Electronic Supplementary Information (EIS)

Isolated single-atom Pt sites for highly selective electrocatalytic hydrogenation of formaldehyde to methanol

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Figure S1. XRD patterns of (a) Pt-SA/Ti₃C₂T_x and (b) Pt-NP/Ti₃C₂T_x. It can be found that no reflection peaks exist for Pt-related crystal in the Pt-SA/Ti₃C₂T_x sample. From the XRD pattern of Pt-NP/Ti₃C₂T_x, the two identified diffraction peaks marked with "#" were observed in the enlarged view, which can be assigned to metallic Pt phase (JCPDS NO. 87-0644). This suggests that the successful preparation of the metallic Pt in the Ti₃C₂T_x.



Figure S2. TEM characterization of the pristine $Ti_3C_2T_x$ sample: (a-d) TEM images; (e-h) STEM image and the corresponding EDS element mapping.



Figure S3. TEM characterization of the as-prepared Pt-NP/Ti₃C₂T_x sample: (a, b) STEM images; (c, d) TEM images; (e-i) STEM image and the corresponding EDS element mapping.



Figure S4. Deconvoluted Pt 4f spectra of Pt-NP/Ti₃C₂T_x. The binding energies at 71.3 and 74.7 eV for Pt 4f are assigned to the Pt 4f_{7/2} and Pt 4f_{5/2}, indicating that the chemical state the element Pt is Pt⁰, which agrees with the XRD results of Pt-NP/Ti₃C₂T_x.



Figure S5. Additional atomic-resolution HAADF-STEM images of $Pt-SA/Ti_3C_2T_x$. These images were taken from randomly selected regions of the sample.



Figure S6. (a-e) STEM image and the corresponding EDS element mapping of the asprepared $Pt-SA/Ti_3C_2T_x$ sample.



Figure S7. AFM characterization of the as-prepared Pt-SA/Ti₃C₂T_x sample: (a, b) The low-magnification AFM images; (c, d) High-magnification AFM image and the corresponding height profiles. It can be found from the AFM images that a large number of ultra-thin nanosheets have been successfully prepared. The thickness of these nanosheets is measured to be within a narrow range of 2.1 ± 0.2 nm.



Figure S8. Nitrogen adsorption/desorption isotherms and corresponding pore size distribution of as-synthesized (a, b) Pt-SA/Ti₃C₂T_x and (c, d) Ti₃C₂T_x. The pore structure and surface properties of the as-prepared samples were characterized by N₂ adsorption/desorption measurements. The as-synthesized Pt-SA/Ti₃C₂T_x and Ti₃C₂T_x nanosheets possess a surface area of 420.9 m² g⁻¹ and 392.23 m² g⁻¹, respectively. Moreover, the Pt-SA/Ti₃C₂T_x sample shows a prominent pore size distribution at 4.7 nm. The Ti₃C₂T_x sample also shows comparable prominent pore size distribution around 5.6 nm.



Figure S9. Synchrotron radiation XANES measurements: (a) XANES curves of Pt-SA/Ti₃C₂T_x at L3-edge; (b) The detail view of the main edges.



Figure S10. Deconvoluted Pt 4f spectra of Pt-SA/Ti₃C₂T_x. The valence states of isolated Pt atoms in Pt-SA/Ti₃C₂T_x was investigated by XPS. As shown, the high-resolution core-level spectra of Pt 4f in Pt-SA/Ti₃C₂T_x display $4f_{7/2}$ and $4f_{5/2}$ doublets due to the spin-orbital splitting. This indicates that the chemical state the element Pt is Pt²⁺.



Figure S11. DOS of Pt-NPs and Pt-SA/Ti₃C₂T_x.



Figure S12. CH₃OH quantification via gas chromatography method: (a) The gas chromatograph signal of different concentrations of chromatographic grade CH₃OH in 0.5 M Na₂SO₄ aqueous solution, and (b) the corresponding calibration curve for the concentration of CH₃OH.



Figure S13. The polarization curves for Pt-NP/Ti₃C₂T_x and Pt-SA/Ti₃C₂T_x in 0.1 M of Na₂SO₄ aqueous solution fed with CH₂O gas.



Figure S14. The electrocatalytic CH₂O hydrogenation performance of commercial Pt/C: (a) Polarization curves in 0.1 M of Na₂SO₄ fed with CH₂O or Ar gas. (b) FEs and yield rates of CH₃OH at various applied potentials. As shown in Figure S14a, the linear sweep voltammetry (LSV) curve of commercial Pt/C in 0.1 M HCl solution fed with Ar display a large current density. In detail, at -1.0 V versus the reversible hydrogen electrode (vs RHE), the current density was -45.0 mA cm⁻². When fed with gaseous CH₂O, this value just increased to -48.5 mA cm⁻². This result demonstrated that the large the current density of Pt/C in 0.1 M HCl solution mainly due to hydrogen evolution reaction rather than CH₂O hydrogenation reaction. Moreover, the maximum value of the Faradaic efficiency and yield rate of CH₃OH were 6.8% and 8.7 mg h⁻¹ mg_{cat}⁻¹, respectively, which were significantly lower than that of Pt-SA/Ti₃C₂T_x.



Figure S15. The FE and the corresponding yield rate of CH₃OH over the Pt-NP/Ti₃C₂T_x catalyst.



Figure S16. Nyquist plots of the as-prepared catalysts.



Figure S17. Cyclic voltammetry curves of (a) $Ti_3C_2T_x$, (b) Pt-NP/Ti_3C_2T_x, and (c) Pt-SA/Ti_3C_2T_x, in the non-Faradaic capacitance current range at scan rates of 5, 10, 15, 20, and 25 mV s⁻¹.



Figure S18. Atomic-resolution HAADF-STEM images of $Pt-SA/Ti_3C_2T_x$ after the consecutive recycling and potentiostat electrolysis tests at -0.8 V vs. RHE. These images were taken from randomly selected regions of the sample.



Figure S19. The electrochemical reaction steps for CH_2O conversion into CH_3OH . As shown, the electrochemical reaction steps for CH_2O conversion into CH_3OH were given. First, gaseous CH_2O is adsorbed on the catalyst surface by van der Waals forces or hydrogen bonding. Then, *OCH₂ converts into *OCH₃ species by interacting with a proton (H⁺) and an electron (e) derived from electrolyte. Subsequently, the *OCH₃ converts into *OHCH₃ species by interacting with another proton (H⁺) and electron (e). Finally, the *OHCH₃ species is desorbed from the surface of catalysts to form liquid CH₃OH. Note that the protons come from the water molecule in electrolyte solutions, which also is the hydrogen sources to form a CH₃OH.

Electrocatalyst	Electrolyte	Potential	Selectivity FE _{CH3OH} (%)	Productivity	Stability (h)	Ref.
Pt-SA/Ti ₃ C ₂ T _x	0.5 M Na ₂ SO ₄	-0.8 V vs. RHE	95.8	$30700 \ \mu g \ h^{-1} \ m g_{cat.}{}^{-1}$	33	This work
BP	0.1 M KHCO ₃	–0.5 V vs. RHE	92	127.5 μ g h ⁻¹ mg _{cat.} ⁻¹	18	S1
CuSAs/TCNFs	0.1 M KHCO ₃	–0.9 V vs. RHE	44	68.4 μ mol m ⁻² s ⁻¹	50	S2
HKUST-1 and CAU-17	0.5 M KHCO ₃	_	8.6	29.7 μmol m ⁻² s ⁻¹	5	S3
Cu ₂ O/ZnO-based electrodes	0.5 M KHCO ₃	–1.3 V vs. Ag/AgCl	17.7	$3.17 \times 10^{-5} \text{ mol } \text{m}^{-2} \text{ s}^{-1}$	1.5	S4
FeS ₂ /NiS	0.5 M KHCO ₃	–0.6 V vs. RHE	64	_	4	S 5
Pd/SnO ₂	0.1 M KHCO ₃	–0.24 V vs. RHE	54.8 ± 2	_	5	S6
RuO ₂ /TiO ₂ /Pt	0.5 M NaHCO ₃	–0.15 V vs. RHE	60.5	_	_	S7
Oxide-derived Cu/C	0.1 M KHCO ₃	-0.3 V vs. RHE	43.2	$12.4 \text{ mg } \text{h}^{-1} \text{ L}^{-1}$	_	S8

Table S1. Selectivity, stability and productivity results of CH₃OH electrosynthesis in this work and previously reported studies.

Electrodeposited thin Cu film	0.5 M KHCO ₃	–0.4 V vs. RHE	38	43 μmol h ⁻¹ cm ⁻²	_	S 9
Cu ₂ O/MWCNTs	0.5 M NaHCO ₃	–1.1 V vs. SCE	38	_	0.33	S10
RuO ₂ /TiO ₂	0.05 M H ₂ SO ₄	–0.58 V vs. RHE	24	_	I	S11
RuO _x /Cu	0.5 M KHCO3	–0.8 V vs. SCE	41.3	_	8	S12
Mo foil on Cu wire	0.2 M Na ₂ SO ₄	–0.3 V vs. RHE	84	_	9	S13
PO-5 nm Co/SL-NG	0.1 M NaHCO ₃	–0.90 V vs. RHE	71.4	$1.1 \text{ mmol } h^{-1} \text{ L}^{-1}$	10	S14
Co(CO ₃) _{0.5} (OH)·0.11H ₂ O	NaHCO ₃	–0.98 V vs. RHE	97.0	145 mmol h ⁻¹ g ⁻¹	10	S15
Cu/Ni	0.05 M KHCO3	–0.9 V vs. RHE	7	_	_	S16
Cu-Au alloy	0.5 M KHCO ₃	–1.1 V vs. SCE	15.9	_	-	S17
Cu ₈₈ Sn ₆ Pb ₆	1.5 M HCl + 0.17 M BaCl ₃	–0.65 V vs. Ag/AgCl	36.3	_	_	S8
Cu _{1.8} Se	0.1 M KHCO ₃	–1.1 V vs. RHE	24	_	25	S19

Cu ₂ O/CNT	0.1 M Na ₂ SO ₄	0.49 V vs. RHE	9	_	4.2	S20
PD-Zn/Ag	0.1 M KHCO ₃	–1.38 V vs. RHE	10.5	13.3 μ mol h ⁻¹ cm ⁻²	8	S21
BDD films	1 M NH ₃	-1.3 V vs. Ag/AgCl	24.3	$0.25 \text{ mg } \mathrm{L}^{-1}$	30	S22
BND	0.1 M KHCO ₃	–1.0 V vs. RHE	<20	_	3	S23
[PYD]@Pd	0.5 M KCl	–0.6 V vs. SCE	35	_	14	S24
[PYD]@Cu-Pt	0.5 M KCl	–0.6 V vs. SCE	37	_	_	S25
[PYD]@Cu-Pd	0.5 M KCl	–0.04 V vs. RHE	26	_	14	S26

^a According to different units, the yield rate of CH₃OH over Pt-SA/Ti₃C₂T_x can be also expressed as 15400 μ g h⁻¹ cm⁻², 1335.14 μ mol m⁻² s⁻¹, 19.2 mmol h⁻¹ L⁻¹, 958.2 mmol h⁻¹ g_{cat.}⁻¹ or 614 mg h⁻¹ L⁻¹.

All of "-" mean that no values were reported for the corresponding parameters in the corresponding references.

References

- S1 S. Mou, T. Wu, J. Xie, Y. Zhang, L. Ji, H. Huang, T. Wang, Y. Luo, X. Xiong, B. Adv. Mater., 2019, 31, 1903499.
- S2 H. Yang, Y. Wu, G. Li, Q. Lin, Q. Hu, Q. Zhang, J. Liu, C. He. J. Am. Chem. Soc., 2019, 141, 12717–12723.
- S3 J. Albo, M. Perfecto-Irigaray, G. Beobide, A. Irabien. J. CO₂ Util., 2019, 33, 157–165.
- S4 J. Albo, A. Sáez, J. Solla-Gullón, V. Montiel, A. Irabien. *Appl. Catal. B*, 2015, 176–177, 709–717.
- S5 S. Zhao, S. Guo, C. Zhu, J. Gao, H. Li, H. Huang, Y. Liu, Z. Kang. RSC Adv., 2017, 7, 1376– 1381.
- S6 W. Zhang, Q. Qin, L. Dai, R. Qin, X. Zhao, X. Chen, D. Ou, J. Chen, T. T. Chuong, B. Wu,
 N. Zheng. Angew. Chem. Int. Ed., 2018, 57, 9475–9479.
- S7 J. Qu, X. Zhang, Y. Wang, C. Xie. *Electrochimi. Acta*, 2005, **50**, 3576–3580.
- S8 K. Zhao, Y. Liu, X. Quan, S. Chen, H. Yu. ACS Appl. Mater. Interfaces, 2017, 9, 5302–5311.
- S9 M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz, J. C. Flake. *J. Electrochem. Soc.*, 2011, 158, E45–E49.
- S10 M. Irfan Malik, Z. O. Malaibari, M. Atieh, B. Abussaud, Abussaud, B. Chem. Eng. Sci., 2016, 152, 468–477.
- S11 A. Bandi. J. Electrochem. Soc., 1990, 137, 2157-2160.
- S12 J. P. Popić, M. L. Avramov-Ivić, N. B. Vuković. J. Electroanal. Chem., 1997, 421, 105–110.

- S13 D. P. Summers, S. Leach, K. W. Frese. J. Electroanal. Chem. Interfacial Electrochem., 1986, 205, 219–232.
- S14 J. Huang, X. Guo, G. Yue, Q. Hu, L. Wang. ACS Appl. Mater. Interfaces, 2018, 10, 44403– 44414.
- S15 J. Huang, Q. Hu, X. Guo, Q. Zeng, L. Wang. Green Chem., 2018, 20, 2967–2972.
- S16 M. Watanabe, M. Shibata, A. Kato, M. Azuma, T. Sakata. J. Electrochem. Soc., 1991, **138**, 3382–3389.
- S17 F. Jia, X. Yu, L. Zhang. J. Power Sources, 2014, 252, 85-89.
- S18 A. Schizodimou, G. Kyriacou. Electrochim. Acta, 2012, 78, 171–176.
- S19 Y. Mi, X. Peng, X. Liu, J. Luo. ACS App. Energy Mater., 2018, 1, 5119–5123.
- S20 E. Kecsenovity, B. Endrődi, Z. Pápa, K. Hernádi, K. Rajeshwar, C. Janáky. J. Mater. Chem. A, 2016, 4, 3139–3147.
- S21 Q. H. Low, N. W. X. Loo, F. Calle-Vallejo, B. S. Yeo. Angew. Chem. Int. Ed., 2019, 58, 2256–2260.
- S22 P. K. Jiwanti, K. Natsui, K. Nakata, Y. Einaga. RSC Adv., 2016, 6, 102214–102217.
- S23 Y. Liu, Y. Zhang, K. Cheng, X. Quan, X. Fan, Y. Su, S. Chen, H. Zhao, Y. Zhang, H. Yu, M.
 R. Hoffmann. *Angew. Chem. Int. Ed.*, 2017, 56, 15607–15611.
- S24 H.-P. Yang, S. Qin, H. Wang, J.-X. Lu. Green Chem., 2015, 17, 5144–5148.
- S25 H.-P. Yang, Y.-N. Yue, S. Qin, H. Wang, J.-X. Lu. Green Chem., 2016, 18, 3216–3220.

S26 H.-P. Yang, S. Qin, Y.-N. Yue, L. Liu, H. Wang, J.-X. Lu. Catal. Sci. Technol., 2016, 6, 6490–6494.