is the ideal gas constant (0.0821 [L * atm / mol * K]).

For the theoretical amount of H₂ gas, the number of mol H₂ gas was theoretically calculated using Faraday's law equation

$$n = (I * t) / (z * F)$$

n is the number of mol H₂ gas, I [A] is the measured current, t [s] is the experiment time, z is the number of electron transfer (for HER, z = 2), and F [C / mol] is the Faraday constant (96,485 [C / mol]).

Table 1. Atomic ratios of Fe₂GeO₄ and Co₂GeO₄ determined by EDS

Catalysts	Fe	Co	Ge	O
Fe ₂ GeO ₄	23.95	-	6.52	69.51
Co ₂ GeO ₄	-	25.38	13.57	61.04

Table S2. Electrochemical impedance parameters from the Fe₂GeO₄ for the urea oxidation reaction.

No.	Potential (V vs. RHE)	R _Ω [Ohm]	R _f [Ohm]	R _{ct} [Ohm]	C _f [F]	C _{dl} [F]	W [Ohm s ^{-1/2}]
1	O (V vs. OCP)	0.5198	8.565	1199	2.267e-3	2.745e-3	16.31
dev.		0.3269	6.295	103.8	1.091e-3	0.1667e-3	8.15
2.	1.30	0.5079	17	606.5	1.96e-3	3.318e-3	9.125
dev.		0.3295	5.941	0.9473e-3	0.2231e-3	0.2231e3	16.73
3.	1.35	0.5052	14.46	14.46	2.217e-3	4.081e-3	8.719
dev.		0.3351	4.034	4.034	1.508e-3	0.4147e-3	18.38
4.	1.40	0.5352	8.52	1.904	4.237e-3	2.933e-3	2.279
dev.		0.2669	12.44	12.65	0.01329	4.132e-3	1.344
5.	1.45	0.5394	1.344	2.557	3.075e-3	7.908e-3	1.203
dev.		0.2758	19.38	19.17	0.01102	0.114	1.071
6.	1.50	0.55	2.259	2.765	0202026	3.378e-3	1.414
dev.		0.2437	20.16	20.21	0.3484	6.03e-3	1.528
7.	1.55	0.5582	0.08386	2.267	3.438e-3	3.082e-3	5.82e-24
dev.		1	1	1	1	1	0
8.	1.60	0.5756	0.07568	0.4175	2.795e-3	3.488e-3	0.4175
dev.		0.3502	9.592	9.637	0.106	0.1651	9.637

Table S3. Electrochemical impedance parameters from the Co_2GeO_4 for the urea oxidation reaction.

No.	Potential (V vs. RHE)	R_Ω [Ohm]	R_f [Ohm]	R_{ct} [Ohm]	C_f [F]	C_{dl} [F]	W [Ohm s ^{-1/2}]
1	O (V vs. OCP)	0.5044	19.27	2691	0.8242e-3	1.138e-3	19.11
dev.		0.3058	4.961	83.58	0.1741e-3	30.44e-6	1.372
2.	1.30	2.051	275.9	6.982	0.01314	0.01021	12.44
dev.		0.3073	78.63	4.996	1.001e-3	0.01347	11.9
3.	1.35	2.071	5.826	47.43	8.98e-3	0.01023	8.39
dev.		0.2327	8.36	26.92	0.01007	5.64e-3	8.719
4.	1.40	2.126	12.48	2.268	8.253e-3.	7.399e-3	2.576
dev.		0.2327	15.25	13.99	0.01932	4.187e-3	1.899
5.	1.45	2.141	2.443	5.981	0.01461	7.657e-3	2.727
dev.		0.2362	17.96	18.65	0.1222	0.01951	1.896
6.	1.50	2.131	5.974	2.676	0.01461	7.657e-3	2.727
dev.		0.2315	29.06	27.62	0.1222	0.01951	1.896
7.	1.55	2.145	6.88	0.3604	5.647e-3	7.062e-3	2.285e-39
dev.		1	1	1	1	1	0
8.	1.60	2.15	1.459	0.2255	5.654e-3	4.007e-3	1.891e-15
dev.		1	1	1	1	1	0

Table S4. Comparison of urea oxidation performances of M_2GeO_4 and other electrocatalysts under 1.00 M KOH with specific urea condition

Catalysts	Support	Potential (V vs. RHE) @ Current density (mA/cm ²)	Urea (M)	Stability	Ref.
Fe_2GeO_4	Ni foam	1.39 @ 10	0.33	24 h	This work
Co_2GeO_4	Ni foam	1.42 @ 10	0.33	24 h	This work
CoP/C	Ni foam	1.354 @ 10	0.1	12 h	2
$CuCo_2O_4$ nanosheets	Ni foam	1.36 @ 10	0.33	15 h	3
CoS_2 nanoneedle array	Ti mesh	1.4 @ 10	0.3	15000 s	4
RuO_2	Ti mesh	1.5 @ 10	0.3	-	4
Co(OH)F	Ni foam	1.25 @ 10	0.7	10 h	5
Co_3Mo_1S	Carbon cloth	1.31 @ 10	0.5	-	6
$CoMoO_4/Co_9S_8$	Ni foam	1.402 @ 10	-	13 h	7
Co_3O_4 nanoarray	Ni foam	1.40 @ 20	0.5	-	8
Ru- $Co_2P/N-C$	Ni foam	1.351 @ 50	0.5	15 h	9
CoRu-MOF	Ni foam	1.43 @ 50	0.5	-	9
RuO_2	Ni foam	1.43 @ 50	0.5	-	9
Pt/C	Ni foam	1.441 @ 50	0.5	-	9
-	Ni foam	1.475 @ 50	0.5	-	9
FeOOH	Ni foam	1.40 @ 100	0.5	600 s	10
$Ni_{60}Cr_{40}/C$	Glassy carbon disk	1.55 @ 90	0.33	2000 s	11
$NiCo_2O_4$	Carbon paper	1.73 @ 5	0.33	-	12
$Co_3O_4-SrCo_3$	Carbon nanofiber	1.73 @ 30	0.33	-	13
$Cu(OH)_2$ nanowire arrays	Cu foam	1.49 @ 10	0.5	12 h	14

Table S5. Energy efficiencies of Pt || M₂GeO₄ cell at 1.7 V.

Electrocatalyst	Fe ₂ GeO ₄	Co ₂ GeO ₄
EE (%)	20.2	20.0

The full cell energy efficiency (EE) with the M₂GeO₄ catalyst is calculated according to the below equation^{15, 16}:

$$\text{Energy Efficiency} = (E_{\text{UOR}} / E_{\text{Full-cell}}) * \text{FE}_{\text{H}_2}$$

where the E_{UOR} is the thermodynamic onset voltage (for HER||UOR, E_{UOR} = 0.37 [V]) and E_{Full-cell} is the applied potential for full cell.

The measured full-cell energy efficiencies of Fe₂GeO₄ and Co₂GeO₄ are 20.2 and 20.0 % at 1.7 V,

References:

1. S. Sultan, M. Ha, D. Y. Kim, J. N. Tiwari, C. W. Myung, A. Meena, T. J. Shin, K. H. Chae and K. S. Kim, Superb water splitting activity of the electrocatalyst Fe₃Co(PO₄)₄ designed with computation aid, *Nature communications*, 2019, **10**, 1-9.
2. J. Zheng, K. Wu, C. Lyu, X. Pan, X. Zhang, Y. Zhu, A. Wang, W.-M. Lau and N. Wang, Electrocatalyst of two-dimensional CoP nanosheets embedded by carbon nanoparticles for hydrogen generation and urea oxidation in alkaline solution, *Applied Surface Science*, 2020, **506**, 144977.
3. C. Zequine, F. Wang, X. Li, D. Guragain, S. R. Mishra, K. Siam, P. K. Kahol and R. K. Gupta, Nanosheets of CuCo₂O₄ as a high-performance electrocatalyst in urea oxidation, *Applied Sciences*, 2019, **9**, 793.
4. S. Wei, X. Wang, J. Wang, X. Sun, L. Cui, W. Yang, Y. Zheng and J. Liu, CoS₂ nanoneedle array on Ti mesh: A stable and efficient bifunctional electrocatalyst for urea-assisted electrolytic hydrogen production, *Electrochimica Acta*, 2017, **246**, 776-782.
5. M. Song, Z. Zhang, Q. Li, W. Jin, Z. Wu, G. Fu and X. Liu, Ni-foam supported Co(OH)₂ and Co-P nanoarrays for energy-efficient hydrogen production via urea electrolysis, *Journal of Materials Chemistry A*, 2019, **7**, 3697-3703.
6. P. Li, Z. Zhuang, C. Du, D. Xiang, F. Zheng, Z. Zhang, Z. Fang, J. Guo, S. Zhu and W. Chen, Insights into the Mo-Doping Effect on the Electrocatalytic Performance of Hierarchical Co_xMo_yS Nanosheet Arrays for Hydrogen Generation and Urea Oxidation, *ACS Applied Materials & Interfaces*, 2020, **12**, 40194-40203.
7. X. Du, C. Huang and X. Zhang, Synthesis of CoMoO₄/Co₉S₈ network arrays on nickel foam as efficient urea oxidation and hydrogen evolution catalyst, *International Journal of Hydrogen Energy*, 2019, **44**, 19595-19602.
8. X. Du, C. Huang and X. Zhang, Co₃O₄ arrays with tailored morphology as robust water oxidation and urea splitting catalyst, *Journal of Alloys and Compounds*, 2019, **809**, 151821.
9. Y. Xu, T. Ren, K. Ren, S. Yu, M. Liu, Z. Wang, X. Li, L. Wang and H. Wang, Metal-organic frameworks-derived Ru-doped Co₂P/N-doped carbon composite nanosheet arrays as bifunctional electrocatalysts for hydrogen evolution and urea oxidation, *Chemical Engineering Journal*, 2021, **408**, 127308.
10. J.-J. Zhang, W.-W. Bao, M.-Y. Li, C.-M. Yang and N.-N. Zhang, Ultrafast formation of an FeOOH electrocatalyst on Ni for efficient alkaline water and urea oxidation, *Chemical Communications*, 2020, **56**, 14713-14716.
11. R. K. Singh and A. Schechter, Electroactivity of NiCr catalysts for urea oxidation in alkaline electrolyte, *ChemCatChem*, 2017, **9**, 3374-3379.
12. A. Schranck, R. Marks, E. Yates and K. Doudrick, Effect of urine compounds on the electrochemical oxidation of urea using a nickel cobaltite catalyst: an electroanalytical and

- spectroscopic investigation, *Environmental science & technology*, 2018, **52**, 8638-8648.
13. Z. K. Ghouri, K. Elsaid, S. Al-Meer and N. A. M. Barakat, Applicable anode based on Co₃O₄-SrCO₃ heterostructure nanorods-incorporated CNFs with low-onset potential for DUFCS, *Applied Nanoscience*, 2017, **7**, 625-631.
 14. W. Shi and J. Lian, Mesoporous Cu(OH)₂ nanowire arrays for urea electrooxidation in alkaline medium, *Materials Chemistry and Physics*, 2020, **242**, 122517.
 15. A. Ozden, Y. Liu, C.-T. Dinh, J. Li, P. Ou, F. P. García de Arquer, E. H. Sargent and D. Sinton, Gold Adparticles on Silver Combine Low Overpotential and High Selectivity in Electrochemical CO₂ Conversion, *ACS Applied Energy Materials*, 2021.
 16. Y. C. Li, G. Lee, T. Yuan, Y. Wang, D.-H. Nam, Z. Wang, F. P. García de Arquer, Y. Lum, C.-T. Dinh and O. Voznyy, CO₂ electroreduction from carbonate electrolyte, *ACS Energy Letters*, 2019, **4**, 1427-1431.