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# Phase Directing Ability of an Ionic Liquid Solvent for the Synthesis of HER-Active Ni<sub>2</sub>P Nanocrystals

Emily J. Roberts,<sup>†</sup> Carlos G. Read,<sup>‡</sup> Nathan S. Lewis,<sup>‡,\*</sup> and Richard L. Brutchey<sup>†,\*</sup>

<sup>†</sup>Department of Chemistry, University of Southern California, Los Angeles, California 90089, USA

<sup>‡</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

**KEYWORDS:** *ionic liquid, nickel phosphide, nanocrystal, electrocatalyst, hydrogen evolution reaction*

**Abstract:** An ionic liquid (IL) solvent was used to synthesize small, phase-pure nickel phosphide (Ni<sub>2</sub>P) nanocrystals. In contrast, under analogous reaction conditions, substitution of the IL for the common high-boiling organic solvent 1-octadecene (ODE) results in phase-impure nanocrystals. The 5-nm Ni<sub>2</sub>P nanocrystals prepared in IL were electrocatalytically active towards the hydrogen evolution reaction. The synthesis in IL was also extended to alloyed Ni<sub>2-x</sub>Co<sub>x</sub>P nanocrystals, where 0.5 ≤ x ≤ 1.5.

Room temperature ionic liquids (ILs) have garnered increased interest because of their unique physicochemical properties relative to traditional organic solvents. For example, ILs are non-flammable, have high thermal and chemical stability, possess a wide liquidus range, and have extremely low vapor pressures (~10<sup>-10</sup> Pa at 25 °C), amongst other properties that result in environmental health and safety benefits relative to traditional organic solvents.<sup>1,2</sup> As a result of these unique properties, ILs are becoming an increasingly attractive class of solvents for the synthesis of colloidal inorganic nanocrystals.

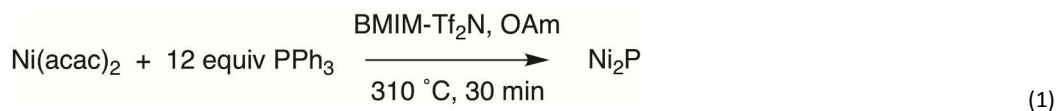
The low interfacial tension possessed by ILs tends to induce rapid nucleation rates, resulting in small particles with high surface-area-to-volume ratios.<sup>2</sup> In addition, ILs can stabilize the surfaces of inorganic nanocrystals through combined electrostatic and steric effects, minimizing agglomeration and Ostwald ripening.<sup>2</sup> Consequently, imidazolium-based ILs have been investigated as dual-functioning solvents and stabilizers for the synthesis of a variety of colloidal inorganic nanocrystals, including metal and metal oxide nanocrystals (e.g., Au, Ag, Pt, Rh, Cu, ZnO, NiO, TiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>).<sup>3-8</sup> Despite the reported thermal stability of many ILs, their practical utilization in high-temperature colloidal nanocrystal syntheses is not well developed.

We report herein the high-temperature synthesis of Ni<sub>2</sub>P nanocrystals as an interesting proof-of-concept reaction. Ni<sub>2</sub>P has attracted considerable interest as a result of the relative Earth abundance of its constituent elements, stability in alkaline as well as acidic media, and catalytic activity for the hydrodeoxygenation of biomass,

the hydrodesulfurization of petrol, and the hydrogen evolution reaction (HER).<sup>9-11</sup> The binary Ni–P phase diagram is complex, with a large number of thermodynamically stable stoichiometries (Ni<sub>3</sub>P, Ni<sub>5</sub>P<sub>2</sub>, Ni<sub>12</sub>P<sub>5</sub>, Ni<sub>2</sub>P, Ni<sub>5</sub>P<sub>4</sub>, NiP, NiP<sub>2</sub>, and NiP<sub>3</sub>), thereby creating a synthetic challenge with respect to accessing phase-pure Ni<sub>2</sub>P. In general, increasing the molar equivalents of phosphide precursor, extending the reaction time, and operating at higher temperatures allow the more phosphorus-rich side of the phase diagram to be accessed for colloidal nanocrystals.<sup>12-14</sup>

Typical methods used to synthesize high-quality colloidal Ni<sub>2</sub>P nanocrystals use traditional organic solvents (e.g., octadecene (ODE), dioctyl ether), expensive and/or reactive phosphide precursors (tri-*n*-octylphosphine (TOP), white phosphorus (P<sub>4</sub>), tris(trimethylsilyl)phosphine (P(TMS)<sub>3</sub>), and tri-*n*-butylphosphine), high temperatures, and/or multiple-step reactions.<sup>10,15-17</sup> Triphenylphosphine (PPh<sub>3</sub>) is a low-cost, less-reactive, and more air-stable phosphide precursor (~15% the cost of TOP in price per mole);<sup>18</sup> however, compared to TOP and P(TMS)<sub>3</sub>, nanocrystals synthesized using PPh<sub>3</sub> are typically large (>45 nm), ill-defined, amorphous, and/or not phase pure.<sup>18-20</sup>

Herein, we report the one-step, heating up synthesis of Ni<sub>2</sub>P nanocrystals using Ni(acac)<sub>2</sub>, PPh<sub>3</sub>, oleylamine (OAm), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM-Tf<sub>2</sub>N) as the IL solvent (Eq. 1, see Supporting Information for detailed experimental). This particular IL solvent was specifically chosen for its superior thermal stability, because weakly coordinating anions are relatively stable with respect to high-temperature decomposition.<sup>7</sup> The ~12 molar equivalents of PPh<sub>3</sub> was used since lower P:Ni precursor ratios resulted in larger, phase-impure nanocrystals. When the reactants were heated to 310 °C at a rate of ~10 °C min<sup>-1</sup> and held at temperature for 30 min, small, phase-pure Ni<sub>2</sub>P nanocrystals were obtained. The isolated yield of the resulting Ni<sub>2</sub>P nanocrystals was 80% relative to the Ni(acac)<sub>2</sub> precursor, as assessed by organic content-corrected thermogravimetric analysis (Figure S1).



All of the diffraction peaks in the powder X-ray diffraction (XRD) pattern of the resulting nanocrystals were ascribable to the hexagonal structure of Ni<sub>2</sub>P (Figure 1a), indicating that the resulting product was crystalline and phase-pure Ni<sub>2</sub>P. The diffraction peaks at 40.87, 44.79, 47.60, and 54.44° 2θ can be indexed to the (111), (021), (210), and (002) reflections, respectively. The lattice parameters were calculated to be *a* = 5.85 and *c* = 3.37 nm, which are in good agreement with those reported for bulk Ni<sub>2</sub>P (PDF#01-089-2742). Scherrer analysis of the peak broadening yielded an average grain size of 5.6 nm. Transmission electron microscope (TEM) images revealed that the resulting Ni<sub>2</sub>P nanocrystals were spherical in shape, with an average diameter of 5.0 ± 0.9 nm, and a standard deviation about

the mean ( $\sigma/d$ ) of 18%. The nanocrystal size is in agreement with the predicted grain size determined by Scherrer analysis, consistent with the formation of single-domain particles (Figure 1b,c). No void spaces within the nanocrystals were observable by high-resolution TEM analysis (Figure 1c), implying that the growth mechanism may not involve the phosphidation of a crystalline Ni intermediate, which typically results in particle hollowing by the Kirkendall effect.<sup>21</sup> A  $d$ -spacing of 0.220 and 0.204 nm was calculated for the observed lattice fringes, corresponding to the (111) and (021) planes of the hexagonal  $\text{Ni}_2\text{P}$  structure, respectively.

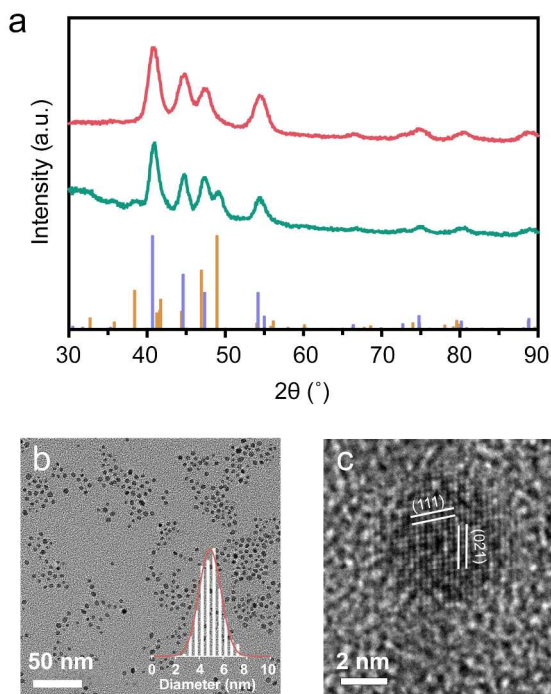


Figure 1. (a) XRD patterns of nickel phosphide nanocrystals synthesized in BMIM-Tf<sub>2</sub>N (red) and 1-octadecene (green) at 310 °C for 30 min. The purple stick pattern represents Ni<sub>2</sub>P and the gold stick pattern represents Ni<sub>12</sub>P<sub>5</sub>. (b) TEM micrograph and corresponding size histogram (inset) of Ni<sub>2</sub>P nanocrystals synthesized in BMIM-Tf<sub>2</sub>N. (c) High-resolution TEM micrograph displaying lattice fringes of the (111) and (021) planes.

When ODE was substituted in place of BMIM-Tf<sub>2</sub>N as the solvent, under otherwise identical reaction conditions, mixed-phased products were obtained after 30 min at 310 °C. These products contained the phosphorus-poor Ni<sub>12</sub>P<sub>5</sub> phase as well as the desired Ni<sub>2</sub>P phase, as indicated by the presence of an additional diffraction peak at  $\sim 49^\circ$   $2\theta$  by XRD that corresponds to the 100% intensity (312) reflection of Ni<sub>12</sub>P<sub>5</sub> (PDF#01-089-2742) (Figure 1a). TEM micrographs revealed that the phase-impure nanocrystals synthesized in ODE were relatively ill-defined and faceted, with the particles being almost twice the average diameter ( $10.9 \pm 2.5$  nm;  $\sigma/d = 23\%$ ) as those synthesized by the analogous

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3 reaction in IL (Figure S2). The relatively smaller size of the resulting nanocrystals synthesized in BMIM-Tf<sub>2</sub>N suggests  
4 that the IL is playing an important role during synthesis, consistent with expectations that ILs can provide shape<sup>22,23</sup>  
5 and size-directing<sup>23-25</sup> capabilities, but this is the first report of obtaining a specific phase by using an IL solvent  
6 instead of traditional organic solvents.  
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10 A variable temperature study was performed to understand in more detail the phase evolution that occurred in  
11 BMIM-Tf<sub>2</sub>N relative to ODE as the solvent (Figure 2). In BMIM-Tf<sub>2</sub>N, nucleation was observed beginning at ~180 °C,  
12 and isolable particles were produced by 220 °C, which is also the temperature at which significant phosphine gas  
13 evolution is observed.<sup>12</sup> In the absence of OAm, no nucleation is observed, indicating that OAm is acting as the  
14 primary reducing agent. When the same molar equivalents of TOP were substituted for PPh<sub>3</sub>, the particles were not  
15 isolatable due to their small size. For all temperatures up to 310 °C, powder XRD patterns of the reaction products  
16 displayed a single broad peak that has previously been assigned to an amorphous Ni-P phase.<sup>26</sup> This diffraction peak is  
17 in agreement with Brock's observation of the formation of an amorphous Ni-P phase when higher P:Ni stoichiometric  
18 ratios are used.<sup>13</sup> In contrast, when ODE is substituted as the solvent, nucleation was not observed until 200-220 °C.  
19 Post-nucleation, nuclei were not isolable in ODE at temperatures below 280 °C due to their small size. Moreover, gas  
20 evolution is not observed in ODE until ~260 °C. Hence, both particle nucleation and phosphine gas evolution occurred  
21 at lower temperatures in the IL solvent than when in ODE. The diffractogram for the reaction product from ODE at  
22 280 °C displayed a similar amorphous Ni-P phase as the particles obtained from the IL solvent, but exhibited a  
23 significant shoulder at 49° 2θ, which can be indexed to the 100% intensity peak of Ni<sub>12</sub>P<sub>5</sub>. In ODE, once the reaction  
24 temperature reached 310 °C for 2 min, a mixed-phase Ni<sub>12</sub>P<sub>5</sub>-Ni<sub>2</sub>P product was obtained, and it has previously been  
25 reported that crystalline Ni<sub>12</sub>P<sub>5</sub> can serve as an intermediate phase to Ni<sub>2</sub>P in ODE.<sup>27</sup> The data are thus consistent with  
26 the hypothesis that evolution of the Ni<sub>2</sub>P phase in the IL solvent does not proceed through an observable Ni<sub>12</sub>P<sub>5</sub>  
27 intermediate, as is observed in ODE, but rather has a delayed amorphous-to-crystalline transition that leads directly  
28 to the crystalline, more phosphorus-rich phase; however, obtaining a high yield required a reaction time of 30 min.  
29 These results imply that the IL may be interacting with the surface and consequently influencing nucleation and  
30 growth.  
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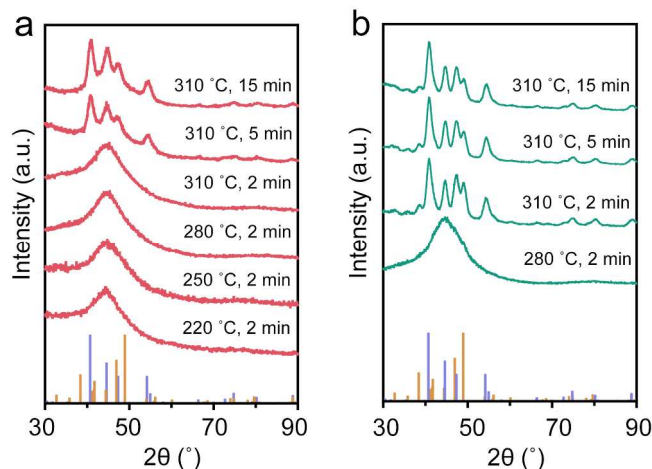


Figure 2. Powder XRD patterns of nickel phosphide nanocrystal syntheses performed at various times and temperatures in (a) BMIM-Tf<sub>2</sub>N and (b) ODE solvents. The purple stick pattern corresponds to Ni<sub>2</sub>P and the gold stick pattern corresponds to Ni<sub>12</sub>P<sub>5</sub>.

To determine if the IL was coordinated to the purified nanocrystal surface, high-resolution X-ray photoelectron spectroscopic (XPS) data were collected showing F 1s and S 2p signals, confirming the presence of the bis(trifluoromethane)sulfonimide anion (Figure S3a,b). Three sets of doublets were observed in the Ni 2p region, with the first set of 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks having binding energies of 852.9 and 870.2 eV, respectively, and possessing the expected spin-orbit splitting ( $\Delta = 17.3$  eV) for Ni species (Figure 3a). The observed Ni 2p<sub>3/2</sub> binding energy is slightly higher than that of metallic Ni (Ni<sup>0</sup> 2p<sub>3/2</sub> = 852.7 eV), consistent with a Ni $\delta^+$  species that is in good agreement with previous reports for Ni<sub>2</sub>P.<sup>28</sup> The remaining doublets, with 2p<sub>3/2</sub> binding energies of 855.8 and 861.0 eV, can be assigned to oxidized surface species (e.g., NiO and NiOOH) and expected satellite peaks, respectively.<sup>29</sup>

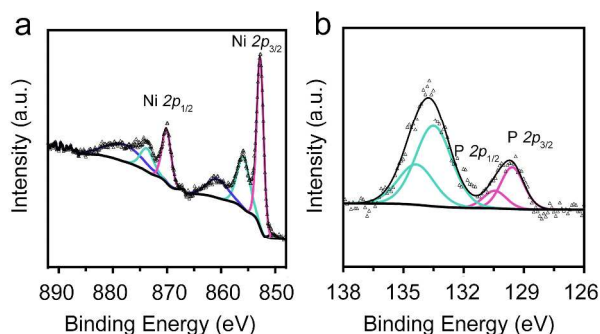


Figure 3. High-resolution XPS spectra of (a) Ni 2p and (b) P 2p regions.

The high-resolution XPS data in the P 2p region exhibited peak envelopes at binding energies of 130.2 and 134.2 eV, each of which consisted of doublets with 2p<sub>3/2</sub> peaks at 129.8 and 134.0 eV, respectively (Figure 3b). Both doublets exhibited the expected spin orbit splitting of 0.8 eV. The peak present at lower binding energies can be

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3 attributed to reduced P species within the Ni<sub>2</sub>P structure, while the doublet at ~134 eV is ascribable to oxidized P<sup>5+</sup>  
4 surface species.<sup>30</sup> The surface oxidation of both Ni and P is a result of storage in air and is not expected to  
5 deleteriously influence the catalytic activity of the Ni<sub>2</sub>P nanocrystals, provided that the material is reduced prior to  
6 catalysis (vide infra).  
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10 To further confirm the presence of BMIM-Tf<sub>2</sub>N on the surface of the nanocrystals, FT-IR spectra of the Ni<sub>2</sub>P  
11 nanocrystals were obtained *post*-purification (Figure S4). Symmetric and asymmetric ν(SO<sub>2</sub>) stretching bands at 1135  
12 and 1350 cm<sup>-1</sup>, and an asymmetric ν(CF<sub>3</sub>) stretching band at 1196 cm<sup>-1</sup>, correspond to the presence of the NTF<sub>2</sub><sup>-</sup>  
13 anion and corroborate the XPS observations. Bands from the overlapping modes of the BMIM<sup>+</sup> cation, including ν(C-C)  
14 and ν(NCH<sub>3</sub>), appear at 1055 cm<sup>-1</sup>, in a region where both OAm and PPh<sub>3</sub> do not exhibit IR-active modes.<sup>31</sup>  
15 Additionally, PPh<sub>3</sub> or oxidized Ph<sub>3</sub>P=O species are likely coordinated to the nanocrystal surface, as indicated by the  
16 appearance of bands appearing at 1436, 1477, and 1581 cm<sup>-1</sup> that are ascribable to phenyl C-C bond stretches.<sup>32</sup> No  
17 IR bands expected for coordinated OAm were observed in the Ni<sub>2</sub>P nanocrystals. The observation of FT-IR bands  
18 corresponding to BMIM-NTf<sub>2</sub> is consistent with the IL acting as a stabilizer.<sup>22</sup> Coordination to the surface thus appears  
19 to influence the resulting phase and morphology, and supports the observation of small, single-phase particles as  
20 compared to the nanocrystals produced in non-coordinating ODE under analogous conditions.  
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30 The HER activity of the Ni<sub>2</sub>P nanocrystals was also evaluated and compared to Ni<sub>2</sub>P nanocrystals that were  
31 synthesized by more conventional routes. The working electrode was prepared by drop-casting a colloidal suspension  
32 of purified Ni<sub>2</sub>P nanocrystals onto a Ti foil substrate (to achieve a mass loading ~1 mg cm<sup>-2</sup>), followed by heating at  
33 400 °C in forming gas (5% H<sub>2</sub>/95% N<sub>2</sub>) for 1 h to remove ligands and reduce any oxidized surface species.<sup>10</sup> A typical  
34 three-electrode set up in 0.5 M H<sub>2</sub>SO<sub>4</sub> (aq) was utilized. Figure 4a presents the polarization data for the Ni<sub>2</sub>P  
35 nanocrystals, along with a standard Pt mesh electrode and a bare Ti foil as working electrodes. The Ni<sub>2</sub>P nanocrystals  
36 exhibited overpotentials of  $\eta_{-10 \text{ mA/cm}^2} = -107 \text{ mV}$  and  $\eta_{-20 \text{ mA/cm}^2} = -125 \text{ mV}$ , as compared to the overpotentials for the  
37 Pt mesh electrode ( $\eta_{-10 \text{ mA/cm}^2} = -12 \text{ mV}$  and  $\eta_{-20 \text{ mA/cm}^2} = -20 \text{ mV}$ ). The bare Ti foil substrate did not exhibit substantial  
38 electrocatalytic activity for HER over this potential range. The Tafel slopes were 30 mV/decade and 70 mV/decade for  
39 Pt mesh and the Ni<sub>2</sub>P nanocrystals, respectively. These overpotentials and Tafel slopes are in accord with the behavior  
40 of Ni<sub>2</sub>P nanocrystal-based electrodes with comparable mass loadings that were synthesized using typical high-boiling  
41 organic solvents.<sup>33</sup> For example, Schaak and coworkers reported an overpotential and Tafel slope of  $\eta_{-10 \text{ mA/cm}^2} = -116$   
42 mV and 46 mV/decade for their Ni<sub>2</sub>P nanocrystals synthesized in ODE using similar reagents.<sup>10</sup> Galvanostatic  
43 measurements at a current density of -20 mA/cm<sup>2</sup> displayed only a slight decrease in potential over the course of 15 h  
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of continuous hydrogen evolution (Figure S5). Cyclic voltammogram sweeps of the Ni<sub>2</sub>P electrode between 0 and -0.2 V vs RHE illustrate the continued activity of the nanocrystals during on and off cycling (Figure S6). Moreover, chronopotentiometric measurements for the Ni<sub>2</sub>P nanocrystals in 1 M NaOH showed that they also exhibit stable operation in alkaline media at -10 mA/cm<sup>2</sup> for more than 10 h (Figure S7).

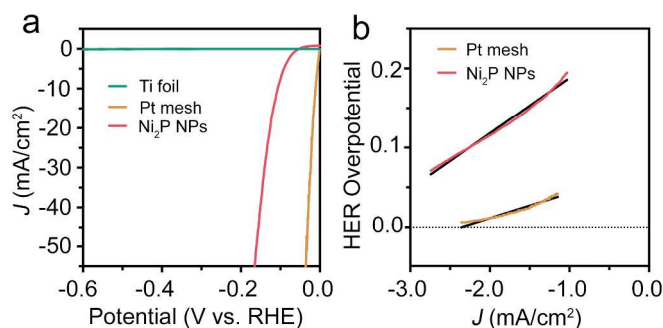


Figure 4. (a) Polarization data in 0.5 M H<sub>2</sub>SO<sub>4</sub> for Ni<sub>2</sub>P nanocrystals synthesized in BMIM-Tf<sub>2</sub>N on a Ti foil substrate, bare Ti foil, and Pt mesh electrode. (b) Corresponding Tafel plots for the Ni<sub>2</sub>P nanocrystal and Pt mesh electrodes.

The synthetic methodology described herein was also extended to the synthesis of phase-pure, mixed-metal Ni<sub>2-x</sub>Co<sub>x</sub>P nanocrystals ( $0.5 \leq x \leq 1.5$ ) by simply adjusting the precursor ratio of Ni(acac)<sub>2</sub> to Co(acac)<sub>2</sub> and increasing the reaction time (see Supporting Information for detailed experimental and characterization). The resulting nanocrystals display a similar size to the Ni<sub>2</sub>P nanocrystals (Figure S8); however, as the concentration of Co increased, the nanocrystals became gradually more faceted and morphologically dissimilar, which has been previously observed for Co-rich Ni<sub>2-x</sub>Co<sub>x</sub>P structures.<sup>11,34</sup>

The composition of the mixed-metal Ni<sub>2-x</sub>Co<sub>x</sub>P nanocrystals was confirmed through a combination of XRD, XPS, and energy dispersive X-ray (EDS) analyses. As the Co content increased, the powder XRD patterns showed a decrease in intensity of the (201) and (210) reflections, and the peak envelope of the (300) and (211) reflections at  $\sim 54^\circ 2\theta$  that appeared as a single peak for  $x \leq 1.0$  split into two resolvable peaks, corresponding to the (002) and (320) reflections of the bulk orthorhombic Co<sub>2</sub>P structure, for  $x = 1.5$  (Figure S9). The unit cell volume increased linearly with increasing Co content for the hexagonal structure ( $x = 0, 0.5, 1.0$ ), confirming that the material was a homogenous solid solution (Figure S10). The experimentally determined composition determined from high-resolution XPS scans of the Ni and Co 2p regions were in close accord with the nominal compositions used during synthesis, indicating facile Co incorporation within the 1 h reaction time (Table S1). The nanocrystals with a Ni<sub>1.0</sub>Co<sub>1.0</sub>P nominal composition were



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3 further examined by EDS mapping, which corroborated that the nominal composition matched the experimental  
4 composition and that the Co and Ni were homogeneously distributed over a cluster of nanocrystals (Figure S12).  
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6 In summary, small, phase-pure Ni<sub>2</sub>P nanocrystals can be synthesized using the IL solvent, BMIM-Tf<sub>2</sub>N. Under  
7 analogous reaction conditions, substituting ODE for the IL instead produced ill-defined, phase-impure nanocrystals,  
8 suggesting that the IL plays an important role in the reaction. XPS and FT-IR spectroscopic evidence confirmed  
9 coordination of the IL to the nanocrystal surface. Despite surface coordination of the IL, the resulting nanocrystals  
10 displayed comparable HER activity to Ni<sub>2</sub>P nanocrystals synthesized by other routes.  
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## 18 **Associated Content**

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20 The Supporting Information is available free of charge on the ACS Publications website at DOI:

21 Experimental; TGA trace of Ni<sub>2</sub>P; TEM micrograph of nanocrystals produced in ODE; additional XPS spectra  
22 of Ni<sub>2</sub>P; FT-IR spectrum of Ni<sub>2</sub>P; additional electrochemical measurements for Ni<sub>2</sub>P; TEM images, XRD, and XPS data  
23 for Ni<sub>2-x</sub>Co<sub>x</sub>P nanocrystals (PDF)  
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## 30 **Author Information**

### 31 **Corresponding Author**

32 \*Email: brutchey@usc.edu; nslewis@caltech.edu  
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## 47 **Abbreviations**

48 acetylacetonate (**acac**)

49 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**BMIM-Tf<sub>2</sub>N**)

50 ionic liquid (**IL**)

51 1-octadecene (**ODE**)  
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3 oleylamine (OAm)

4 trioctylphosphine (TOP)

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6 triphenylphosphine (PPh<sub>3</sub>)  
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## TOC Graphic

