Supporting Information (SI) for:

Advantageous Crystalline-Amorphous Phase Boundary for Enhanced Electrochemical Water Oxidation

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EXPERIMENTAL SECTION

Catalyst Preparation (Co$_2$B and F-Co$_2$B): All chemicals were purchased from Sigma-Aldrich and used without further purification. To prepare Co$_2$B powder, a solution of cobalt chloride (CoCl$_2$·6H$_2$O, 20 mL, concentration 0.5 M) in a round-bottomed flask was flushed with argon for de-aeration and maintained at 0°C in an ice-bath. A 1.0 M sodium borohydride (NaBH$_4$) in 0.1 M sodium hydroxide (NaOH) was prepared separately and added drop-wise using a syringe to the CoCl$_2$ solution. A dark precipitate was instantaneously formed that was collected by filtration. The collected precipitate was washed with distilled (DI) water and ethanol several times and stored in vacuum-oven for 24 h. The dried-powder was subjected to pyrolysis at 600 °C under argon for 2 h. For F-Co$_2$B, appropriate amounts of ammonium fluoride (NH$_4$F) were mixed with CoCl$_2$ solution, and preparation was identical with that for Co$_2$B.

Catalyst Characterizations: Field-emission scanning electron microscopy (FE-SEM; model S4800; Hitachi) was used to study the surface morphologies of the samples. Transmission electron microscopy (TEM; Talos F200X; Thermo Fisher Scientific) equipped with an energy dispersive X-ray (EDX) was used to acquire TEM, and elemental mapping, images. Structural characterization was determined by X-ray diffraction (XRD; D/MAX-2500/PC; Rigaku) patterns using a diffractometer with Cu-Kα radiation ($\lambda = 0.15418$ nm) at 40 kV and 100 mA. The surface electronic states and composition of the samples, were analyzed by X-ray photoelectron spectroscopy (XPS; VG ESCALAB 200i; Thermo Fisher Scientific). XPS survey and high-resolution scans were conducted with pass energies of, respectively, 100 and 20 eV.

Electrochemical Measurements: The electrochemical performance of the catalysts was evaluated in 1.0 M KOH using a three-electrode electrochemical cell with a rotating disk electrode (RDE) which was controlled by an electrochemistry workstation (Autolab PGSTAT; Metrohm). Titration vessel (height: 80 mm, outer diameter: 78 m, volume: 90 ml) made by clear glass was used as a testing cell. The distance between working and reference electrodes was about 1 cm. In a typical preparation of the working electrode, a powder of 4 mg was dispersed in a Nafton$^\text{®}$ solution (30 μL, 5 wt.%) of water (1 mL) and ethanol (volume ratio 3:1). A homogeneous ink formed after 20 min ultrasonication. A 5 μL of the catalyst ink was drop-cast onto the surface of a glassy-carbon (GC) RDE electrode which had a diameter of 3
mm to yield a catalyst loading of 0.285 mg cm$^{-2}$. The working electrode was air-dried for 24 h under ambient conditions. The electrolyte was purged with O$_2$ before measurements. During measurement the RDE electrode was rotated at 2,000 rpm to remove any bubbles. Hg/HgO and graphite rod were used, respectively, as the reference electrode and counter electrode. Prior to electrochemical measurement the working electrode was subjected to continuous potential cycling from 1.0 to 1.7 V$_{RHE}$ until reproducible voltagrams were obtained. To determine the resistance of the solution ($R_s$) electrochemical impedance spectroscopy (EIS) was measured at open circuit potential (OCP) in the frequency range 1 to 50, kHz. $R_s$ was estimated from the resulting Nyquist plot and used for ohmic drop correction based on the relation $E_c = E_m - iR_s$, where $E_c$ is, respectively, $iR$-corrected potential and $E_m$ is the measured potential. The potentials were calibrated against a reversible hydrogen electrode (RHE). Linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV s$^{-1}$ from 1.2 to 2.0, V$_{RHE}$. Cyclic voltammetry (CV) was used to measure the electrochemical effective surface area (ECSA). The test was performed in an O$_2$-saturated 1.0 M KOH solution to estimate the electrochemical double-layer capacitance ($C_{dl}$) at non-Faradaic overpotentials. CV scans were conducted at scan rates 20, 40, 60, 80, 100, and 120, mV s$^{-1}$ over a voltage range 1.41 to 1.46, V$_{RHE}$. The difference in current density between the anodic and cathodic sweeps ($J_{anodic} - J_{cathodic}$) at 1.435 V$_{RHE}$ was plotted as a function of the scan rate in which the slope is equal to twice the $C_{dl}$ of the catalyst. Electrochemical impedance spectroscopy (EIS) was performed over a frequency range of 0.1 to 100, kHz under OCP and an applied voltage of 0.50, 0.52, 0.54, and 0.60, V with an ac perturbation of 10 mV.

**Density Functional Theory Calculations:** Density functional theory (DFT) calculations were performed using Vienna Ab initio Simulation Package (VASP) code within the generalized gradient approximation (GGA-PBE). All were performed using a cut-off energy of 400 eV. For bulk and slab modeling a 2×2×2 expanded supercell from unitcell (96 atoms, Fig.1) was employed. For the slab model, an 18Å thick vacuum-layer was placed within the periodic cells repeated in the z-axis to obviate interactions. A supercell model of amorphous Co$_2$B with OH, O, OOH adsorptions on the surface Co atoms with coordination numbers of 1, 2, 3, and 4 was used in DFT modeling. Then, adsorption energy was calculated for the amorphous structures, where the strongest adsorption energies were used for the consideration of energy landscape. In order to check the validity of DFT calculations on amorphous phase, binding energies
between the surface Co and intermediates, such as OH, O, OOH, were calculated in three different supercell models with amorphous phase. The results showed that Co atoms in each amorphous Co$_2$B supercell having highest OH adsorption energy did not have exactly the same coordination number with B. However importantly, adsorption energy of OH was increased as coordination number of Co-B increases and the highest adsorption energies for three different amorphous Co$_2$B supercell models were similar as, -3.90, -3.94, -3.95 eV. In addition, the second highest adsorption energies in the three different supercell models of amorphous Co$_2$B were also very close to each other as -3.57, -3.56, and -3.54 eV. Thus, these results can support validity of our DFT calculations on the amorphous Co$_2$B system, although other factors still may exist which needs to be considered for further enhancing validity DFT calculations in amorphous materials.$^{S3-S5}$

**Calculation of turnover frequency (TOF):** TOF is calculated from,

$$\text{TOF} = j \times \frac{A}{4 \times F \times N_s}$$

where $j$, $A$, $F$ and $N_s$ are, respectively, current density at a certain overpotential (A cm$^{-2}$), surface area of the working electrode (cm$^{-2}$), Faraday constant (96,458 C mol$^{-1}$), and concentration of activie sites in the catalysys (mol cm$^{-2}$). $N_s$ for oxygen evolution reaction (OER) was determined by CV measuremments at different scan rates in the voltage range where redox reaction occurs. The peak current is plotted against scan rate where the slope has the linear relationship,

$$\text{Slope} = n^2 F^2 A N_s / 4RT$$

in which $n$, $R$, and $T$ are, respectively, the number of electrons transferred (here $n = 1$), ideal gas constant and absolute temperature.$^{S6-S8}$ The linear relationship between $N_s$ and scan rate was derived from the Nernst equation,

$$E = E_0' + \frac{RT}{nF} \ln \frac{C_{ox}(t)}{C_{red}(t)}$$

where $E_0'$ and C(t) are the potential of redox species and the time-dependent concentrations of redox producs, respectively. Assuming that there is no bulk concentration, the current (i) can be obtained as the concentration variation of the oxidized species,
\[ i = -nFV \frac{dC_{\text{ox}}(t)}{dt} \]

where \( n \) = number of transfer electrons, \( V \) and \( t \) are volume and time, respectively. Given the constant of the total concentration,

\[ C_T = C_{\text{ox}}(t) + C_{\text{red}}(t) \]

\( C_{\text{ox}}(t) \) can be described as follow,

\[ C_{\text{ox}}(t) = \frac{C_T \exp \left[ \frac{nF(E - E^{0'})}{RT} \right]}{1 + \exp \left[ \frac{nF(E - E^{0'})}{RT} \right]} \]

by differentiating the equation of \( C_{\text{ox}}(t) \) with respect to \( t \) and substituting into equation of \( i \), the \( i \) can be obtained as,

\[ i = \frac{n^2F^2V C_T \nu \exp \left[ \frac{nF(E - E^{0'})}{RT} \right]}{RT \left( 1 + \exp \left[ \frac{nF(E - E^{0'})}{RT} \right] \right)^2} \]

where \( \nu \) is the scan rate, which is equal to \(- \frac{dE}{dt}\). Since \( E = E^{0'} \) at peak current, and \( VC_T \) can be replaced by \( ANS \), finally we can get,

\[ i = \frac{n^2F^2 ANS \nu}{4RT} \]

Hence, the linear relationship between the oxidation peak current and scan rate can be used to estimate the number of redox active sites.

**Determination of collection efficiency for RRDE:**

The collection efficiency of RRDE system was calibrated in 0.1 M KOH with a 10 mM potassium ferricyanide, \( K_3\text{Fe(CN)}_6 \), electrolyte. The ferrocyanide/ferricyanide half reaction is a simple and single-electronic reaction that is frequently used as the standard method for calculating collection efficiency of RRDE system.
\[ \text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-} \] (Reduction of ferricyanide)

\[ \text{Fe(CN)}_6^{4-} + e^- \rightarrow \text{Fe(CN)}_6^{3-} \] (Oxidation of ferrocyanide)

Initially, both ring and disk electrodes were fixed at sufficiently positive potential, and then the potential sweep towards negative voltage were performed on the disk electrode with scan rate of 10 mV s\(^{-1}\). The potential of ring electrode was fixed at a positive potential (oxidizing) and rotation speed was held at 500, 1000, and 1600 rpm during the measurement. Figure Rxx shows the collected voltage-current plots at the both of ring and disk electrodes. The collection efficiency of RRDE system was calculated by the measured ratio of the ring limiting current to the disk limiting current (Fig.Sxx), which was about 0.2005.

\[ N_{\text{collection efficiency}} = - \frac{i_{\text{limiting,ring}}}{i_{\text{limiting,disk}}} \]

**Ultraviolet Photoelectron Spectroscopy:** Work function analysis was conducted using ultraviolet photoelectron spectroscopy (UPS; Thetaprobe; Thermo).

**X-ray Absorption Spectroscopy:** X-ray absorption spectroscopy (XAS) of the powder samples was measure at 1D KIS-PAL XAS beamline at the Pohang Light Source (PLS-II) equipped with bending magnet and operated at an energy of 3.0 GeV with a maximum storage current of 300 mA. The beamline comprised a double-crystal Si (111) monochromator detuned to 40% to suppress higher order harmonic content from the beam. The beamline is operating in an energy range of 4 to 16 KeV with an energy resolution (\(\Delta E/E\)) of \(2 \times 10^{-4}\). The optical components consist of a tangential focusing and collimating mirror. The beam size was 2 (horizontal) \(\times\) 1 (vertical) mm (focused) during XAS measurements. The data were collected in transmission mode with argon-nitrogen gas-filled ionization chambers as detectors. Co metallic reference foil was also measured simultaneously to calibrate the data. The data were analyzed using the ATHENA software package.\(^5\)\(^9\) The EXAFS data was plotted in the \(k\)-range of 0.2 to 1.0 nm\(^{-1}\) with \(k^2\)-weight in Hanning window and in an R-range of 0 to 0.6 nm. Fourier transformation (FT) of the EXAFS oscillations were plotted without phase-correction and the actual bond lengths are longer with a shift in x-axis than the plotted.
Figure S1. Low-resolution TEM images of F-Co$_2$B, a) bright-field, b) dark-field.
Figure S2. Line profiles for marked regions as “1” and “2”.

Figure S3. XRD patterns for F-Co$_2$B, Co$_2$B and the as-prepared samples.
Figure S4. a) Dark-field TEM image and corresponding EDX mapping image for b) Co (red), c) B (blue), d) O (green) and e) F (cyan) elements for F-Co$_2$B with f) quantitative mapping results.
**Figure S5.** EDX line profile across the c-a interface of F-Co$_2$B. Red and green lines are Co and O, respectively.

**Figure S6.** XPS spectra for a) B 1s and b) O 1s for F-Co$_2$B.
Figure S7. Theoretically generated scattering paths for Co$_2$B without phase-corrected. (b) The crystal structure of Co$_2$B where Co atoms are shown in blue and B atoms in green color.

Figure S8. a) SEM image of Co$_2$B b) Low-resolution TEM image of Co$_2$B and corresponding EDS mapping images for Co, O, and B.
Figure S9. CV scans measured at a voltage range from 1.40 to 1.46 V_{RHE} (no iR-compensation), where a capacitive current flows, with scan rates, respectively, 20, 40, 60, 80, 100 and 120, mV s^{-1} for a) Co\textsubscript{2}B and b) F-Co\textsubscript{2}B.

Figure S10. SEM image of F-Co\textsubscript{2}B.
Figure S11. SEM images of F-Co$_2$B with varying F (respectively, 15, 40 and 60, %).

Figure S12. a) LSV curves (scan rate 5 mV s$^{-1}$) for F-Co$_2$B with varying F and b) corresponding Tafel plots measured in 1M KOH solution.
Figure S13. Computed $C_{dl}$ values using CV data measured in a capacitive region (1.40 to 1.46 V$_{RHE}$, no $iR$-compensation) at scan rates, respectively, 20, 40, 60, 80, 100 and 120, mV s$^{-1}$ in 1 M KOH solution.

Figure S14. Low-resolution dark-filed TEM images of F-Co$_2$B with different F amounts.
Figure S15. Overpotential for affording a current density of 10 mA cm\(^{-2}\) of F-Co\(_2\)B catalysts with different F amounts.

Figure S16. RRDE data for F-Co\(_2\)B. (Inset shows schematic of the experimental set-up).
Figure S17. LSV-RRDE calibration curves for calculation of a collection efficiency (N) using 0.1 M KOH with 10 mM K$_3$Fe(CN)$_6$.

Figure S18. CV of a) F-Co$_2$B and b) Co$_2$B at different scan rates of 5, 10, 15, 20 and 25, mV s$^{-1}$ in 1 M KOH.
**Figure S19.** Linear relationship of the oxidation peak currents vs. scan rate at 1.46 V in the CVs (Fig. S12) for a) F-Co$_2$B and b) Co$_2$B.

**Figure S20.** Chronoamperometry curves for a) F-Co2B and b) Co2B under an applied voltage 1.55 V$_{RHE}$ in 1M KOH.
**Figure S21.** CV cycle of F-Co$_2$B loaded on nickel foam, RuO$_2$ loaded on nickel foam, and bare nickel foam, respectively. Measurements were performed 1.0 M KOH solution with a scan rate of 5 mV s$^{-2}$.

**Figure S22.** Chronoamperometry curve for F-Co$_2$B loaded on nickel foam generating at a constant voltage for generating an current density of about 100 mA cm$^{-2}$ in 1M KOH under applied voltage of 1.43 V$_{RHE}$. 

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**Figure S23.** UPS spectra of a) Co$_2$B and b) F-Co$_2$B for computing work functions.

**Figure S24.** TEM images of F-Co$_2$B after 20 min OER under varying (0.54 to 0.50) applied voltage.
**Figure S25.** *Ex-situ* HR-TEM images for F-Co$_2$B after 20 min OER under varying (0.54 to 0.50) applied voltage.
Figure S26. a,b) Low and high-resolution TEM and SAED pattern images for F-Co$_2$B following 10 h electrocatalytic water oxidation in 1 M KOH c-h) Corresponding elemental (Co, O, B, and F) mapping images.
Figure S27. Quantitative analysis for EDS mapping data (Fig. S17d) for post-OER F-Co$_2$B.

Figure S28. XRD pattern for F-Co$_2$B before and after 10 h OER in 1 M KOH.
Figure S29. XPS spectra of a) Co 2p and b) O 1s for F-Co$_2$B following long-term (12 h) OER in 1 M KOH.

Figure S30. Changed coordinate number of amorphous Co$_2$B from 3 to 2(red circles) and 4(purple circles) (right). Blue, green and grey spheres indicate Co, B, and F atoms, respectively.
Figure S31. Calculated DOS for crystal (black line) and amorphous (blue line) Co$_2$B phases, respectively.
Table S1. A comparison of catalytic OER activity for F-Co2B with transition metal borides, sulfides, selenides and phosphides in alkaline media.

<table>
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<th>Catalyst</th>
<th>Electrolyte</th>
<th>(\eta^{10}) (mV)</th>
<th>(\eta^{100}) (mV)</th>
<th>Tafel slope (mV dec(^{-1}))</th>
<th>Loading amount (mg cm(^{-2}))</th>
<th>Reference</th>
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<td>1 M KOH</td>
<td>320</td>
<td>-</td>
<td>32</td>
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<td>170</td>
<td>-</td>
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<td>380</td>
<td>297</td>
<td>3.0</td>
<td>S27</td>
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*Overpotential for affording a current density of 10 mA cm\(^{-2}\); **Overpotential for affording a current density of 100 mA cm\(^{-2}\).
References for SI


