Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information for:

Using Earth Abundant Materials for the Catalytic Evolution of Hydrogen from Electron-Coupled-Proton-Buffers

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Contents

SI-1: General Experimental Remarks:

The solvents used throughout the experimental procedures were purchased from Sigma Aldrich. All chemicals purchased for the synthesis of the earth abundant catalysts were purchased from Sigma Aldrich. Nafion N-117 (0.18mm thick) membrane, used in the H-cells, was purchased from Alfa Aesar. Carbon felt, used as a high surface area working electrode, was purchased from either Alfa Aesar (43199, 3.18mm thick, 99.0%) or FuelCellStore (AvCarb G100 Soft Graphite Battery Felt, 3.2mm thick, 99%). Nitrogen (OFN) and argon (Pureshield) gas cylinders were purchased from BOC. All chemical reagents and solvents were used as purchased. Solutions, both electrolytes and compounds for testing, were made up in reagent grade water (18 $M\Omega cm^{-1}$ resistivity). The pH of solutions was determined using a Hanna HI 9124 waterproof pH meter. Synthesis of the nickel phosphide catalysts was conducted in a custom built schlenk line, using dried nitrogen as the atmospheric gas. Powder XRD was performed on a Panalytical X'Pert Pro using Cu Kα1 radiation over a $5^o \leq 2\theta \leq 85^o$ range for 1 hour with a step size of 0.0167^o. SEM-EDX samples were taken using a Philips XL30 ESEM (Environmental Scanning Electron Microscope) using a tungsten source (acceleration voltage = 25kV) and a secondary electron detector. EDX measurements were taken with an Oxford Instruments X-act spectrometer with a silicon drift detector that had been coupled to the microscope device. The samples were coated in gold at 25 keV using a gold splutter coater to prevent charging of their surfaces. ICP-OES was performed on an Agilent 5100 and calibrated to a range (0.5ppm to 10ppm) of measured ppm solutions of Ni and P.

SI-2: Electrochemical methods

Three-electrode electrochemical studies were performed on either a CH Instruments CHI760D or a Biologic SP-150 potentiostat. Unless otherwise stated, all cyclic voltammetry electrochemistry experiments were performed using a 3mm glassy carbon disc working electrode (Princeton Applied Research), a large area Pt mesh or Pt wire counter electrode and a saturated Ag/AgCl reference electrode (BASi) under room temperature, pressure and ambient atmospheric conditions. Cyclic voltammetry experiment solutions were conducted in a 1 pot system that was not stirred and iR compensation was enabled. Linear sweep voltammetry experiments were conducted using either a 3mm diameter glassy carbon working electrode (Princeton Applied Research) or a 1.6mm inner diameter carbon paste electrode using a mixture of carbon paste (BASi Japan) and the catalyst to be tested in a 1:4 of catalyst to carbon paste. A large area Pt mesh or Pt wire was used as a counter electrode and an Ag/AgCl reference electrode (BASi) were also used under room temperature, pressure and ambient atmospheric conditions. Linear sweep voltammetry experiments were conducted at a scanning speed of $0.1Vs^{-1}$ with stirring and iR compensation enabled. Bulk electrolysis reactions were carried out in a custom built H-cell arrangement, where a piece of Nafion N-117 (0.178mm thick) separated the counter and working electrode compartments. The counter compartment used a large area Pt mesh or Pt wire (BASi) as an electrode and was stirred vigorously to remove any gas bubbles accumulating on the counter electrode. The working compartment contained a large area (1cm x 4cm) carbon felt working electrode attached *via* a silver wire (Alfa Aesar) to the leads of the potentiostat along with an Ag/AgCl reference electrode (BASi). The working compartment was stirred vigorously and bubbled with argon gas throughout the experiment to remove any oxygen from the solution. All potentials were converted to RHE voltages using E(RHE) = E(Ag/AgCl) + 0.197V + 0.059*pH).

Each POMs redox potentials were determined *via* cyclic voltammetry. The reduction potentials of each POM were noted and used to fully electrochemically reduce each POM by two electrons under continuous bubbling of argon. These reduced POMs were then introduced to each catalyst in an argon filled gas measurement setup. Each experiment was video recorded for 5 minutes to obtain the starting rate and left overnight to obtain the total volume of gas evolved from the combination of catalyst and POM. The gases produced were tested using gas chromatography to confirm the production of hydrogen.

SI-3: Electrochemical testing and reduction of redox mediators

Cyclic Voltammetry

The testing process involved firstly determining the redox potentials of the various POMs. 10 ml of a 25 mM solution for each POM to be tested was made up using deionised water for the cyclic voltammetry experiments. The upper and lower potentials scanned were altered between each POM to observe the full set of redox waves with a scanning rate of 0.1V s^{-1} and an unstirred solution. iR compensation was used in all instances. 10 and 100 cycles (i.e. alternating reduction and oxidation) were used to determine the redox potentials of the POMs and the stability over multiple redox reactions.

Electrochemical reduction

Typically, 25 ml of a 0.1 M solution of the POMs would be prepared in deionised water with a final pH of: STA = 0.61, PTA = 0.42, SMA = 0.69 and PMA = 0.42. Each was placed in the working compartment of a two-compartment H-cell. All POMs dissolved readily in water except with SMA, which came as a solution and was diluted to 0.1 M. The counter compartment was filled with 1 M H_3PO_4 (pH = 0.84) and equipped with a large area Pt mesh counter electrode. 1 M Phosphoric acid was chosen as the electrolyte for the gas evolving side of the H-cell in order to maintain a pH and ionic concentration similar to the mediator containing working compartment. Phosphate was also chosen for its relative stability to both oxidation and reduction. Both chambers were separated by a Nafion membrane to allow for the movement of protons between the two chambers but prevent the movement of anions. All solutions were bubbled with argon, stirred vigorously and kept under an argon atmosphere throughout the experiment. Each POM was reduced by two electrons at their equivalent 2 electron reduction potentials by passing 482.43 C of charge at the working electrode. STA was reduced at –0.327 V, PTA was reduced at –0.278 V, SMA was reduced at +0.428 V and PMA was reduced at +0.522 V, all vs RHE. Degassing of the solutions was essential to prevent reoxidation of the reduced species *via* atmospheric oxygen, otherwise a lower yield of gas evolution was always observed.

SI-4: Hydrogen evolution from ECPB's in the presence of purchased and synthesised catalysts

Pt/C (1% wt, 50 mg), Ni_5P_4 (bulk, 50 mg), Ni_2P (bulk, 50 mg), MoS_2 (bulk, 50 mg), Mo_2C (bulk, 50 mg) and Ni_2P (1% /10% wt silica, 50 mg) were tested for catalytic hydrogen evolution from reduced POMs STA, PTA, PMA and SMA. 25 ml of a 0.1 M solution of a 2e- reduced POM was prepared *via* bulk electrolysis and 20 ml was used in the spontaneous hydrogen evolution reaction. The theoretical amount of hydrogen that could be evolved in a complete $2e^-$ re-oxidation of each POM is 48.9 ml at 25 °C (see Equation S1). If only 1-electron oxidation occurred, then only 24.45 ml would be produced and the resulting mediator solution would contain the 1-electron reduced form.

The 2-electron reduced mediator was reacted with the various catalysts as follows. A RBF with a schlenk tap was equipped with a stirrer bar and 50 mg of each catalyst. *Via* a pressure-equalising dropping funnel, the freshly reduced compounds were added to the catalyst under an argon atmosphere and stirred vigorously. The evolving gas was captured in a measuring cylinder filled with water, connected *via* tubing and the schlenk tap (see Figure S1)

The oxidised forms of the POMs were also tested but no gas evolution was observed.

$$\frac{C_{redox} \times V_{redox} \times z \times V_{ideal}}{2} = Theoretical\ H_2\ volume$$

Equation S1: Theoretical volume of hydrogen that can be evolved from a redox mediator in L (C_{redox} = Concentration of redox mediator in mol L^{-1}, V_{redox} = Volume of redox mediator in L, z = number of electrons, V_{ideal} = Volume of an ideal gas at 25°C = 24.465 L mol^{-1})

Previously used catalysts Mo_2C and Ni_2P (10% wt silica) were utilised a second time with freshly reduced 0.1M STA in a setup similar to the previous paragraph. From the initial usage, the catalysts were filtered from the POM solution, washed thoroughly with water and dried in a desiccator overnight. A small loss of catalyst mass was observed as it was not possible to collect 100% of the catalyst from the filter paper. The results of reusing the catalysts are recorded in section SI-8

Figure S1: Hydrogen evolving test rig

SI-5 Theory of variation of hydrogen evolution

Taking STA as an example, the two processes occurring when 2 electron reduced STA is oxidised by a catalyst can be described as below:

1. $H_6[SiW_{12}O_{40}] \rightarrow H_5[SiW_{12}O_{40}] + e^- + H^+$ E = -0.22 V vs NHE

   $2H^+ + 2e^- \rightarrow H_2$ E = 0 V vs NHE

And

2. $H_5[SiW_{12}O_{40}] \rightarrow H_4[SiW_{12}O_{40}] + e^- + H^+$ E = 0.01 V vs NHE

   $2H^+ + 2e^- \rightarrow H_2$ E = 0 V vs NHE

For redox equations 1.

$E_{cell} = E_{reduction} – E_{oxidation} = 0\text{ V} – (-0.22\text{ V}) = 0.22\text{V}$

From the Nernst Equation:

$$\Delta E = E_{cell} - \frac{0.059\ V}{n} \log Q$$

Q is < 1 when STA is in the $[SiW_{12}O_{40}]^{-6}$ form, then the $\frac{0.059\ V}{n} \log Q$ term is negative and therefore ΔE is positive (thus reaction is spontaneous, according to the Nernst equation in the form shown in Equation 1 of the main text)

The equilibrium constant, K, for the oxidation of 2 electron reduced STA to 1 electron reduced STA is $2.87*10^7$ and therefore favours the 1 electron reduced STA formation $[SiW_{12}O_{40}]^{-5}$.

For redox equations 2.

$E_{cell} = E_{reduction} – E_{oxidation} = 0\text{ V} – 0.01\text{ V} = -0.01\text{ V}$

E_{cell} is negative, thus the reaction of $[SiW_{12}O_{40}]^{-5} \rightarrow [SiW_{12}O_{40}]^{-4}$ will not go to completion. However when the equilibrium constant is calculated, K = 0.458. As K < 1 the reaction will not go to completion but only a certain quantity of $[SiW_{12}O_{40}]^{-5}$ will be converted to $[SiW_{12}O_{40}]^{-4}$ before an equilibrium is established.

Therefore a 100% oxidation of $[SiW_{12}O_{40}]^{-6} \rightarrow [SiW_{12}O_{40}]^{-4}$ would not occur, and variations in % theoretical H_2 obtained (see Tables 2, 3 and S2) can be attributed to differences in the catalysts HER potentials

For PTA, the two oxidation steps would be:

1. $H_5[PW_{12}O_{40}] \rightarrow H_4[PW_{12}O_{40}] + e^- + H^+$ E = -0.066 V vs NHE

   $2H^+ + 2e^- \rightarrow H_2$ E = 0 V vs NHE

And

2. $H_4[PW_{12}O_{40}] \rightarrow H_3[PW_{12}O_{40}] + e^- + H^+$ E = 0.21 V vs NHE

   $2H^+ + 2e^- \rightarrow H_2$ E = 0 V vs NHE

For redox equations 1.

$E_{cell} = E_{reduction} – E_{oxidation}$ = 0 V – (-0.066 V) = 0.066V

Q is < 1 when PTA is in the $[PW_{12}O_{40}]^{-5}$ form, then the (-(0.059/n)log Q) term is positive and therefore ΔE is positive (thus reaction is spontaneous, according to the Nernst equation in the form shown in Equation 1 of the main text)

The equilibrium constant, K, for the oxidation of 2 electron reduced PTA to 1 electron reduced PTA is 172.7 and therefore favours the 1 electron reduced PTA formation $[PW_{12}O_{40}]^{-4}$.

For redox equations 2.

$E_{cell} = E_{reduction} – E_{oxidation}$ = 0 V – 0.21 V = -0.21 V

E_{cell} is negative, thus the reaction of $[PW_{12}O_{40}]^{-4} \rightarrow [PW_{12}O_{40}]^{-3}$ will not go to completion. When the equilibrium constant is calculated, K = 7.61 * 10^{-8}. As K <<< 1 the reaction will barely occur, which corresponds well with the data reported in Tables 2, 3 and S2.

In both cases, ΔG (from equation 1 of the main text) becomes 0 when ΔE becomes 0 and the reaction ceases to be spontaneous. This occurs when the $\frac{0.059\,V}{n} log\, Q$ term of the Nernst equation equals E_{cell}.

SI-6: Catalyst Synthesis

Ni_5P_4

Ni_5P_4 was synthesised following the procedure from Li *et al.*[1] 0.172 g of $Ni(acac)_2$ (Nickel (II) acetylacetonate) and 10 ml of OAm (oleylamine) were added to a 100 ml 2 neck RBF which was attached to a condenser with a schlenk line connected. The second opening was stoppered and a partial vacuum was established for 20 minutes at 120 °C to remove any water and air from the system. After 20 minutes, the vacuum was turned off and a nitrogen flow was established. The stopper was replaced with a rubber septum and 10 ml of TOP (tri-n-octylphosphine) was syringed into the flask under a nitrogen atmosphere. The rubber septum was replaced by a stopper and the heating mantle was set to ~360 °C for 3 hours. During this time, white phosphorus was emitted from the reaction which was contained within the RBF due to a positive nitrogen pressure. The system was allowed to cool to room temperature naturally by removing the heating mantle and suspending the RBF in air (still connected to the schlenk line and with a nitrogen flow). Once cooled, the black precipitate was washed by firstly sonicating in chloroform for 10 minutes then precipitated with ethanol in a centrifuge. This was repeated 3 times with the washings becoming clear over the course of the repeated washings. Finally, acetone was used to wash the sample 3 times *via* centrifuge and the black powder was dried under vacuum.

Ni_2P

Synthesis of Ni_2P was carried out using a procedure from Laursen *et al.*[2] 0.385 g of $Ni(acac)_2$ was placed in a 2 neck round bottom flask with 2.5 g TOPO (tri-n-octylphosphone oxide). To the RBF was attached a condenser connected to a schlenk line, while the other neck was stoppered.

The RBF was degassed *via* a process of vacuum then refilling the vacated chamber with nitrogen gas three times over the course of 30 minutes. A positive nitrogen pressure was established while the stopper was replaced with a rubber septum. 10 ml of TOP was syringed into the RBF and the stopper was replaced. The heating mantle was set to ~390 ^{o}C and left for 150 minutes under nitrogen. During this time, white phosphorus was emitted from the reaction which was contained within the RBF due to a positive nitrogen pressure. Once the reaction was complete, the flask was removed from the heat source and left to cool to room temperature naturally. The resulting black solution and precipitate was transferred to a centrifuge tube using hexane then diluted to a 4:10:1 ratio by volume using hexane : ethanol : acetic acid. The solution was centrifuged for five minutes and the black powder was recovered. This powder was washed with the same 4:10:1 mixture twice more giving a clear effluent and black pellet at the bottom of the centrifuge tube. The black pellet was washed three times with acetone by centrifuging for 5 minutes at 4000rpm and decanting the solution. The resulting powder was then dried under vacuum in a desiccator.

MoS_2

Synthesis of MoS_2 was carried out following the procedure of Wu *et al.*[3] 0.88 g $(NH_4)_6Mo_{7\text{-}}O_{24}.4H_2O$ (ammonium molybdate tetrahydrate) and 0.94 g CH_3CSNH_2 (thioacetamide) were dissolved in 50 ml NH_4OH (ammonium hydroxide) with stirring to form a homogenous solution. This solution was transferred to a 100 ml Teflon-lined stainless steel autoclave and heated to 220 ^{o}C, at a heating rate of 10 K min^{-1}, for 13 hours. The reaction vessel was cooled to room temperature naturally and the solution plus precipitate was transferred to a centrifuge tube. The samples were collected *via* centrifuging for 5 mins at 4000 rpm before being washed with water and ethanol (three times each for 5 mins at 4000 rpm). The washed product was dried at 60 °C overnight. The catalyst was annealed at 400 °C in air for 2 hours after drying.

α-Mo_2C

Synthesis of α-Mo_2C was carried out following the procedure of Kojima *et al.*[4] Molybdenum oxide (MoO_3) was heated under an ammonia flow (68 ml min^{-1}) at 6 °C min^{-1} to 350 °C, which was then decreased to 1 °C min^{-1} to reach 700 °C and held for 2 hours. This created a γ-Mo_2N precursor that was passivated at ambient temperature using a gas mixture of <0.1 % O_2 and N_2 for 2 hours. The precursor was then heated under a methane/hydrogen gas flow ($CH_4 + 4H_2$) (12 ml min^{-1}) at 6 °C min^{-1} to 350 °C, which was then decreased to 1 °C min^{-1} to reach 700 °C and held for 2 hours before being quenched to room temperature.

Ni_2P (1 % / 10 % wt on Silica)

Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) was dissolved in 10 mL of deionised water and this was added to a silica gel support whilst stirring thoroughly for 30 mins. The supported metal was dried at 100 °C overnight. Diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) (Sigma Aldrich >99 %) was then dissolved in 10 mL of deionised water and this was added to the supported metal precursor, whilst stirring for 30 mins. The mixture was dried at 100 °C overnight. The supported catalyst was calcined in static air at 500 °C for 6 hrs, to ensure decomposition of any nitrates and ammonia that may be still present within the support.

A reduction was carried out in a silica glass fixed bed flow reactor under a hydrogen/argon gas mixture (BOC 75 % H_2: 25 % Ar). The flow rate of the reduction was 60 mL min^{-1}. When synthesising Ni_2P the reduction was carried out at 700 °C for 4 hrs.

SI-7: Characterisation of catalysts

Ni_5P_4 (Bulk)

XRD

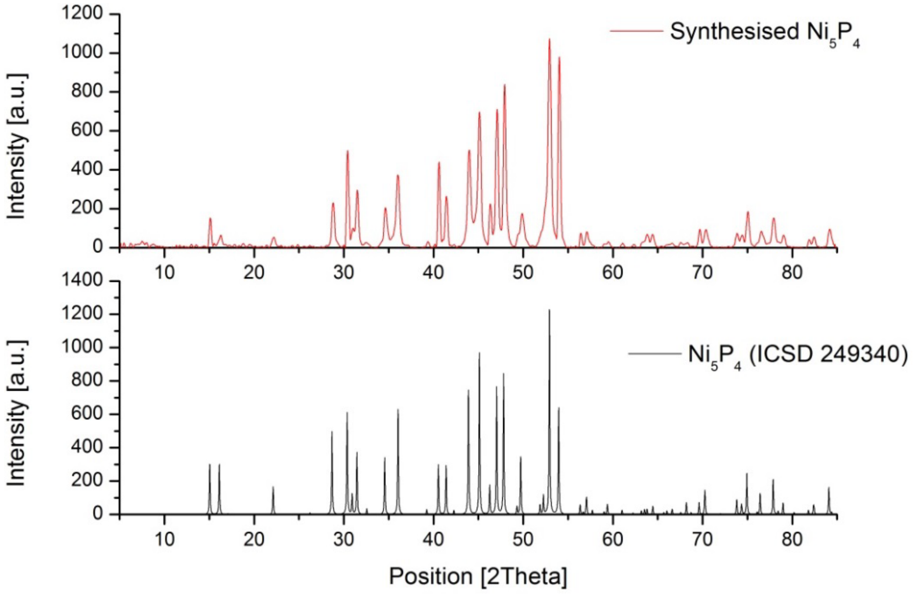


Figure S2: XRD pattern for Ni_5P_4 (bulk) and ICSD reference.

SEM

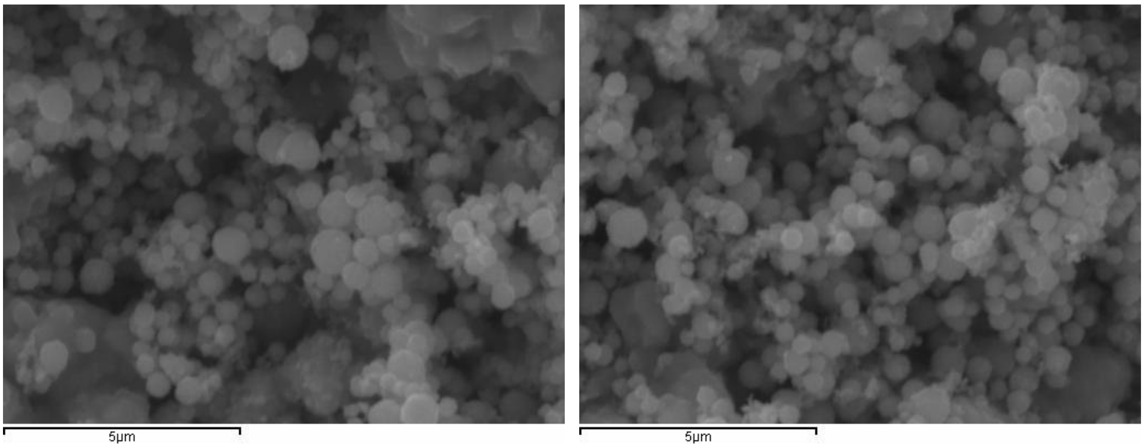


Figure S3: SEM images of Ni_5P_4 (bulk) particles.

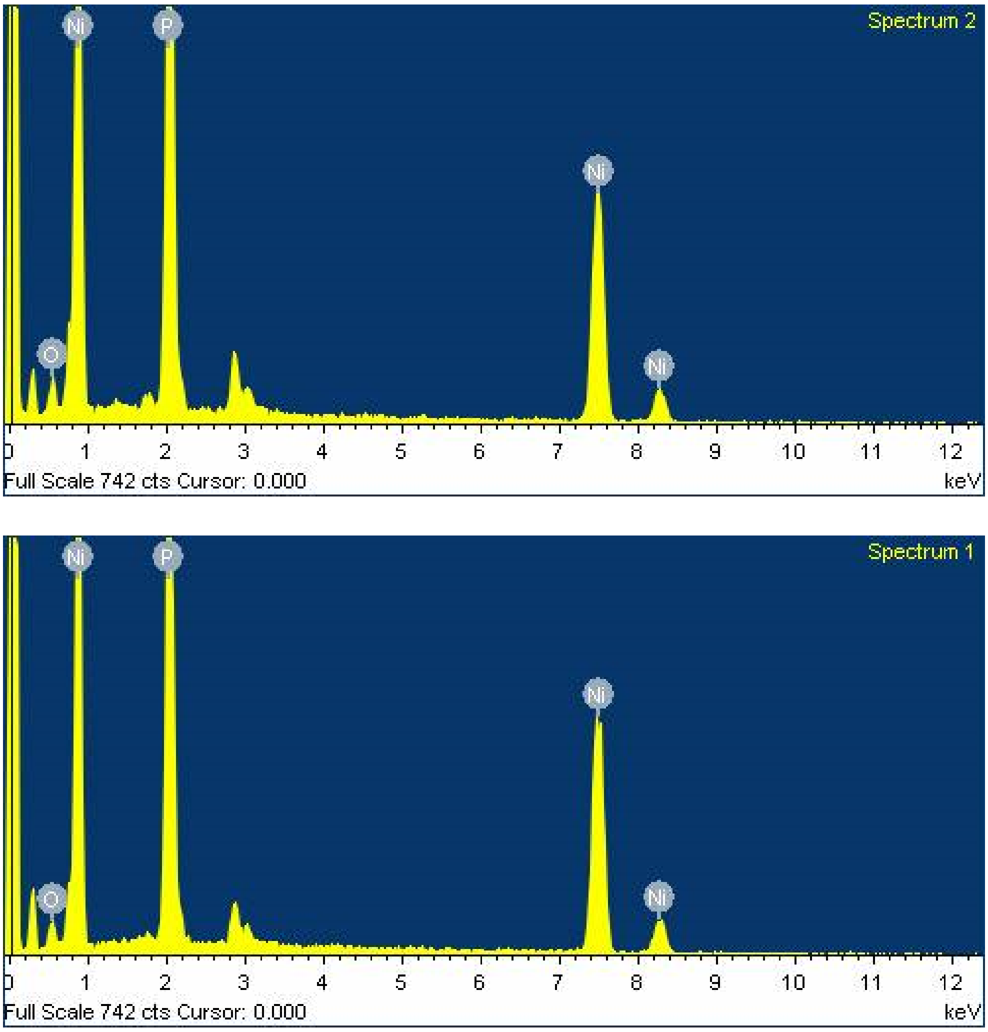


Figure S4: EDX samples of Ni_5P_4 (bulk).

Ni_2P (Bulk)

XRD

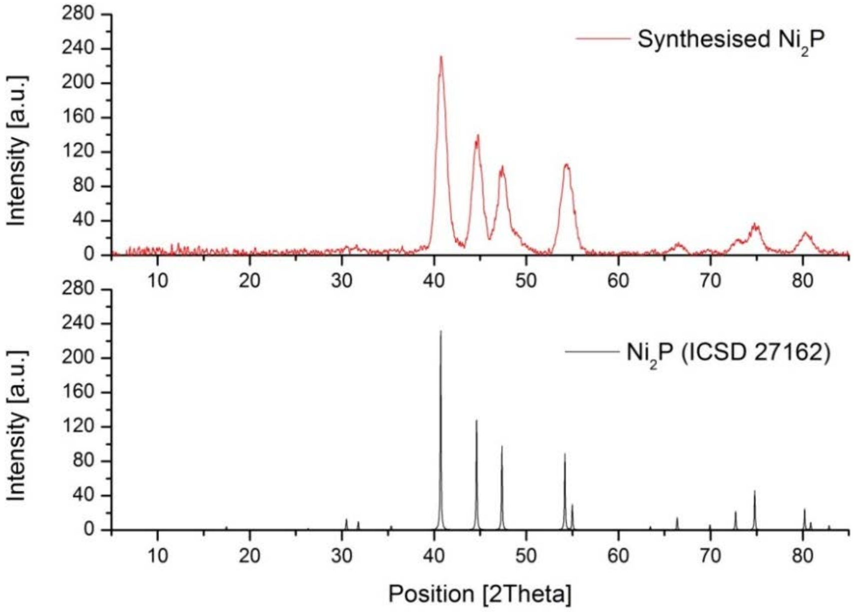


Figure S5: XRD pattern for Ni_2P (bulk) and ICSD reference.

SEM

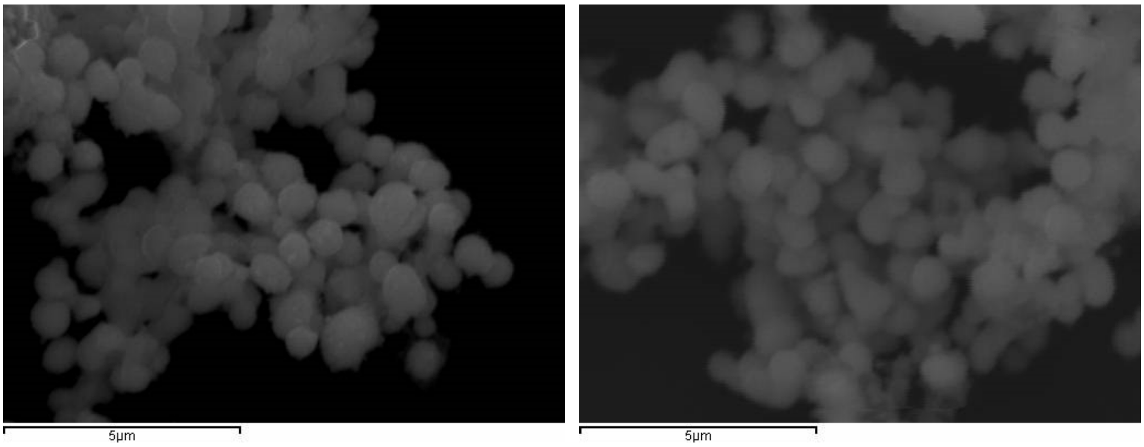
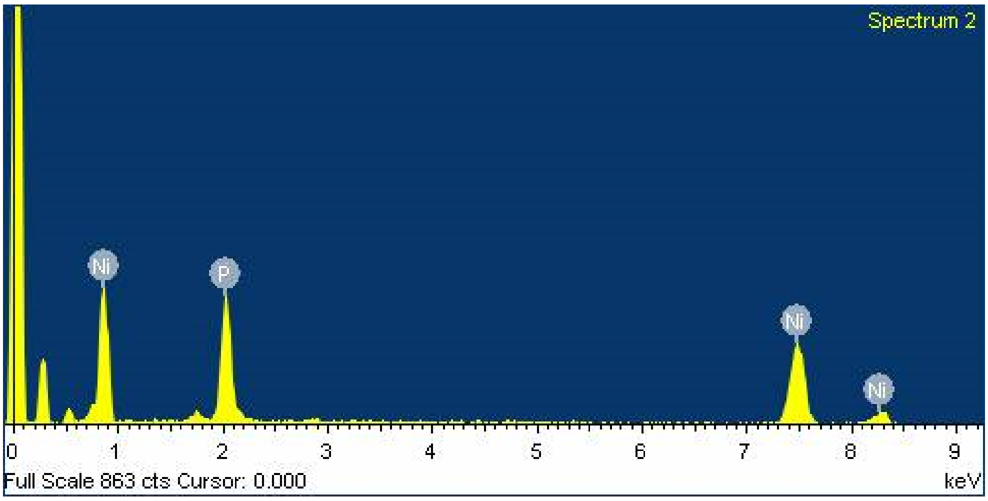


Figure S6: SEM images of Ni_2P (bulk) particles.



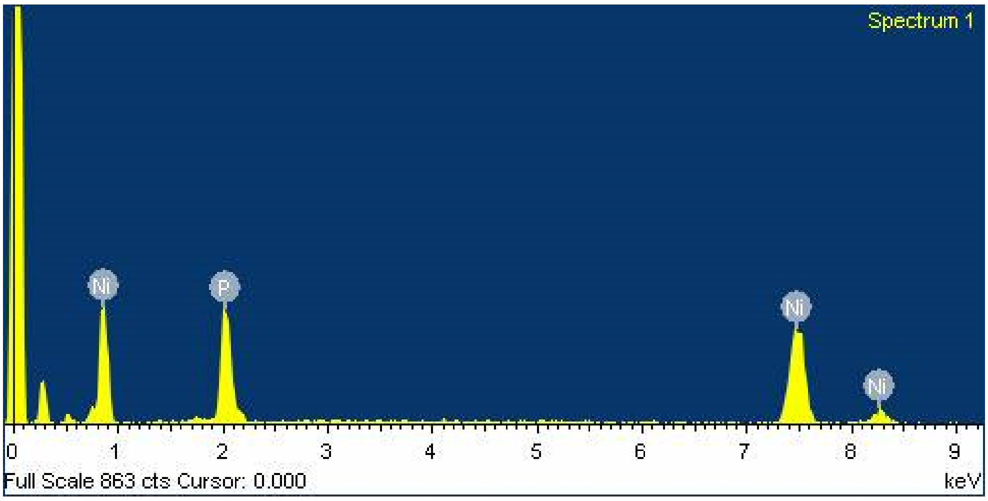


Figure S7: EDX samples of Ni_2P (bulk).

Mo_2C (Bulk)

XRD

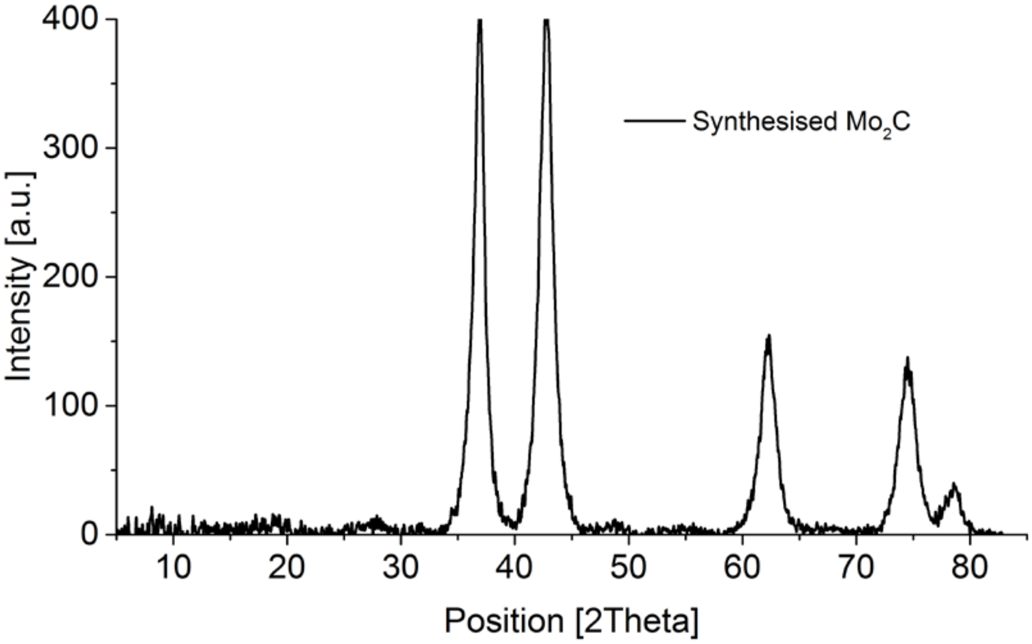
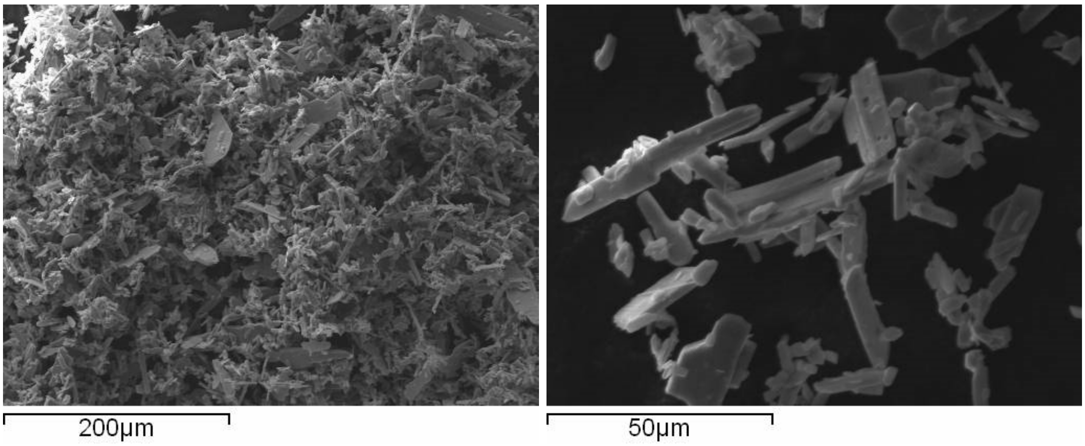


Figure S8: XRD pattern for Mo_2C (bulk).

- XRD Confirmed from Kojima *et al*.[4]

SEM



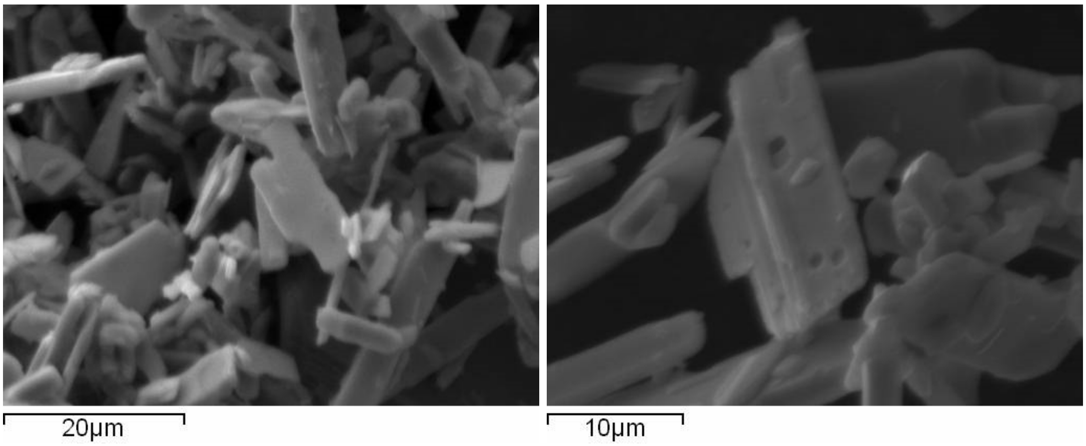


Figure S9: SEM images of Mo_2C (bulk) particles.

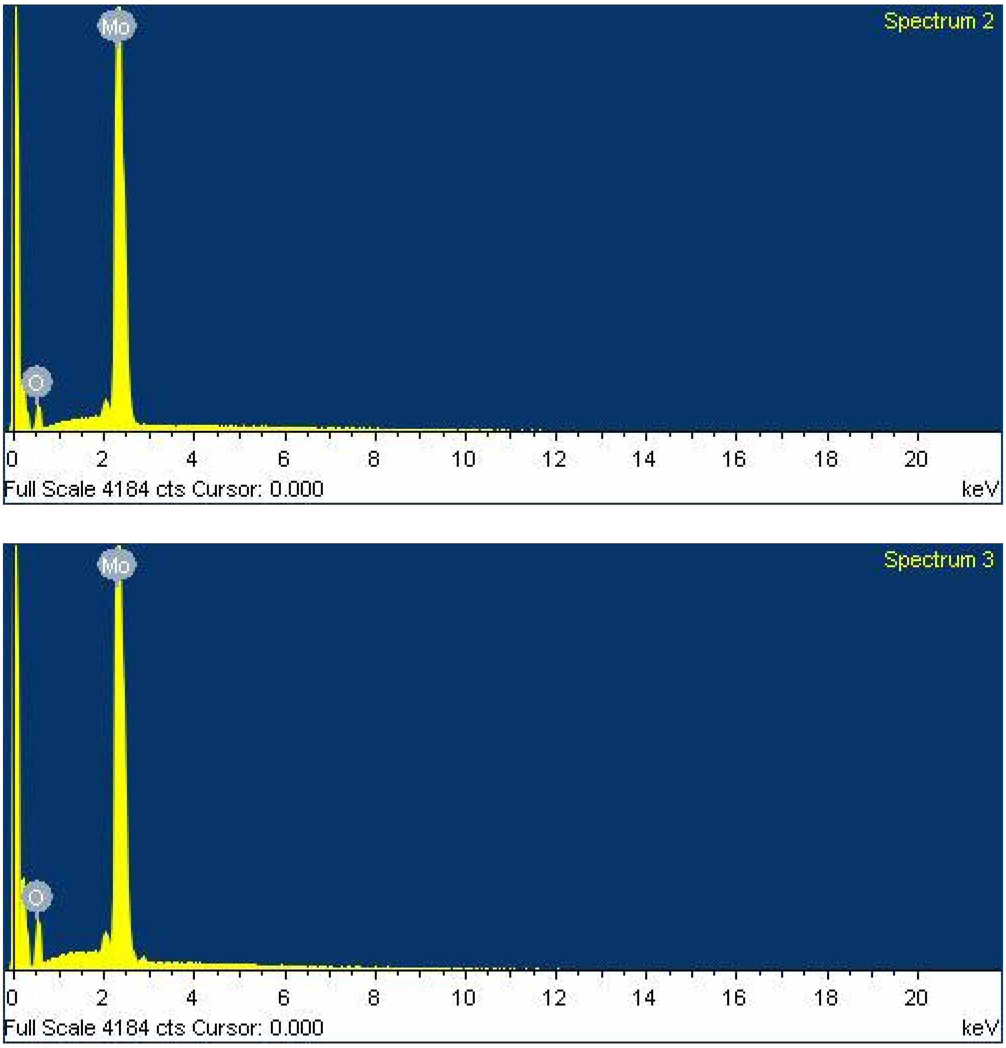


Figure S10: EDX samples of Mo_2C (bulk).

MoS_2 (Bulk)

XRD

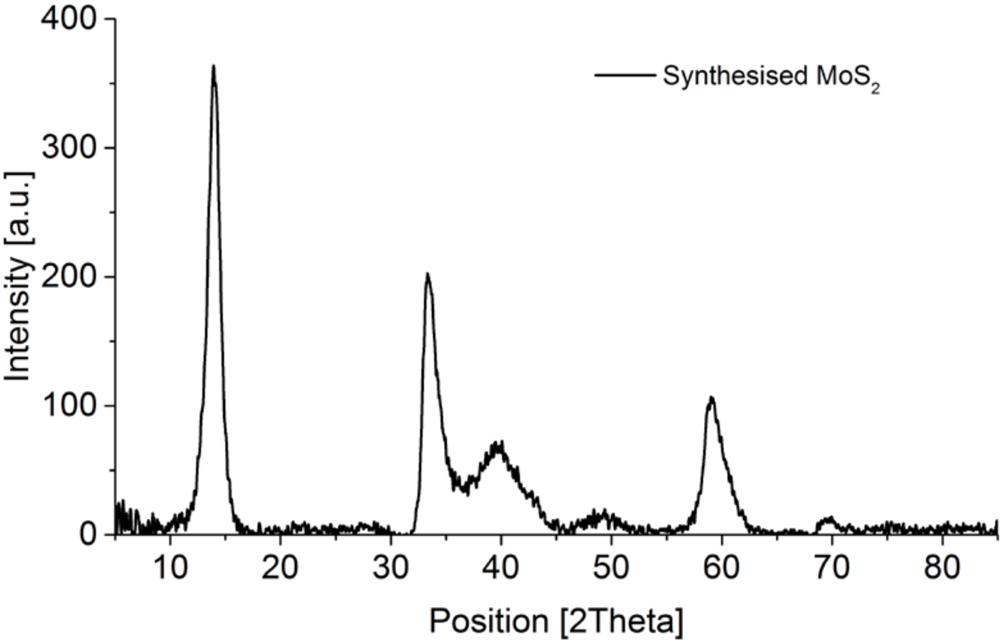
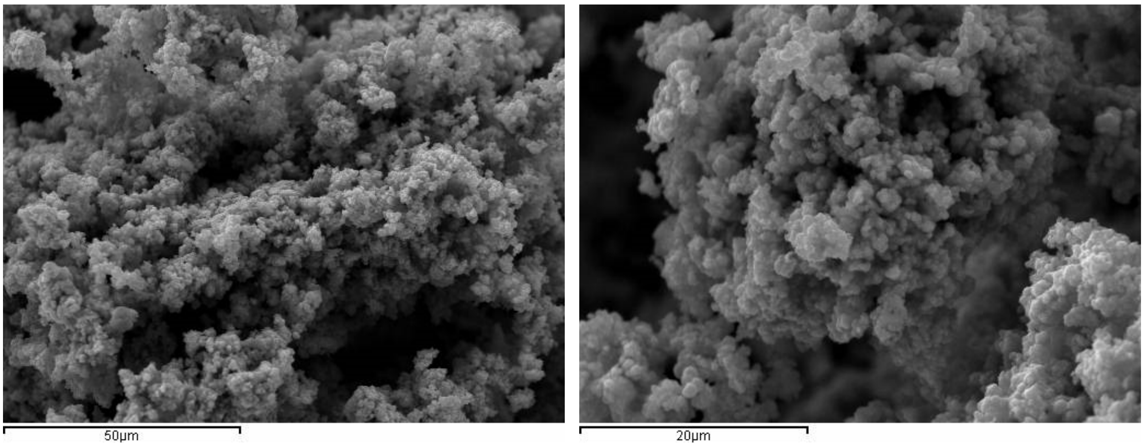


Figure S11: XRD pattern for MoS_2 (bulk).

- XRD confirmation taken from Wu *et al.*[3]

SEM



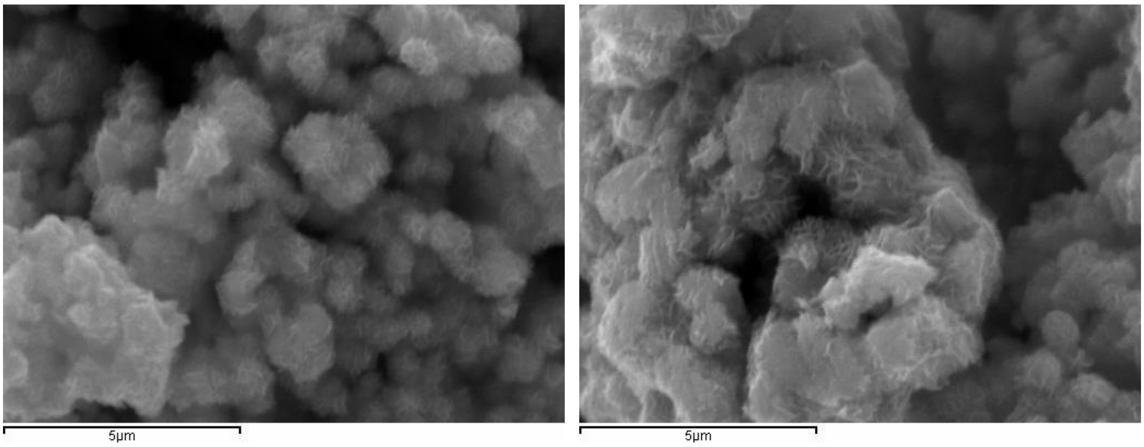


Figure S12: SEM images of MoS_2 (bulk) particles.

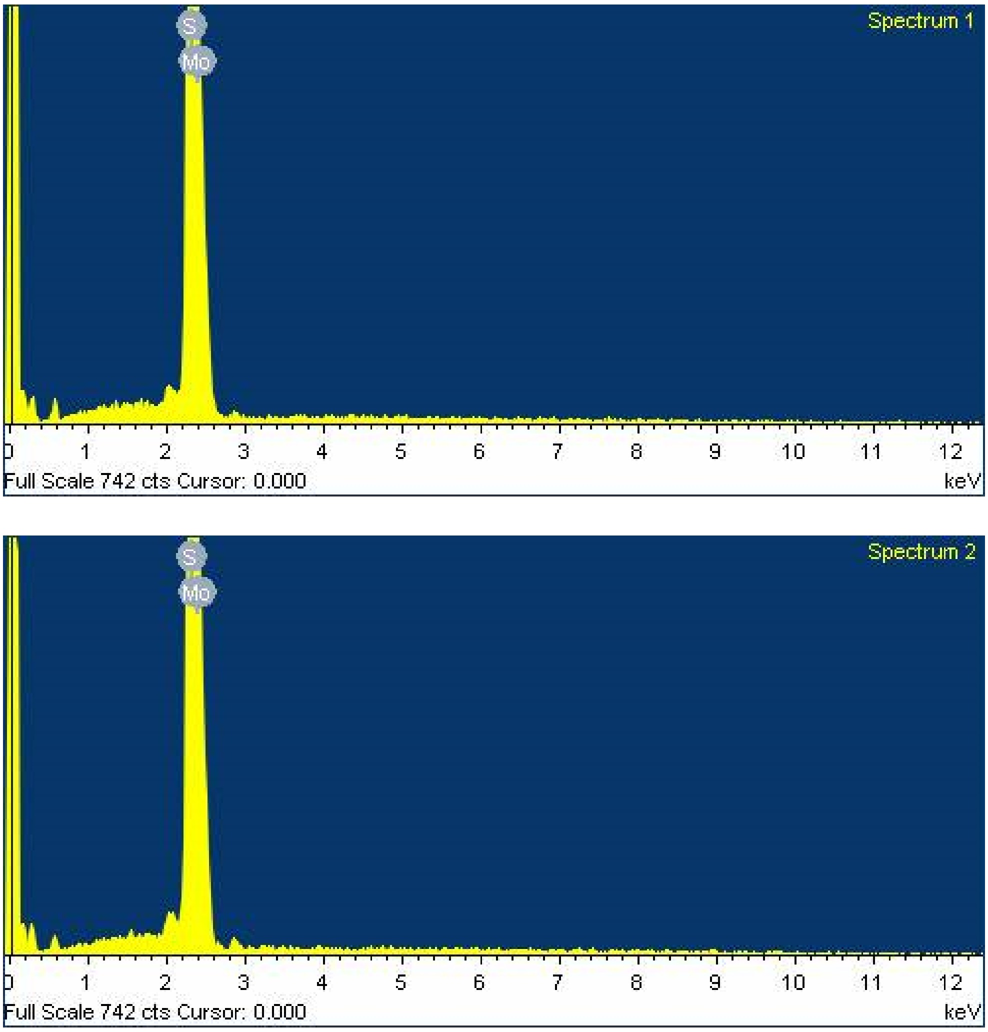


Figure S13: EDX samples of MoS_2 (bulk).

Ni_2P (10 % wt silica)

XRD

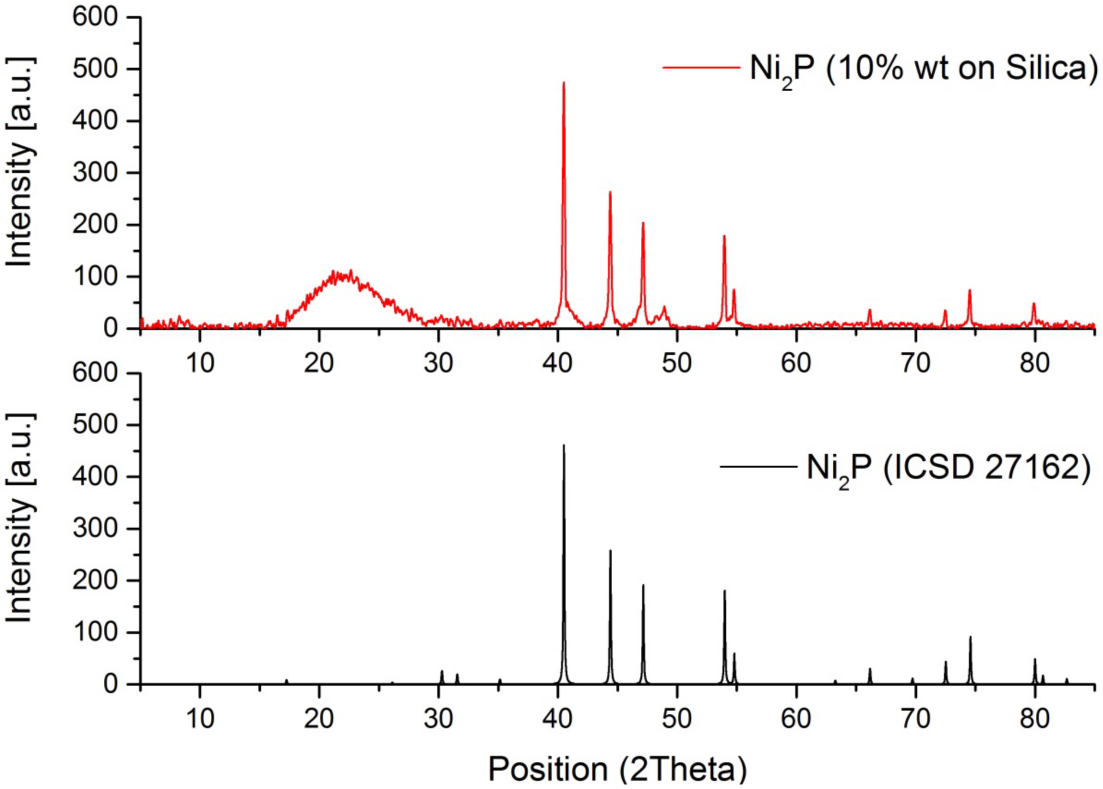


Figure S14: XRD pattern for Ni_2P (10 % wt silica) and ICSD reference.

SEM

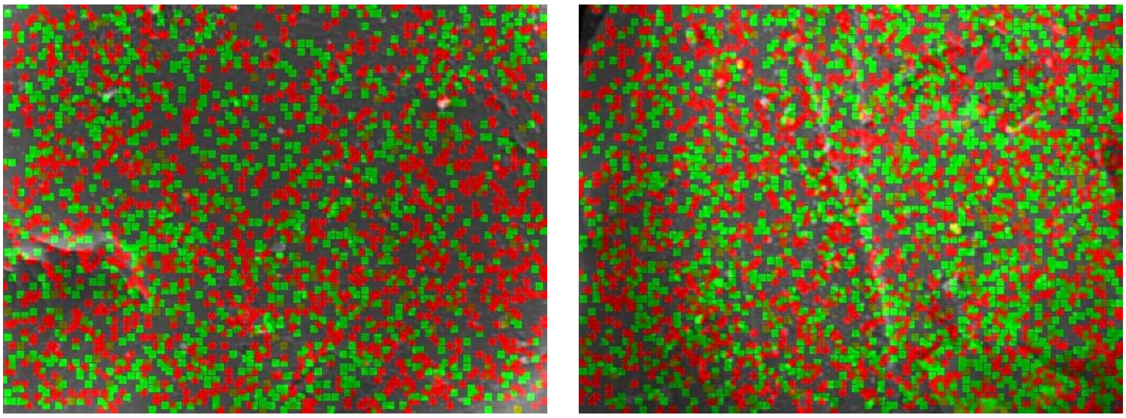


Figure S15: SEM images of Ni_2P (10 % wt silica) with composition shown (Nickel = Red, Phosphorus = Green).

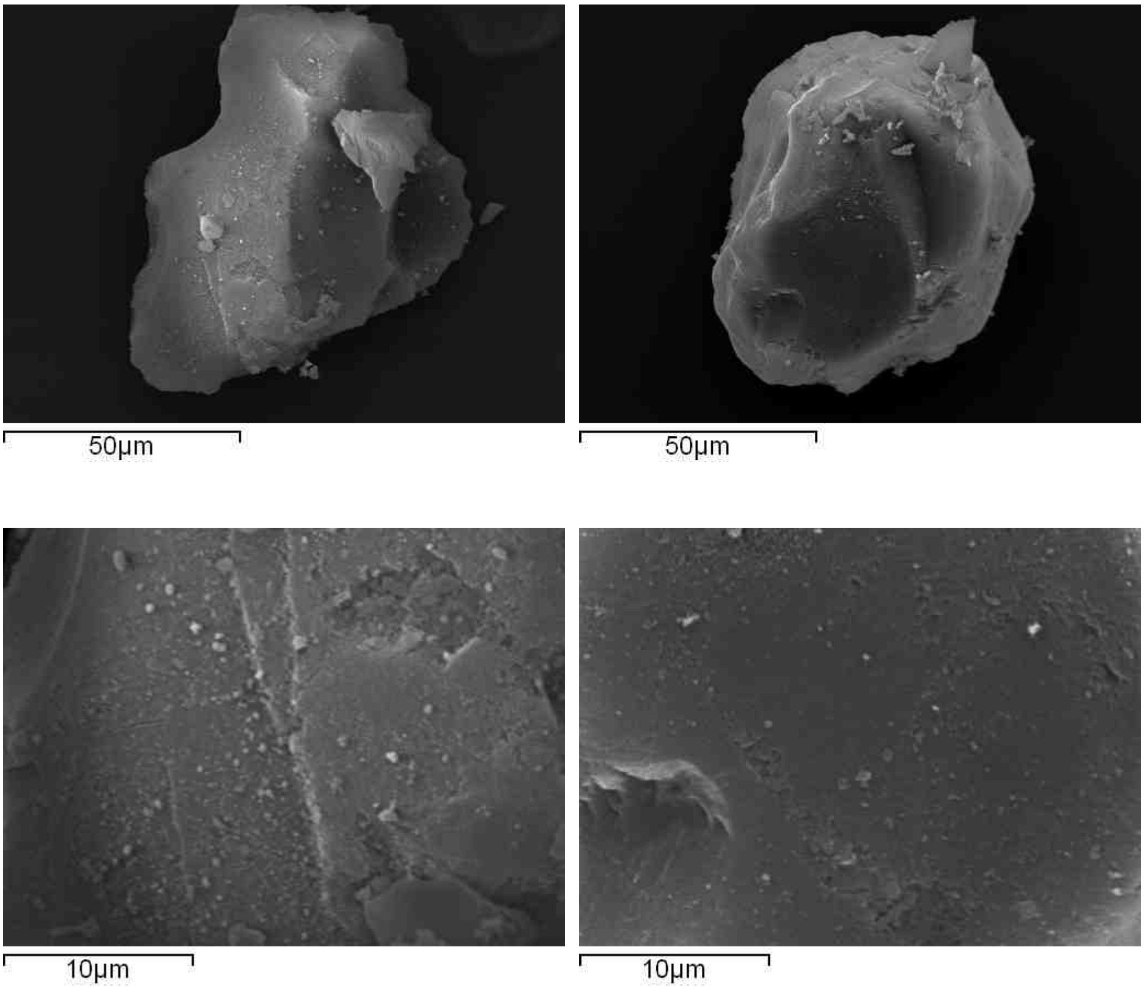
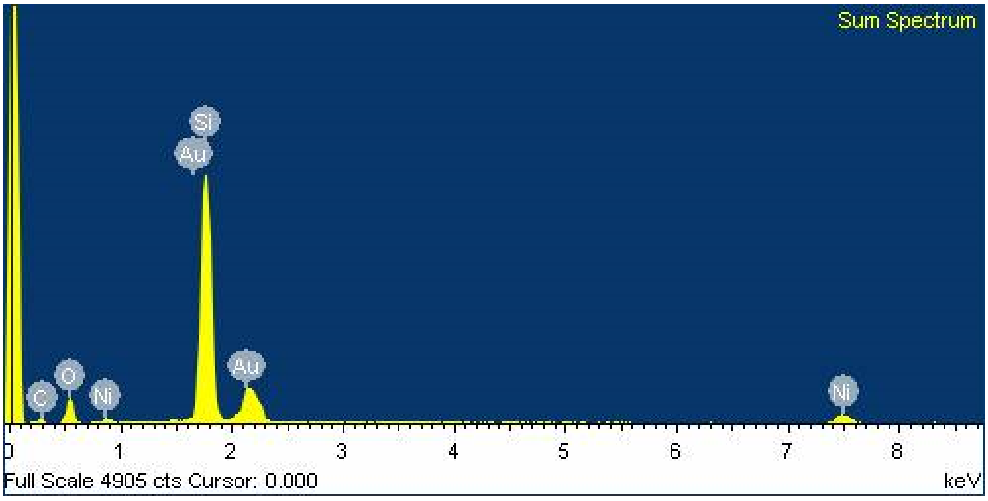


Figure S16: SEM images of Ni_2P (10 % wt silica) particles.



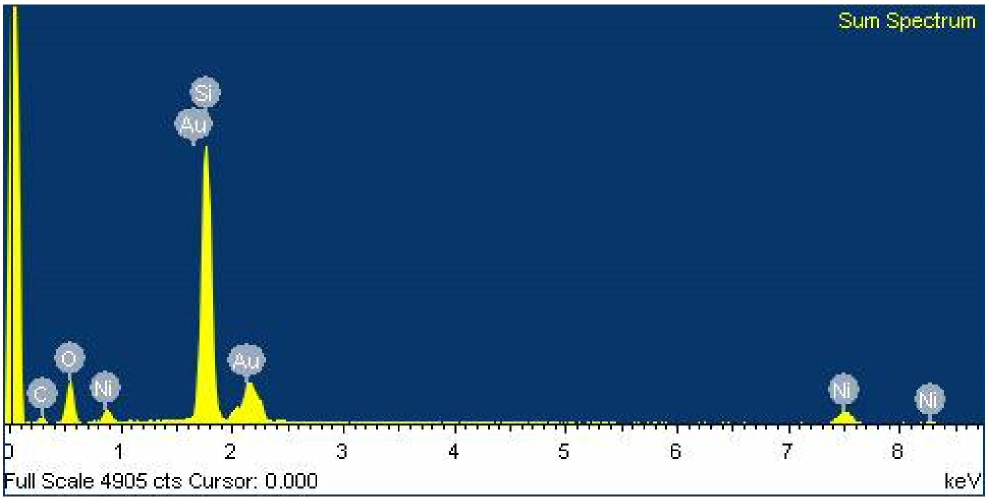


Figure S17: EDX samples of Ni_2P (10 % wt silica).

- Gold coating blocks out the phosphorus signal

<u>ICP</u>

Ni_2P (10 % wt on Silica):

Theory: Ni = 7.912 %, P = 2.088 % (Ni_2P),

Actual: Ni = 8.411 %, P = 2.047 % ($Ni_{2.17}P$)

Ni$_2$P (1 % wt silica)

XRD

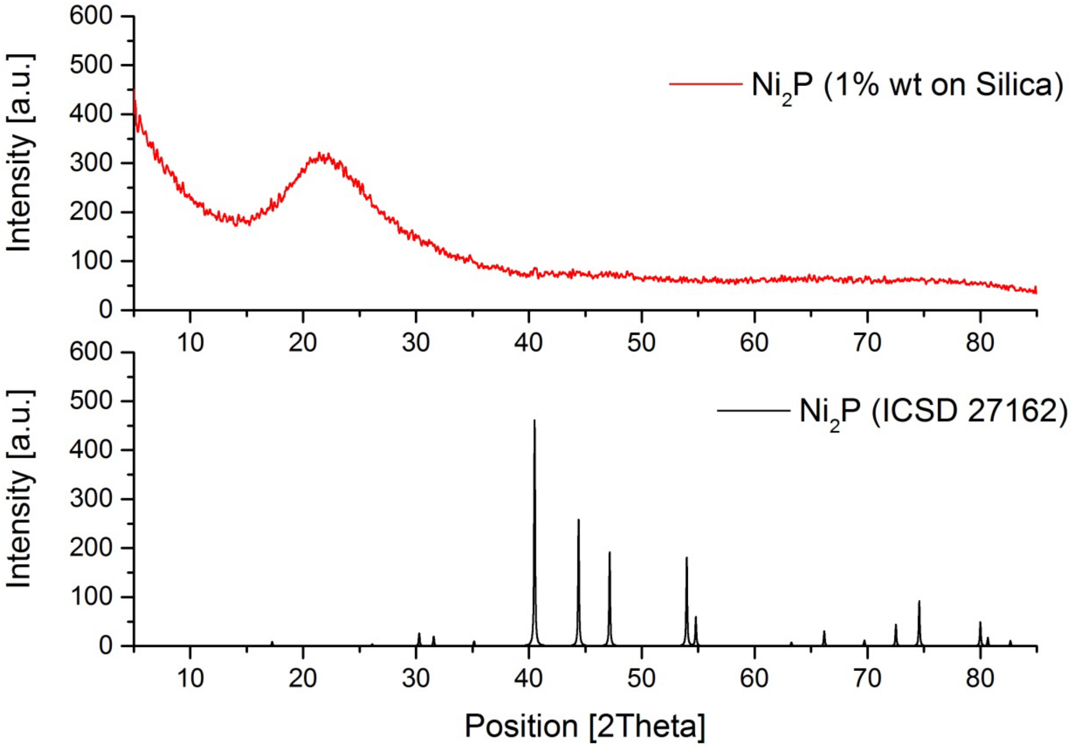


Figure S18: XRD pattern for Ni$_2$P (1 % wt silica) and ICSD reference.

SEM

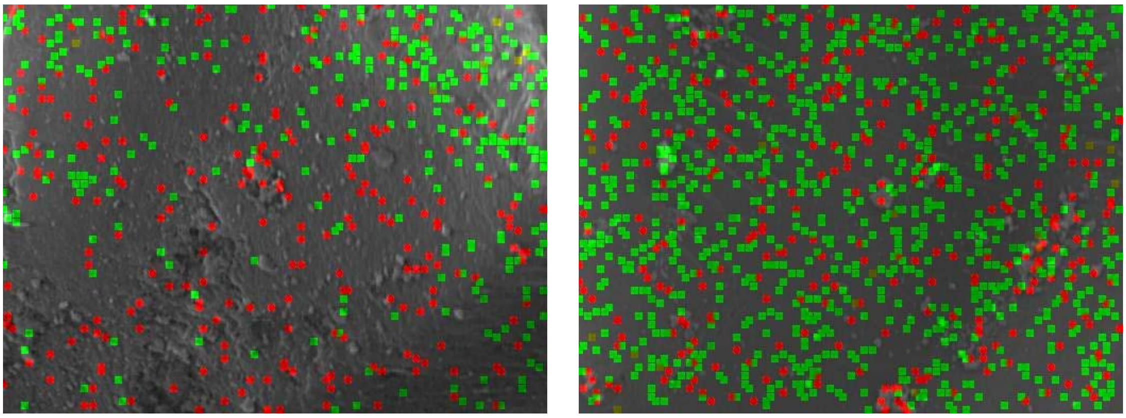


Figure S19: SEM images of Ni$_2$P (1 % wt silica) with composition shown (Nickel = Red, Phosphorus = Green).

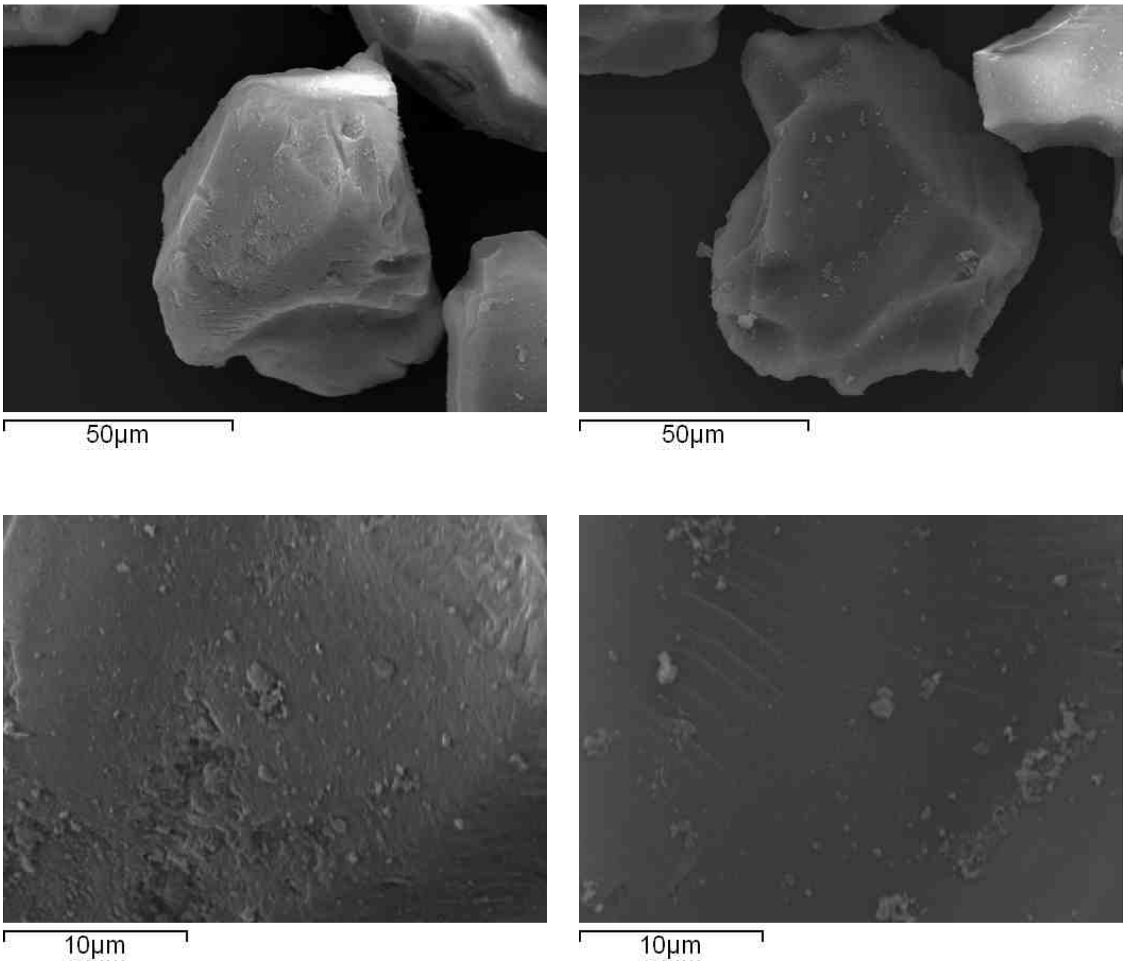
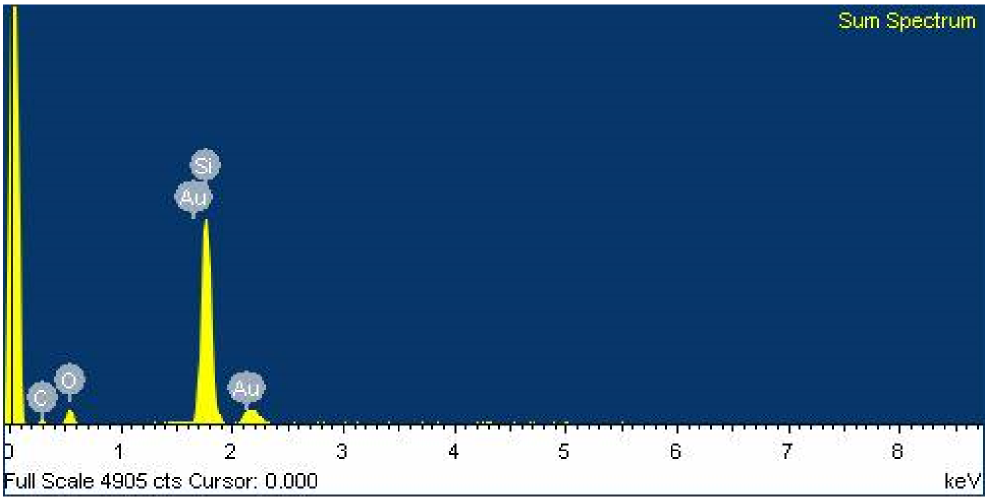


Figure S20: SEM images of Ni_2P (1 % wt silica) particles.



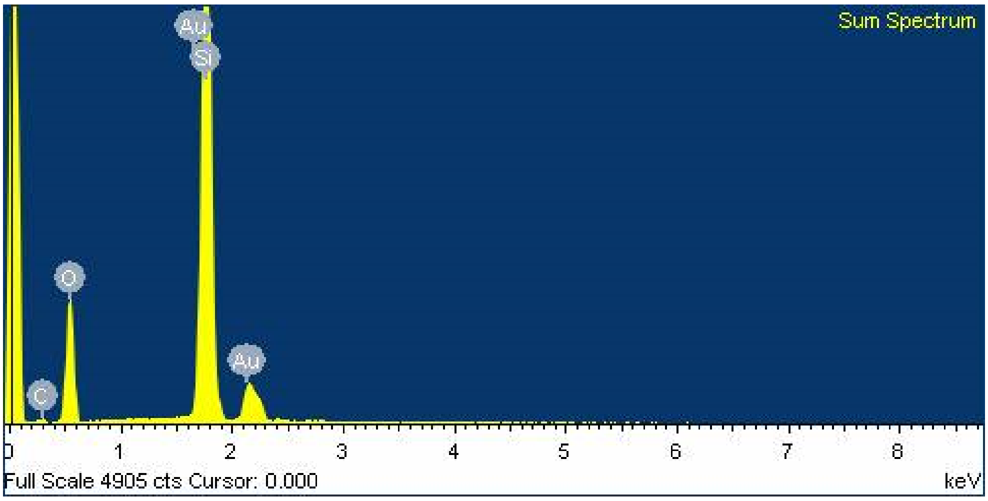


Figure S21: EDX samples of Ni_2P (1 % wt silica).

- Gold coating was used to prevent charging, however the catalyst loading was too low to observe any signals.

ICP

Ni_2P (1 % wt on Silica):

Theory: Ni = 0.791 %, P = 0.209 % (Ni_2P),

Actual: Ni = 0.693 %, P = 0.174 % ($Ni_{2.10}P$)

SI-8: SMA and PMA CV's overlaid onto HER onset graphs

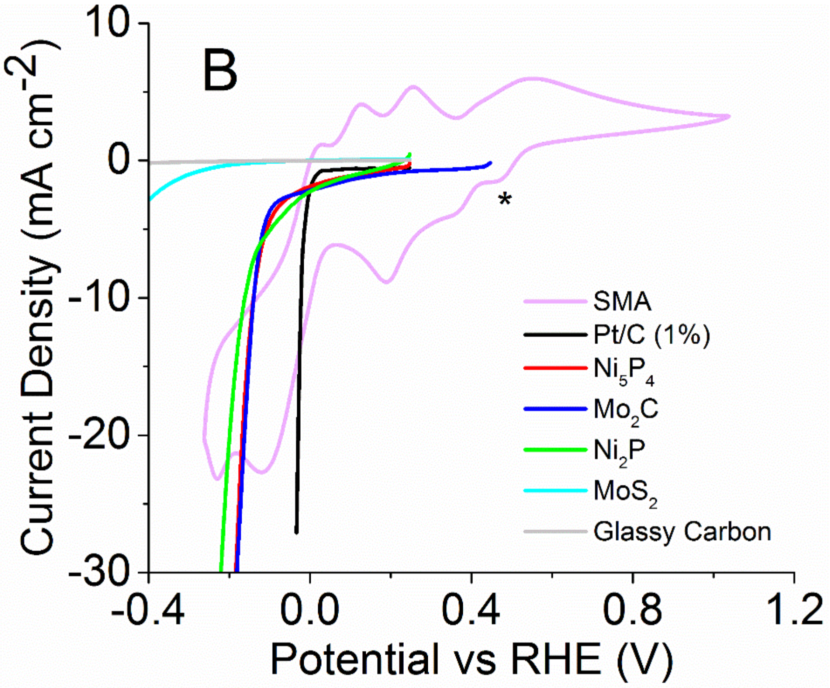


Figure S22: Linear sweep voltammetry of catalysts tested and CV of SMA overlaid to show where the redox values are with respect to each catalysts HER onset. (* = Extent POM was reduced to)

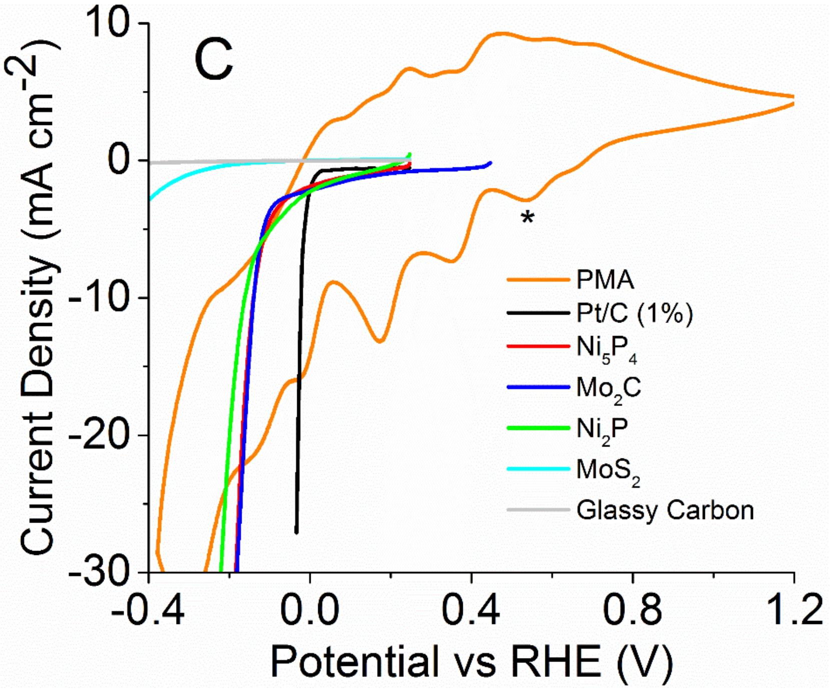


Figure S23: Linear sweep voltammetry of catalysts tested and CV of PMA overlaid to show where the redox values are with respect to each catalysts HER onset. (* = Extent POM was reduced to)

SI-9: Reusability of earth abundant catalysts with STA

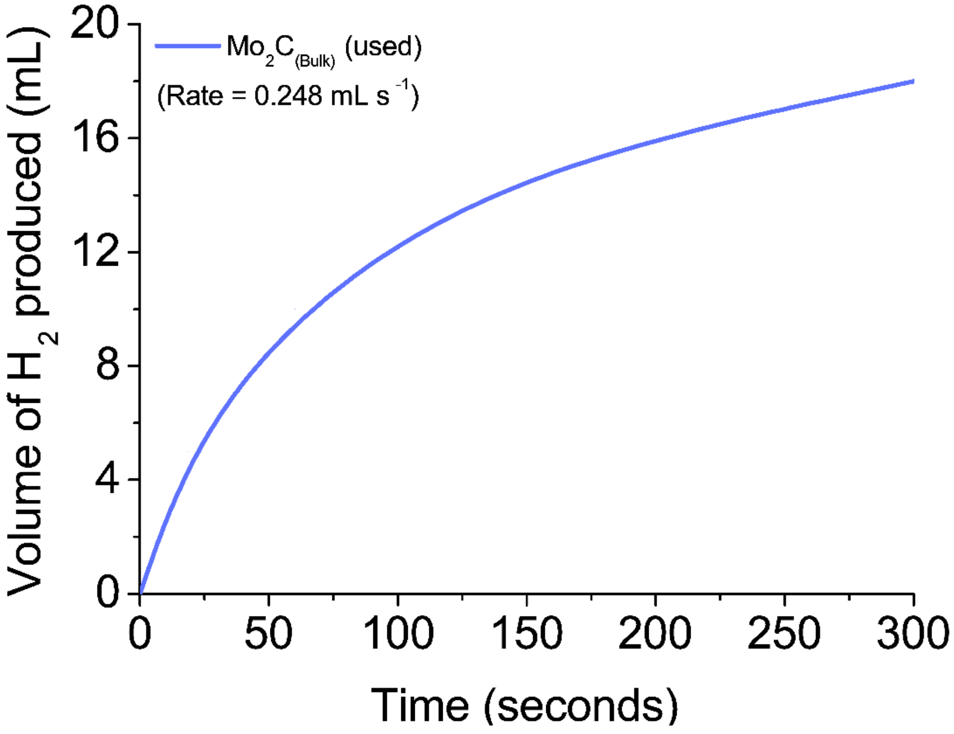


Figure S24: Hydrogen produced over time with previously used Mo$_2$C (bulk) catalyst in 0.1M STA

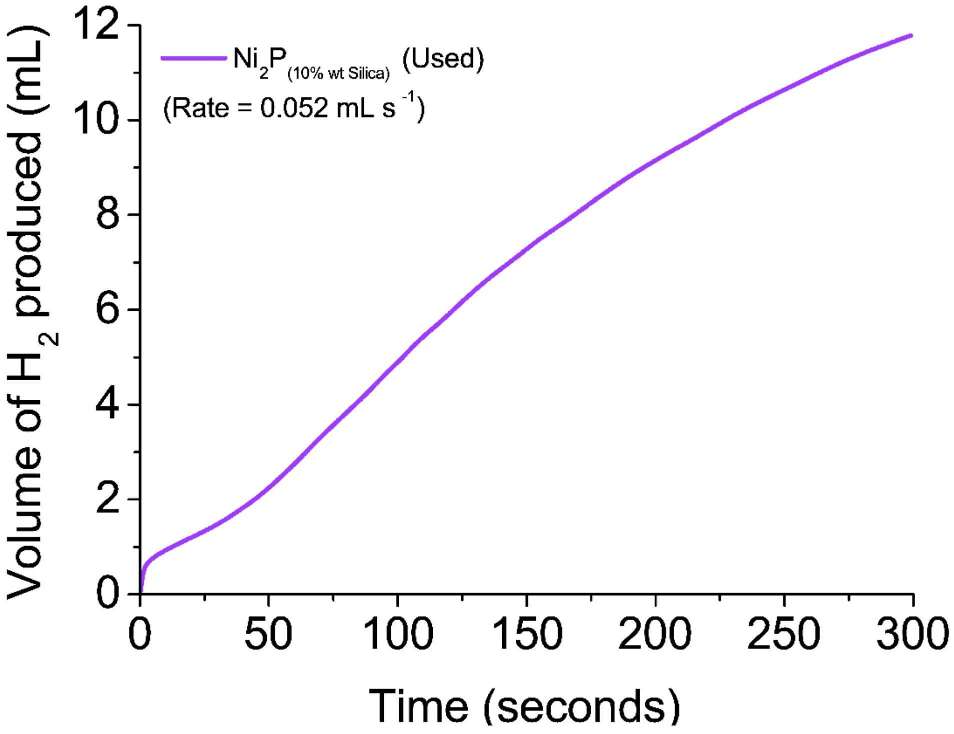


Figure S25: Hydrogen produced over time with previously used Ni$_2$P (10% wt silica) catalyst in 0.1M STA

SI-10: Tables

Catalyst	HER onset potential (vs RHE) (V)
Pt/C (1%)	0.0214
Ni_5P_4	-0.0993
Mo_2C	-0.1179
Ni_2P	-0.1348
MoS_2	-0.4052
Glassy Carbon	-0.7895

Table S1: HER onset potentials for various catalysts used in paper

	Silicotungstic Acid		Phosphotungstic Acid		Silicomolybdic Acid		Phosphomolybdic Acid	
Catalyst	% theoretical H2 obtained (After 18hrs)	H_2 production rate (mmol hr^{-1} mg^{-1})	% theoretical H2 obtained (After 18hrs)	H_2 production rate (mmol hr^{-1} mg^{-1})	% theoretical H2 obtained (After 18hrs)	H_2 production rate (mmol hr^{-1} mg^{-1})	% theoretical H2 obtained (After 18hrs)	H_2 production rate (mmol hr^{-1} mg^{-1})
Pt/C (1% wt)	63.2	573.0	48.5	249.525	0	0	0	0
Ni_5P_4	60.2	1.198	44.6	0.205	0	0	0	0
Mo_2C	49.7	1.006	26.6	0.226	0	0	0	0
MoS_2	42.9	0.438	18.4	0.038	0	0	0	0
Ni_2P	51.0	0.250	42.9	0.039	0	0	0	0
Ni_2P (10% wt)	51.3	2.060	34.8	1.001	0	0	0	0
Ni_2P (1% wt)	53.1	9.418	8.2	0.883	0	0	0	0

Table S2: All catalysts (Bulk + Supported) with total decoupling volume and H2 production rate (mmols of H2 released per hour, per mg of catalyst) for the 4 POMs tested.

Reference	Catalyst	Amount of catalyst used [mg]	Precious metal loading [mg]	H_2 evolution rate [L h^{-1}]	H_2 evolution rate [mmol h^{-1} mg^{-1}]	Mols of Electrolyte [mol]	H_2 evolution rate [mol h^{-1} mg^{-1} mol^{-1}]
5	Mo_2C (2%)	192	3.84	3.76	144.0	0.0016 (V^{2+})	90.00
6	Pd/C (10%) (Prev. Work)	50	5	14.7	121.0	0.01 (STA)	12.10
6	Rh/C (5%) (Prev. Work)	50	2.5	18.0	294.0	0.01 (STA)	29.40
6	Pt/C (1%) (Prev. work)	50	0.5	15.6	1275	0.01 (STA)	127.5
(This Work)	Pt/C (1%)	50	0.5	7.01 3.14	573.0 256.6	0.002 (STA) 0.002 (PTA)	286.5 128.3
(This Work)	Ni_5P_4 (Bulk)	50	50	1.47 0.25	1.198 0.205	0.002 (STA) 0.002 (PTA)	0.599 0.103
(This Work)	Mo_2C (Bulk)	50	50	1.23 0.41	1.006 0.338	0.002 (STA) 0.002 (PTA)	0.503 0.205
(This Work)	MoS_2 (Bulk)	50	50	0.54 0.04	0.438 0.038	0.002 (STA) 0.002 (PTA)	0.219 0.019
(This Work)	Ni_2P (Bulk)	50	50	0.31 0.08	0.250 0.039	0.002 (STA) 0.002 (PTA)	0.125 0.020
(This Work)	Ni_2P (10%)	50	5	0.25 0.12	2.060 1.001	0.002 (STA) 0.002 (PTA)	1.030 0.501
(This Work)	Ni_2P (1%)	50	0.5	0.12 0.011	9.418 0.883	0.002 (STA) 0.002 (PTA)	4.709 0.442

Table S1: Table detailing current work, previous work and a similar system with H2 evolution rates normalised to both mass of catalyst used and mols of electrolyte used (mols of H2 released per hour, per mg of catalyst, per mol of electrolyte).

SI-11: References:

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