Article Carbon Monoxide-Assisted Synthesis of Nickel Cobalt Phosphide Nanorods for the Hydrogen Evolution Reaction

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Abstract: The development of efficient and costeffective catalysts for hydrogen evolution reaction (HER) is crucial for the advancement of electrochemical water splitting technology. Here, we report a novel synthetic method for the preparation of single-crystalline NiCoP nanorods with tunable aspect ratios using a carbon monoxide (CO)-assisted, trioctylphosphine (TOP)-mediated approach. The introduction of CO gas at different temperatures allows for the control of the nanorod growth, resulting in various aspect ratios while maintaining a hexagonal



crystal structure and a composition of 1:1 Ni/Co as NiCoP. Our results demonstrate that the NiCoP nanorods with higher aspect ratios exhibit improved HER activity and stability, with the highest aspect ratio nanorods showing the lowest overpotential and Tafel slope in both acidic and alkaline media. This study highlights the importance of controlling the size and morphology of bimetallic phosphide nanoparticles to optimize their catalytic activity for HER, providing new insights into the design and optimization of nanostructured catalysts for electrochemical water splitting applications.

Keywords: CO; NiCoP; nanorods; DFT; HER

1. Introduction

Transition metal phosphides have emerged as a promising class of catalysts in various industrial applications, including water splitting for hydrogen production [1–5], biomass hydrogenation or hydrodeoxygenation [6], as well as energy conversion and storage [7,8]. Their exceptional properties and abundance make them attractive alternatives to precious metals in these applications, allowing for lower costs. Notably, transition metal phosphides have been extensively explored for the hydrogen evolution reaction (HER) since the seminal work of one of the nickel phosphides (Ni₂P) as an alternative to Pt for HER reported by Schaak and Lewis in 2013 [9]. Studies have demonstrated the importance of controlling the size and morphology of nickel phosphide nanoparticles to optimize their catalytic activity for HER [5]. For example, one-dimensional (1D) nanostructures, such as nanorods and nanowires, have been demonstrated to exhibit enhanced HER activity [10–13]. Theoretical calculations have shown that the nickel bridge sites on the surface of the long side of the 1D nanostructures, which grow along the [001] direction of the hexagonal Ni₂P, exhibit lower Tafel slopes for HER compared to the (001) facet [10]. Other studies have provided evidence that 1D Ni₂P can expose a Ni₃P₂ surface, generated during HER, as active sites, or offer the possibility of tuning the surface roughness to enhance HER [11].

On the other hand, adding a secondary metal to create bimetallic phosphides has resulted in significantly improved catalytic activity, often surpassing that of their monometallic counterparts [14,15]. The enhanced performance is thought to stem from synergistic electronic and structural modifications that alter the characteristics of the active sites. Ni_xCo_yP_z is one of the most active catalysts, as predicted by theoretical calculations and confirmed by the experimental results [14,15]. A composition study of Ni_{2-x}Co_xP ($0 \le x \le 2$) nanocrystals for HER



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showed that these electrocatalysts exhibited enhanced activity, with NiCoP showing particularly promising performance and excellent long-term stability [16]. Building on these findings, this work focuses on the synthesis of the NiCoP nanorods using a CO-assisted, trioctylphosphine (TOP)-mediated method, and investigates the effects of aspect ratios on the HER electrocatalytic activity.

The TOP-mediated synthesis is a solution-based method of metal phosphides involving TOP as the phosphorus source. Back in the early 2000s, TOP and trioctylphosphine oxide (TOPO) were used for the synthesis of iron phosphides nanorods and nanowires by Liu and coworkers [17]. The method was generalized to several mono-metal phosphide nanorods including MnP, Co_2P , FeP, and Ni_2P by Hyeon and coworkers [18]. Some of the progress was later summarized by Brock and coworkers for the synthesis of MnP, FeP, and Fe₂P with their magnetic and catalytic applications [19]. Recently, Zhang and coworkers used Co_2P nanorods as seeds to grow Co_2P/MP_x (M = Fe, Ni, Mn, and Cu) core/shell nanorods, which were then loaded them onto a support for further annealing to form CoMP_x nanorods [20]. However, it remains challenging to synthesize single-crystalline bimetallic phosphide nanorods using this method.

In this work, we report a TOP-mediated method assisted by the in-situ generated CO for the synthesis of single-crystalline NiCoP nanorods with different aspect ratios. The method introduces in-situ generated CO into our previously-established synthesis for nickel phosphides [21], in which the equimolar metal precursors are thermally decomposed in the presence of oleylamine (OLAM) and TOP, resulting in the synthesis of single-crystalline NiCoP nanorods. Depending on the stage of CO introduced to the reaction, the aspect ratio could be tuned from 1:3 to 1:16 while maintaining hexagonal crystal structure the same as that of Ni₂P and a composition of 1:1 Ni/Co as NiCoP. The crystallinity and growth direction of the resulting NiCoP were characterized by high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS). The NiCoP nanorods are single-crystalline in nature and growing preferentially along the [001] direction. The role of CO in the synthesis was investigated by monitoring the kinetics of the formation and disappearance of metal-TOP complex. The electrocatalytic activities and stabilities of these nanostructures for HER were compared, revealing a positive correlation between aspect ratio and electrocatalytic performance.

2. Experimental Methods

2.1. Chemicals and Materials

Nickel(II) acetylacetonate (Ni(acac)₂, 96%) and cobalt(II) acetylacetonate (Co(acac)₂, 99%) were purchased from Acros Organics, Geel, Belgium. 1-octadecene (ODE, 90%) was purchased from Alfa Aesar, Lancashire, United Kingdom. Oleylamine (OLAM, 70%) and methoxy-polyethylene glycol acetic acid (PEG-COOH, M.W. = 5000) were purchased from Sigma-Aldrich, St. Louis, MO, USA. Trioctylphosphine (TOP, 90%) was purchased from Thermo Scientific, Waltham, MA, USA. Toluene was purchased from Macron Fine Chemicals, Radnor, PA, USA. Ethanol (200 proof) was purchased from Koptec, King of Prussia, PA, USA. Sulfuric acid (95–98%, ACS) and potassium hydroxide (KOH) pellets were purchased from J.T. Baker, Radnor, PA, USA. Formic acid (\geq 88.0%, ACS) was purchased from VWR BDH Chemicals, Radnor, PA, USA. Hexane and chloroform were purchased from EMD Millipore, Burlington, MA, USA. Ultrapure water (18.2 M Ω) was obtained from a Milli-Q Integral system (Rahway, NJ, USA). The chemicals were used directly as purchased, unless further specified.

2.2. Synthesis of NiCoP Nanorods

The NiCoP nanorods were synthesized using thermal decomposition of Ni and Co precursors simultaneously in the presence of TOP, OLAM, and CO. Typically, Ni(acac)₂ (25.7 mg, 0.1 mmol) and Co(acac)₂ (25.7 mg, 0.1 mmol) were added to a 3-neck round-bottom flask, followed by adding 4 mL of ODE and 1 mL of OLAM. The reaction flask was equipped with a magnetic stirring bar, a condenser, and a Schlenk line under Ar protection. The reaction mixture was degassed for 10 min under Ar. Prior to heating, 1 mL of TOP was injected into the reaction mixture under magnetic stirring. The reaction mixture was heated to 300 °C and held at this temperature for 20 min. In order to form nanorods, CO was introduced to the reaction mixture during the heating process twice, using a balloon. Briefly, CO was generated by mixing 10 mL of sulfuric acid and 10 mL of formic acid in a single neck round-bottom flask equipped with a balloon via a syringe and a needle. After the formed CO inflated the balloon, the balloon was transferred to the reaction flask and left there for 10 s. During this process, the CO-filled balloon was introduced to the reaction mixture with a noticeable smog that was observed. Details regarding CO generation and introduction are provided in the Supporting Information (Figure S1). For nanorods with a low aspect ratio, CO was introduced at 175 and 280 °C, respectively. In this two-step CO addition process, CO

was generated via one reaction for 10 min prior to the first injection. Each CO introduction delivered 3.2 ± 0.32 mL under approximate ideal gas conditions.

2.3. Synthesis of CoNiP Spherical Nanoparticles (Nanospheres)

The nanospheres were synthesized using the same method, except that no CO was introduced to the mixture during the reaction.

2.4. UV-Vis Measurement

The UV-vis spectra were acquired by diluting 10 μ L of solution at different temperatures or time points from the reaction of interest in 2 mL of ODE at 60 °C in a quartz cuvette. Warmed ODE at 60 °C was used as a blank. In a typical reaction, 100 μ L aliquots were taken out by a 1 mL syringe equipped with a long needle from the reaction at each temperature or time point into 1-dram glass vials. From these aliquots, a 10 μ L quantity was taken out by a 50 μ L glass syringe for dilution in 2 mL of warmed ODE prior to the UV-vis measurement.

2.5. Characterization

The transmission electron microscope (TEM) images were taken using a TEM (JEOL JEM-1011, Tokyo Japan) with an acceleration voltage of 100 kV. Each TEM sample was prepared by drop-casting 5–10 μ L of diluted nanoparticle suspension on a 200-mesh carbon-formvar coated copper grid. Powder X-ray diffraction (XRD) patterns were recorded using a diffractometer (Rigaku XtaLAB Synergy-S, Tokyo, Japan) with a Cu K_a radiation source. A sample pellet of 100 μ g was dried using a N₂ stream before it was loaded on a nylon loop for XRD measurement. Elemental concentrations of the samples were measured using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific iCAP Q, Waltham, MA, USA). The samples were digested using nitric acid and diluted in 2 vol.% nitric acid as a matrix into the concentration range of 1–100 ppb. High-resolution TEM (HRTEM) images were collected using a JEOL ARM200CF (Tokyo, Japan) operated at 200 kV equipped with dual CEOS GmbH C_s correctors and a Gatan K3 IS detector for image collection. Scanning transmission electron microscopy—annular dark-field (STEM-ADF) images and energy dispersive spectroscopy (EDS) maps were collected using a FEI Talos S/TEM (Waltham, MA, USA) operated at 200 kV with a Super-X EDS system. Annular dark-field (ADF) images were collected with an inner acceptance angle of approximately 30–35 mrad.

2.6. Electrochemical Measurements

All electrochemical measurements were performed in a 3-electrode cell setup using a potentiostat (Biologic SP-150, Seyssinet-Pariset, France). A glassy carbon (GC) rotating disk electrode (0.2 cm^2) was used as the working electrode. Prior to preparation of catalyst inks, the nanoparticle samples were transferred into an ethanol suspension via a ligand exchange process where 2 mL of each sample in toluene was stirred with 2.5 mg of PEG-COOH dissolved in 5 mL of chloroform for 6 h, followed by purification with hexane, ethanol, water, and subsequently resuspended in ethanol. The catalyst ink was prepared by mixing 500 µL of ~2 mg/mL nanoparticle suspension in ethanol with 50 µL of a 0.04 wt.% Nafion solution and drop-casted onto the GC electrode with a catalyst loading of 50 µg/cm².

The electrochemical measurements were performed in both acidic and basic media with the working electrode rotated at a rate of 2400 rpm controlled by an electrode rotator (Pine Research, Durham, NC, USA). For the measurement in acidic medium, 0.5 M H₂SO₄ was used as an electrolyte, while a Ag/AgCl, double junction electrode (Pine Research, Durham, NC, USA) was used as the reference electrode, and a graphite rod seated inside a fritted glass tube (Pine Research, Durham, NC, USA) was used as the counter electrode. The potential conversion followed: E (vs. RHE) = E (vs. Ag/AgCl) + (0.0591 × pH) + E^o(Ag/AgCl), where pH is 1 and E^o(Ag/AgCl) is 0.199 V. For the measurements in alkaline medium, 1 M KOH was used as the electrolyte, while a Hg/HgO electrode (CHI) was used as the reference electrode, and a home-customized Pt foil or Pt wire (~4.7 cm²) seated inside a fritted glass tube (Pine Research) was used as the counter electrode. The potential conversion followed: E (vs. RHE) = E (vs. Hg/HgO) + (0.0591 × pH) + E^o(Hg/HgO), where pH is 14 and E^o(Hg/HgO) is 0.98 V. Nitrogen was used to purge the electrolyte solution for 5 min prior to the electrochemical measurements. Linear sweep voltammetry (LSV) was carried out at a scan rate of 10 mV/s from 0 to -0.5 V vs. RHE. An 85% iR correction was applied to all scans. The stability tests were performed at 10 mA/cm² for 2 h.

3. Results and Discussion

The synthesis of NiCoP at a stoichiometric ratio of 1:1:1 was carried out in the presence of OLAM at elevated temperature using Ni(acac)₂ and Co(acac)₂ at an equimolar ratio as metal precursors, and TOP as the phosphorus source. During the reaction, CO gas, which was generated by the decomposition of formic acid by sulfuric acid [22], was introduced via a balloon, syringe and needle at different temperatures for 10 s. Figure 1A illustrates the reaction scheme of the synthesis. Depending on how the CO was added during the reaction, three distinct morphologies of NiCoP nanostructures were formed: the spherical nanoparticles or nanospheres (NSs), the nanorods with low aspect ratio (LAR NRs), and the nanorods with high aspect ratio (HAR NRs). TEM images reveal that the NSs have an average size of 17.9 ± 2.3 nm (Figure 1B), while the LAR NRs exhibit lengths of 53.3 ± 7.8 nm and widths of 16.8 ± 2.6 nm, resulting in an aspect ratio of 3.2 (Figure 1C). In contrast, the HAR NRs display lengths of 50.4 ± 5.2 nm and widths of 6.7 ± 0.9 nm, yielding an aspect ratio of 7.5 (Figure 1D). XRD analysis indicates that all of these nanostructures exhibit a set of the peaks at 41.02, 44.94, 47.62, ~55 (specifically, 54.48, 54.79 and 55.38), 75.48, and 80.94 degrees of 2θ , which can be indexed to the XRD pattern of NiCoP (COD1008056) [23–25]. The ICP-MS results, listed in Table S1, confirm that the composition of the nanostructures is approximately 1:1:1.



Figure 1. (A) Schematic illustrating the synthesis of NiCoP nanostructures. (**B**–**D**) TEM images of the NiCoP nanostructures: (**B**) nanospheres (NSs) with an average size of 17.9 ± 2.3 nm; (**C**) low-aspect-ratio nanorods (LAR NRs) with a length of 53.3 ± 7.8 nm and a width of 16.8 ± 2.6 nm, resulting in an aspect ratio of 3.2; (**D**) high-aspect-ratio nanorods (HAR NRs) with a length of 50.4 ± 5.2 nm and a width of 6.7 ± 0.9 nm, resulting in an aspect ratio of 7.5. (**E**,**F**) XRD patterns of the corresponding samples in (**B**–**D**): (**E**) NS; (**F**) LAR NR; and (**G**) HAR NR, which can be indexed to the XRD pattern of the crystal structure of NiCoP labeled in blue.

In the absence of CO gas, the reaction yielded spherical NiCoP nanoparticles. To further elucidate their structure, HRTEM and EDS mapping were employed. The results reveal a mixture of single-crystalline and polycrystalline nanoparticles. A representative single-crystalline nanoparticle, shown in Figure 2A, exhibits lattice spacings corresponding to the $(0\bar{2}1)_{NiCoP}$ and $(1\bar{2}\bar{1})_{NiCoP}$ crystallographic planes, viewed from the [412] zone axis of hexagonal NiCoP similar to hexagonal Ni₂P. In contrast, Figure 2B illustrates a polycrystalline nanoparticle

with distinct grain boundaries within the particle. Notably, EDS maps (Figure 2D–F) demonstrate that Ni, Co, and P are uniformly distributed throughout each particle, irrespective of their crystallinity, indicating no elemental segregation.



Figure 2. HRTEM and EDS mapping of NiCoP NS: (**A**) HRTEM image of the nanoparticle with lattice spacings marked with $d_1 = (0\overline{2}1)_{\text{NiCoP}}$ and $d_2 = (1\overline{2}\overline{1})_{\text{NiCoP}}$. (**B**) HRTEM image of a polycrystalline nanoparticle with the grain boundary and particle outlined in red. (**C**–**F**) EDS mapping of Ni, Co, and P in two nanoparticles, with an ADF image inset in (**C**). Simplified scale bars of 7 nm are used in (**D**–**F**) for data visibility.

Upon addition of CO gas at 175 and 240 °C, the reaction resulted in nanorods with low aspect ratio. HRTEM analysis of a representative LAR NR, shown in Figure 3A, reveals that it is single-crystalline in nature. The crystallographic orientation of the LAR NR is characterized by a lateral direction along the [110] axis and a longitudinal direction along the [001] axis. It is implied that the reaction conditions promote the growth of the NiCoP nanostructures along the [001] direction, leading to the formation of nanorods. These observations are consistent with previous studies on the growth of mono-metal phosphide Ni₂P nanorods, which also exhibit growth along the [001] direction of the hexagonal Ni₂P crystal structure [26,27]. Furthermore, the EDS mapping (Figure 3B–E) indicates a uniform distribution of Ni, Co, and P throughout individual particles, with no apparent elemental segregation. Based on these results, the addition of CO facilitates the formation of single-crystalline seeds that lead to elongation of the nanoparticles into nanorods.

The introduction of CO gas at 175 and 280 °C led to the formation of nanorods with high aspect ratio. Similarly, HRTEM analysis of a representative HAR NR (Figure 4A) confirms its single-crystalline nature, with growth occurring along the [001] direction and a lateral direction along the [110] axis, analogous to that of the LAR NR. It is noted that the [112] direction is not aligned with the long axis of the rod, likely due to out-of-plane rotation as the rod is in a cluster instead of lying flat on the TEM grid as in Figure 3A. While most HAR NRs exhibit a uniform distribution of Ni, Co, and P throughout the particle, occasional deviations are observed, where excess Co is present at specific locations (indicated by arrows), coinciding with the absence of Ni, suggesting segregation. P is consistently present throughout normal and Co-rich regions. Compared to LAR NRs, the second addition of CO gas at a higher temperature allows the thinner rods to form while both LAR NRs and HAR NRs

have similar length. The temperature of second CO gas addition affects the growth of the NRs in the lateral direction.



Figure 3. HRTEM and EDS mapping of NiCoP LAR NR: (A) HRTEM image of a thick rod with orientation indicated. (B–E) EDS mapping of Ni, Co, and P in three rods, with an ADF image inset in (B). Simplified scale bars of 40 nm are used in (C–E) for data visibility.



Figure 4. HRTEM and EDS mapping of NiCoP HAR NR: (A) HRTEM image of a thin rod with orientation indicated (B) Lower magnification ADF image of thin rod morphology. (C) ADF image and (D–G) EDS mapping of two rods with arrows indicating areas of Co segregation/Ni depletion. P was excluded from the composite map in (D) to highlight the Ni/Co segregation. Simplified scale bars of 10 nm are used in (E–G) for data visibility.

Since CO plays an important role in the synthesis to promote the growth of NiCoP nanorods, we carried out additional experiments using various CO addition conditions to explore their effects on the nanorod formation. We determined whether two CO additions are necessary. For comparison, we performed a single addition of CO gas at the three different temperatures previously chosen: 175, 240, and 280 °C while keeping all other conditions the same as the reaction without CO addition. The results are shown in Figure 5. The TEM images display the size and shape of the nanoparticles. Upon CO addition at 175 °C, the size of the nanoparticles has a length of 51.0 \pm 6.0 nm and a width of 29.6 \pm 3.8 nm, resulting in an aspect ratio of 1.7, whereas both CO additions at 240 and 280 °C resulted in spherical particles with similar average sizes of 9.0 \pm 1.5 nm and 11.9 \pm 1.3 nm, respectively. The XRD patterns of these three samples indicate that they match well with the hexagonal NiCoP, the same as those of LAR NR and HAR NR. Based on these results, we found that the addition of CO at 175 °C is important for the formation of elongated particles. The additional CO gas that was introduced to the reaction allowed for the reduction of the lateral dimension of the nanorods, resulting in the increase of the aspect ratio of the rods.



Figure 5. TEM images (A–C) and XRD patterns (D–F) of products obtained from reactions with a single CO addition at 175 °C (A,D), 240 °C (B,E), and 280 °C (C,F).

To further investigate the effects of CO on the reaction kinetics, we carried out UV-vis measurements on the aliquots taken out from the reactions for NS, LAR NR, and HAR NR at various stages. The resulting UV-vis spectra of the aliquots for each reaction are presented in Figure 6. According to our previous study, the peak at 313 nm can be attributed to electronic transition of Ni(0)-TOP complex [21]. However, we could not find the spectral signature for Co(0)-TOP which is expected to exhibit a peak at 378 nm based on our theoretical prediction (Figure S1). Although Co precursor is present, the Ni(0)-TOP complex is expected to form initially due to the lower redox potential of Ni²⁺ to Ni(0) compared to that of Co²⁺ to Co(0). In the absence of CO gas, the peak intensity at 313 nm increases gradually with the rising temperature, reaching its maximum at 280 °C, and then decreases and disappears after being held at 300 °C for 5 min (Figure 6A). Based on the TEM results, the reaction forms a mixture of single-crystalline and polycrystalline spherical nanoparticles with no anisotropic growth.

In the presence of CO gas, CO can play multiple roles in the reaction, including acting as a chelating ligand to coordinate with the metal center, a reducing agent to reduce the metal cation, and a capping ligand that adsorbs onto the particle surface. In particular, CO has been introduced as reducing agent in the shape and composition-control of platinum alloy nanocrystals by Yang and co-workers [28,29]. In our case, the first CO addition at 175 °C facilitates the reduction of metal precursors, as evident from the jump in the intensity of the peak at 313 nm for LAR NR (Figure 6B) and HAR NR (Figure 6C) compared to that of NS. The TEM study also supports that the first CO addition also facilitates the formation of single crystals which serves as the seeds for the growth of metal phosphide nanorods. Since the nucleation of the reactions occurs at around 220 °C, the second addition of CO at a higher temperature can act as a reducing agent to reduce the metal precursors, as well as a capping agent to guide the nanocrystal growth. The addition of CO at a higher temperature suppresses the lateral growth of the nanorod, thereby increasing the aspect ratio of the nanorods.



Figure 6. UV-vis spectra of reaction aliquots taken at various stages during the synthesis of NS (**A**), LAR NR (**B**), and HAR NR (**C**). (**D**) Plots of absorbance at 313 nm as a function of temperature for each reaction, with data points beyond 300 $^{\circ}$ C corresponding to reactions held at 300 $^{\circ}$ C for extended periods (5, 10, 15, and 20 min), as indicated by the green arrow pointing from the dashed green line.

We also investigated the effects of the reaction time on the nanorod growth. We extended the reaction time at 300 °C from 20 min to 60 min, while keeping the other reaction conditions constant for each set of reactions. Extending reaction time increases the aspect ratios of nanorods, as shown in Figure 7A–C. For a single CO addition at 175 °C, the nanorods grew to a length of 64.4 ± 12.8 nm and a width of 33.0 ± 4.7 nm, with an aspect of 2.0 after 60 min of reaction, compared to 1.7 after 20 min of reaction. For dual CO additions at 175 and 240 °C, the nanorods resulted in a length of 58.3 ± 7.6 nm and a width of 16.1 ± 2.2 nm, with an aspect ratio of 3.6 after 60 min of reaction, versus 3.2 after 20 min of reaction. For dual CO additions at 175 and 280 °C, the reaction yielded a mixture of thinner nanorods (99.0 ± 20.8 nm in length and 6.6 ± 1.2 nm) width with an aspect ratio of 15 and thicker nanorods (78.5 ± 7.3 nm in length and 16.2 ± 2.7 nm) width with an aspect ratio of 4.8 after 60 min of reaction. The comparison of dimensional information for different reaction conditions is listed in Table S2. The XRD patterns in Figure 7D–F, confirm that all the nanorods are composed of hexagonal NiCoP.

We conducted a comparative study of the HER activities of 1D nanostructures in both acidic and alkaline media. The LSV experiments were performed at a scan rate of 10 mV/s in 0.5 M H₂SO₄ and 1 M KOH, respectively. In the acidic medium (0.5 M H_2SO_4), we observed that the HER overpotential at a current density of 10 mA/cm² decreased with increasing aspect ratio of the nanostructures. Specifically, the HAR rods exhibited the lowest overpotential of 187 mV, while the LAR rods and NS particles showed similar overpotentials of 237 and 264 mV, respectively, as illustrated in Figure 8A. Further analysis of the LSV data using Tafel plots revealed that the Tafel slopes for the HAR rods, LAR rods, and NS particles were 56, 66, and 88 mV/dec, for their overpotential ranges of 125-182 mV, 169-236 mV, and 175-262 mV, respectively (Figure 8B). These values suggest that the HER mechanism on the HAR rods proceeds via a Volmer-Heyrovsky pathway, whereas the LAR rods and NS particles follow a Volmer mechanism. The result is based on the general consideration that Tafel slop can provide insights into the reaction mechanism of HER on the catalyst surface with the theoretical values for the Volmer step, the Heyrovsky step, and the Tafel step in the HER to be 120, 40, and 30 mV/dec [30,31]. In contrast, when the same catalysts were tested in an alkaline medium (1 M KOH), the HER overpotential at 10 mA/cm² increased compared to the acidic condition, in agreement with the findings for other catalysts such as noble metals due to water as the proton source in the HER under the alkaline conditions [32,33]. Notably, the HAR rods still exhibited the lowest overpotential of 412 mV, while the LAR rods and NS particles showed higher overpotentials of approximately 500 mV, as shown in Figure 8C. Tafel analysis in the alkaline medium yielded slopes of 101, 142, and 146 mV/dec in the potential ranges of 306–460 mV, 342–495 mV, and 348–500 mV for the HAR rods, LAR rods, and NS particles, respectively (Figure 8D). These values indicate that the HER mechanism on the HAR rods also proceeds via a Volmer-Heyrovsky pathway, whereas the LAR rods and NS particles follow a Volmer mechanism. Based on these results, we conclude that the 1D nanostructures enhance the catalytic activity for HER by promoting the Heyrovsky mechanism and optimizing the hydrogen binding energy, which is associated with a more efficient hydrogen evolution process.

Figure 7. TEM images (A–C) and XRD patterns (D–F) of products obtained from reactions with a single CO addition at 175 °C (A,D), dual CO additions at 175 and 240 °C (B,E), and dual CO additions at 175 and 280 °C (C,F).

Figure 8. HER evaluation on NS, LAR NR, and HAR NR under acidic and alkaline media: (**A**,**B**) LSVs at a scan rate of 10 mV/s in 0.5 M H₂SO₄ and their Tafel plots; and (**C**,**D**) LSVs at a scan rate of 10 mV/s in 1 M KOH and their Tafel plots. The current density is normalized by the geometric surface area (0.2 cm^2) of the GC rotating disk electrode. The oscillation in the LSVs at high negative potentials (>-0.3 V vs. RHE) is due to the bubble formation on the catalyst surface.

The electrochemically active surface area (ECSA) of each catalyst was evaluated using the double layer capacitance (C_{dl}) method, a widely accepted technique for determining the ECSA of electrocatalysts [34–36]. This method measures the capacitance of the double layer formed at the electrode-electrolyte interface, which is assumed to be directly proportional to the ECSA. To determine the ECSA, cyclic voltammetry (CV) was performed on each catalyst in the non-Faradaic region (±50 mV of open circuit potential, OCP), where no redox reactions occur, with their scan rate varying from 1 to 250 mV/s. The C_{dl} was calculated from the slope of the linear relationship between the current obtained at OCP and scan rate. The ECSA was then calculated using the equation: ECSA = C_{dl}/C_s , where C_s is the specific capacitance of the material. The values of C_s used in this study were 0.035 cm² for acidic conditions and 0.040 cm² for basic conditions, which are typical values reported in the literature [36]. The results show that HAR NR has a significantly higher ECSA than LAR NR and NS under acidic conditions, indicating that it has a more extensive surface area available for electrochemical reactions (Figure S3 and Table S3). This is likely due to the unique morphology of HAR NR, which may provide more active sites for HER. In contrast, under basic conditions, the ECSA of HAR NR is less pronounced in this environment (Figure S4 and Table S4). The LSVs normalized by the ECSA of each catalyst were plotted in Figure S5.

We further investigate the stability of NS, LAR NR, and HAR NR for HER under acidic and alkaline conditions using chronopotentiometry (CP). The CP experiments were conducted at a constant current density of 10 mA/cm². Figure 9A illustrates the potential changes as a function of time in 0.5 M H₂SO₄, revealing distinct stability profiles for each material. Notably, the overpotential increases at rates of -10.0 mV/h and -12.9 mV/hfor HAR NR and LAR NR, respectively. In contrast, NS exhibits a decrease in overpotential at a rate of 0.4 mV/h, suggesting that its surface may undergo reconstruction to facilitate HER. To further assess activity after the stability test, we performed LSV before and after the CP experiments, with the results presented in Figure S6. The LSV data indicate a slight decrease in HAR NR activity, negligible change in LAR NR activity, and an increase in NS activity. Under alkaline conditions, HAR NR demonstrates superior stability compared to NS and LAR NR, with overpotential increases of -3.8 mV/h, -7.0 mV/h, and -20.9 mV/h for HAR NR, NS, and LAR NR, respectively (Figure 9B). Notably, the CP experiments induce a significant enhancement in the catalytic activity of all three materials, as evidenced by a substantial decrease in overpotential at 10 mA/cm². Specifically, the overpotentials decrease from 421 mV to 180 mV for HAR NR, and from 500 mV to 280 mV for both LAR NR and NS (Figure S7). The enhancement of HER activity can be attributed to the structural evolution of the phosphide catalysts to their corresponding hydroxide phases under the alkaline conditions [37,38]. The aspect ratio of the nanostructures plays a crucial role in determining the HER activity and stability, with higher aspect ratios leading to improved performance. These findings have important implications for the design and optimization of nanostructured catalysts for electrochemical water splitting applications.

Figure 9. Chronopotentiometry (CP) evaluation on NS, LAR NR, and HAR NR by recording the potential changes while holding the current density at 10 mA/cm² under acidic and alkaline media: (A) in 0.5 M H_2SO_4 ; and (B) in 1 M KOH.

4. Conclusions

We have successfully synthesized single-crystalline NiCoP nanorods with tunable aspect ratios using a Coassisted, TOP-mediated approach. The introduction of CO gas at different temperatures allows for the control of the nanorod growth, resulting in various aspect ratios while maintaining a hexagonal crystal structure and a composition of 1:1 Ni/Co as NiCoP. The electrocatalytic activities of these nanostructures for the HER were investigated, revealing a positive correlation between aspect ratio and electrocatalytic performance. Our results demonstrate that the NiCoP nanorods with higher aspect ratios exhibit improved HER activity and stability, with the highest aspect ratio nanorods showing the lowest overpotential and Tafel slope. Our results are in line with previous studies on the Ni₂P 1D nanostructures, which have shown that the Ni bridge sites on the surface of the long side of these nanostructures, oriented along the [001] direction of the hexagonal Ni₂P crystal structure, exhibit enhanced HER activity compared to the (001) facet [10]. The enhanced performance is thought to stem from synergistic electronic and structural modifications that alter the characteristics of the active sites. The study highlights the importance of controlling the size and morphology of bimetallic phosphide nanoparticles to optimize their catalytic activity for HER. The findings have significant implications for the design and optimization of nanostructured catalysts for electrochemical water splitting applications, which is crucial for the development of sustainable energy systems.

Supplementary Materials: The following supporting information can be downloaded at: https://media.sciltp.com/articles/ others/2506201608320087/MI-1091-SI-proofreading.pdf, CO generation setup and experimental details, ICP-MS results, DFT calculation of the UV-vis spectrum of Co(0)-TOP4 complex, ECSA measurement, LSVs normalized by ECSA, LSVs before and after CP measurements. References [39–42] are cited in the Supplementary Materials.

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