Colloidal Ni_{2-x}Co_xP nanoparticles for the hydrogen evolution reaction

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ABSTRACT

A cost-effective and scalable approach was developed to produce monodisperse Ni_{2-x}Co_xP nanoparticles (NPs) with composition tuned over the entire range ($0 \leq x \leq 2$). Ni_{2-x}Co_xP NPs were synthesized using low-cost, stable and low-toxicity triphenyl phosphite (TPOP) as phosphorous precursor, metal chlorides as metal precursors and hexadecylamine (HDA) as ligand. The synthesis involved the generation of intermediate Ni-P amorphous NPs and the posterior crystallization and simultaneous incorporation of Co. The composition, size and morphology of the NPs could be controlled simply by varying the ratio of Ni and Co precursors and the amount of TPOP and HDA. Ternary Ni_{2-x}Co_xP based electrocatalysts exhibited enhanced electrocatalytic activity toward hydrogen evolution reaction (HER) compared to binary phosphides. In particular, NiCoP electrocatalysts displayed the lowest overpotential of 97 mV at $J=10 \text{ mA cm}^{-2}$ and an excellent long-term stability. DFT calculations of the Gibbs free energy for hydrogen adsorption at the surface of Ni_{2-x}Co_xP NPs showed NiCoP to have the most appropriate composition to optimize this parameter within the whole Ni_{2-x}Co_xP series. However, the hydrogen adsorption energy was demonstrated not to be the only parameter controlling HER activity in Ni_{2-x}Co_xP.

1. INTRODUCTION

The development of highly active electrocatalysts not based on Pt or Pt-group metals (PGMs) for the HER in acidic conditions has become a priority to reduce cost and allow extensive commercialization of PEM fuel cells. In this direction, particular transition-metal phosphides are being evaluated as potentially viable alternative electrocatalysts.¹⁻¹¹ Some transition metal phosphides are characterized not only by low cost and toxicity, but also excellent electrical conductivities and proper densities of states to allow an effective HER. While binary phosphides have reached performances relatively close to those of PGMs, ternary and multinary phosphides, with additional degrees of freedom to tune electronic band structure and surface chemistry, are expected to further close the gap with actual best HER catalysts.¹²⁻¹⁶

A crucial challenge that currently limits the use of metal phosphides as HER catalysts and for its wider range of applications is the lack of cost-effective approaches to produce nanostructures of these materials with properly adjusted properties. This limitation is particularly critical for multinary phosphides. Currently, multinary metal phosphide NPs are generally produced from the phosphorization of metal or metal oxide nanoparticles using toxic and expensive phosphorus sources such as phosphane, trioctylphosphine (TOP), (trimethylsilyl)phosphine (TMSP), as well as red/white phosphorus. Besides, because it involves two steps, this common strategy presents additional limitations in terms of cost and control of composition and structural parameters of multinary phosphides.

Among ternary phosphides, $\text{Ni}_{2-x}\text{Co}_x\text{P}$ has been demonstrated an excellent catalyst for HER and OER as well as an excellent electrode material for supercapacitor and lithium ion batteries.¹⁷⁻²³ Microstructured $\text{Ni}_{2-x}\text{Co}_x\text{P}$ has been synthesized through hydrothermal method by reacting metal chlorides with white phosphorus or NaH_2PO_2 .^{24,25} $\text{Ni}_{2-x}\text{Co}_x\text{P}$ has been also synthesized through annealing of Ni_xCo_y alloys within a phosphane gas atmosphere^{17,18} or through the reaction of pre-formed colloidal Ni_xCo_y NPs with trioctylphosphine (TOP).^{26,27}

We recently demonstrated triphenyl phosphite (TPOP) as a cheap, stable and less-toxic phosphorous precursor that can be used to produce a range of binary metal phosphides.²⁸ Motivated by the expectation of expanding the use of TPOP to the synthesis of ternary metal phosphides, we show here the possibility of producing $\text{Ni}_{2-x}\text{Co}_x\text{P}$ ($0 \leq x \leq 2$) NPs using metal chlorides and this phosphorus source. We further scaled up the synthesis procedure to the gram scale and tested these $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs for HER in acidic solution. The performance of these materials toward HER is analyzed as a function of the composition and explained using DFT calculations of the Gibbs free energy for hydrogen adsorption on the surface of these materials.

2. EXPERIMENTAL SECTION

Chemicals: Triphenyl phosphite (TPOP, 99%) was purchased from Alfa Aesar. 1-Octadecene (ODE, 90%), hexadecylamine (HDA, technical grade 90%), nickel (II) chloride (CoCl_2 , 98%), cobalt (II) chloride (CoCl_2 , 98%) and hexafluorophosphoric acid (HPF_6 , 65 wt%), carbon-supported Pt NPs (Pt/C, 10 wt% Pt) and Nafion (5 wt% in a mixture of low aliphatic alcohols and water) were purchased from Sigma Aldrich. Chloroform, isopropanol and acetone were of analytical grade and obtained from various sources. Milli-Q water was supplied by a PURELAB flex from ELGA. All precursors and solvents were used without further purification.

Synthesis of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs ($0 \leq x \leq 2$): All reactions were carried out under argon atmosphere using standard Schlenk line techniques. In a typical synthesis, the proper amount of NiCl_2 and CoCl_2 (overall 1.0 mmol) and 2.4 g (10 mmol) of HDA were combined with 10.0 mL of ODE and 2.6 mL (10 mmol) of TPOP in a 50 mL flask equipped with a condenser. The system was heated to 150 °C under argon flow (30 mL min^{-1}) and maintained at this temperature for 1 h to remove low boiling point impurities, moisture and oxygen. The temperature was then increased to the solvent boiling point (about 290 °C) in 20 min and kept there for 1 h. Afterward, the mixture was allowed to cool to 200 °C by removing the heating mantle and then cooled rapidly to room temperature with a water bath. The black product was isolated by precipitation with acetone. To remove as much organics as possible, two redispersion and precipitation cycles using chloroform and acetone were additionally carried out.

The synthesis of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs was scaled up in a 500 mL flask containing 1.3 g (10 mmol) of NiCl_2 and 1.3 g (10 mmol) of CoCl_2 , 52 mL (200 mmol) of TPOP, 48 g (200 mmol) of HDA and 100 mL of ODE. The temperature was maintained at 150 °C for 2 h under argon flow and afterward increased to the solvent boiling point. After 2h reaction, the reaction mixture was cooled down and purified as detailed above.

Different sizes of spherical NiCoP NPs were prepared following the same procedure, using 65 mg (0.5 mmol) of NiCl_2 and 65 mg (0.5 mmol) of CoCl_2 but different amounts of TPOP. Different morphologies were produced by tuning the amount of HDA in the reaction as detailed in the results section.

Ligand removal: $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs dispersed in chloroform (~50 mg in 10 mL) were mixed with an equal volume fraction of 6.3 wt % HPF_6 in formamide solution to form a two phase system. The mixture was vigorously stirred at room temperature. The final formamide solution containing the NPs was washed several times with chloroform to remove all the remaining organic ligands surrounding the NPs. The precipitate was collected after drying at room temperature for later application.

Characterization: Transmission electron microscopy (TEM) characterization was carried out using a ZEISS LIBRA 120, operating at 120 KV and a JEOL 1011 operating at 100kV. Carbon-coated TEM grids from Ted-Pella were used as substrates. High-resolution TEM (HRTEM) studies were conducted using a field emission gun FEI Tecnai F20 microscope at 200 kV with a point-to-point resolution of 0.19 nm. High angle annular dark-field (HAADF) STEM was combined with electron energy loss spectroscopy (EELS) in the Tecnai F20, by using a GATAN QUANTUM filter. Scanning electron microscopy (SEM) analyses were carried out using a ZEISS Auriga microscope with an energy dispersive X-ray spectroscopy (EDS) detector operating at 20 kV. Powder X-ray diffraction (XRD) patterns were collected directly from the as-synthesized NPs dropped on Si (501) substrate using a Bruker-AXS D8 Advanced X-ray diffractometer with Ni-filtered (2 μm thickness) Cu K radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. A LynxEye linear position-sensitive detector was used in reflection geometry. X-ray photoelectron spectroscopy (XPS) was carried out on a SPECS system equipped with an Al anode XR50 source operating at 150 mW and a Phoibos 150 MCD-9 detector. The pressure in the analysis chamber was below 10^{-7} Pa. The area analyzed was about 2 mm $\times$ 2

mm. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). Binding energy values were corrected using the C 1s peak at 284.8 eV. Fourier transform infrared spectroscopy (FTIR) was performed on an Alpha Bruker FTIR spectroscopy with a platinum attenuated total reflectance (ATR) single reflection module.

Catalyst preparation: The catalyst ink for electrochemical measurements was prepared by mixing 5 mg of Ni_{2-x}Co_xP NPs, 5 mg of carbon powder (Vulcan XC-72), 2 mL of deionized water/isopropanol (v/v = 1:1) and 35 μ L of 5 wt % of Nafion solution. The mixture was sonicated for 30 min to form a homogeneous catalyst ink. A glassy carbon electrode (GCE, 5 mm in diameter) was polished using diamond paper and 0.05 μ m alumina slurry sequentially, followed by ultrasonication in ethanol and water for 1 min. The cleaned GCE was dried under argon flow at room temperature. Onto the GCE, 10 μ L of catalyst ink were drop casted and then dried at room temperature.

Electrochemical measurements: Electrochemical measurements were conducted at room temperature on a BioLogic Electrochemical workstation in a standard three-electrode cell using a modified GCE as working electrode, Pt mesh as counter electrode and Ag/AgCl as reference electrode. The HER polarization curves were obtained in 0.5 M H₂SO₄ electrolyte, which was degassed by bubbling hydrogen for 30 min before measurement. The HER polarization curves were tested from 0 to -0.7 V versus Ag/AgCl at a scan rate of 5 mV s⁻¹. The time dependency of catalytic currents during electrolysis for NiCoP NPs was tested in 0.5 M H₂SO₄ at η = 150 mV under stirring to remove the generated gas bubbles.

DFT calculations: The density functional calculations were conducted by using the Vienna ab initio simulation package (VASP),^{29,30} we selected the Projector augmented wave method (PAW) to describe the interaction between the atomic cores and electrons, with a kinetic cut-off of 300 eV.³¹ The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was applied.³² The Ni_{2-x}Co_xP(200) surfaces were modeled by supercell slab containing four (0001) atomic layers to eliminate the polarity with a vacuum gap of ~15 Å. A Monkhorst-Pack grid of size of 6×6×1 was used to sample the surface Brillouin zone. The lowest two layers were fixed and the other layers were fully relaxed. The convergence criterion for total energies was set to 10⁻⁶ eV, simultaneously residual force were converged to 0.01 eV Å⁻¹ during relaxation. All bulk and slab structure of Ni_{2-x}Co_xP crystals are presented in **Figures S1** and **S2** (supporting information, SI). The differential adsorption energy ΔE_H can be calculated by using the equation:

$$\Delta E_H = E(\text{Ni}_{2-x}\text{Co}_x\text{P} + \text{H}^*) - E(\text{Ni}_{2-x}\text{Co}_x\text{P}) - 1/2 E(\text{H}_2)$$

where $E(\text{Ni}_{2-x}\text{Co}_x\text{P} + \text{H}^*)$ represents the total energy of Ni_{2-x}Co_xP with H atom adsorbed on surfaces, $E(\text{Ni}_{2-x}\text{Co}_x\text{P})$ is the total energy of Ni_{2-x}Co_xP slabs, and $E(\text{H}_2)$ is the energy of a hydrogen molecule in gas phase. Ni_{2-x}Co_xP structures with an adsorbed H atom are presented in **Figure S2**. Our calculations showed that H atom would always be absorbed on the same active site of the (0001) surface of Ni_{2-x}Co_xP, that is on the hollow site where the H atom bonds with three metal atoms.

ΔE_H does not include the contributions from the vibrational motion and the entropy. The Gibbs free energy for hydrogen adsorption can be calculated with the equation including these corrections:

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{\text{ZPE}} + \Delta_{0 \rightarrow 298.15\text{K}} \Delta H_H - T \Delta S_H$$

where the ΔE_{ZPE} represents the zero point correction between adsorbed hydrogen and hydrogen in gas phase, which can be obtained from frequency calculation, the $\Delta_{0 \rightarrow 298.15\text{K}} \Delta H_H$ means enthalpy change from 0K to 298.15K which approaches to half of $\Delta_{0 \rightarrow 298.15\text{K}} \Delta H_{\text{H}_2}$, and the $T \Delta S_H$ means the entropy changes from H* to H₂ in gas phase, which is approximately equivalent to 1/2 $T \Delta S_{\text{H}_2}$.³³⁻³⁴ Detail data are presented in **Table S1**.

3. RESULTS AND DISCUSSION

$\text{Ni}_{2-x}\text{Co}_x\text{P}$ ($0 \leq x \leq 2$) NPs were produced from the reaction in solution of nickel and cobalt chlorides with TPOP in the presence of HDA (see experimental section for details). Composition was tuned by simply adjusting the ratio of nickel and cobalt chlorides in the precursor solution. **Figure 1** displays representative TEM micrographs of the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs produced following this procedure. Spherical NPs were obtained for $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs with $x \leq 1.0$ and elongated NPs or nanorods for $x \geq 1.2$. The NP size and aspect ratio increased when increasing the amount of Co. **Table 1** displays the nominal composition and the experimental metal ratios measured by SEM-EDX. Notice that the final NP composition correlated well with the nominal metal ratios introduced.

Figure 1. TEM images of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs with different compositions: $x = 0$ (a), 0.2 (b), 0.6 (c), 1 (d), 1.2 (e), 1.4 (f), 1.8 (g), 2 (h). Scale bars = 50 nm.

Table 1. Ni:Co metal ratios (nominal and EDX) and average NP size (TEM) of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs.

Ni:Co ratio		Average size (nm)	
Nominal	EDX	Length	Width
2.00:0.00	2.00:0.00	7.6 ± 0.8	
1.80:0.20	1.81:0.19	9 ± 1	
1.40:0.60	1.40:0.60	13 ± 2	
1.00:1.00	1.03:0.97	12 ± 2	
0.80:1.20	0.82:1.18	11 ± 1	7 ± 1
0.60:1.40	0.54:1.46	9.0 ± 0.7	5.3 ± 0.6
0.20:1.80	0.17:1.83	10 ± 1	3.6 ± 0.7
0.00:2.00	0.00:2.00	33 ± 6	6 ± 1

Ni_2P and Co_2P share the same hexagonal crystal phase (P62m space group) and have similar lattice parameters. Thus, taking into account the small size of the crystal domains, $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs with different compositions displayed very similar XRD patterns (**Figure 2**). However as the amount of Ni decreased, NPs crystallinity decreased.

Figure 2. XRD patterns of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs. From bottom to top: $x = 0, 0.2, 0.6, 1.0, 1.2, 1.4, 1.8, 2$. Reference patterns of Ni_2P (PDF #65-9706) and Co_2P (PDF #54-0413) are also displayed at the bottom and top of the graph, respectively.

HRTEM micrographs of NiCoP (**Figure 3**) and $\text{Ni}_{0.4}\text{Co}_{1.6}\text{P}$ (**Figure S4** and **S5**) NPs confirmed the hexagonal crystal phase and demonstrated the NPs to be single crystal. A slight decrease of the lattice parameters from NiCoP ($a = b = 5.834 \text{ \AA}$ and $c = 3.353 \text{ \AA}$ as visualized along the $[0001]$ zone axis) to $\text{Ni}_{0.4}\text{Co}_{1.6}\text{P}$ ($a = b = 5.795 \text{ \AA}$ as visualized along the $[10-10]$ direction) was detected by HRTEM. This small variation of the lattice parameter was consistent with the increased amount of Co, which has a slightly larger ionic radius than Ni. EELS compositional maps showed the two metals, Ni and Co, and also P to be homogeneously distributed within each NP, although a slight excess of Co was detected at the NP surface and a small excess of Ni was measured within the NP. All NPs analyzed had similar metal ratios and no binary NP could be detected after extensive EELS characterization.

Figure 3. HRTEM micrograph of NiCoP NPs (a), detail of the NP in yellow (b) and its corresponding power spectrum (c). STEM-EELS elemental composition maps (d) and quantification maps (e) of NiCoP NPs.

XPS analysis (**Figure 4**) of the Ni $2p_{3/2}$ region of NiCoP NPs showed Ni to be present at the NP surface in two different chemical states, which we associated to NiP (852.9 eV) and a Ni^{2+} or Ni^{3+} chemical environment (856.7 eV).³⁵⁻⁴⁰ An additional satellite peak was also observed at 862.2 eV.⁴¹ The ratio between the two nickel chemical states was: $Ni^{2+/3+}/NiP = 1.45$. The Co $2p_{3/2}$ spectrum was fitted with four peaks associated to CoP (778.2 eV), a Co^{2+} chemical environment (781.7 eV), and two satellite peaks (785.6 eV and 788.0 eV).^{42,43} The amount of Co^{2+} was three times larger than that of CoP: $Co^{2+}/CoP=3.05$. Two phosphorous chemical states were identified from the XPS analysis of the P 2p electronic states. A P $2p^{3/2}$ peak at 129.5 eV matched with the binding energy expected from P in a metal phosphide environment, thus we related it to P within the NiCoP structure.^{41,42} A second P $2p^{3/2}$ peak at higher binding energy, 133.1 eV was assigned to a phosphate environment.^{41,44} The ratio between the two phosphorous chemical states was: $MP/PO = 1.02$. From the XPS analysis, we conclude that the NP surface, the outermost 1-2 nm, was oxidized to a $NiCoPO_x$, while below this surface layer the chemical environment of Ni, Co and P corresponded to that of a NiCoP with a slight sharing of electrons from Ni and Co, showing electronic states with higher binding energies than the metal, to P, which shows lower binding energies than zero-valent P.

Figure 4. XPS spectra of NiCoP NPs in the Ni 2p (a), Co 2p (b) and P 2p (c) regions.

In terms of stoichiometry, XPS analysis showed a clear excess of phosphorous at the NP surface: $P/(Ni+Co)=2.9$. This excess of P might be related to the presence of TPOP as surface ligand and to the stripping of metal ions from the NP surface during the purification procedure.²⁷ The metal ratio obtained from XPS analysis showed a slight excess of cobalt, $Co/Ni=0.9$, which was consistent with the EELS compositional maps showing an excess of Co at the NP surface. This slight surface segregation of Co was also consistent with the higher ratio Co^{2+}/CoP measured, when compared with $Ni^{2+/3+}/NiP$, and it could have been generated by the surface oxidation itself owing to the slightly lower electronegativity of Co than Ni, and thus its higher tendency to react with oxygen.

To study the mechanism of formation of the $Ni_{2-x}Co_xP$ NPs, we analyzed aliquots of a reacting mixture at different reaction temperatures and times (**Figure 5**). We selected the NiCoP composition for this study. From the first solid product recovered, at 230 °C, only Ni and P were detected by EDX. The XRD pattern of these initial NPs displayed a weak and broad peak at ca. 62°, indicating a close to amorphous atomic structure. As the reaction temperature increased to 260 °C, Co was introduced within the NPs and the Co/Ni ratio increased to ca. $Co/Ni = 0.46$. The XRD pattern of the material produced at 260 °C showed a broad reflection at around 61°. Additionally a small peak at ca. 40°, around the position of the main XRD peak of the hexagonal phase of NiCoP, started to appear, demonstrating the formation of a crystalline lattice with the proper phase. By the time when the solution reached the set reaction temperature, 290 °C, the ratio of Co/Ni had increased to $Co/Ni=0.67$. At this point, the broad XRD peak had shifted to about 51°, while the peak corresponding to the (111) reflection of NiCoP had become much more intense. As the reaction time increased, with the solution at 290 °C, more cobalt was introduced into the lattice up to a final $Co/Ni=0.94$ for this particular sample. Meanwhile, NPs crystallinity continuously improved (**Figure 5**). It should be pointed out that Ni_2P and Co_2P hexagonal phases display two different metal coordination sites, the tetrahedral geometry (M1) site and the square pyramidal geometry (M2) site (**Figure S11**). The square pyramidal geometry site is larger than the tetrahedral site.⁴⁵ Therefore, in a NiCoP crystal, the slightly larger Co^{2+} ions are expected to occupy the larger M2 site, while slightly smaller Ni^{2+} ions would occupy the M1 sites.⁴⁶

Figure 5. a) XRD patterns obtained from aliquots extracted from a NiCoP NP reaction mixture at different temperatures and reaction times. b) Ratio of the Co and Ni composition, Co/Ni, in the solid products precipitated from aliquots, as measured by EDX.

To analyze the influence of TPOP and HDA on the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NP size and geometry, NPs were grown from solutions containing different amounts of these compounds. **Figure 6** shows the TEM images, size distribution histograms and XRD patterns of the NiCoP NPs obtained from the reaction of 1 mmol of metal chlorides with different amounts of TPOP, from 3 to 20 mmol. As the amount of TPOP increased, the average size of the obtained NiCoP NPs increased from 8 ± 1 to 24 ± 3 nm. We believe that TPOP plays a double role in the formation of the precursor metal complexes: as phosphorous source and as reducing agent. It is through this second role that it controls the NP size. As the amount of TPOP increases, a faster growth rate is obtained during the first stage of the synthesis, thus the free monomer concentration is more rapidly reduced, limiting the number of nucleation events and thus the number of NPs formed.⁴⁷

Figure 6. Representative TEM micrographs (a), size distribution histograms (b) and XRD patterns (c) of NiCoP NPs produced using 1 mmol of metals and 3 mmol, 10 mmol or 20 mmol of TPOP, as indicated. Scale bars = 100 nm.

Figure 7 shows the TEM images, size distribution histograms and XRD patterns of the NiCoP NPs obtained from the reaction of the 1 mmol of metal chlorides with 10 mmol TPOP, in the presence of different amounts of HDA, from 10 mmol to 1 mmol. With excess amounts of HDA, quasi spherical NiCoP NPs were formed. However, as the amount of HDA was reduced, the NiCoP NP morphology became elongated and at equivalent metal and HDA concentrations, NiCoP nanorods were produced. We believe HDA to also play different roles in the reaction mixture. The presence of HDA is essential for the metal chlorides to be dissolved in the ODE solution. HDA reacts with the chlorine ions present in solution from the dissolution of the metal chlorides to form a hexadecylammonium chloride ($\text{HDA} \cdot \text{HCl}$) complex. This $\text{HDA} \cdot \text{HCl}$ complex probably binds at the NiCoP NPs surface influencing their growth. HDA itself also binds at the NiCoP NPs surface, playing a key role in controlling their growth and colloiddally stabilizing them in solution. We

hypothesize that the HDA·HCl complex preferentially binds at particular NP facets, while HDA binds at NiCoP sites throughout the whole NP surface.⁴⁸ When excess amounts of HDA are present in the reaction mixture, no preferential growth direction is defined due to the unselective binding of HDA. However, when stoichiometric amounts of HDA and metal chlorides are present, most of the HDA will be occupied in the formation of the HDA·HCl complex, which selective binding results in the growth of NiCoP nanorods. XRD patterns showed the increase of the relative intensity of the (111) reflection with the nanorods formation, confirming this one to be the preferential growth direction.

Figure 7. Representative TEM micrographs (a), size distribution histograms, including width and length for the elongated NPs (b) and XRD patterns (c) of NiCoP NPs produced from the reaction of 1 mmol of metals in the presence of 10 mmol, 2 mmol and 1 mmol of HDA. Scale bars = 100 nm.

The synthetic protocol proposed here was characterized by an excellent reproducibility and production yields above 90% after purification. The two types of precursor used, metal chlorides and TPOP, are relatively low cost, are stable in ambient conditions and present a low-toxicity. The synthetic protocol was designed to make use of a heating up strategy to facilitate up scaling. We explored the scale up of the present synthetic procedure to the production of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NP at the gram scale. We simply increased a factor 20 the amounts of metal chlorides, TPOP and HDA, but increased just a factor 10 the volume of solvent, ODE, thus raising a two-fold the concentration. We also prolonged both the initial solvent cleaning step and the reaction time to 2 h. The $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs produced from this straightforward scaling up showed an excellent quality with very narrow size distributions, a high reproducibility and above 90% yields (**Figure 8**).

Figure 8. a) Representative TEM micrograph and b) size distribution histogram of the NiCoP NPs produced in a scaled up procedure resulting in over 1g of NPs per batch (c).

FTIR spectra were consistent with the presence of HDA ligands at the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NP surface (**Figure 9**). FTIR peaks at 2910 and 2847 cm^{-1} were attributed to C-H stretching vibrations of alkyl groups from HDA. The peaks at 1464 and 722 cm^{-1} were assigned to C-H bending vibrations and the peak at 1605 cm^{-1} corresponded to the N-H bending vibration. For free HDA, two clear peaks at 1050 and 914 cm^{-1} were assigned to the C-N and C-C stretching vibration, respectively. However, those peaks appeared merged in a broad band centered at 1032 cm^{-1} in the FTIR spectrum from the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs. Organic ligands were stripped from the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs surface through mixing them with HPF_6 in formamide solution to form a two phase system that was vigorously stirred at room temperature. The absence of stretching modes of C-H, C-C and C-N in the final $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs confirmed the elimination of HDA from the NP surface.

Figure 9. FTIR of TPOP, HDA, NiCoP NPs before and after ligand removal.

The electrocatalytic activity of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs with different composition was tested toward the HER in acidic conditions. Electrodes were prepared by drop casting onto a GCE an ink prepared by mixing $\text{Ni}_{2-x}\text{Co}_x\text{P}$

NPs with carbon powder and Nafion (see experimental section for details). Electrochemical measurements were conducted at room temperature in a standard three-electrode cell using the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NP-based catalyst as working electrode, a Pt mesh as counter electrode and Ag/AgCl as reference electrode. The HER polarization curves were obtained in H_2 -saturated 0.5 M H_2SO_4 aqueous solutions. **Figure 10a** shows linear sweep voltammograms (LSVs) of the electrodes produced from $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs with different compositions. Data for the GCE and a commercial Pt/C electrocatalysts was also plotted as a reference. Figure 10b shows the overpotential at $J=10 \text{ mA cm}^{-2}$ as a function of the composition. As expected, the Pt/C catalyst showed an excellent HER performance with a very low overpotential, while the bare GCE showed negligible HER activity. Binary Ni_2P exhibits HER activity with an overpotential of 136 mV at $J=10 \text{ mA cm}^{-2}$. As cobalt was introduced within ternary $\text{Ni}_{2-x}\text{Co}_x\text{P}$ NPs, improved performances were obtained and the overpotential at $J=10 \text{ mA cm}^{-2}$ decreased down to 97 mV for NiCoP NPs. When increasing the amount of Co above the Co:Ni=1:1 metal ratio, worse electrocatalytic properties were again measured until an overpotential of 118 mV was measured for Co_2P . Notice that the overpotential of the electrode based on NiCoP NPs was lower than that obtained from most other non-noble metal-based electrocatalysts reported for HER in acid media, including MoS_2 , MoN , CoSe_2 , WS_2 , Ni_3S_2 , Co_2P , FeP , $\text{WS}_{2(1-x)}\text{P}_{2x}$, $\text{Mn}_{0.05}\text{Co}_{0.95}\text{Se}_2$ and CoMoS_3 (**Table S2** and **S3**).

To understand the variation of catalytic activity with the composition, we investigate the HER pathways on $\text{Ni}_{2-x}\text{Co}_x\text{P}$ catalysts by DFT calculations. A series of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ ($x=0, 0.33, 0.67, 1, 1.33, 1.67, 2$) crystals were created with the hexagonal crystal phase (**Figure S1**). The HER pathway is generally depicted as a three-state diagram, with an initial state of $\text{H}^+ + e$, an intermediate adsorbed H^* , being $*$ the adsorption site, and a final product of $1/2\text{H}_2$ in acidic media.⁴⁹⁻⁵⁰ The lower the Gibbs free energy of the adsorbed atomic hydrogen, ΔG_{H^*} , the stronger the bond between this adsorbed hydrogen and the catalyst. Materials that bind hydrogen atoms too strongly, do not allow the hydrogen release thus blocking active sites and failing to efficiently evolve hydrogen. On the other hand, materials that bind hydrogen too weakly, hinder the step of proton/electron-transfer because they fail to stabilize the intermediate state, thus also prevent an efficient HER to take place.³⁴ ΔG_{H^*} is thus a reasonable descriptor to evaluate the HER activity of catalysts. Taking into account this unique descriptor, the Sabatier principle predicts a volcano distribution of the catalyst performance as a function of ΔG_{H^*} , peaking at $\Delta G_{\text{H}^*}=0$.

To deep inside the observed dependence of the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ catalysts performance toward HER, we calculated ΔG_{H^*} on the most active (0001) surface of $\text{Ni}_{2-x}\text{Co}_x\text{P}$ crystals. **Figure 10c** shows the relationship between the value of ΔG_{H^*} and Co content, indicating that the value of ΔG_{H^*} decreased with Co content increasing. When the percentage of Co was 50% (NiCoP), the value of ΔG_{H^*} is -0.025eV, which is the minimum $|\Delta G_{\text{H}^*}|$ value among all the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ compositions tested (calculation details are given in **Table S1**). This result is consistent with the experimental results showing the NiCoP catalysts to have the highest activity toward HER among the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ series measured.

We observed that the DFT calculated ΔG_{H^*} rapidly separated from the optimum value when increasing the cobalt concentration above $x=1$, while the ΔG_{H^*} variation in the Ni rich side was not so abrupt. This result does not match with the moderate performance change obtained when moving from NiCoP to Co_2P , if compared with the stronger loss of performance measured when moving from NiCoP to Ni_2P . Therefore, additional parameters, beyond ΔG_{H^*} need to be considered to explain the compositional dependence of the $\text{Ni}_{2-x}\text{Co}_x\text{P}$ catalysts performance toward HER.

The stability of NiCoP for HER was analysed through chronoamperometric measurements. The NiCoP catalyst exhibited a high stability toward HER at about 30 mA cm^{-2} for 12 h, with a current density decrease of ca. 11% during the 12 h period (**Figure S12**).

Figure 10. a) Polarization curves of GCE, Ni_{2-x}Co_xP and Pt/C in 0.5 M H₂SO₄ solution. b) Overpotential at 10 mA cm⁻² as a function of composition for the different Ni_{2-x}Co_xP electrocatalysts. c) Free-energy diagram for atomic hydrogen adsorption on the Ni_{2-x}Co_xP (0001) surface. d) Overpotential at 10 mA cm⁻² as a function of the Gibbs free energy for atomic hydrogen adsorption at the Ni_{2-x}Co_xP surface.

4. CONCLUSION

In summary, monodispersed Ni_{2-x}Co_xP (0 ≤ x ≤ 2) NPs were synthesized using metal chlorides as metal precursors, TPOP as phosphorus precursor and HDA as ligand. Different compositions, sizes and morphologies could be prepared simply by tuning the ratio of metal chlorides, TPOP and HDA, respectively. The synthetic approach was up-scaled to the production of Ni_{2-x}Co_xP at the gram scale with yields above 90%. Ni_{2-x}Co_xP NPs, mixed with carbon black and Nafion, showed notable HER activities. In particular, NiCoP electrocatalysts showed best performances with an overpotential of 97 mV at 10 mA cm⁻², and significant long-term stability. The dependence of the catalyst performance with the composition qualitatively matched the variation of the Gibbs free energy for atomic hydrogen adsorption at the Ni_{2-x}Co_xP surface. Ni-rich compositions were characterized by too low adsorption energies that were not effective for proton reduction, while Co-rich NPs showed to high binding energies that limited hydrogen desorption, thus blocking adsorption sites. This low-cost and straightforward method for Ni_{2-x}Co_xP NPs showed potential application for industrial production of catalysts for HER. Furthermore, such a synthetic protocol is expected to be expanded as a general strategy for other ternary metal phosphides.

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