# Supplementary Information

**A fast and general approach to carbon coated Janus metal/oxide hybrid for catalytic water splitting**

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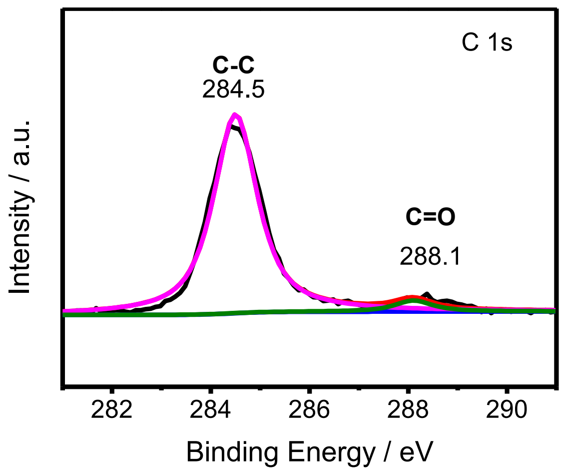


**Figure S1.** XPS spectra of C 1s for CoMo/$CoMoO_x$.

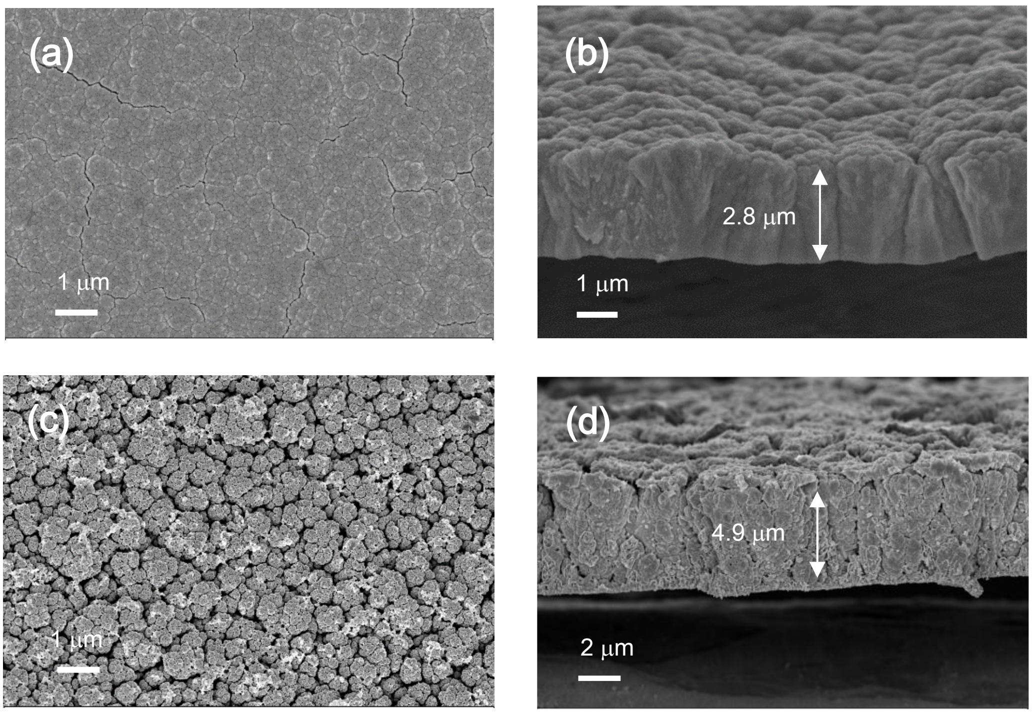


**Figure S2.** SEM images of (a, b) CoMo and (c, d) CoMo/$CoMoO_x$.

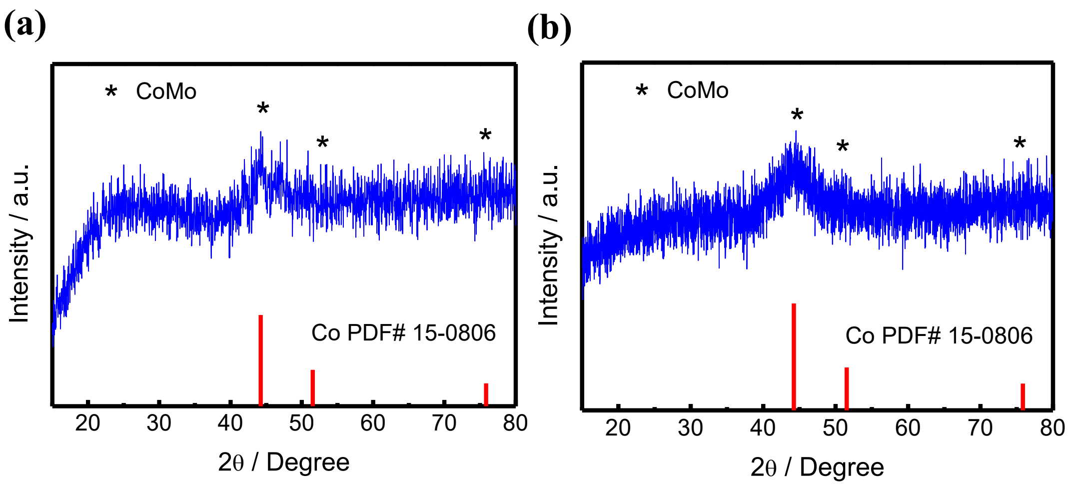


**Figure S3.** XRD patterns of (a) CoMo/$CoMoO_x$ and (b) CoMo.

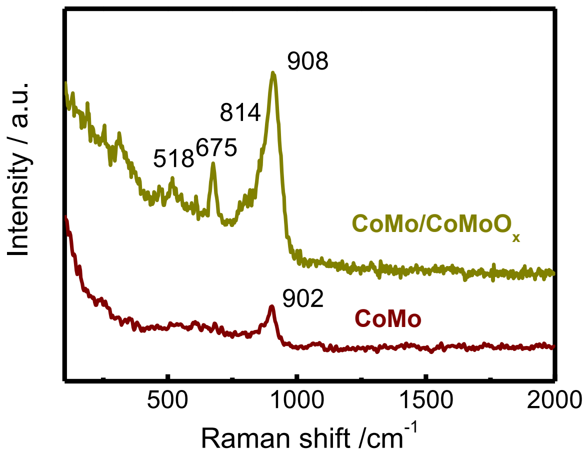


**Figure S4.** Raman spectra of CoMo/$CoMoO_x$ and CoMo.

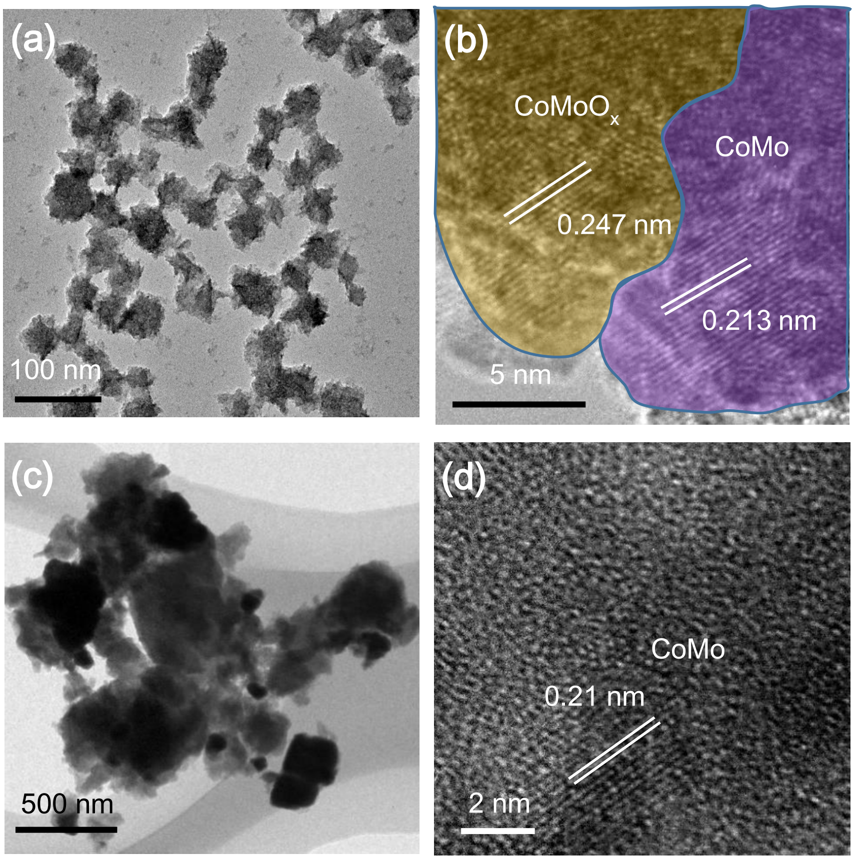


**Figure S5.** (a) Low magnification TEM image and (b) HRTEM image for CoMo/CoMoO$_x$. (c) Low magnification TEM image and (d) HRTEM image for CoMo.

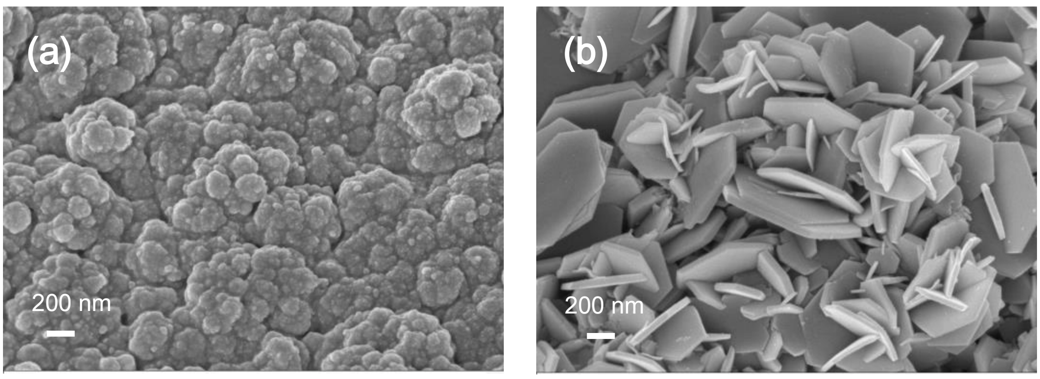


**Figure S6.** SEM images of (a) CoMo/CoMoO$_x$@C and (b) CoMo/CoMoO$_x$ after stability test.

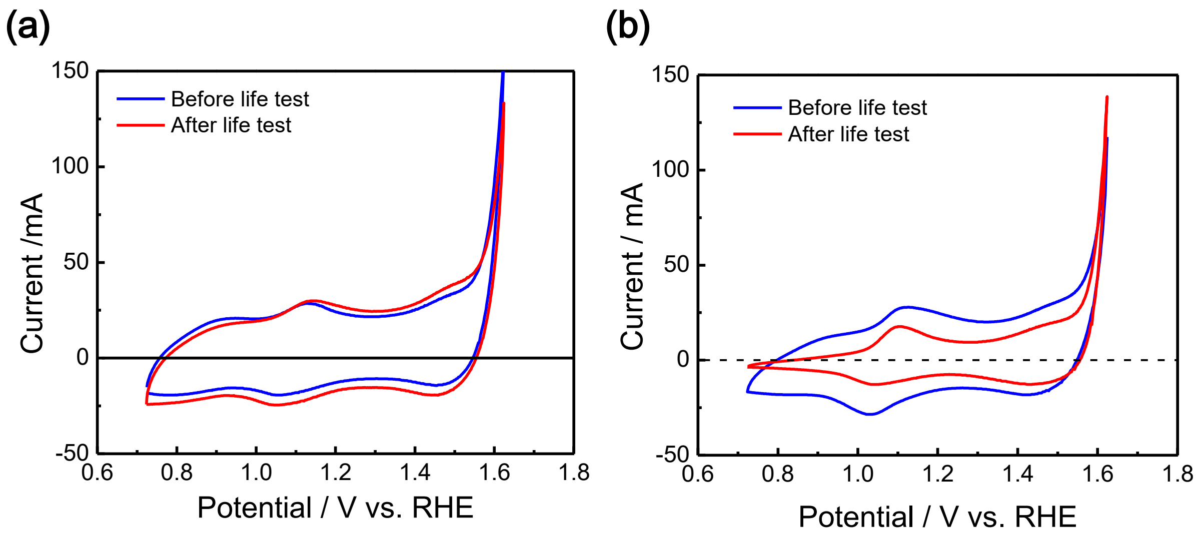


**Figure S7.** CV curves of (a) CoMo/CoMoO$_x$@C and (b) CoMo/CoMoO$_x$ recorded in 1M KOH at a scan rate of 100 mV $s^{-1}$.

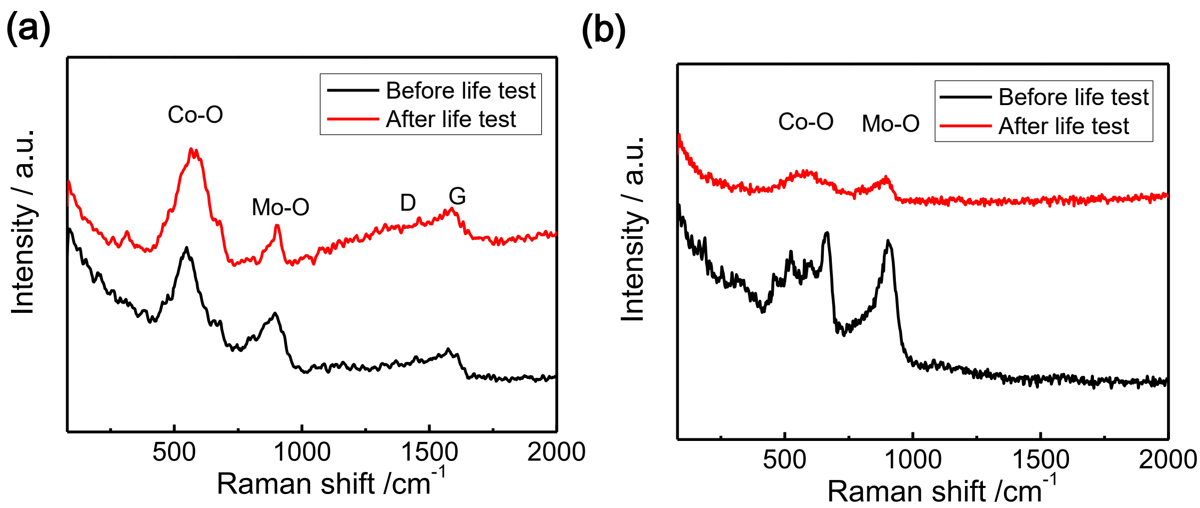


**Figure S8.** Raman spectra of (a) CoMo/CoMoO$_x$@C and (b) CoMo/CoMoO$_x$.

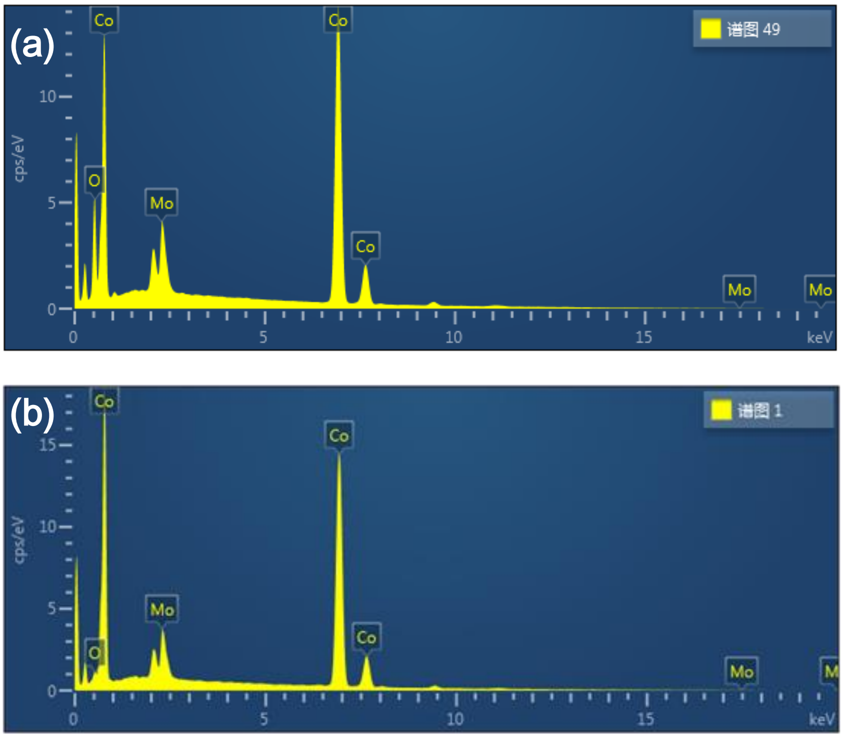


**Figure S9.** Energy dispersive X-ray (EDX) spectra of CoMo/CoMoOx (a) before and (b) after stability test.

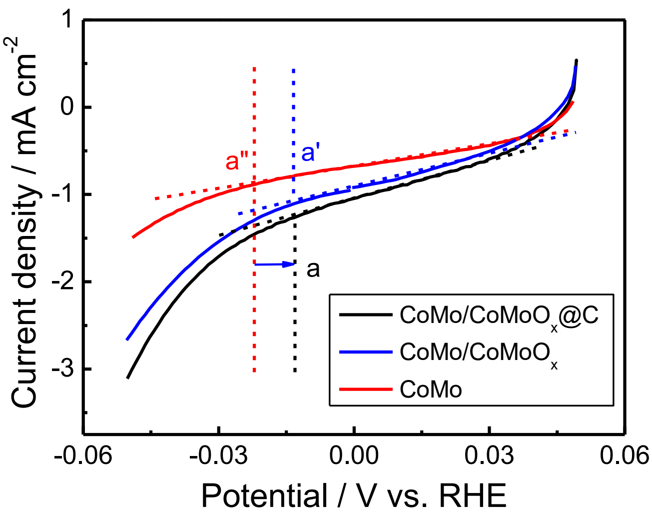


**Figure S10.** LSV curves measured in 1 M KOH at a scan rate of 1 mV $s^{-1}$. Symbols a, a' and a'' refer to the onset potential of hydrogen adsorption.

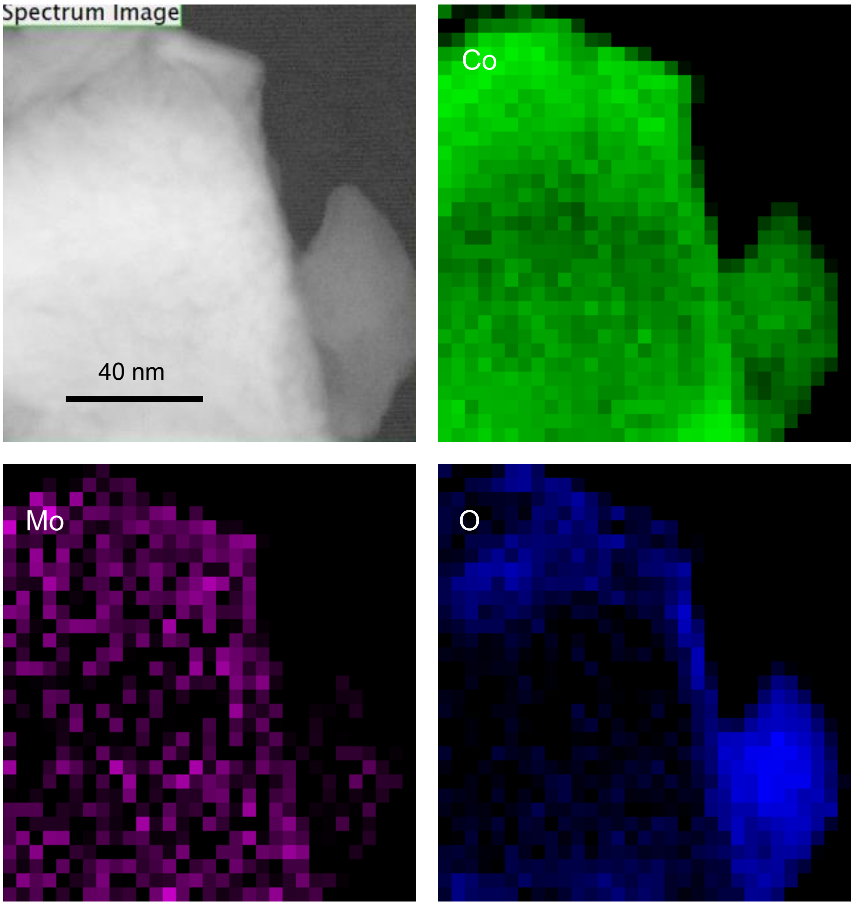


**Figure S11.** Elemental mapping images of CoMo obtained by normal cathodic deposition at 20 mA cm$^{-2}$ without plasma arcing.

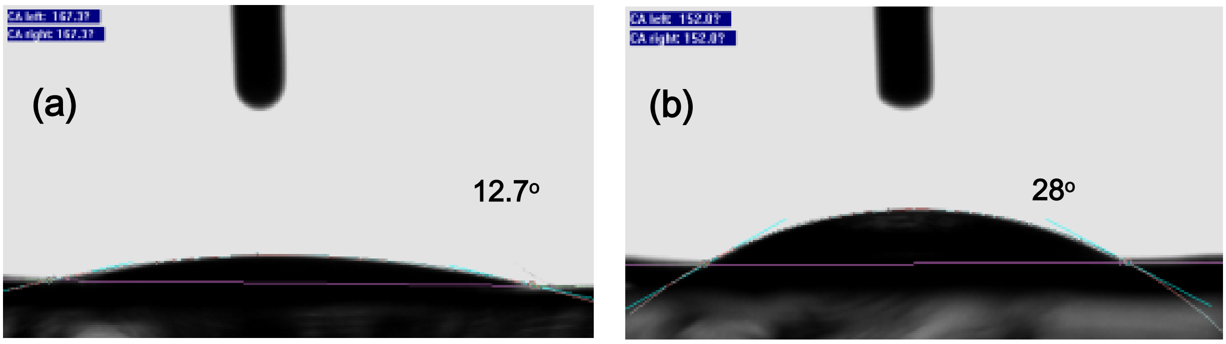


**Figure S12.** Contact angle of (a) CoMo/CoMoO$_x$@C and (b) CoMo/CoMoO$_x$.

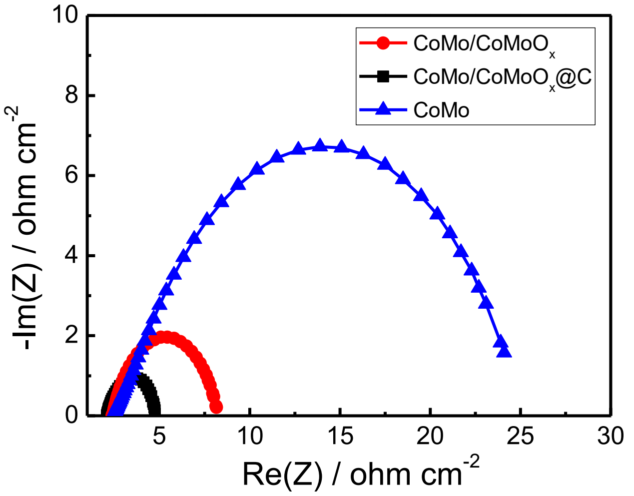


**Figure S13.** Nyquist plots obtained at an HER overpotential of 80 mV in 1 M KOH.

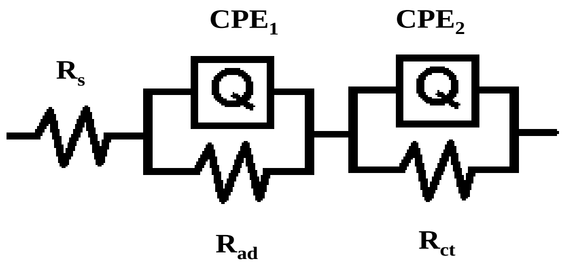


**Figure S14.** Equivalent circuit used to fit the EIS data.

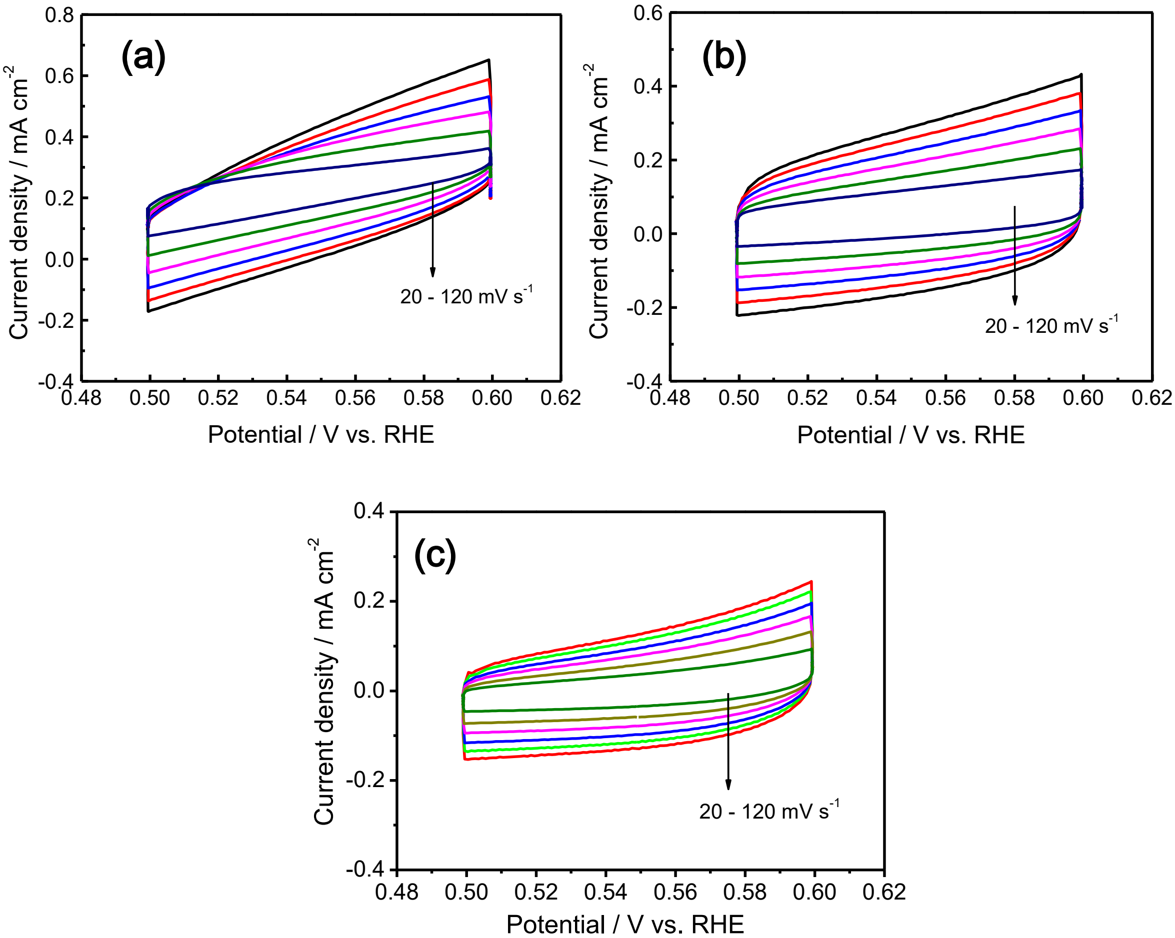


**Figure S15.** CV curves recorded in 1M KOH at different scan rates in the region of 0.5~0.6 V vs. RHE for (a) CoMo/$CoMoO_x$@C, (b) CoMo/$CoMoO_x$ and (c) CoMo.

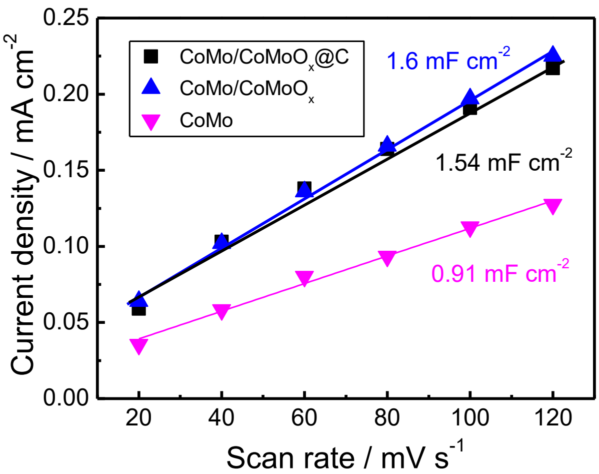


**Figure S16.** Plots showing the extraction of the electrochemical double layer capacitance ($C_{dl}$).

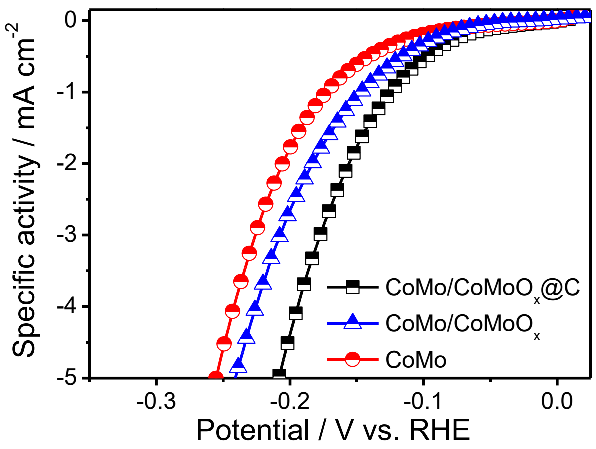


**Figure S17.** Specific activity obtained from the normalization of the HER current by the ECSA.

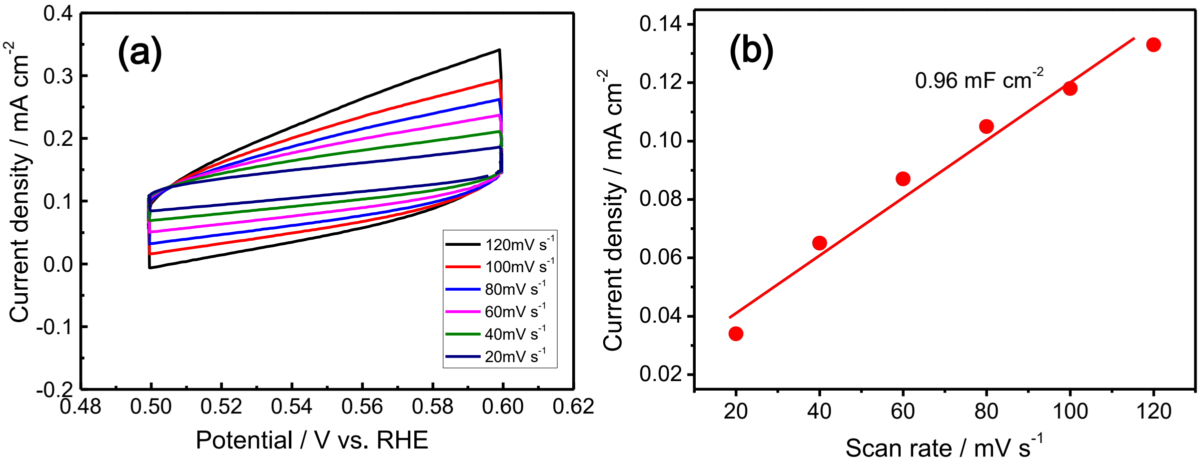


**Figure S18.** (a) CV curves for heat-treated CoMo/$CoMoO_x$@C (100ºC for 12 hours), and (b) the extraction of the electrochemical double layer capacitance ($C_{dl}$). Solution: 1M KOH.

The $C_{dl}$ was 0.96 mF $cm^{-2}$ for CoMo/$CoMoO_x$@C after the heat treatment at 100 ºC. The ECSA was 24 $cm^2$ assuming that the specific capacitance of a planar surface was 40 μF $cm^{-2}$.

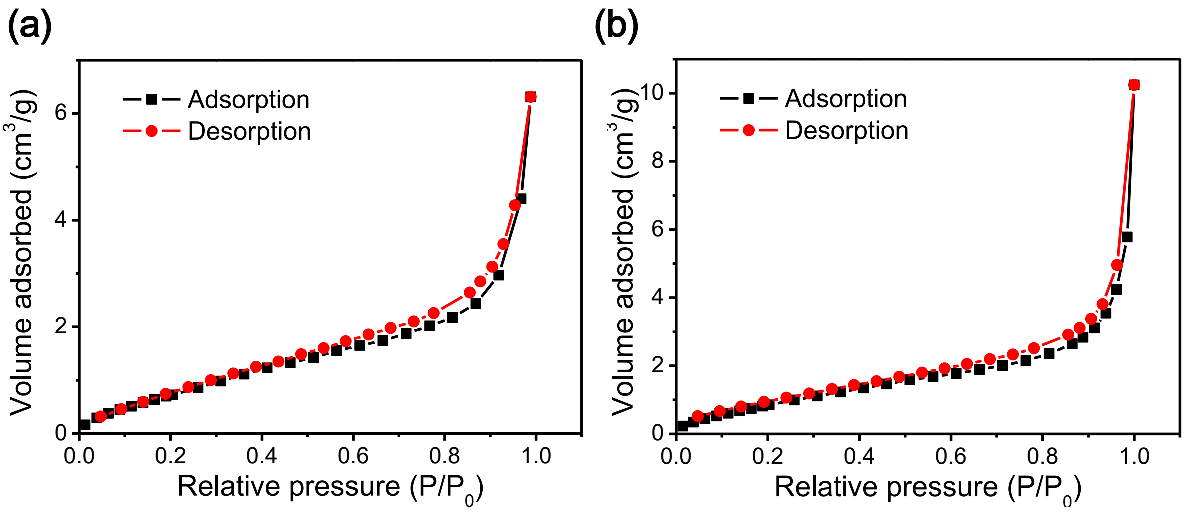


**Figure S19.** The Brunauer-Emmett-Teller (BET) isotherms for (a) as-prepared and (b) heat-treated CoMo/CoMoO$_x$@C (100°C for 12 hours).

The overall isotherm of both materials can be identified as type IV according to the IUPAC classification. The BET surface area was 3.72 and 3.86 $m^2$ $g^{-1}$ for as-prepared and heat-treated CoMo/CoMoO$_x$@C, respectively. The small surface area was attributed to the wrapping of nanoparticles by carbon layer.

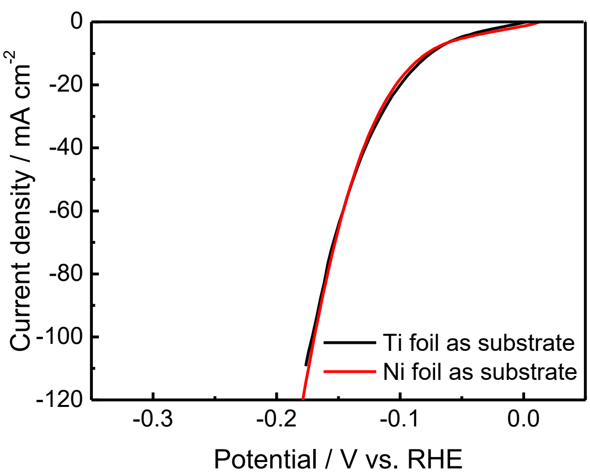


**Figure S20.** The iR-corrected linear sweep voltammetry (LSV) curves of CoMo/CoMoO$_x$@C prepared on different substrates. Scan rate: 5 mV $s^{-1}$. Solution: 1M KOH.

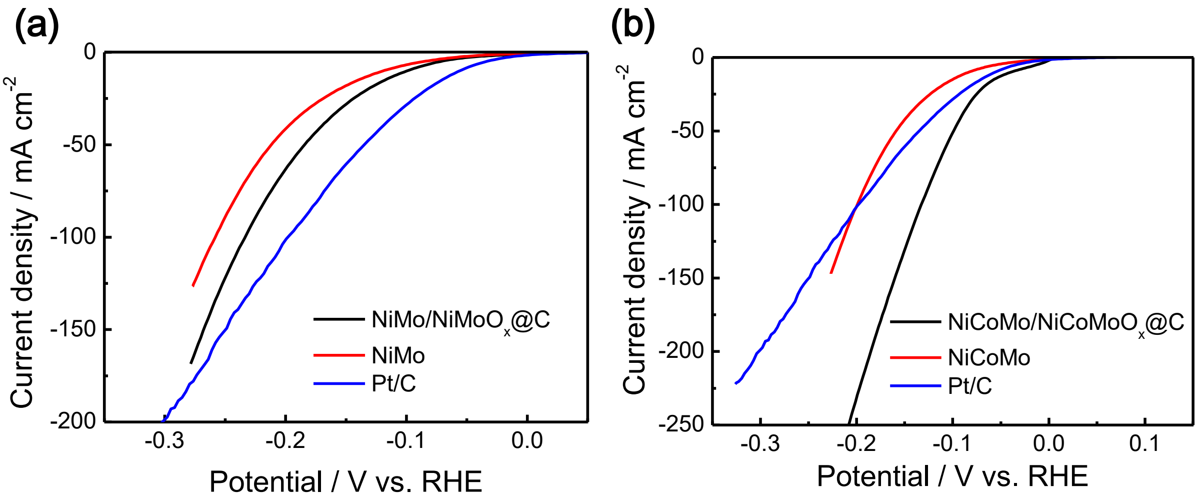


**Figure S21.** The iR-corrected LSV curves of (a) NiMo/$NiMoO_x$@C and NiMo, and (b) NiCoMo/$NiCoMoO_x$@C and NiCoMo. Scan rate: 5 mV $s^{-1}$. Solution: 1M KOH.

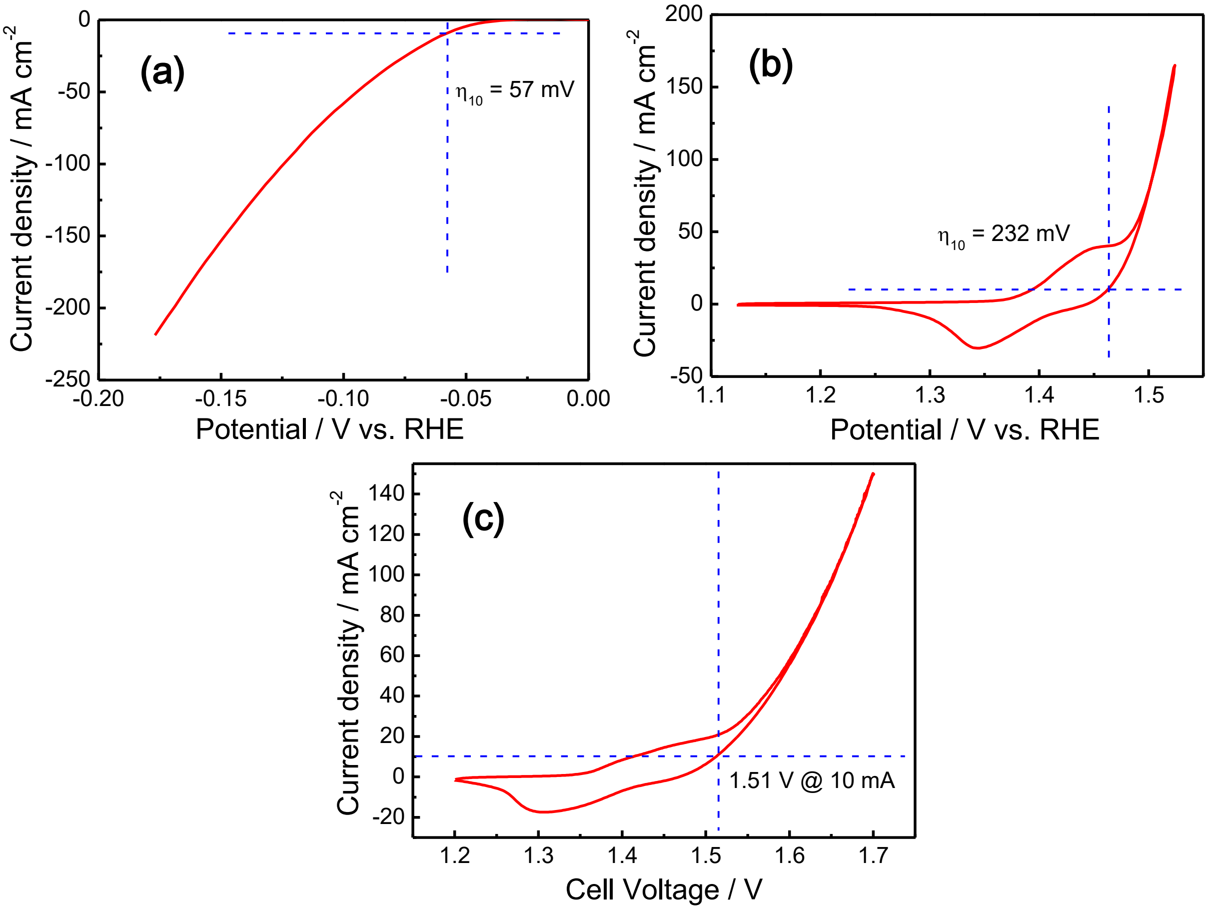


**Figure S22.** The iR-corrected electrocatalytic measurements of NiFeMo/$NiFeMoO_x$ in 1 M KOH. (a) LSV, (b) CV, and (c) the overall water splitting. Scan rate: 5 mV $s^{-1}$.

**Table S1.** Performance comparison between $CoMo/CoMoO_x@C$ and recently reported non- precious HER catalysts.

| Material | Solution | Current collector | $\eta_{10}$(mV) | Tafel slope (mV $dec^{-1}$) | Reference |
|---|---|---|---|---|---|
| $CoMo/CoMoO_x$ @C | 1M KOH | Planar, copper foil | 76 | **75.2** | **This work** |
| $FeCo/Co_2P@NPCF$[1] | 1M KOH | Glassy carbon | 260 | 120 | Adv. Energy. Mater. 2020 |
| $CoMn/CoMn_2O_4$[2] | 1M KOH | 3D, nickel foam | 69 | 90 | Adv. Funct. Mater. 2020 |
| Co@N-CNTs@rGO[3] | 1M KOH | Glassy carbon | 108 | 55 | Adv. Mater. 2018 |
| $C\text{-}Ni_{1\text{-}x}O$[4] | 1M KOH | Nickel foam | 27 | 36 | Nat. Commun. 2020 |
| $LSC\&MoSe_2$[5] | 1M KOH | Glassy carbon | >200 | 34 | Nat. Commun. 2019 |
| Ni-CoP/HPFs[6] | 1M KOH | Glassy carbon | 92 | 71 | Nano Energy 2019 |
| $Ni\text{-}N_x\text{-}C$[7] | 1M KOH | Exfoliated graphene foil | 147 | 114 | Energy Environ. Sci. 2019 |
| $NiCoS@HsGDY@Ni,Co\text{-}MoS_2$[8] | 1M KOH | Carbon paper | 100 | 89.5 | Nat. Commun. 2019 |
| $Zn_{0.08}Co_{0.92}P$ nanowall array[9] | 1M KOH | Titanium mesh | 67 | 39 | Adv. Energy Mater. 2017 |
| NiCoP/rGO[10] | 1M KOH | Carbon paper | 209 | 124.1 | Adv. Funct. Mater. 2016 |
| $CoO_x@CN$[11] | 1M KOH | Glassy carbon | 232 | N. A. | J. Am. Chem. Soc. 2015 |
| $MoNi_4$[12] | 1M KOH | Nickel foam | 15 | 30 | Nat. Commun. 2017 |
| $MoS_2/Ni_3S_2$[13] | 1M KOH | Nickel foam | 110 | 83 | Angew. Chem. 2016 |
| $sc\text{-}Ni_2P^{-}/NiHO$[14] | 1M KOH | Nickel foam | 60 | 75 | Angew. Chem. 2019 |
| $o\text{-}CoSe_2\|P$[15] | 1M KOH | Glassy carbon | 104 | 69 | Nat. Commun. 2018 |
| Ni/NiO[16] | 1M NaOH | Nickel foam | 46 mV @ 20 mA $cm^{-2}$ | 65 | J. Mater. Chem. A 2016 |

| | | | | | |
|---|---|---|---|---|---|
| NiO/Ni-CNT[17] | 1M KOH | Glassy carbon | 80 | 82 | Nat. Commun. 2014 |
| Iron-nickel sulfide ultrathin nanosheets[18] | 0.5M $H_2SO_4$ | Glassy carbon | 105 | 40 | J. Am. Chem. Soc. 2015 |
| Mo-doped $Ni_3S_2$ nano-rods[19] | 1M KOH | Nickel foam | 278 mV @ 100 mA $cm^{-2}$ | 72.9 | J. Mater. Chem. A 2017 |
| NiMo hollow nanorod[20] | 1M KOH | Ti mesh | 92 | 76 | J. Mater. Chem. A 2015 |
| $NiMo_3S_4$/CTs[21] | 0.5M $H_2SO_4$ | Carbon textile | 156 | 46.2 | Nano Energy 2018 |
| $Ni_3FeN$/r-GO[22] | 1M KOH | Nickel foam | 94 | 90 | ACS Nano 2018 |

**Table S2.** Elemental percentage of CoMo/$CoMoO_x$ before and after stability test.

| Elements | Before test / wt.% | After test / wt.% |
|---|---|---|
| O | 10.9 | 1.1 |
| Co | 69.9 | 85.6 |
| Mo | 19.2 | 13.3 |

**Table S3**. Electrical elements fitted by the equivalent circuit in Figure S14.

| | $R_s$ / Ω | $CPE_1$ / mF | $R_{ad}$ /Ω | $CPE_2$ / mF | $R_{ct}$ /Ω |
|---|---|---|---|---|---|
| CoMo/$CoMoO_x$@C | 2.10 | 523 | 0.88 | 730 | 1.80 |
| CoMo/$CoMoO_x$ | 2.39 | 630 | 0.92 | 715 | 5.88 |
| CoMo | 2.45 | 490 | 1.43 | 720 | 20.81 |

**Table S4.** Comparison of overall water splitting performance between NiFeMo/NiFeMoOx and recently reported catalysts.

| **Material** | **Solution** | **Current collector** | **Potential @ 10mA/cm²** | **Reference** |
|---|---|---|---|---|
| NiFeMo/$NiFeMoO_x$ | 1M KOH | Planar, copper foil | 1.51 | **This work** |
| LSC&$MoSe_2$[5] | 1M KOH | Ni mesh | 2.3V @ 100 mA /cm² | Nat. Commun. 2019 |
| CoFeZr oxides nanosheets[23] | 1M KOH | 3D, Ni foam | 1.63 | Adv. Mater. 2019 |
| FeCo/$Co_2P$@NPCF[1] | 1M KOH | Carbon paper | 1.68 | Adv. Energy. Mater. 2020 |
| Ni NP/Ni-N-C[7] | 1M KOH | Graphite foil | 1.58 | Energy & Environ. Sci. 2019 |
| NC–NiCu–NiCuN[24] | 1M KOH | 3D, nickel foam | 1.56 | Adv. Funct. Mater. 2018 |
| O-CoMoS[25] | 1M KOH | Carbon fiber cloth | 1.6 | ACS Catalysis 2018 |
| $Ni_3FeN$/r-GO[22] | 1M KOH | 3D, Ni foam | 1.6 | ACS Nano 2018 |
| Pt-$CoS_2$/CC[26] | 1M KOH | Carbon cloth | 1.55 | Adv. Energy Mater. 2018 |
| NiCoP/rGO[10] | 1M KOH | Carbon fiber paper | 1.59 | Adv. Funct. Mater. 2016 |
| NiFe LDH@NiCoP/NF[27] | 1M KOH | 3D, Ni foam | 1.57 | Adv. Funct. Mater. 2018 |
| $Fe_{0.09}Co_{0.13}$-$NiSe_2$[28] | 1M KOH | Carbon fiber cloth | 1.52 | Adv. Mater. 2018 |
| $Ni_2P$@NiFe hydroxide[29] | 1M KOH | 3D, Ni foam | 1.51 | Chem. Sci. 2018 |
| Ni-Fe NP[30] | 1M KOH | 3D, Ni foam | 1.47 | Nat. Commun. 2019 |
| $Ni_2Fe_1$-Mo[31] | 1M KOH | 3D, Ni foam | 1.66 | J. Mater. Chem. A 2018 |
| EG/$Co_{0.85}Se$/NiFe LDH[32] | 1M KOH | Graphite foil | 1.67 | Energy & Environ. Sci. 2016 |
| V-CoP@a-$CeO_2$[33] | 1M KOH | Carbon cloth | 1.56 | Adv. Funct. Mater. 2020 |

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