Reversing Mg suppression effect on Co-Site water oxidation of $MgCo_2O_4$ based on vanadium-atom electronic affinity synergy with Mg sites toward electronic redistribution

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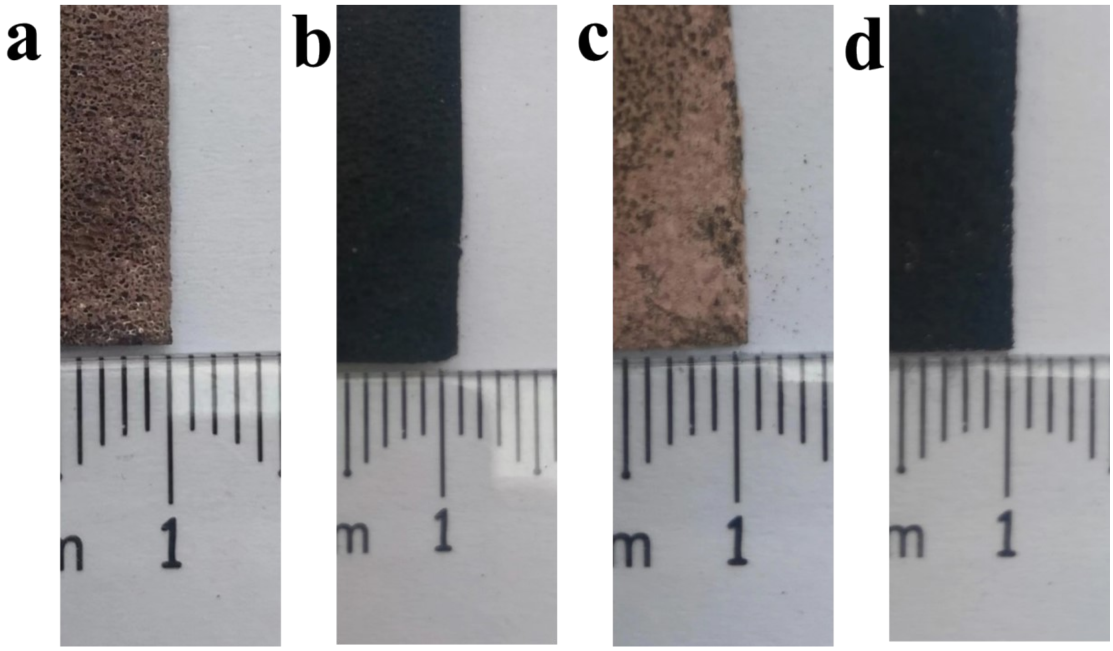

Fig. S1 The optical images of (a) V-$CoOOH@MgCO_3$, (b) V-$MgCo_2O_4@MgO$, (c) $CoOOH@MgCO_3$ (d) $MgCo_2O_4@MgO$.

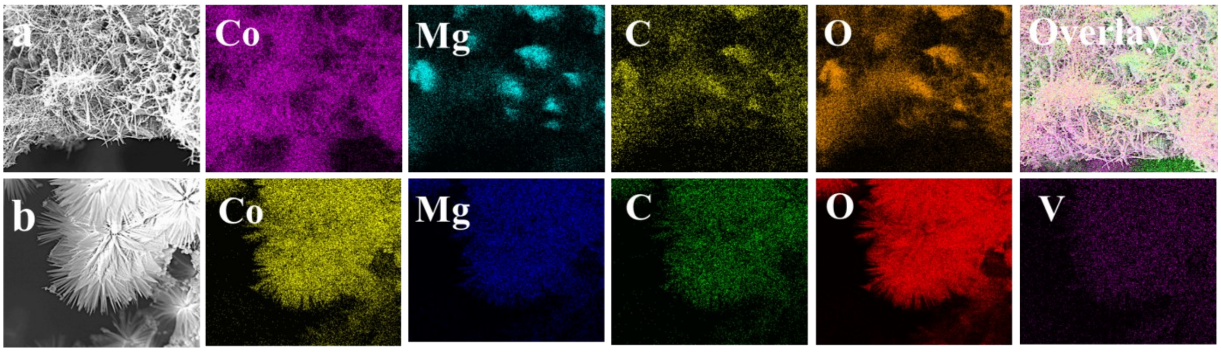

Fig. S2 The SEM images of (a) $MgCo_2O_4$@MgO (b) V-CoOOH@$MgCO_3$ and their corresponding EDX element mapping images.

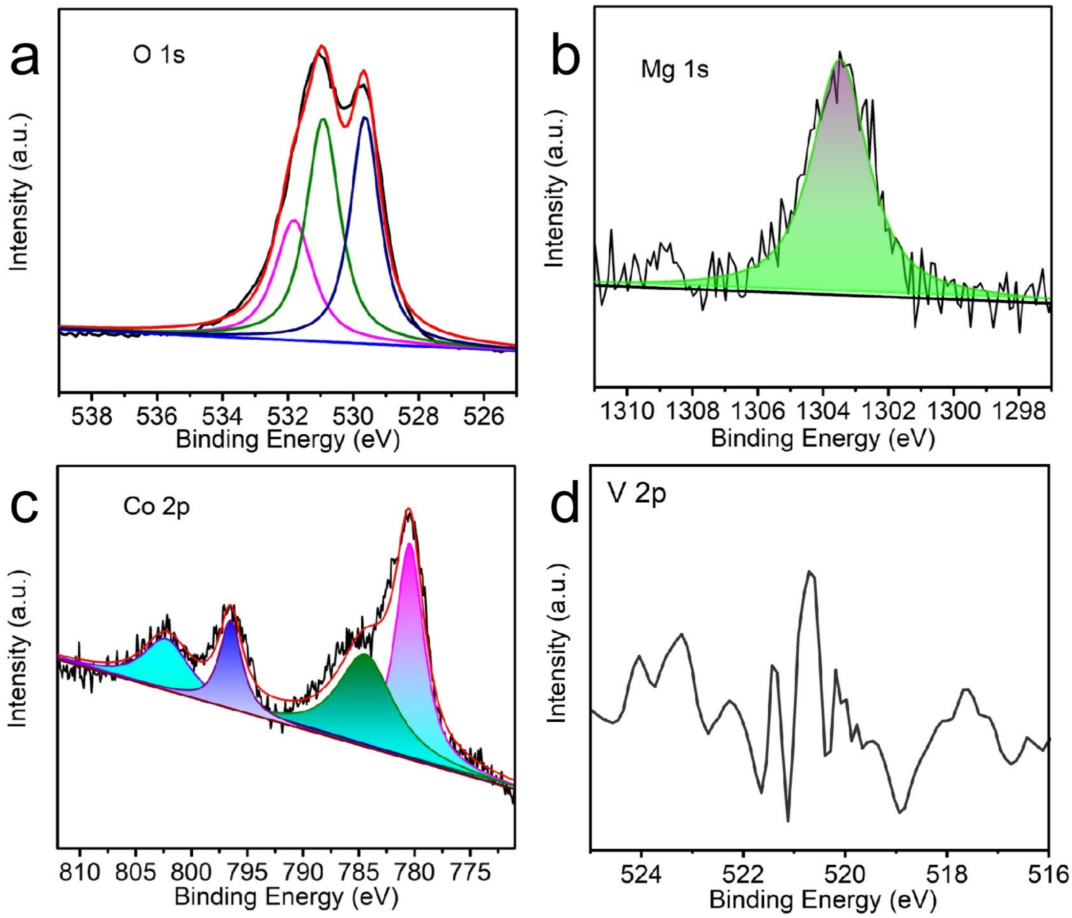

Fig. S3 XPS spectra of (a) O 1s, (b) Mg 1s, (c) Co 2p, (d) V 2p for $MgCo_2O_4$@MgO.

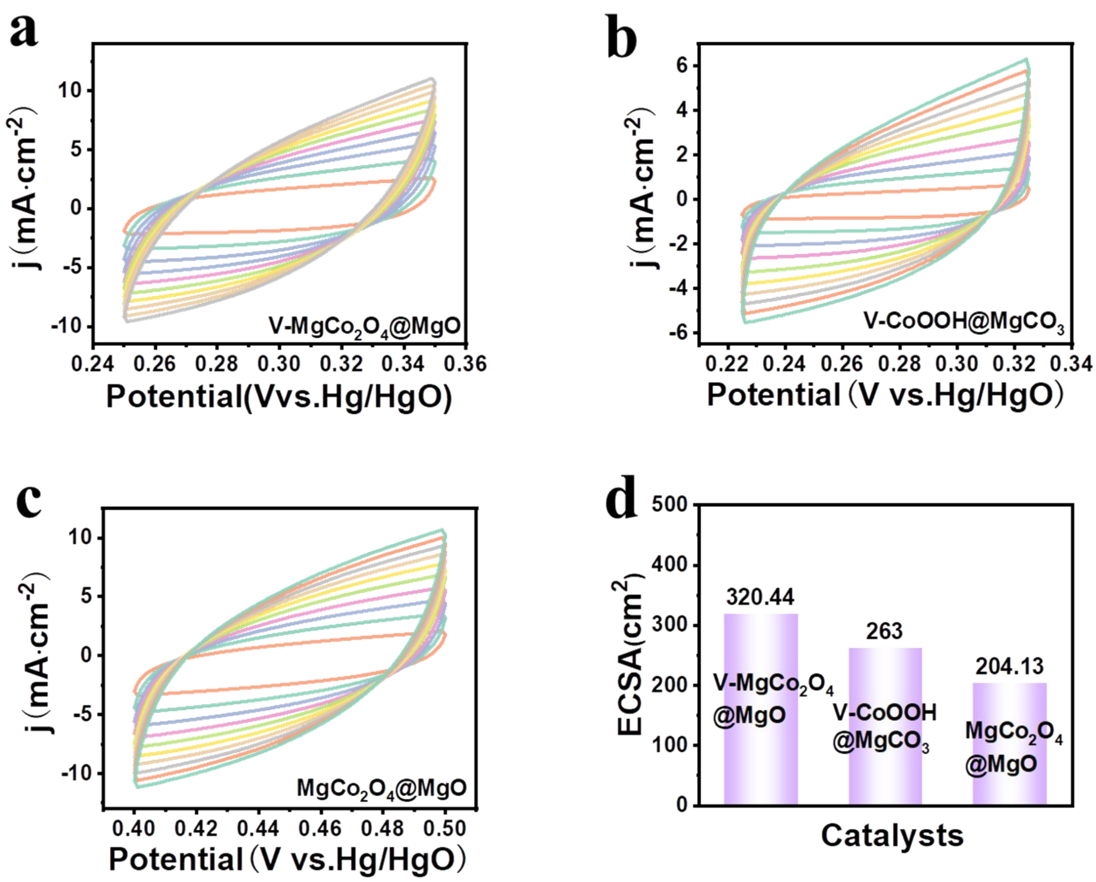

Fig. S4 CVs for (a) V-$MgCo_2O_4$@MgO, (b) V-CoOOH@$MgCO_3$, (c) $MgCo_2O_4$@MgO at scan rates from 10 to 100 mV·s^{-1} in 1.0 M KOH. (d) ECSA values of V-$MgCo_2O_4$@MgO, V-CoOOH@$MgCO_3$ and $MgCo_2O_4$@MgO.

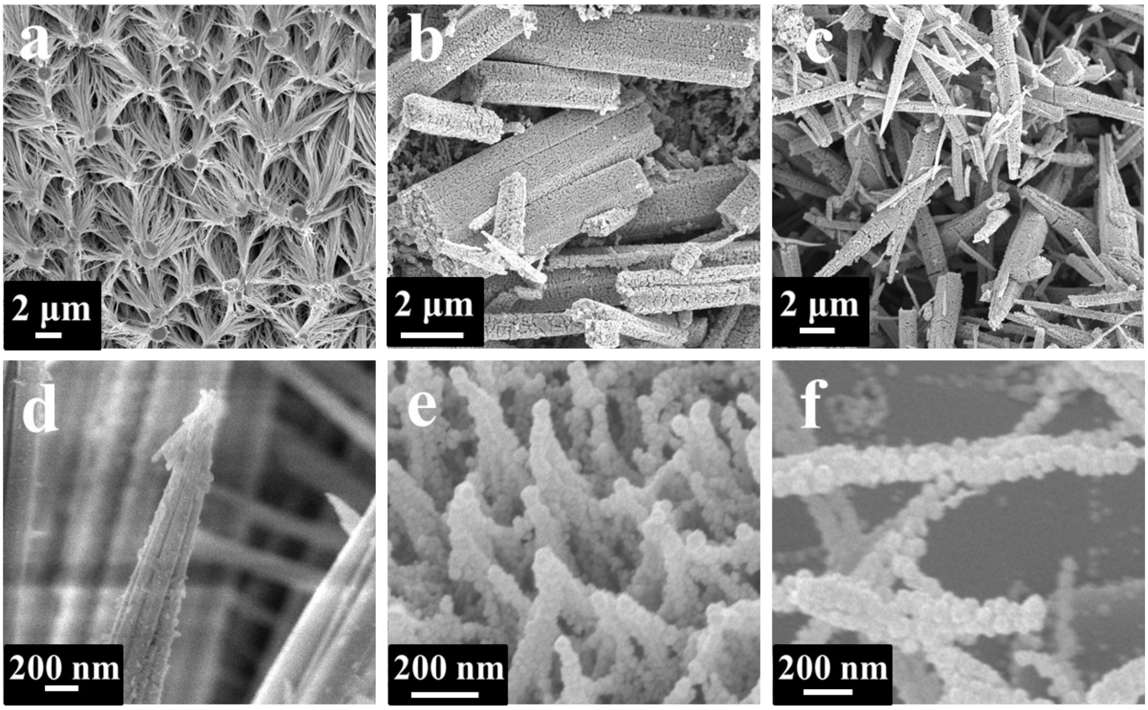

Fig. S5 The SEM images of (a and d) V-$CoOOH@MgCO_3$, (b and e) V-$MgCo_2O_4@MgO$ and (c and f) $MgCo_2O_4@MgO$ after electrolysis for 24 hours at different magnifications.

Table S1. *Comparison of OER performances for V-$MgCo_2O_4$@MgO with other electrocatalysts recently reported in 1.0 M KOH.*

Catalyst	**η@100mA cm^{-2} (mV)**	**Ref.**
V-$MgCo_2O_4$@MgO	240	This work
Ni_5P_4/NiP_2/NiFe LDH	243	*J. Mater. Chem. A* **2018**, *6*, 13619−13623.
$Fe(PO_3)_2$	221	*P NATL A SCI.* **2017**, *114*, 5607−5611.
CoNiP@LDH	249	*ACS Appl. Energy Mater.* **2018**, *1*, 623−631.
CoFe@CoNi	262	*Chem. Cat. Chem.* **2022**, *14*, e202200347.
Ni@NiFe LDH	269	*J. Mater. Chem. A* **2019**, *7*, 21722−21729.
NiFe LDHs	280	*Adv. Energy Mater.* **2018**, *8*, 1703341.
NiMoN/NiF	294	*ACS Appl. Mater. Interfaces* **2018**, *10*, 30400−30408.
$CoSe_2$/CoP	299	*Part. Part. Syst. Charact.* **2018**, *35*, 1800135.
Cu@CoFe LDH	300	*Nano Energy* **2017**, *41*, 327−336.
Ni_3FeN	300	*ACS Catal.* **2018**, *8*, 9686−9696.
FeOOH/Co/FeOOH	309	*Angew. Chem.-Int. Edit.* **2016**, *55*, 3694−3698.
$W_{0.5}Co_{0.4}Fe_{0.1}$/NF	310	*Angew. Chem.-Int. Edit.* **2017**, *56*, 4502−4506.
Oxygenated-$CoSe_2$-$MoSe_2$	310	*ACS Catal.* **2018**, *8*, 4612−4621.
NiFeCr/NF	318	*Energy Environ. Sci.* **2020**, *13*, 4225−4237.

$Fe_{0.09}Co_{0.13}$-$NiSe_2$	330	*Adv. Mater.* **2018**, *30*, 1802121.
$Ni_{0.94}Fe_{0.06}Se_2$	332	*J. Mater. Chem. A* **2020**, *8*, 8113−8120.
CoFe-PBA	339	*J. Mater. Chem. A* **2021**, *9*, 2135−2144.
$Fe_{0.96}S/Fe(OH)_3$	341	*Appl. Catal. B-Environ.* **2019**, *246*, 337−348.
CoOOH/Cu	358	*ACS Sustain. Chem. Eng.* **2021**, *9*, 12300−12310.
Ni-B/NF	360	*Nanotechnology* **2016**, *27*, 12LT01.
Fe-CoO	370	*Inorg. Chem. Front.* **2020**, *7*, 3327−3339.
CoFe(OH)x	371	*Catal. Sci. Technol.* **2020**, *10*, 215−221.
NiMoN-CF	389	*ChemSusChem* **2018**, *11*, 3198−3207.
NiO/Co_3O_4	394	*ACS Catal.* **2021**, *10*, 12376−12384.
two-tiered NiSe	410	*Adv. Energy Mater.* **2018**, *8*, 1702704.
Ni3N	420	*J. Am. Chem. Soc.* **2015**, *137*, 4119−4125.
NiCoP/C	430	*Angew. Chem.-Int. Edit.* **2017**, *56*, 3897−3900.
NiO_X/Ni	469	*Nanoscale* **2020**, *11*, 22261−22269.
Ni_3FeN/CC	494	*ACS Appl. Mater. Interfaces* **2018**, *10*, 3699−3706.

Table S2. *Comparison of HER performances for V-$MgCo_2O_4$@MgO with other electrocatalysts recently reported in 1.0 M KOH.*

Catalyst	η@10mA cm^{-2} (mV)	Ref.
V-$MgCo_2O_4$@MgO	105	This work
$NiCo_2P_x$	58	*Adv. Mater.* **2017**, *29*, 1605502.
$Ni_{0.89}Co_{0.11}Se_2$	85	*Adv. Mater.* **2017**, *29*, 1606521.
NiP_2 NS/CC	102	*Nanoscale* **2014**, *6*, 13440−13445.
CoMnP/Ni_2P/NF	108	*J. Mater. Chem. A* **2021**, *9*, 22129−22139.
NiMoN film	109	*Adv. Energy Mater.* **2016**, *6*, 1600221.
NiFeP/SG	115	*Nano Energy* **2019**, *58*, 870−876.
ReS_2/CFP	116	*Nano Energy* **2018**, *46*, 305−313.
Co_4N-$VN_{1-x}O_x$/CC	118	*Appl. Catal. B-Environ.* **2018**, *241*, 521−527.
$NiCo_2O_4$@$CoMoO_4$/NF-7	121	*J. Mater. Chem. A* **2018**, *6*, 16950−16958.
Co_xNi_yP	129	*Adv. Funct. Mater.* **2017**, *27*, 1703455.
Ni_2P	136	*Nano Res.* **2020**, *13*, 2098−2105.
FeNi-LDH/CoP/CC	138.6	*Angew. Chem.-Int. Edit.* **2019**, *58*, 11903−11909.
3D-MoS_2/G	143	*Nano Energy* **2019**, *61*, 611−616.

FeCoNi	149	*ACS Catal.* **2017**, *7*, 469−479.
NiCoFeP/C	149	*ChemComm* **2019**, *55*, 10896−10899.
CoNiP@NF	155	*J. Mater. Chem. A* **2016**, *4*, 10195−10202.
$(Ni_{0.33}Co_{0.67})S_2$ NWs/CC	156	*ACS Appl. Mater. Interfaces* **2018**, *10*, 27723−27733.
Co_2P/Co foil	157	*J. Mater. Chem. A* **2017**, *5*, 10561−10566.
FeP_2–NiP_2@PC	179	*ACS Appl. Mater. Interfaces* **2020**, *12*, 727−733.
Co_1Mn_1CH/NF	180	*J. Am. Chem. Soc.* **2017**, *139*, 8320−8328.
Co_xP/N-doped C	187	*Carbon* **2019**, *145*, 694−700.
CoP/Ni_2P	200	*RSC Adv.* **2021**, *11*, 22467−22472.
Ni_3Se_2	203	*Nano Energy* **2016**, *24*, 103−116.
Co_2P/CoNPC	208	*Adv. Mater.* **2020**, *32*, 2003649.
CoP	209	*J. Am. Chem. Soc.* **2018**, *140*, 2610−2618.
$CoNi_2Se_4$	220	*ChemComm* **2017**, *53*, 5412−5415.
bulk MoB	225	*Angew. Chem.-Int. Edit.* **2012**, *51*, 12703−12706.
FeCo/Co_2P@NPCF	260	*Adv. Energy Mater.* **2020**, *10*, 1903854.
Co_2P@N, P-PCN	360	*J. Mater. Chem. A* **2016**, *4*, 15501−15510.