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Supporting Information

Synergistic Electronic Interaction in RhCo Catalyst Regulated by Vanadium-Molybdenum Oxide for Enhanced Alkaline Hydrogen Evolution

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Characterization

SEM images were captured using a ZEISS GeminiSEM 300 scanning electron microscope operating at 15 kV. TEM and elemental mapping images were acquired using a Talos FEI Tecnai G2 F20 with an acceleration voltage of 200 kV. XRD analysis was performed on a Rigaku Ultimate IV X-ray diffractometer equipped with Co-Kα radiation (λ = 1.79 Å). The scanning rate for XRD measurements was set at $4°\cdot min^{-1}$, ranging from 10° to 80°. XPS measurements were conducted using a PHI 5000 Versa probe XPS instrument, employing non-monochromatic Al-Kα X-ray as the excitation source. EPR measurements were carried out using an EMX plus 6-1 spectrometer with the experimental temperature set at 70 K. The conversion time was set at 50 ms, modulation amplitude at 0.8 mT, and modulation frequency at 100 kHz.

Electrochemical measurements

To obtain the polarization curve, a linear sweep voltammetry (LSV) was performed with a sweep rate of 5 $mV\cdot s^{-1}$. The LSV curve was plotted with the logarithm of the standard potential against the current density to obtain the Tafel diagram. The electrochemical double layer capacitance (Cdl) was measured using cyclic voltammetry (CV) with potential scan rates of 100, 80, 60, 40, and 20 $mV\cdot s^{-1}$. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 100 kHz to 1 Hz to investigate the material's electrical properties. All the electrochemical tests were conducted under room temperature conditions to assess the performance of the material in the three-electrode system.

To prepare the catalyst, start by dispersing 4 mg of electrocatalyst and 30 μL of a 5% nafion solution in a mixture of 1 mL water and ethanol (3:1) using ultrasonication. Continue the dispersion for 15 minutes until a mixed ink is formed. Next, spread 14 μL of the ink onto a glass carbon electrode with a diameter of 5 mm. Allow the ink to naturally dry before using the electrode. As a result, the sample will have a loading capacity of 0.277 mg cm^{-2}.

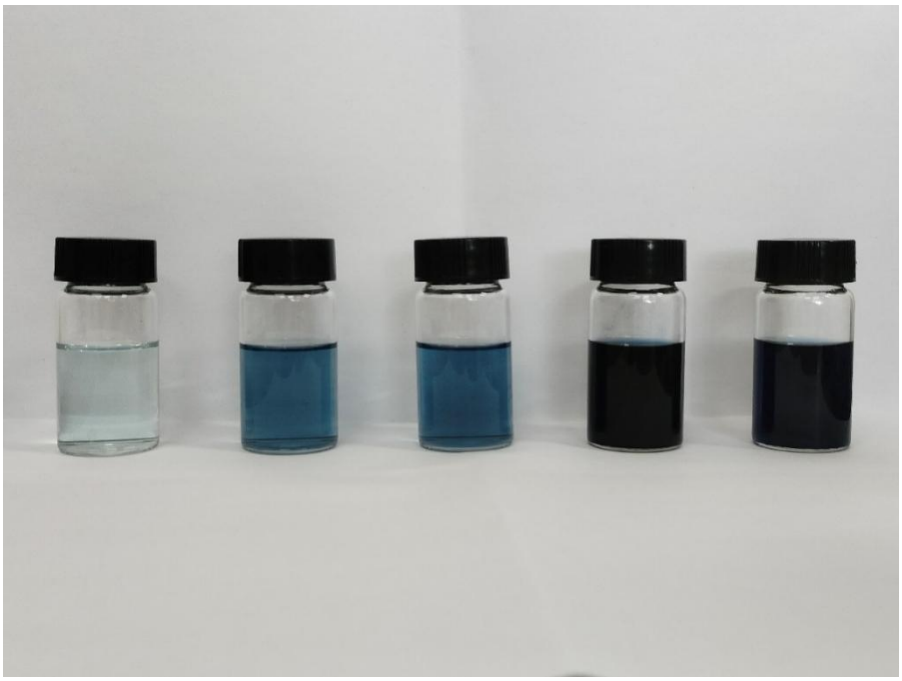


Figure S1. Digital image of vanadium powder and molybdenum powder（V:Mo=1:1） mixed in hydrogen peroxide ethanol solution for each hour.

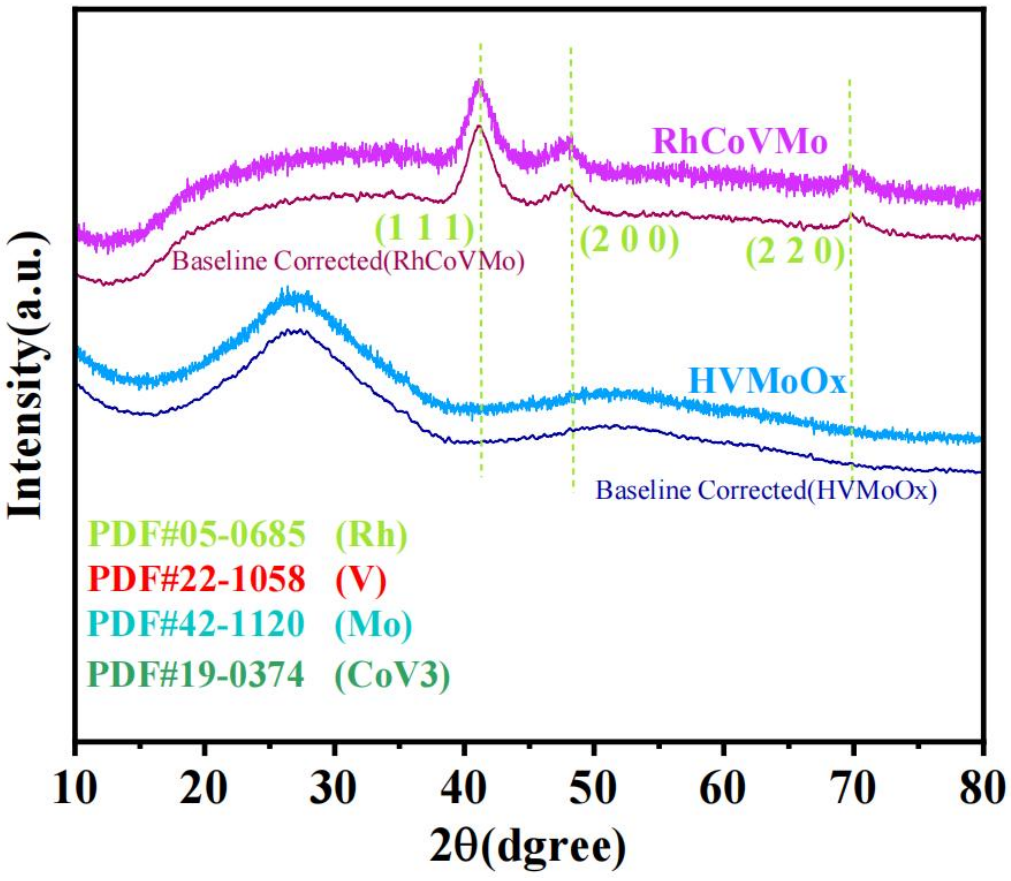


Figure S2. XRD patterns of $RhCoVMo_x$ and $HVMoO_x$ before and after baseline correction

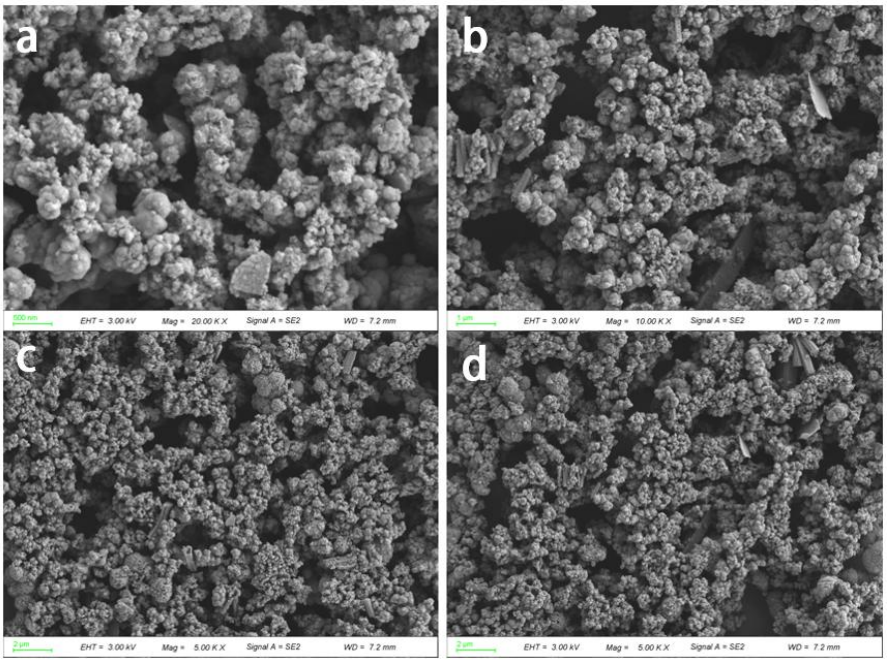


Figure S3. SEM images at different scales for RhCoVMoO (a) 500nm, (b) 1μm, (c) 2μm, (d) 2μm.

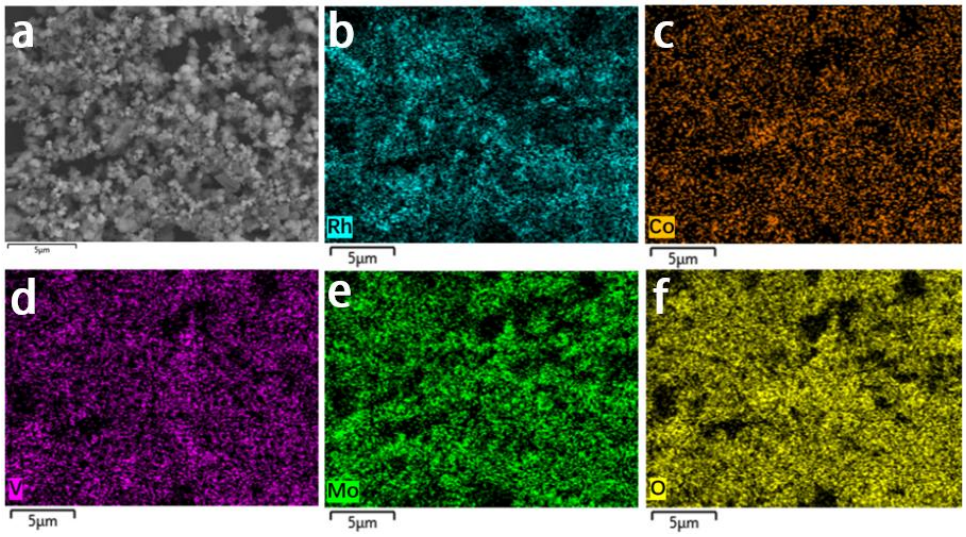


Figure S4. (a) SEM images and corresponding EDX mapping of (b) Rh, (c) Co, (d) V, (e) Mo and (f) O element for RhCoVMoO(V:Mo=1:1).

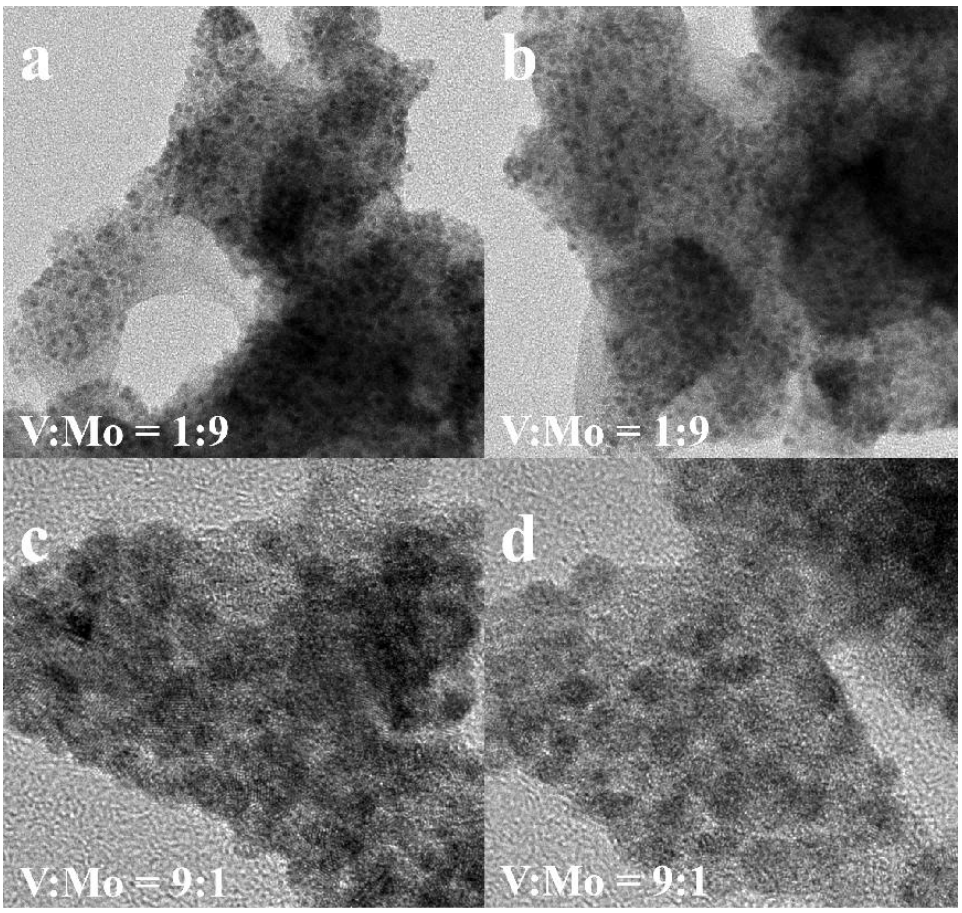


Figure S5. TEM images of control samples with different V:Mo ratios

(a-b) TEM images of the V:Mo = 1:9 sample; (c-d) TEM images of the V:Mo = 9:1 sample.

(b-

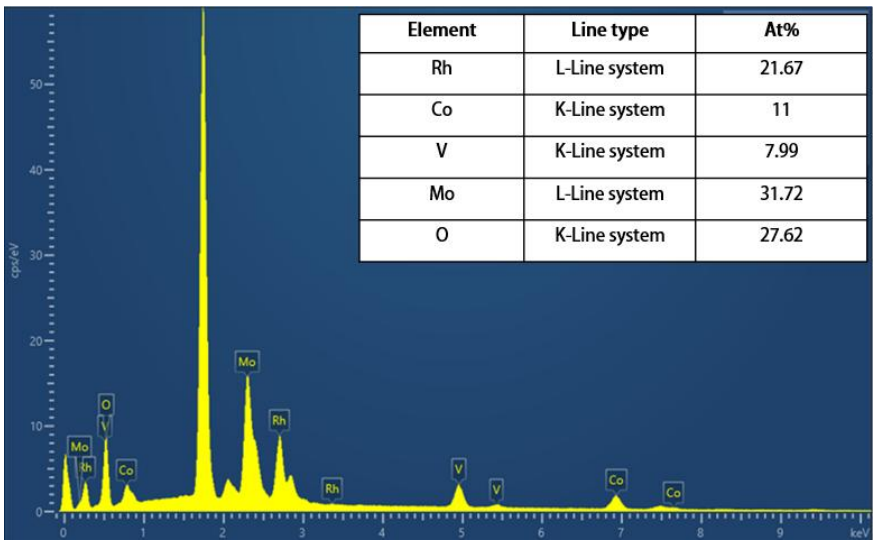
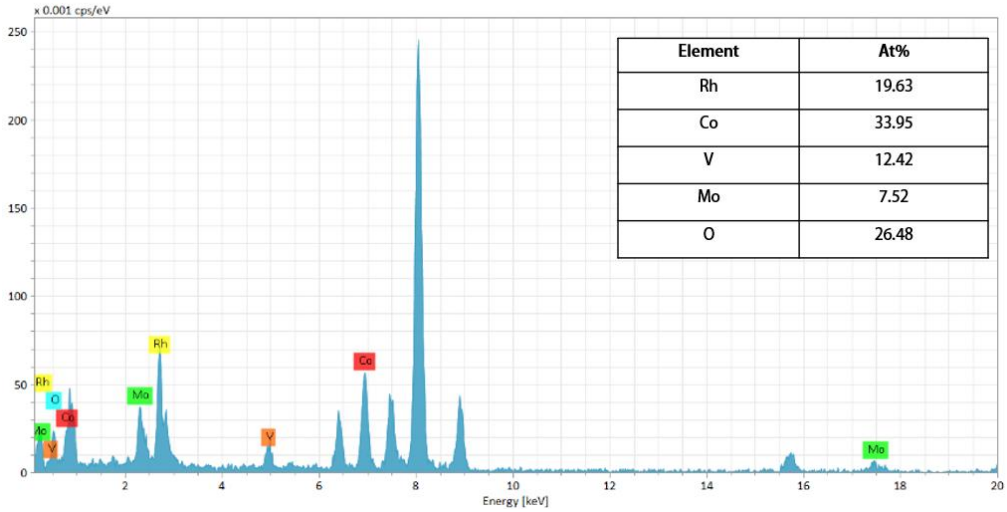


Figure S6. The distribution of the total spectrum of RhCoVMoO(V:Mo=1:1) in SEM.



Element	At%
Rh	19.63
Co	33.95
V	12.42
Mo	7.52
O	26.48

Figure S7. The distribution of the total spectrum of RhCoVMoO(V:Mo=1:1) in TEM.

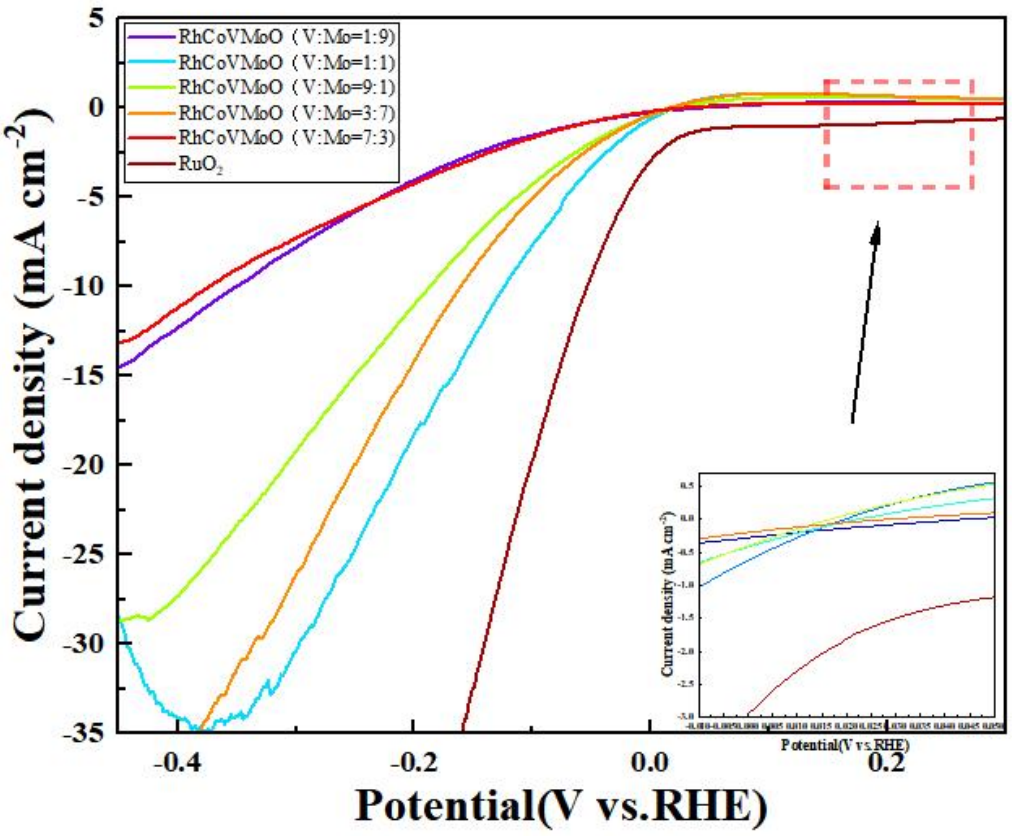


Figure S8. Raw HER LSV curves without iR correction (1.0 M KOH)

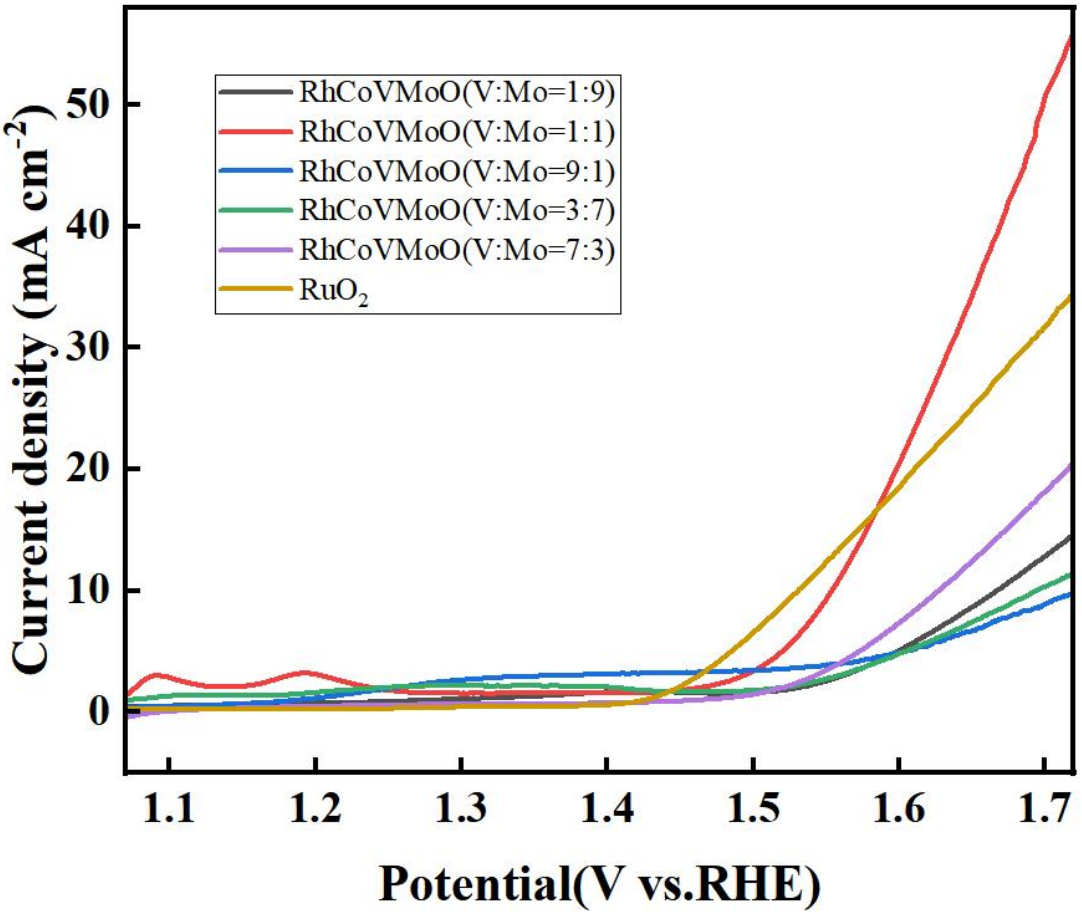


Figure S9. Original LSV curves (without iR correction) of $RhCoVMoO_x$ catalysts with different V:Mo ratios and commercial RuO_2 in 1.0 M KOH (scan rate = 5 $mV \cdot s^{-1}$).

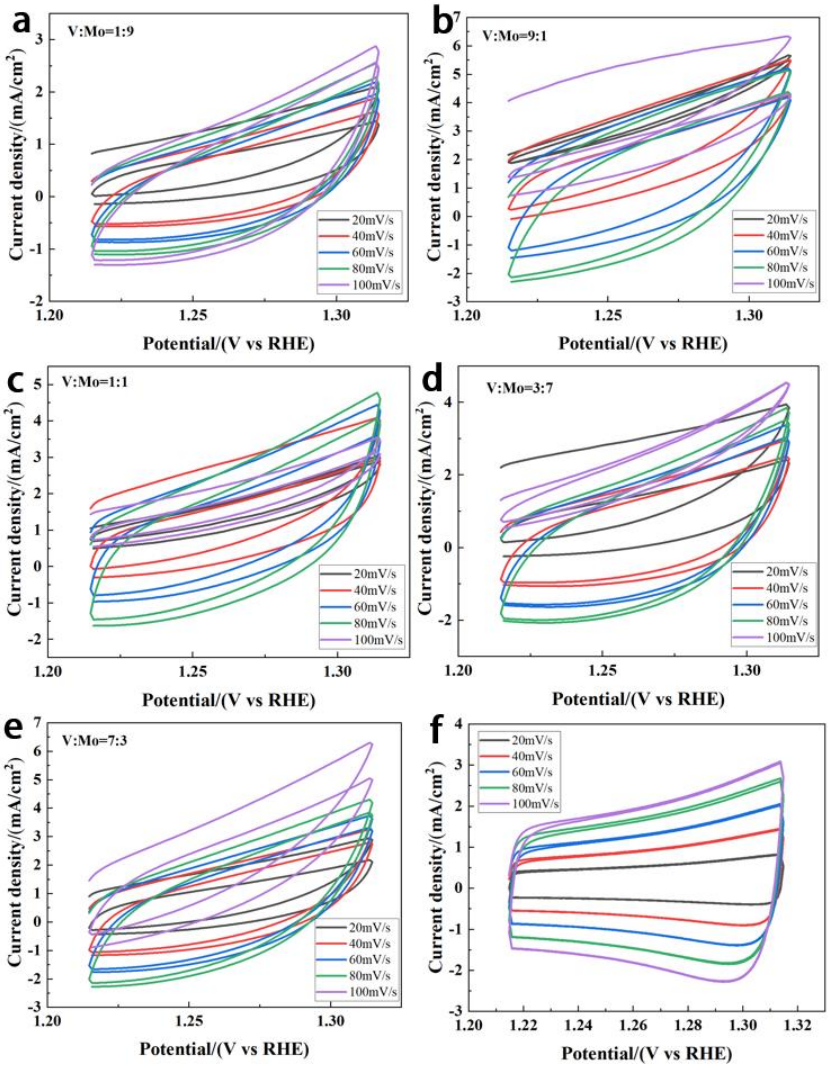


Figure S10. CV curves of RhCoVMoO（V:Mo=1:9）, RhCoVMoO（V:Mo=9:1）, RhCoVMoO（V:Mo=1:1）, RhCoVMoO（V:Mo=3:7）, RhCoVMoO（V:Mo=7:3）catalysts and RuO_2 in the double layer region at different scan rates.

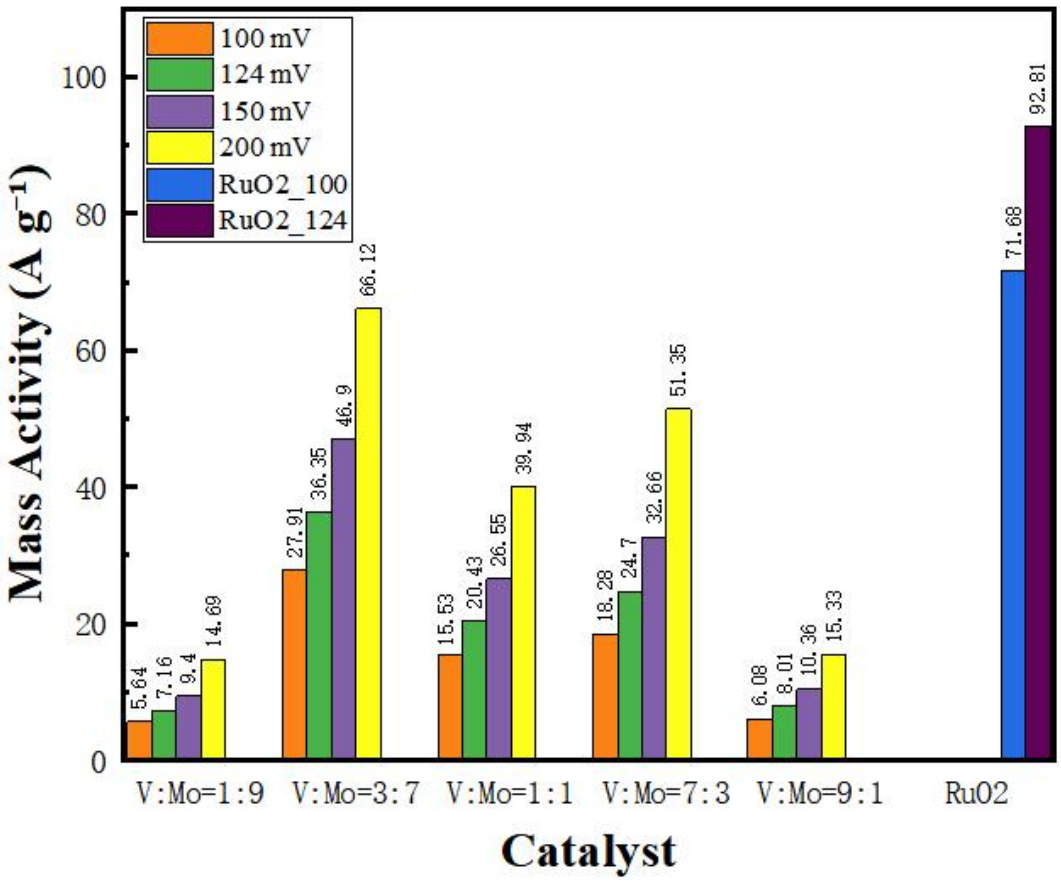


Figure S11. Mass activity of $RhCoVMoO_x$ catalysts with different V:Mo ratios and commercial RuO_2 at various overpotentials for HER. Mass activity was calculated by normalizing the measured current density (from Figure 5a) to the catalyst loading mass (0.277 mg·cm^{-2}). The V:Mo = 1:1 catalyst exhibits a mass activity of 20.43 A g^{-1} at 124 mV, which is higher than most other $RhCoVMoO_x$ compositions except for V:Mo=3:7 (36.35 A g^{-1}). RuO_2 is included as a benchmark.

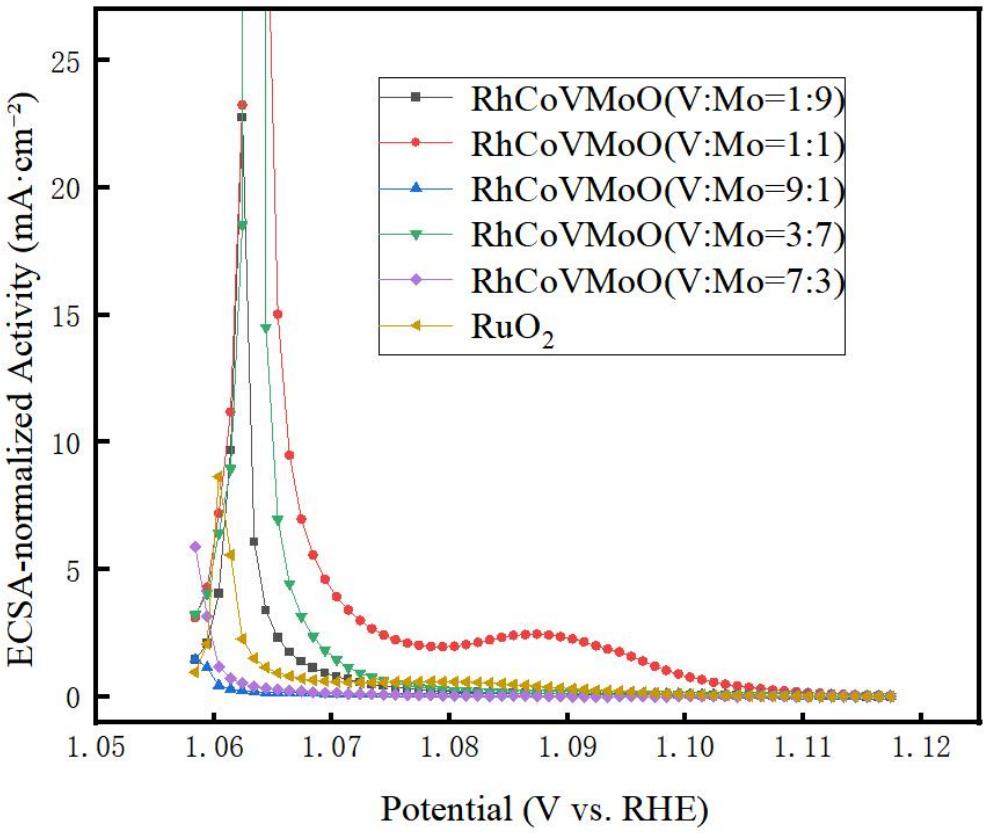


Figure S12. ECSA-normalized activity curves of $RhCoVMoO_x$ catalysts with different V:Mo ratios and commercial RuO_2 in 1.0 M KOH (scan rate = 5 $mV \cdot s^{-1}$).

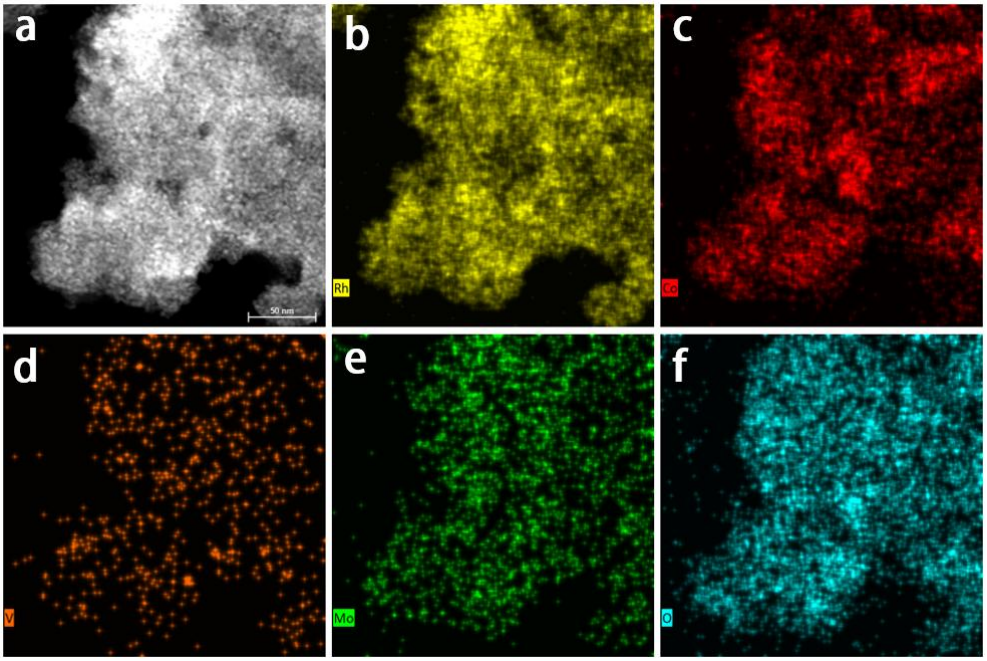
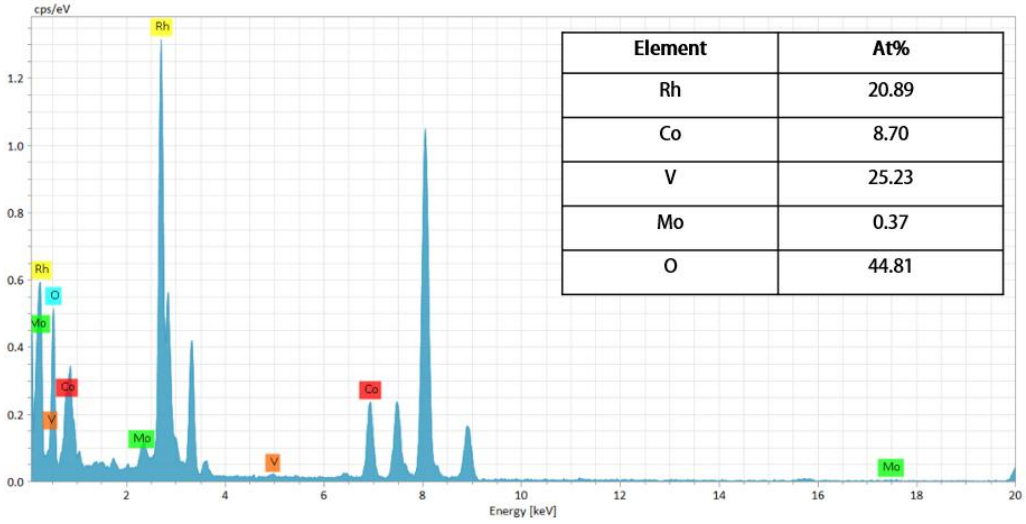


Figure S13. TEM of RhCoVMoO after the stability test.



Element	At%
Rh	20.89
Co	8.70
V	25.23
Mo	0.37
O	44.81

Figure S14. Elemental composition of $RhCoVMoO_x$ after 240 h stability test.

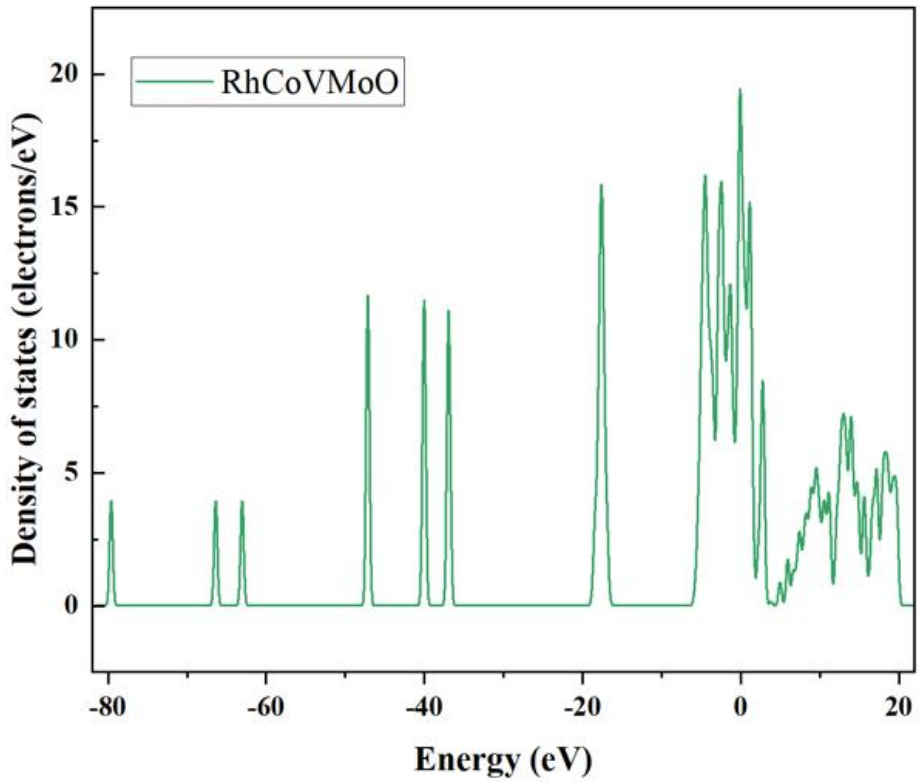


Figure S15. Calculated density of states (DOS) for RhCoVMoO.

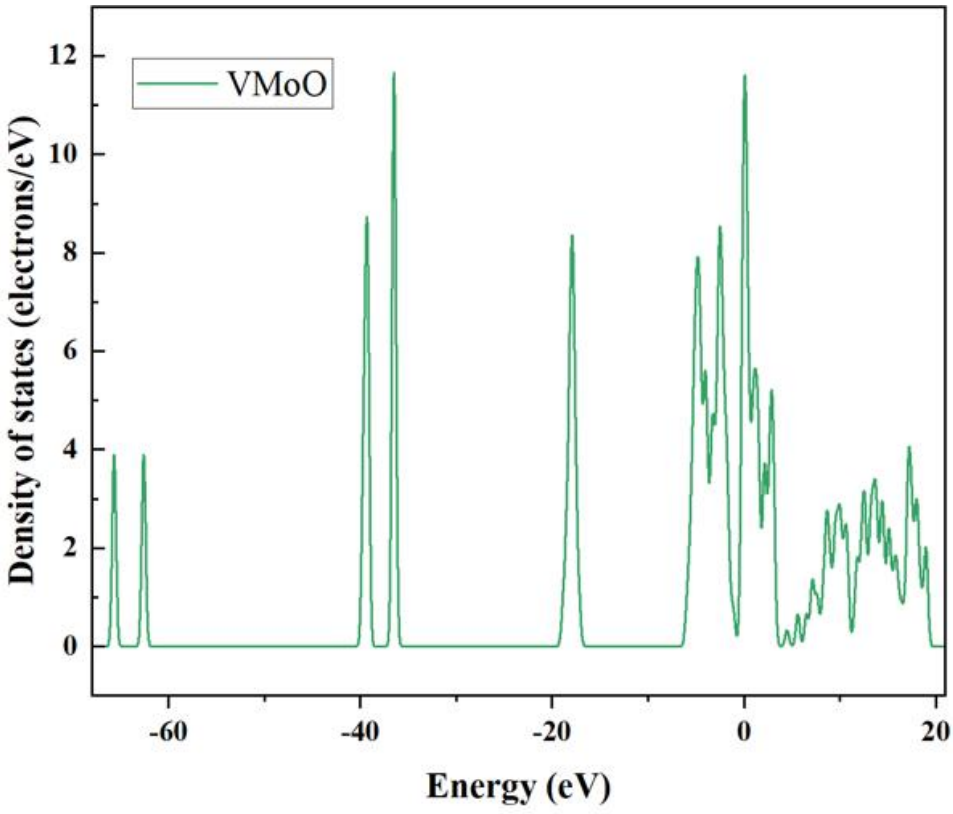


Figure S16. Calculated density of states (DOS) for VMoO.

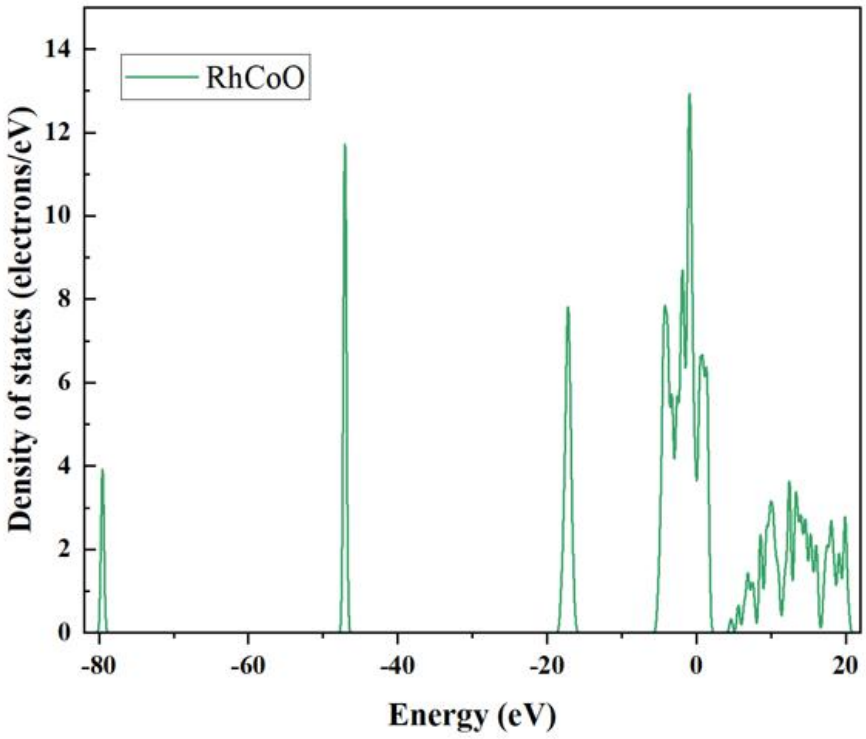


Figure S17. Calculated density of states (DOS) for RhCoO.

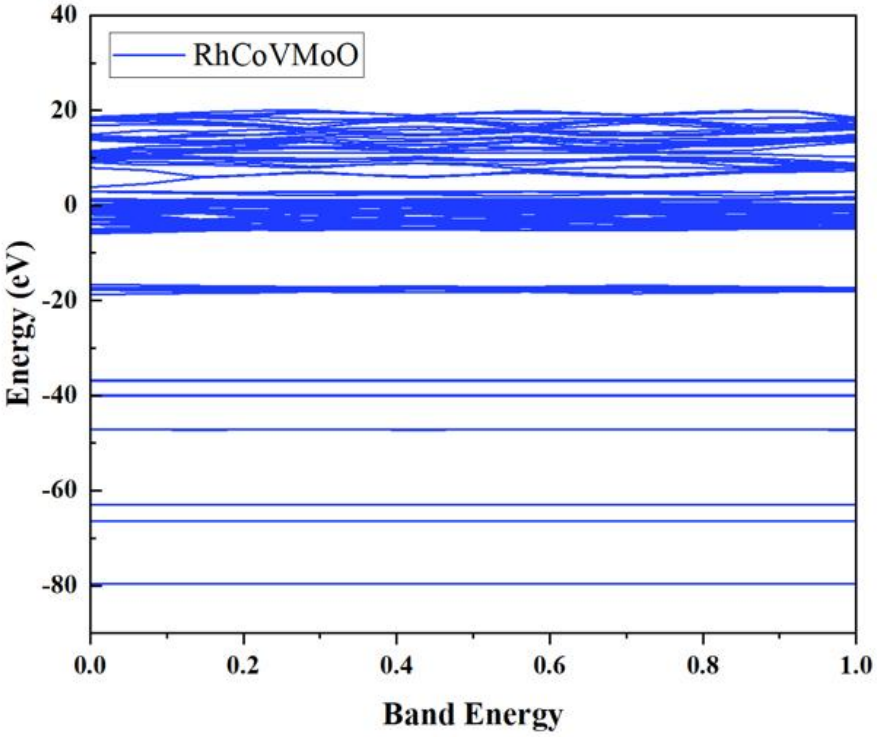


Figure S18. Calculated band structure of RhCoVMoO.

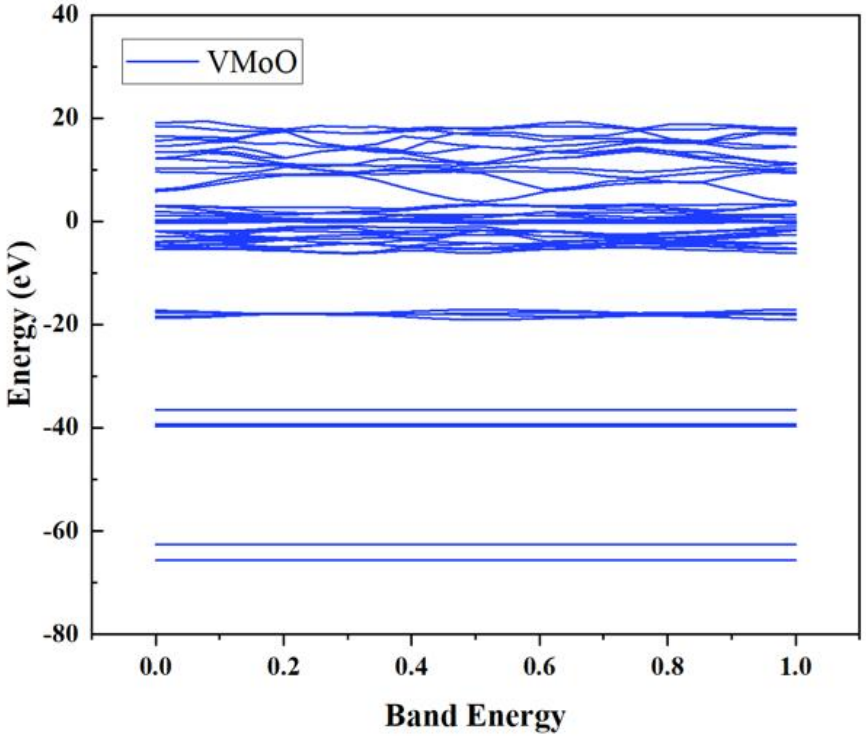


Figure S19. Calculated band structure of VMoO.

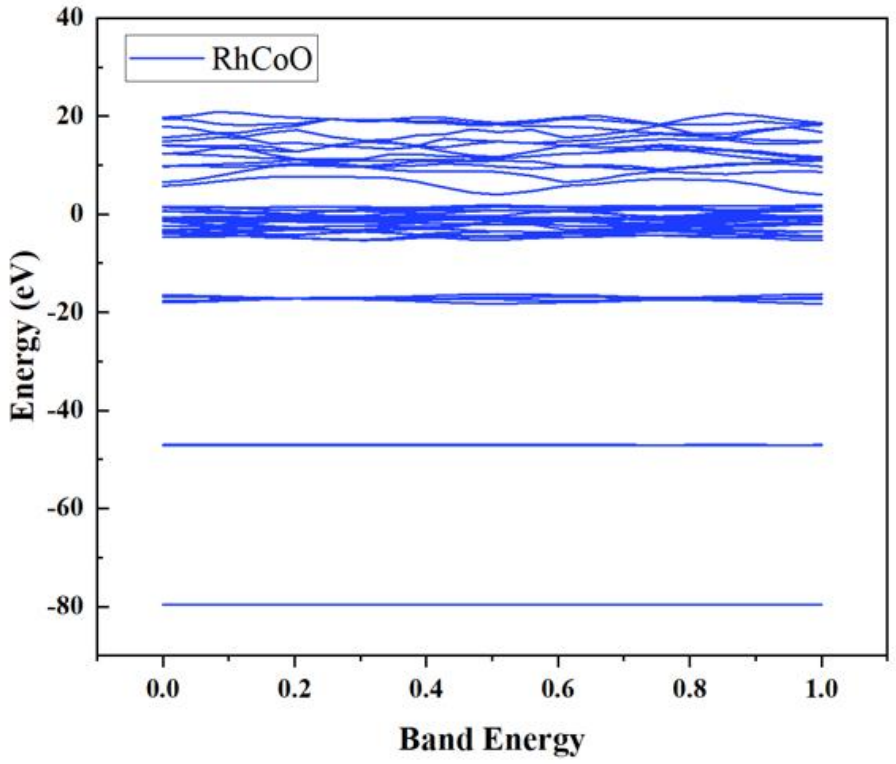


Figure S20. Calculated band structure of RhCoO.

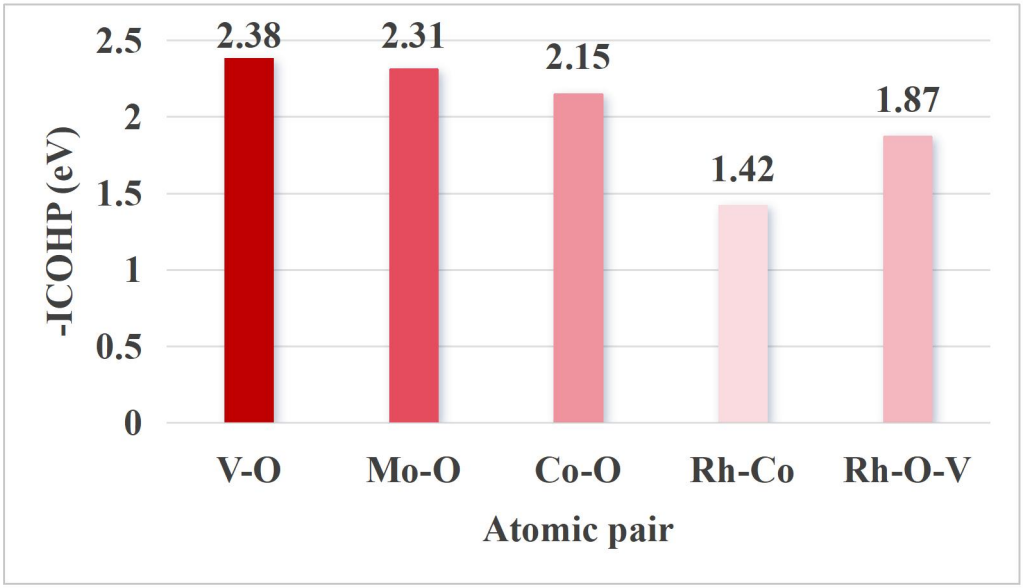


Figure S21. -ICOHP values of key atomic pairs in the RhCoVMoO_x model.