Supporting Information for

Engineering Transition Metal Catalysts for Large-Current-Density Water Splitting

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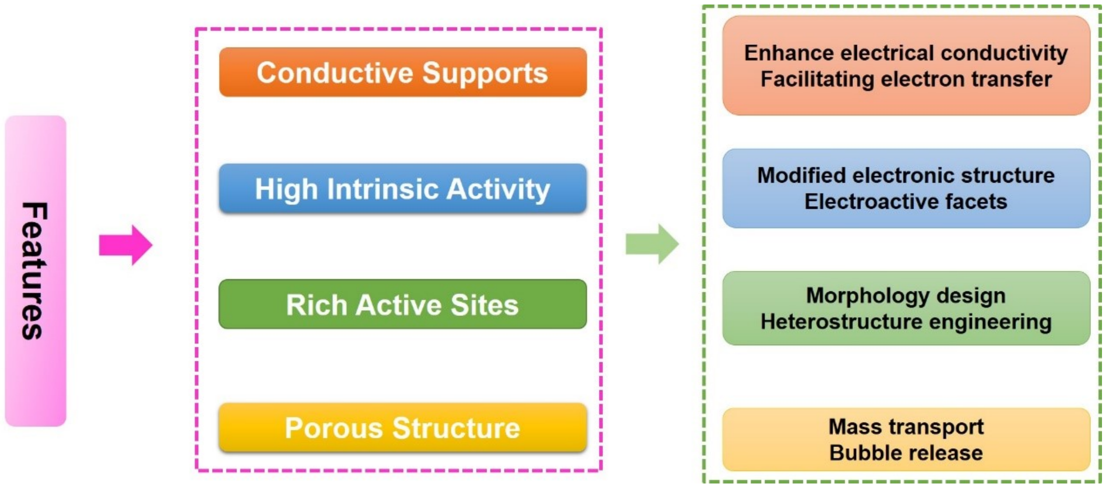

Fig.S1 Schematically showing the features of transition metal catalysts for large-current-density water splitting.

1. Transition metal borides

Transition metal borides (TMBs), with the features of low-cost, environmentally benign, and high catalytic performance, have also been widely adopted as advanced electrocatalysts for driving water electrolysis. Despite these advantages, the applications of TMBs toward industrial water electrolysis were also hindered by the complicated complex preparation methods for the catalyst and unsatisfied catalytic properties. After enormous endeavors devoted, an apparent enhancement in electrocatalytic performance has been clearly observed in TMBs, and many TMB catalysts can even achieve a current density of higher than 1000 mA cm^{-2} for HER, OER, and overall water splitting. As a distinctive example, Guo et al. have developed a facile electroless plating strategy for the successful fabrication of Co-B/Ni electrode (**Fig.S2a, b**), which can afford 10 mA cm^{-2} at overpotentials of only 140 mV for OER and 70 mV for HER (**Fig.S2c**) [1]. More importantly, Co-B/Ni electrode can also survive at a large current density of 1000 mA cm^{-2} for over 20 h without performance degradation in strong alkaline solution. Moreover, the electroless plating has also been demonstrated to be versatile for the synthesis of a series of TMBs, and all of them are also uncovered to be highly active toward HER and OER. A perfect integration of active catalyst and favorable structure was found to be responsible for the excellent performance of these electrodes.

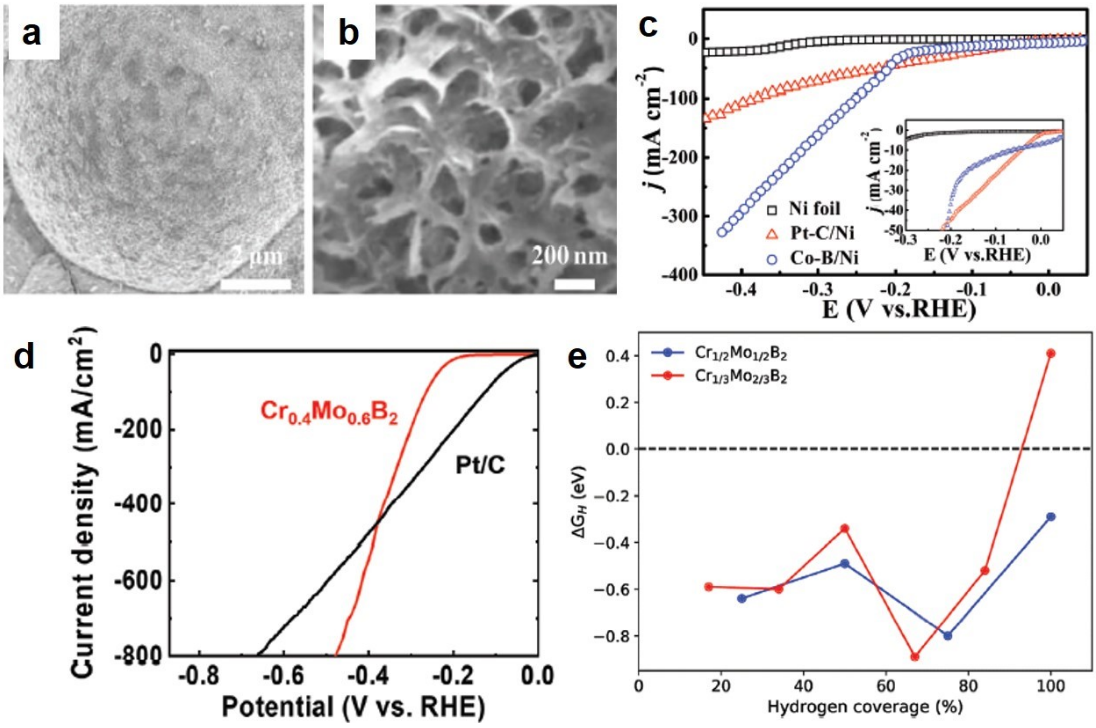

Fig.S2 (a) Representative SEM images of the Co-B/Ni electrode. (b) LSV polarization curves of different catalysts toward HER. (c) HER polarization curves of Pt/C and $Cr_{0.4}Mo_{0.6}B_2$. Reproduced with the permission from [1], 2018, Wiley-VCH. (d) ΔG_{H*} on the (110) surfaces of $Cr_{1-x}Mo_xB_2$ (x = 1/2, 2/3) plotted as a function of hydrogen coverage. Reproduced with the permission from [2], 2020, Wiley-VCH.

More recently, Fokwa et al. reported full solid solution $Cr_{1-x}Mo_xB_2$ (x = 0, 0.25, 0.4, 0.5, 0.6, 0.75, 1) for boosting HER electrocatalysis in 0.5 M H_2SO_4 solution [2].

Impressively, such $Cr_{1-x}Mo_xB_2$ shows an intriguing canonic-like behavior of the c lattice parameter that perfectly correlates with its HER activity, as it requires 180 mV less overpotential to drive an 800 mA cm^{-2} current density (**Fig.S2d**), superior to Pt/C. DFT calculations demonstrated that the mixed metal/B (110) layer promoted hydrogen evolution more efficiently for x = 0.6 (**Fig.S2e**). These researches have further confirmed the great potential of TMBs for boosting large-current-density water splitting.

2. Transition metal carbides

In general, electronic properties of catalyst play a crucial role in determining its electroctalytic performance. Optimizing the electronic properties of electrocatalysts is another principle that should be paid attention to since OER is a multistep reaction. Contrary to transition metal oxides, transition metal carbides may be promising alternatives for water oxidation thanks to their distinct electronic properties and high electrical conductivity. Therefore, TMCs have also been extensively researched and adopted as high-performance electrode materials for boosting water splitting electrocatalysis. For instance, Wu and workers have developed a new type of advanced electrocatalysts by hybridizing metallic Ni_3C nanoparticles with conductive carbon (Ni_3C/C). Interestingly, the intrinsically metallic character of Ni_3C phase facilitates the electron transfer, meanwhile, the conductive carbon support can also greatly promote the charge transport on the surface of the catalyst (**Fig.S3a, b**). As a result, the synergistic contributions of Ni_3C and conductive carbon support greatly boost the electrocatalytic OER reaction, rendering them to be promising OER electrocatalysts with ultrahigh current density.

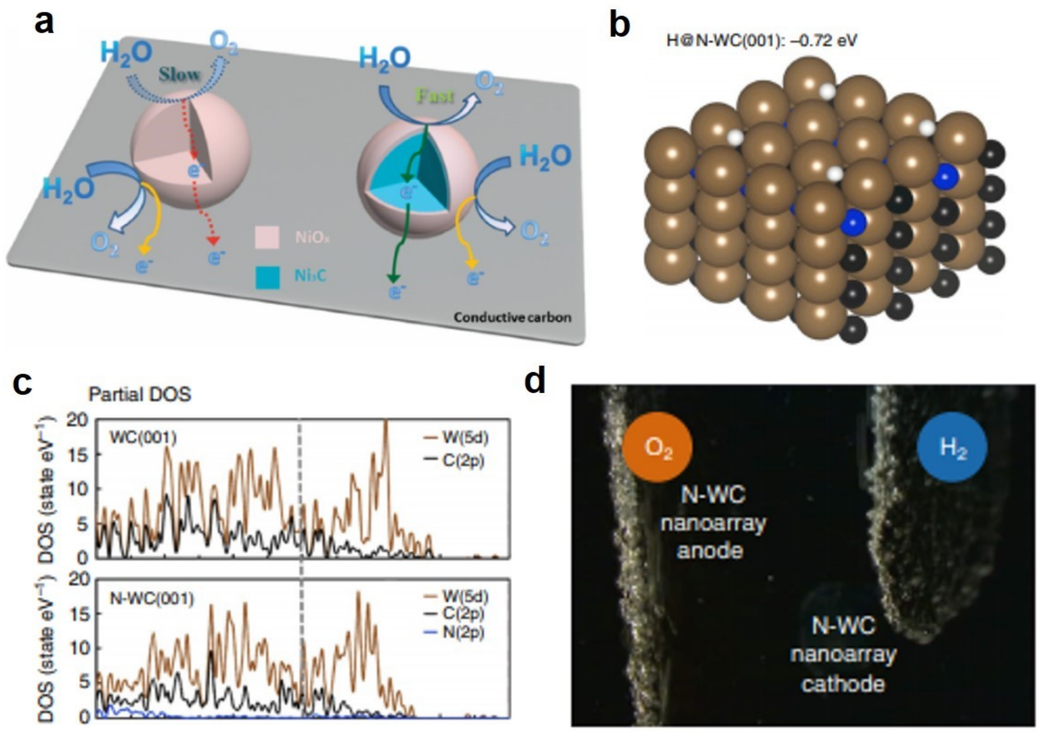

Fig.S3 (a) Schematic illustration of the electrocatalytic water oxidation based on NiO_x/C and NiC/C. (b) Hydrogen binding geometry and hydrogen binding energy on H@N-WC (001). Reproduced with the permission from [3], 2016, Wiley-VCH. (c) PDOS of WC (001) and N-WC (001). (d) Photo of water splitting based on bifunctional N-WC arrays. Reproduced with the permission from [4], 2018, Nature Publishing Group.

In addition to outstanding OER performance, the inherently electronic properties also endow TMCs with superb electrocatalytic HER properties. A representative example is demonstrated by Sun and coworkers [4], they have synthesized the N-doped WC nanoarray structures, in which the N doping modifies the surface energy level to optimize hydrogen binding and thus promote HER kinetics (**Fig. S3c, d**). More importantly, it is also demonstrated that the N-doped WC nanoarray can also exhibit enchanting electrocatalytic OER performance, rendering them as advanced bifunctional electrocatalysts for overall water splitting.

Table S1 Summary of TMCs for OER electrocatalysis

Electrocatalyst	Electrolyte	Current density (mA cm^{-2})	η (mV) @10 mA cm^{-2}	Reference
NiFe LDH/MXene	1 KOH	500	300	[5]
$NiFe_2O_4$ /NiFe LDH	1 KOH	1000	265	[6]
Sn−Ni_3S_2/NF	1 KOH	1000	580	[7]
N, Fe-NiSe@NIF	1 KOH	1000	290	[8]
(Ni−MoO_2)@C/N F NWs	1 KOH	2000	400	[9]
P-NiCoV-LTH/NF	1 KOH	1000	373	[10]
CoO_x−RuO_2/NF	1 KOH	1500	420	[11]
Fe_2P-Co_2P/CF	1 KOH	1000	317	[12]
Ni_3Fe/FeV_2O_4	1 KOH	1500	350	[13]
Fe-CoP	1 KOH	1000	428	[14]
$Ni_{0.8}Fe_{0.2}$− AHNA	1 KOH	1078	260	[15]
$Fe_{13.7\%}$-Ni_3S_2	1 KOH	500	245	[16]

Table S2 Summary of TMCs for HER electrocatalysis

Electrocatalyst	Electrolyte	Current density (mA cm^{-2})	η (mV)	Reference
$CoP@Ni_2P$	1 KOH	500	209	[17]
$Ni_{2(1-x)}Mo_{2x}P$	1 KOH	1000	294	[18]
Ni_5P_4/NiP_2	0.5 M H_2SO_4	2000	237	[19]
MoS_2/Ni_3S_2	0.5 M H_2SO_4	1000	200	[20]
A-NiCo LDH/NF	1 KOH	1000	381	[21]
$NC/Ni_3Mo_3N/NF$	1 KOH	570	500	[22]
NiCoS	1 KOH	1000	430	[23]
$F-Co_2P/Fe_2P/IF$	1 KOH	3000	304.4	[24]
NiFe LDH/MXene	1 KOH	500	205	[25]
MoS_2/CNF	0.5 M H_2SO_4	1000	450	[26]
$Sn-Ni_3S_2/NF$	1 KOH	1000	570	[27]
$N-MoO_2/Ni_3S_2$ NF	1 KOH	1000	517	[28]
P-MNS/NF	0.5 M H_2SO_4	1000	243	[29]

References

[1] W. Hao, R. Wu, R. Zhang, Y. Ha, Z. Chen, L. Wang, Y. Yang, X. Ma, D. Sun, F. Fang, Y. Guo, Electroless Plating of Highly Efficient Bifunctional Boride-Based Electrodes toward Practical Overall Water Splitting, Adv. Energy Mater. 8(26) (2018) 1801372.

[2] H. Park, E. Lee, M. Lei, H. Joo, S. Coh, B.P.T. Fokwa, Canonic-Like HER Activity of $Cr_{1-x}Mo_xB_2$ Solid Solution: Overpowering Pt/C at High Current Density, Adv. Mater. 32(28) (2020) e2000855.

[3] K. Xu, H. Ding, H. Lv, P. Chen, X. Lu, H. Cheng, T. Zhou, S. Liu, X. Wu, C. Wu, Y. Xie, Dual Electrical-Behavior Regulation on Electrocatalysts Realizing Enhanced Electrochemical Water Oxidation, Adv. Mater. 28(17) (2016) 3326-3332.

[4] N. Han, K.R. Yang, Z. Lu, Y. Li, W. Xu, T. Gao, Z. Cai, Y. Zhang, V.S. Batista, W. Liu, X. Sun, Nitrogen-doped tungsten carbide nanoarray as an efficient bifunctional electrocatalyst for water splitting in acid, Nat. Commun. 9(1) (2018) 924.

[5] M. Yu, Z. Wang, J. Liu, F. Sun, P. Yang, J. Qiu, A hierarchically porous and hydrophilic 3D nickel–iron/MXene electrode for accelerating oxygen and hydrogen evolution at high current densities, Nano Energy 63 (2019) 103880.

[6] Z. Wu, Z. Zou, J. Huang, F. Gao, $NiFe_2O_4$ Nanoparticles/NiFe Layered Double-Hydroxide Nanosheet Heterostructure Array for Efficient Overall Water Splitting at Large Current Densities, ACS Appl. Mater. Interfaces 10(31) (2018) 26283-26292.

[7] J. Jian, L. Yuan, H. Qi, X. Sun, L. Zhang, H. Li, H. Yuan, S. Feng, Sn-Ni_3S_2 Ultrathin Nanosheets as Efficient Bifunctional Water-Splitting Catalysts with a Large

Current Density and Low Overpotential, ACS Appl. Mater. Interfaces 10(47) (2018) 40568-40576.

[8] J. Chen, J. Chen, H. Cui, C. Wang, Electronic Structure and Crystalline Phase Dual Modulation via Anion-Cation Co-doping for Boosting Oxygen Evolution with Long-Term Stability Under Large Current Density, ACS Appl. Mater. Interfaces 11(38) (2019) 34819-34826.

[9] G. Qian, J. Chen, L. Luo, T. Yu, Y. Wang, W. Jiang, Q. Xu, S. Feng, S. Yin, Industrially Promising Nanowire Heterostructure Catalyst for Enhancing Overall Water Splitting at Large Current Density, ACS Sustain. Chem. Eng. 8(32) (2020) 12063-12071.

[10] Q. Liu, J. Huang, X. Zhang, L. Cao, D. Yang, J.-h. Kim, L. Feng, Controllable Conversion from Single-Crystal Nanorods to Polycrystalline Nanosheets of NiCoV-LTH for Oxygen Evolution Reaction at Large Current Density, ACS Sustain. Chem. Eng. 8(43) (2020) 16091-16096.

[11] T. Yu, Q. Xu, G. Qian, J. Chen, H. Zhang, L. Luo, S. Yin, Amorphous CoO_x-Decorated Crystalline RuO_2 Nanosheets as Bifunctional Catalysts for Boosting Overall Water Splitting at Large Current Density, ACS Sustain. Chem. Eng. 8(47) (2020) 17520-17526.

[12] X. Liu, Y. Yao, H. Zhang, L. Pan, C. Shi, X. Zhang, Z.-F. Huang, J.-J. Zou, In Situ-Grown Cobalt–Iron Phosphide-Based Integrated Electrode for Long-Term Water Splitting under a Large Current Density at the Industrial Electrolysis Temperature, ACS Sustain. Chem. Eng. 8(48) (2020) 17828-17838.

[13] H. Zhang, G. Qian, T. Yu, J. Chen, L. Luo, S. Yin, Interface Engineering of Ni_3Fe and FeV_2O_4 Coupling with Carbon-Coated Mesoporous Nanosheets for Boosting Overall Water Splitting at 1500 mA cm^{-2}, ACS Sustain. Chem. Eng. 9(24) (2021) 8249-8256.

[14] L.M. Cao, Y.W. Hu, S.F. Tang, A. Iljin, J.W. Wang, Z.M. Zhang, T.B. Lu, Fe-CoP Electrocatalyst Derived from a Bimetallic Prussian Blue Analogue for Large-Current-Density Oxygen Evolution and Overall Water Splitting, Adv. Sci. 5(10) (2018) 1800949.

[15] C. Liang, P. Zou, A. Nairan, Y. Zhang, J. Liu, K. Liu, S. Hu, F. Kang, H.J. Fan, C. Yang, Exceptional performance of hierarchical Ni–Fe oxyhydroxide@NiFe alloy nanowire array electrocatalysts for large current density water splitting, Energy Environ. Sci. 13(1) (2020) 86-95.

[16] X. Wang, W. Zhang, J. Zhang, Z. Wu, Fe-Doped Ni_3S_2 Nanowires with Surface−Restricted Oxidation Toward High-Current-Density Overall Water Splitting, ChemElectroChem 6(17) (2019) 4550-4559.

[17] M. Jin, X. Zhang, R. Shi, Q. Lian, S. Niu, O. Peng, Q. Wang, C. Cheng, Hierarchical CoP@Ni_2P catalysts for pH-universal hydrogen evolution at high current density, Appl. Catal. B: Environ. 296 (2021) 120350.

[18] L. Yu, I.K. Mishra, Y. Xie, H. Zhou, J. Sun, J. Zhou, Y. Ni, D. Luo, F. Yu, Y. Yu, S. Chen, Z. Ren, Ternary $Ni_{2(1-x)}Mo_{2x}P$ nanowire arrays toward efficient and stable hydrogen evolution electrocatalysis under large-current-density, Nano Energy 53 (2018) 492-500.

[19] W. Chen, I.K. Mishra, Z. Qin, L. Yu, H. Zhou, J. Sun, F. Zhang, S. Chen, G.E. Wenya, Y. Yu, Z.M. Wang, H.-Z. Song, Z. Ren, Nickel phosphide based hydrogen producing catalyst with low overpotential and stability at high current density, Electrochim. Acta 299 (2019) 756-761.

[20] S. Xue, Z. Liu, C. Ma, H.-M. Cheng, W. Ren, A highly active and durable electrocatalyst for large current density hydrogen evolution reaction, Sci. Bull. 65(2) (2020) 123-130.

[21] H. Yang, Z. Chen, P. Guo, B. Fei, R. Wu, B-doping-induced amorphization of LDH for large-current-density hydrogen evolution reaction, Appl. Catal. B: Environ. 261 (2020) 118240.

[22] Y. Chen, J. Yu, J. Jia, F. Liu, Y. Zhang, G. Xiong, R. Zhang, R. Yang, D. Sun, H. Liu, W. Zhou, Metallic Ni_3Mo_3N Porous Microrods with Abundant Catalytic Sites as Efficient Electrocatalyst for Large Current Density and Superstability of Hydrogen Evolution Reaction and Water Splitting, Appl. Catal. B: Environ. 272 (2020) 118956.

[23] C. Wang, M. Zhu, Z. Cao, P. Zhu, Y. Cao, X. Xu, C. Xu, Z. Yin, Heterogeneous bimetallic sulfides based seawater electrolysis towards stable industrial-level large current density, Appl. Catal. B: Environ. 291 (2021) 120071.

[24] X.-Y. Zhang, Y.-R. Zhu, Y. Chen, S.-Y. Dou, X.-Y. Chen, B. Dong, B.-Y. Guo, D.-P. Liu, C.-G. Liu, Y.-M. Chai, Hydrogen evolution under large-current-density based on fluorine-doped cobalt-iron phosphides, Chem. Eng. J. 399 (2020) 125831.

[25] M. Yu, Z. Wang, J. Liu, F. Sun, P. Yang, J. Qiu, A hierarchically porous and hydrophilic 3D nickel–iron/MXene electrode for accelerating oxygen and hydrogen

evolution at high current densities, Nano Energy 63 (2019) 103880.

[26] Z. Zhang, Y. Wang, X. Leng, V.H. Crespi, F. Kang, R. Lv, Controllable Edge Exposure of MoS_2 for Efficient Hydrogen Evolution with High Current Density, ACS Appl. Energy Mater. 1(3) (2018) 1268-1275.

[27] J. Jian, L. Yuan, H. Qi, X. Sun, L. Zhang, H. Li, H. Yuan, S. Feng, Sn-Ni_3S_2 Ultrathin Nanosheets as Efficient Bifunctional Water-Splitting Catalysts with a Large Current Density and Low Overpotential, ACS Appl. Mater. Interfaces 10(47) (2018) 40568-40576.

[28] L. Wang, J. Cao, C. Lei, Q. Dai, B. Yang, Z. Li, X. Zhang, C. Yuan, L. Lei, Y. Hou, Strongly Coupled 3D N-Doped MoO_2/Ni_3S_2 Hybrid for High Current Density Hydrogen Evolution Electrocatalysis and Biomass Upgrading, ACS Appl. Mater. Interfaces 11(31) (2019) 27743-27750.

[29] Y. Tong, D. Feng, P. Chen, Dual Modification Strategy of Nickel Sulfide as pH-Universal Catalysts for Hydrogen Production at Large Current Density, ACS Sustain. Chem. Eng. 9(31) (2021) 10601-10610.