Supporting Information

MXenes enhance electrocatalytic water electrolysis of NiFe layered double hydroxides through bifunctional heterostructuring

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Fig. S1 (a) Geometric structures of β -Ni(OH)₂, top view (up) and side view (down). Antiferromagnetic configuration is used. Up and down arrows show Ni atoms' magnetic moment orientation. Supercell is shown as gray box. (b) Calculated β -Ni(OH)₂ energy band gap and Ni atom's magnetic moment as a function of U_{eff} parameter. The ranges of experimental data are shown by the arrows in the Fig.. (c) β -Ni(OH)₂'s DOS and pDOS. The Fermi energy is shifted to zero.



Fig. S2 (a) Geometric structures of γ -FeOOH, top view (up) and side view (down). Antiferromagnetic configuration (AFM-II order) is used. Up and down arrows show Fe atoms' magnetic moment orientation. Supercell is shown as gray box. (b) Calculated γ -FeOOH energy band gap and Fe atom's magnetic moment as a function of U_{eff} parameter. The ranges of experimental data are shown by the arrows in the Fig.. (c) γ -FeOOH's DOS and *p*DOS. The Fermi energy is shifted to zero.



Fig. S3 Detailed pDOS of NiFe-LDH. All metal-3d and O-2p orbitals are shown here.



Fig. S4 (a) Calculated density of states (DOS) and (b) projected density of states (*p*DOS) of NiFe-LDH using B3LYP method. The Fermi level is shifted to zero.



Fig. S5 (a) Gibbs free energy diagrams of NiFe-LDH OER pathways using B3LYP method. The reaction energy barrierrs are shown with arrows. (b) pDOS of NiFe-LDH O-2p orbitals and metal-3d orbitals using B3LYP method. The p-band and d-band centers of spin-up (cyan line) and spin-down (blue line) states are shown in the Fig..



Fig. S6 The *p*DOS and geometric structure (side view) of (a) $Ti_4N_3O_2$, (b) $Ti_2MoC_2O_2$, (c) $Ti_3C_2O_2$, (d) $Ti_4C_3O_2$, and (e) $Mo_3C_2O_2$. Sky blue, orange, yellow, dark blue, and red balls represent Ti, Mo, C, N, and O atoms, respectively. Supercell is shown as gray box.



Fig. S7 Reaction intermediate H^* adsorbed on (a) $Ti_4N_3O_2$, (b) $Ti_2MoC_2O_2$, (c) $Ti_3C_2O_2$, (d) $Ti_4C_3O_2$, and (e) $Mo_3C_2O_2$ surfaces during HER processes. Top view (up) and side view (down).



Fig. S8 Geometric structure of NiFe-LDH/Ti₄C₃O₂ heterostructures within different interfacial stacking types of AA (left) and AB stacking (right). As marked by the black dash lines, AA stacking means that the O atoms of $Ti_4C_3O_2$ layer are directly on the top of the upmost hydroxide (-OH) terminates of NiFe-LDH layer, while AB stacking means that the O atoms of $Ti_4C_3O_2$ layer are aligned with the below -OH of NiFe-LDH layer. After the fully optimization of the structures, AB stacking slid to AA stacking indicates that AA stacking is the most energetically stable structure.



Fig. S9. (a) Interfacial charge transfer (unit *e*) of NiFe-LDH/Ti₄C₃O₂ heterostructure as a function of interlayer distance reduction. The amount of charge transfer from NiFe-LDH to Ti₄C₃O₂ increases following decreasing of interlayer distance. (b) Charge density difference distribution and (c) DOS of 0% and 30% distance reduction structures. Isosurface level is $0.02e/Å^3$.