## **Supporting Information**

The Role of Phosphate Group in Doped Cobalt Molybdate: Improved Electrocatalytic Hydrogen Evolution Performance

Siyu Zhao<sup>1</sup>, Jasper Berry-Gair<sup>1</sup>, Wenyao Li<sup>2,3</sup>, Guoqiang Guan<sup>5</sup>, Manni Yang<sup>1</sup>, Jianwei Li<sup>1</sup>, Feili Lai<sup>5</sup>, Furio Corà<sup>1</sup>, Katherine Holt<sup>1</sup>, Dan J.L. Brett<sup>3</sup>, Guanjie He<sup>1,3,4</sup>\* and Ivan P. Parkin<sup>1</sup>\*

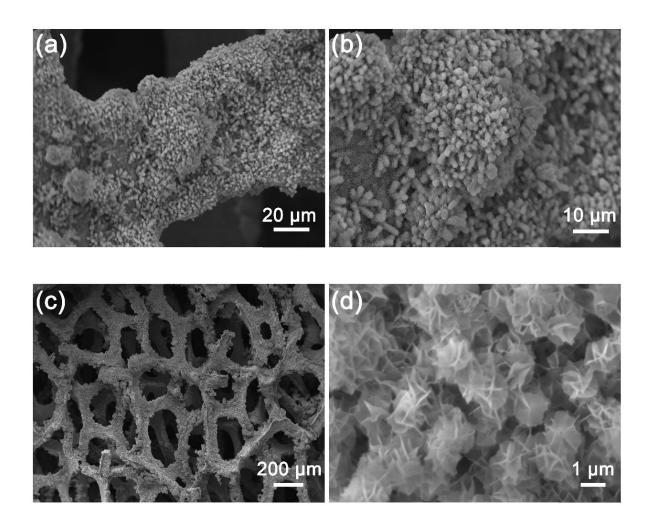
<sup>1</sup>Christopher Ingold Laboratory, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K. Email: g.he@ucl.ac.uk; i.p.parkin@ucl.ac.uk

<sup>2</sup>School of Materials Engineering, Shanghai University of Engineering Science, Shanghai 201620, China.

<sup>3</sup>Electrochemical Innovation Lab, Department Chemical Engineering, University College London, London WC1E 7JE, U.K.

<sup>4</sup>School of Chemistry, University of Lincoln, Joseph Banks Laboratories, Green Lane, Lincoln, LN6
7DL, United Kingdom

<sup>5</sup>State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China



**Figure S1.** (a, b) SEM image of Ni Foam/CMO-350. (c, d) SEM image of Ni Foam/CMP-350.

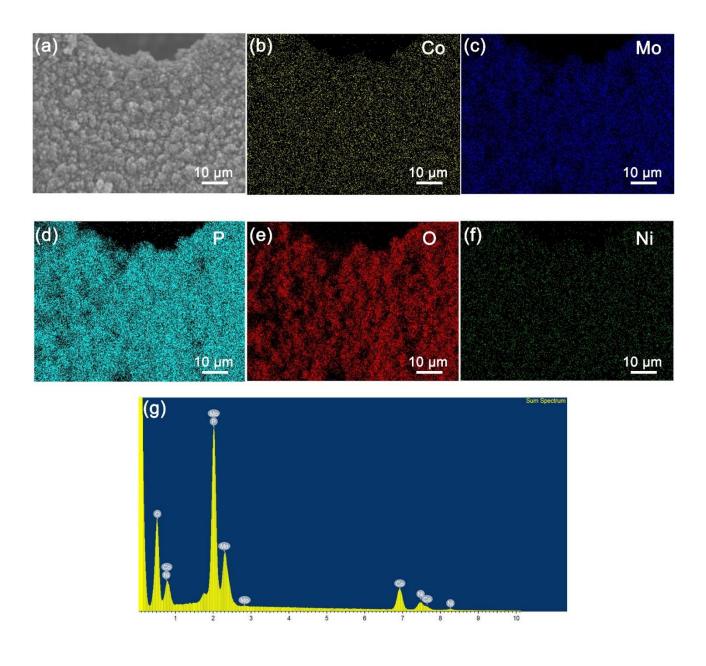


Figure S2. EDX mapping images of Ni foam/CMP-350.

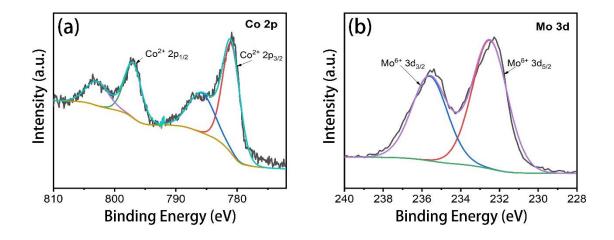


Figure S3. XPS spectra of (a) Co, (b)Mo of Ni Foam/CMO-350

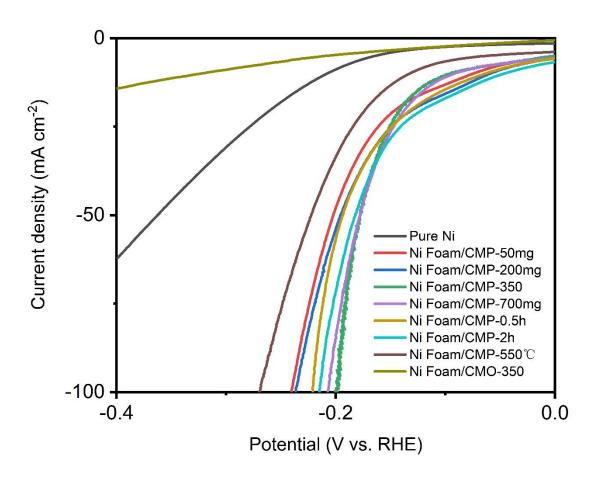
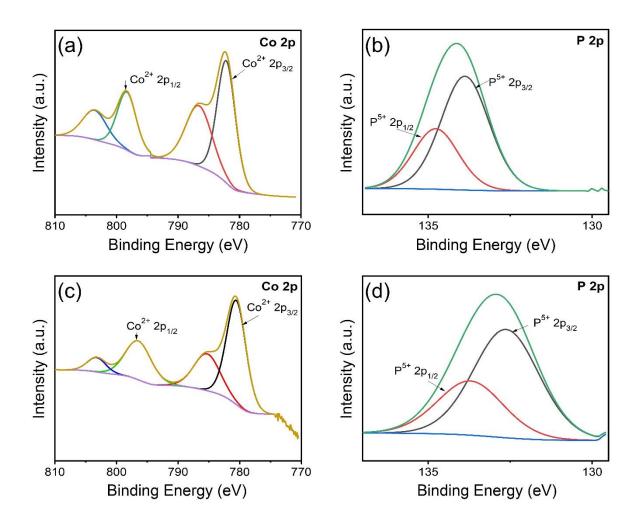


Figure S4. Polarization curves of electrodes in 1M KOH.



**Figure S5.** XPS spectra of Ni foam/CMP-350 before (a) Co 2p, (b) P 2p and after (c) Co 2p, (d) P 2p stability test (j = 10mA cm<sup>-2</sup>, 48h).

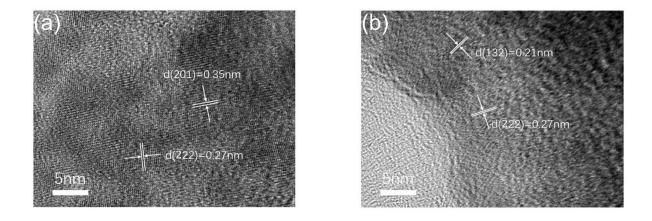
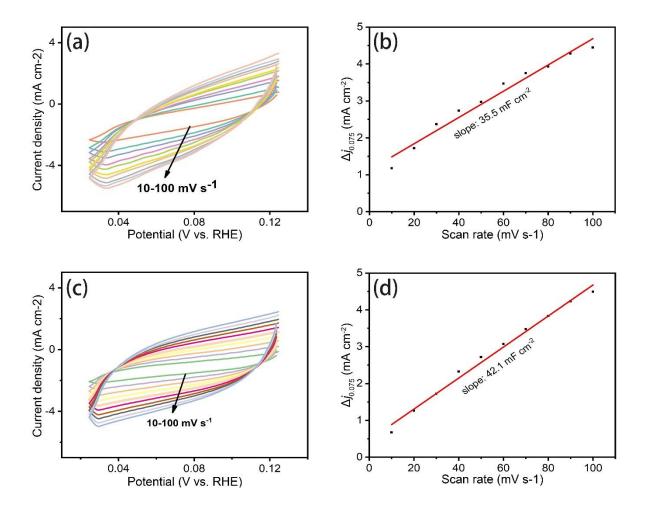
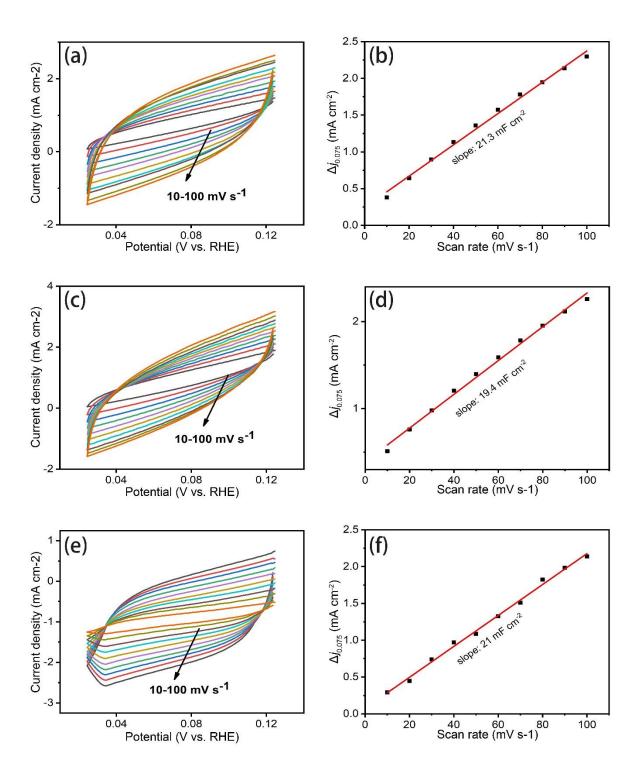


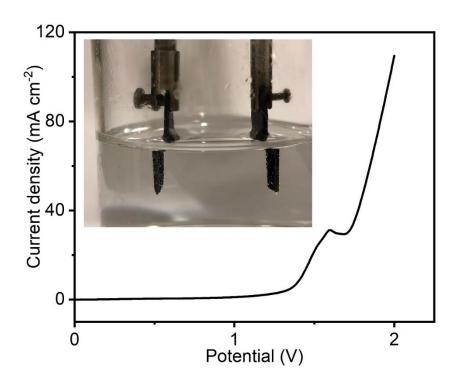
Figure S6. TEM images of Ni Foam/CMP-350 before (a) and after (b) stability test.



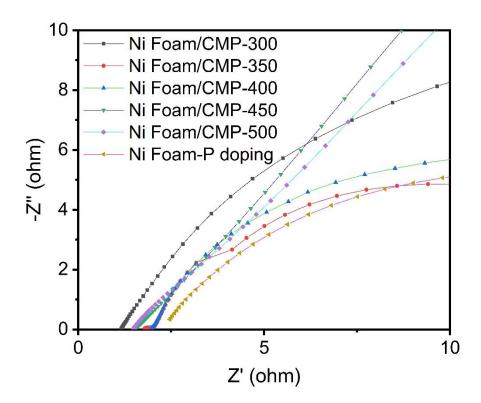
**Figure S7.** (a) CVs of Ni Foam/CMP-350 with different scan rates from 10 to 100 mV s-1. (b) The capacitive current at 0.075 V as a function of the scan rate for Ni Foam/CMP-350. (c) CVs of Ni Foam/CMP-500 with different scan rates from 10 to 100 mV s-1. (d) The capacitive current at 0.075 V as a function of the scan rate for Ni Foam/CMP-500.



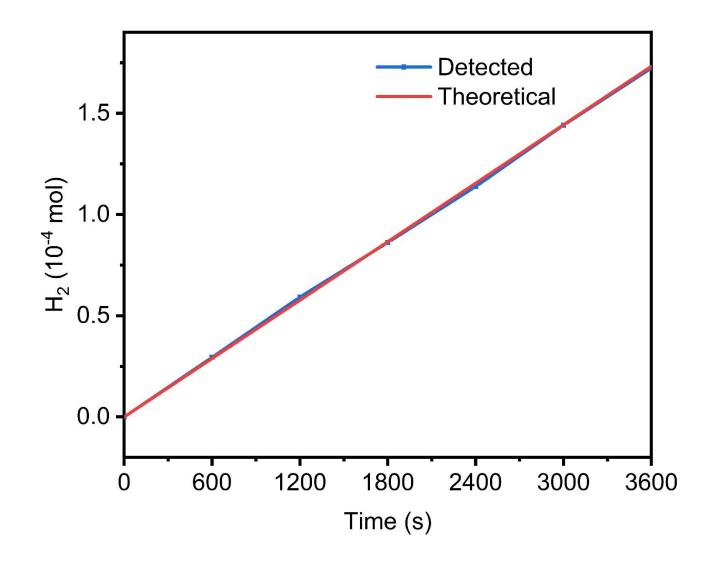
**Figure S8.** (a) CVs of Ni foam/CMP-300 with different scan rates from 10 to 100 mV s<sup>-1</sup>. (b) The capacitive current at 0.075 V as a function of the scan rate for Ni foam/CMP-300. (c) CVs of Ni foam/CMP-400 with different scan rates from 10 to 100 mV s<sup>-1</sup>. (d) The capacitive current at 0.075 V as a function of the scan rate for Ni foam/CMP-400. (e) CVs of Ni foam/CMP-450 with different scan rates from 10 to 100 mV s<sup>-1</sup>. (f) The capacitive current at 0.075 V as a function of the scan rate for Ni foam/CMP-450.



**Figure S9.** Polarization curve of Ni Foam/CMP-350 catalyst for overall water splitting in 1M KOH at a scan rate of 2mV/s. Ni Foam/CMP-350 electrodes were used as both working and counter electrodes. Inset: Graph of two-electrodes cell during reaction.



**Figure S10.** Nyquist plots of electrochemical impedance spectra (EIS) of sample electrodes recorded in 1M KOH solution.



**Figure S11.** The theoretical (red) and detected (blue) values represent the expected and observed amount of H2 produced versus time for Ni foam/CMP-350.

**Table S1.** The XPS quantitative results of Ni foam/CMP electrodes prepared at different conditions.

Sample	Co:P
Ni foam/CMP-0.5h	1:3.63
Ni foam/CMP-2h	1:3.38
Ni foam/CMP-50mg	1:1.48
Ni foam/CMP-200mg	1:2.59
Ni foam/CMP-500mg	1:3.66
Ni foam/CMP-700mg	1:5.16

**Table S2.** Experimental and computational lattice parameters for β-CoMoO<sub>4</sub> and P-doped β-CoMoO<sub>4</sub>. Computational and experimental values match well, and there is little overall change after P-doping.

	a / Å	b / Å	c / Å	α/°	β/°	γ/°
CoMoO <sub>4</sub>	10.21	9.27	7.022	90.0	106.9	90.0
Experimental						
CoMoO <sub>4</sub>	10.26	9.31	7.07	90	107.4	90
Computational						
P-CoMoO <sub>4</sub>	10.14	9.29	6.97	90	107.0	90
Computational						