

Supplemental Information

Mild and Selective Hydrogenation of Nitrate to Ammonia in the Absence of Noble Metals

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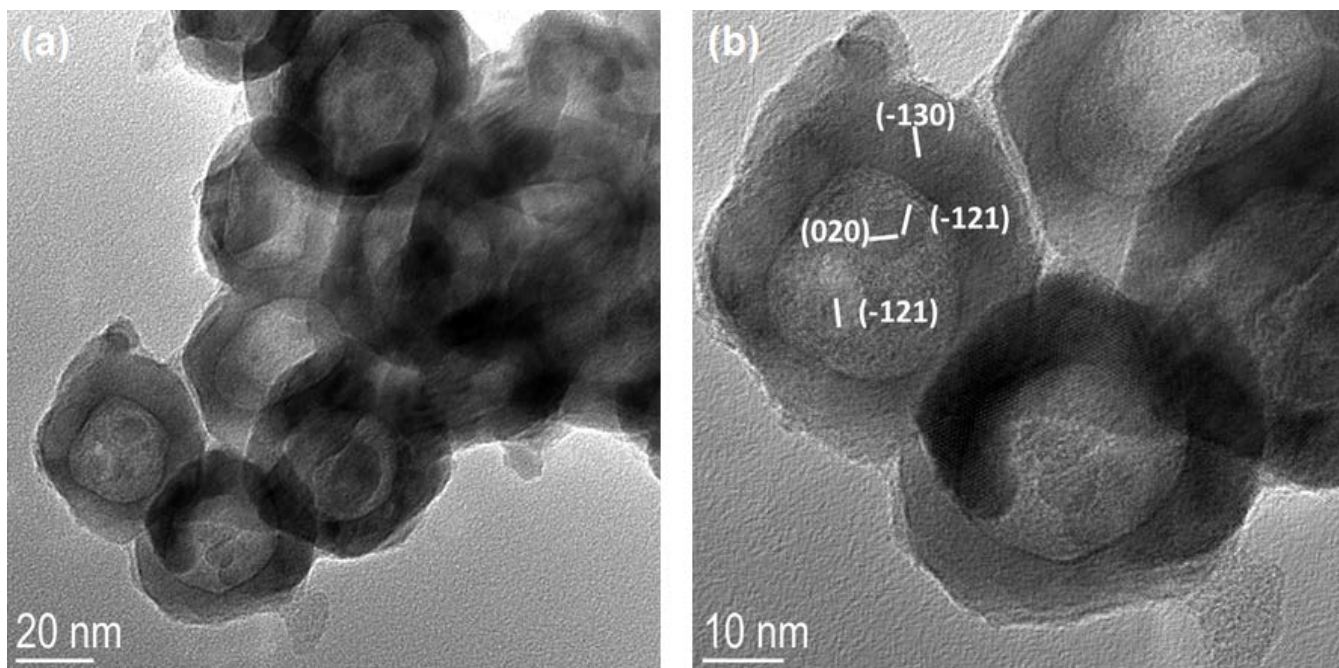


Figure S1. Representative TEM images of Ni_2P nanocrystals, made by our previously reported method,^{S1} and annealed under 1 atm H_2 for 1 h at 400°C .^{S2} Several characteristic lattice fringes are visible at high magnification (b), for example $d = 2.54 \text{ \AA}$ (020), 2.21 \AA (-121), and 1.92 \AA (-130).

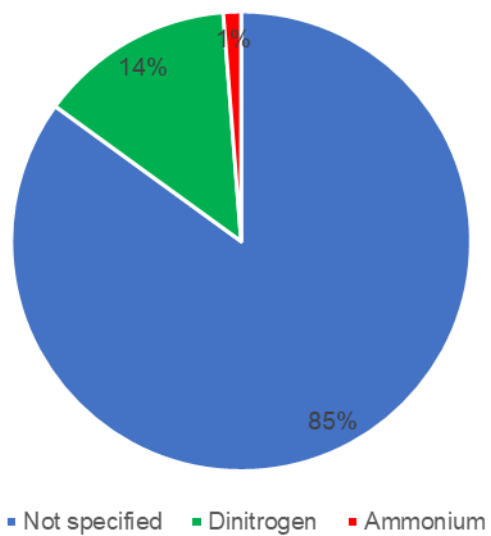


Figure S2. Selectivity of NO_3^- hydrogenation catalysts reported between 1984-present.^{S3}

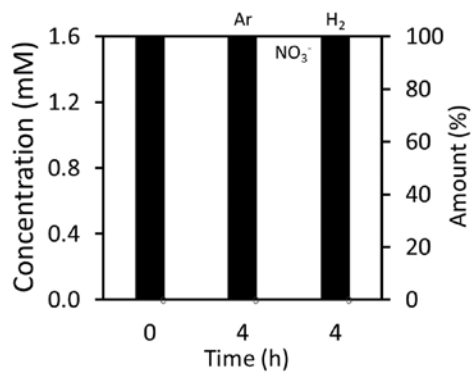


Figure S3. Results (lack of-) of NO₃⁻ hydrogenation in the absence of catalyst.

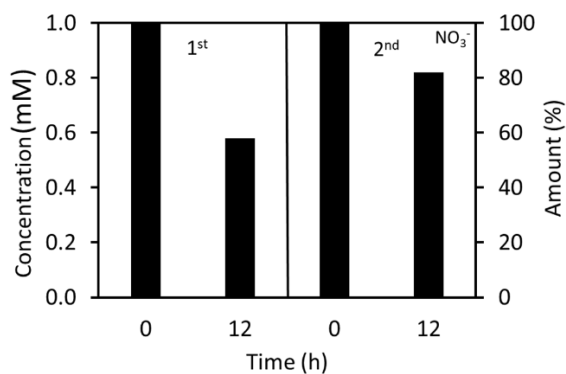


Figure S4. Results of NO₃⁻ hydrogenation without H₂ flow (initial pH = 3).

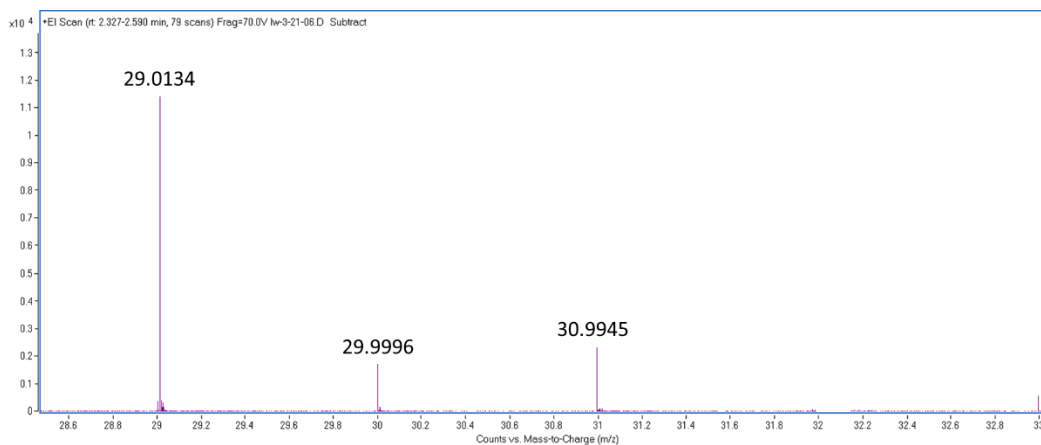


Figure S5. GC-MS analysis of headspace following hydrogenation of Na¹⁵NO₂ (98%).

Table S1. Hydrogenation of Aqueous NO₃⁻-Relevant Reactants over Activated Ni₂P and Ni Catalysts.^a

#	Catalyst ^a	Reactant (mM)	t (h)	pH ₀ ^b (pH _f)	Remain. reactant (mM) (con-ver./%)	Product(s) (mM)	Selectivity (%)	TON ^c (TOF ^d /h)	R _g ^e (10 ⁻⁴ mol·h ⁻¹ ·g ⁻¹) (R _a ^f , 10 ⁻⁶ mol·h ⁻¹ ·m ⁻²)
1	Ni ₂ P ^g	NaNO ₃ (1.6)	4	2 (2)	1.6 (0)	none	Nd ^k	0 (0)	0 (0)
2	Ni ₂ P	NaNO ₃ (1.6)	4	2 (5)	0.02 (99)	NH ₄ ⁺ (1.5)	96	18.9 (4.7)	11.9 (26.1)
3	Ni ₂ P	NaNO ₃ (2.0)	4	2 (6)	0.02 (99)	NH ₄ ⁺ (1.9)	96	23.4 (5.9)	14.9 (32.7)
4	Ni ₂ P	NaNO ₃ (1.6)	24	7 (7)	1.3 (16)	nd	nd	3.0 (0.1)	0.38 (0.83)
5	none	NaNO ₃ (1.6)	4	2 (2)	1.6 (0)	nd	nd	nd	nd
6	Ni ₂ P	NaNO ₃ (1.6) ^h	24	7 (7)	1.6 (0)	nd	nd	0 (0)	0 (0)
7-1	Ni ₂ P	NaNO ₃ (1.0) ^h	12	3 (3)	0.57 (43)	nd	nd	5.1 (0.4)	1.08 (2.37)
7-2	7-1	NaNO ₃ (1.0) ^h	12	3 (3)	0.82 (18)	nd	nd	7.2 ^l (0.3)	0.76 (1.68)
8-1	Ni ₂ P	NaNO ₃ (1.0)	12	3 (4)	0.16 (84)	nd	nd	9.9 (0.8)	2.10 (4.63)
8-2	8-1	NaNO ₃ (1.0)	12	4 (4)	0.22 (78)	nd	nd	19.1 ^l (0.8)	2.03 (4.46)
8-3	8-2	NaNO ₃ (1.0)	12	4 (3)	0.39 (61)	nd	nd	26.3 ^l (0.7)	1.86 (4.09)
8-4	8-3	NaNO ₃ (1.0)	12	3 (3)	0.36 (64)	nd	nd	33.9 ^l (0.7)	1.79 (3.95)
9-1	Ni ₂ P	NaNO ₃ (1.5)	12	3 (3)	0.23 (85)	nd	nd	15.1 (1.3)	3.18 (6.99)
9-2	9-1	NaNO ₃ (1.5)	12	3 (3)	0.36 (76)	nd	nd	28.6 ^l (1.2)	3.01 (6.64)
9-3	9-2	NaNO ₃ (1.5)	12	3 (3)	0.80 (47)	nd	nd	36.9 ^l (1.0)	2.59 (5.71)
9-4	9-3	NaNO ₃ (1.5)	12	3 (3)	0.80 (47)	nd	nd	45.2 ^l (0.9)	2.38 (5.25)
10-1	Ni ₂ P	NaNO ₃ (2.0)	10	2 (1)	0.32 (84)	nd	nd	19.8 (2.0)	5.04 (11.1)
10-2	10-1	NaNO ₃ (2.0)	12	1 (1)	0.52 (74)	nd	nd	37.3 ^l (1.7)	4.31 (9.49)
10-3	10-2	NaNO ₃ (2.0)	8	1 (1)	1.36 (32)	nd	nd	44.9 ^l (1.5)	3.80 (8.37)
11	Ni ₂ P	NaNO ₂ (0.5)	4	2 (2-3)	0.01 (98)	NH ₄ ⁺ (0.19)	39	5.8 (1.5)	3.68 (8.09)
12	Ni ₂ P	NaNO ₂ (1.6)	4	2 (2-3)	0 (100)	NH ₄ ⁺ (0.20)	13	18.9 (4.7)	12.0 (26.4)
13	Ni ₂ P	98% Na ¹⁵ NO ₂ (1.6) ⁱ	4	2 (7)	0.24 (85)	NH ₄ ⁺ (0.72)	53	16.1 (4.0)	10.2 (22.5)
14	Ni ₂ P	NO _(g) (1 atm) ^h	4	2 (2)	nd	NO ₃ ⁻ (13), NO ₂ ⁻ (19), NH ₄ ⁺ (1.2)	nd	nd	nd
15	Ni ₂ P	NO _(g) (1 atm)	4	2 (1)	nd	NO ₃ ⁻ (3.0), NO ₂ ⁻ (1.8), NH ₄ ⁺ (1.0)	nd	nd	nd
16	none	NO _(g) (1 atm)	4	2 (2)	nd	NO ₃ ⁻ (13), NO ₂ ⁻ (10)	nd	nd	nd
17	Ni	NaNO ₃ (2.0)	4	2 (3)	1.7 (17)	(NO _{x(g)}) ^j	nd	nd	nd
18	Ni ₂ P + NiO	NaNO ₃ (2.0)	4	2 (6-7)	0.73 (64)	NH ₄ ⁺ (1.13)	89	nd	nd
19	Ni ₂ P + Ni(OH) ₂	NaNO ₃ (2.0)	4	2 (6-7)	1.26 (37)	NH ₄ ⁺ (0.72)	97	nd	nd
20	Ni ₂ P + Na ₃ PO ₄	NaNO ₃ (2.0)	4	2 (7)	1.28 (36)	NH ₄ ⁺ (0.72)	100	nd	nd
21	Ni ₂ P + Ni ₃ (PO ₄) ₂	NaNO ₃ (2.0)	4	2 (6-7)	1.45 (28)	NH ₄ ⁺ (0.52)	95	nd	nd

^a10 mg activated catalyst (H₂-annealed), 60 °C, 1 atm H₂/Ar flow. ^bInitial pH values (pH₀) lower than 7 were achieved by adding either HCl or H₂SO₄ (see Methods). ^cTON = moles of converted substrate / moles of surface active Ni₂P sites. ^dTOF = TON/time. ^eReaction-rate-per-gram-catalyst (R_g) = moles of converted substrate / (time × grams of catalyst). ^fReaction-rate-per-surface-area (R_a) = moles of converted substrate / (time × surface area of catalyst). ^gNon-activated Ni₂P (as made). ^hNo H₂/Ar flow. ⁱBatch reaction (closed vessel). ^jAssumed/not tested, see refs. 25 & 78 in main manuscript. ^kNot determined. ^lCumulative (sum) for all cycles.

Table S2. XPS Measurements of Nanocrystalline Ni₂P NO₃⁻ Hydrogenation Catalysts.^a

Assignment, energy (eV)	As made Ni ₂ P	H ₂ -anld. Ni ₂ P	Ni ₂ P 1 cycle
Ni ^{δ+} 2p _{3/2} 853.0(1)	40%	34%	32%
Ni ²⁺ (NiO) 2p _{3/2} 853.6(1)	4%	none	none
Ni ²⁺ (NiO) 2p _{3/2} satellite 1 855.3(1)	13%	none	none
Ni ²⁺ (NiO) 2p _{3/2} satellite 2 860.8(1)	10%	none	none
Ni ²⁺ (Ni(OH) ₂) 2p _{3/2} 855.7(1)	none	3%	3%
Ni ²⁺ (Ni(OH) ₂) 2p _{3/2} satellite 1 856.5(1)	none	16%	17%
Ni ²⁺ (Ni(OH) ₂) 2p _{3/2} satellite 2 862.3(1)	none	14%	15%
Ni ^{δ+} 2p _{1/2} ^b 870.3(1)	20%	17%	16%
Ni ²⁺ (NiO) 2p _{1/2} ^b 870.9(1)	2%	none	none
Ni ²⁺ (NiO) 2p _{1/2} satellite 1 ^b 872.6(1)	6%	none	none
Ni ²⁺ (NiO) 2p _{1/2} satellite 2 ^b 878.1(1)	5%	none	none
Ni ²⁺ (Ni(OH) ₂) 2p _{1/2} ^b 873.0(1)	none	1%	1%
Ni ²⁺ (Ni(OH) ₂) 2p _{1/2} satellite 1 ^b 873.8(1)	none	8%	9%
Ni ²⁺ (Ni(OH) ₂) 2p _{1/2} satellite 2 ^b 879.6(1)	none	7%	8%

P ³⁻ 2p _{3/2} ^c	68%	57%	63%
129.1(4)			
P ⁵⁺ 2p _{3/2} ^c	32%	43%	37%
133.2(7)			

^aCalibrated using C 1s peak at 284.6 eV as reference. Assignments agree with NIST XPS database^{S4} as well as previous reports.^{S5,S6} ^bNi 2p_{3/2} - Ni 2p_{1/2} spin-orbit splitting $\Delta = 17.3$ eV. ^cP 2p_{3/2} - P 2p_{1/2} spin-orbit splitting $\Delta = 0.87$ eV, P 2p_{3/2} overlaps P 2p_{1/2}.

Additional Computations

NO₃ adsorption. As noted previously,^{S7} single metal (“monometallic”) palladium catalysts are unable to reduce nitrate, perhaps indicating that nitrate cannot bind or coordinate to monometallic palladium sites. To address this challenge, we encase the ions explicitly with water clusters, and balance the charge with H₃O⁺. Using this method, we obtain the adsorption energy of NO₃⁻ on Pd(111) to be close to zero, supporting the claim that nitrate do not adsorb at palladium. However, the same method also predicts nitrate does not adsorb on Cu(111) either. Further refinement may be necessary.

Comparison between Pd(111), Ni(111) and Ni₂P(001) surface. Table S3 lists some key adsorption energies of various adsorbates on Ni₂P(001), Ni(111), and Pd(111). Geometries are obtained from PBE calculations in a vacuum. For Ni₂P(001), we also calculate the adsorption energies in solution using VASPsol. Aside from the difference in coverage dependence for H adsorption, another key difference is in the reduction pathway for NO₃⁻ (Figure S6). On Ni₂P(001), the predominant pathway seems to be H + NO₃⁻ → OH + NO₂. For Ni(111) and Pd(111), the reaction H + NO₃⁻ → O + HNO₂ is slightly more favored, if one considers the difference in the initial and final energies only.

Table S3. Adsorption Energies of Different Reactants on Select Metal Surfaces.

	Ni ₂ P(001)		Ni(111)	Pd(111)	Reference
	Vacuum	Water	Vacuum	Vacuum	
1 H ^a	-0.72	-0.70	-0.59 (r7×r7)	-0.63 (r7×r7)	H ₂ (g)
2 H ^a	-0.36	-0.35	-0.59 (2×2)	-0.62 (2×2)	
3 H ^a	-0.18	-0.17	-0.58 (r3×r3)	-0.62 (r3×r3)	
NO ₃	-2.40	-2.51	-2.24 (2×2)	-1.78 (2×2)	NO ₃ (g)
NO ₂	-2.17	-2.57	-1.97 (2×2)	-1.64 (2×2)	NO ₂ (g)
NO	-2.32	-2.33	-2.48 (2×2)	-2.30 (2×2)	NO (g)
OH	-3.55	-3.32	-3.37 (2×2)	-2.58 (2×2)	OH (g)
NO ₂ +OH	-2.08	-1.87	-2.14 (r7×r7)	-1.10 (r7×r7)	HNO ₃ (g)
HNO ₂ +O	-0.93		-2.26 (2×2)	-1.16 (2×2)	HNO ₃ (g)
H+OH	-0.02	0.23	-0.55 (r7×r7)	0.07 (r7×r7)	H ₂ O (g)
O (1 ML)	-2.01	-2.04	-2.38 (2×2)	-1.40 (2×2)	O ₂ (g)

^aNumber of H per unit cell area. Unit cells for fcc(111) metal calculations (with 1 H per unit cell) are chosen to roughly cover the same regime of H coverage (per unit area) as on Ni₂P.

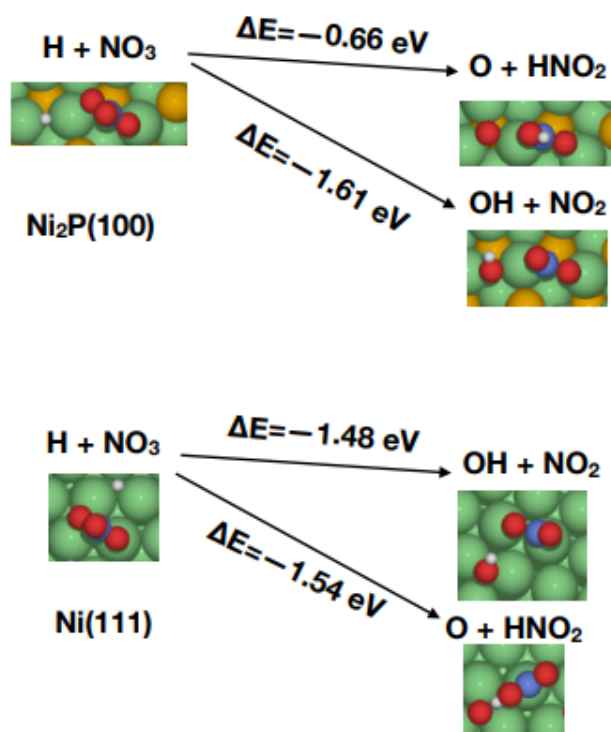


Figure S6. Reaction energies for the reduction of NO₃ on Ni₂P(001) and Ni(111).

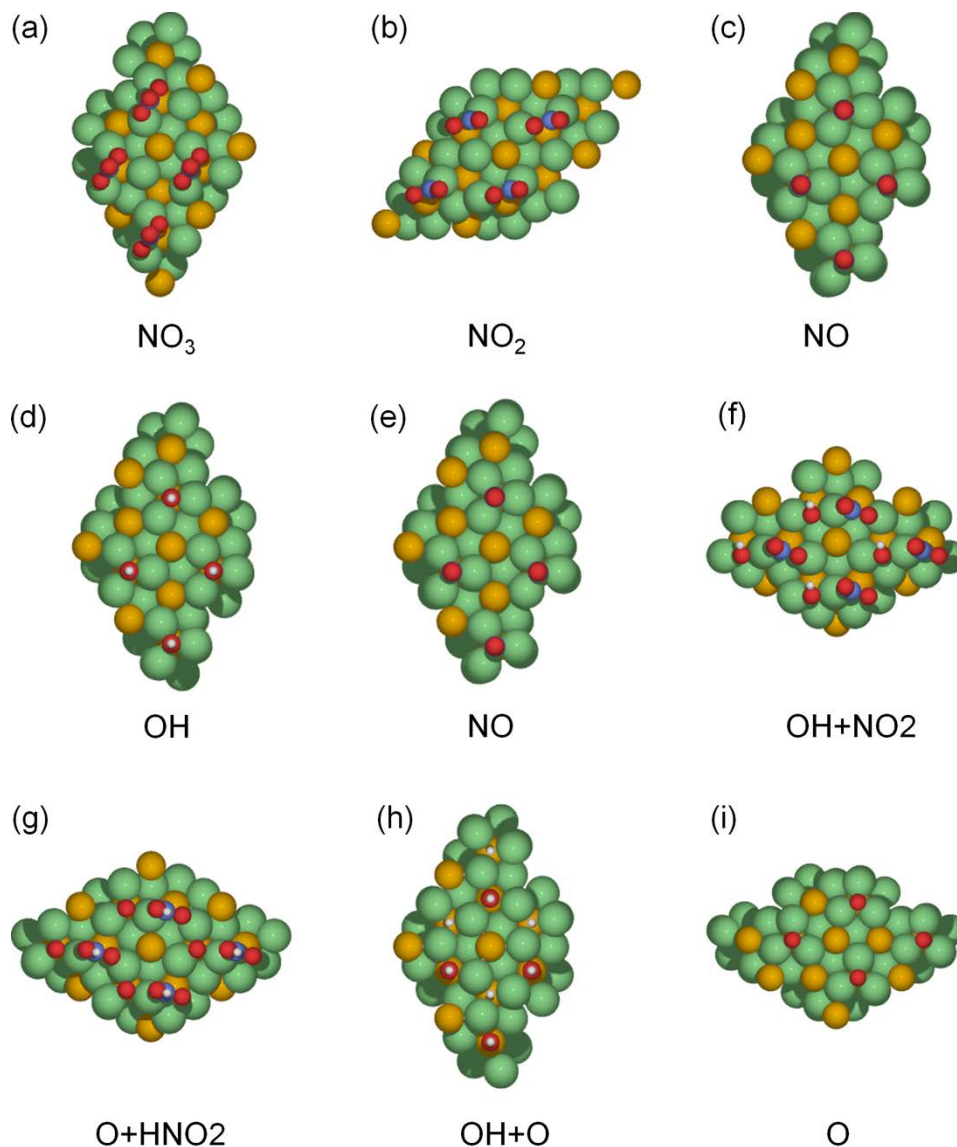


Figure S7. Configuration of other adsorbates on $\text{Ni}_2\text{P}(001)$.

^{S1} Andaraarachchi, H. P.; Thompson, M. J.; White, M. A.; Fan, H.; Vela, J. Phase-Programmed Nanofabrication: Effect of Organophosphite Precursor Reactivity on the Evolution of Nickel and Nickel Phosphide Nanocrystals. *Chem. Mater.* **2015**, *27*, 8021–8031

^{S2} Popczun, E. J.; McKone, J. R.; Read, C. G.; Biacchi, A. J.; Wiltrout, A. M.; Lewis, N. S.; Schaak, R. E. Nanostructured Nickel Phosphides as an Electrocatalyst for the Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2013**, *135*, 9267–9270.

^{S3} *Web of science*, version 5.32; Clarivate Analytics: Philadelphia, PA, 2019 (accessed Aug 23, 2019).; Searched using the keywords “nitrate hydrogenation” and “nitrate reduction” between 1984-present.

^{S4} *NIST X-ray Photoelectron Spectroscopy Database*, srdata.nist.gov/xps/ (accessed on Aug 24, 2019).

^{S5} Roberts, E. J.; Read C. G.; Lewis, N. L.; Brutchey, R. L. Phase Directing Ability of an Ionic Liquid Solvent for the Synthesis of HER-Active Ni_2P Nanocrystals. *ACS Appl. Energy Mater.* **2018**, *1*, 1823–1827.

^{S6} Pan, Y.; Liu, Y.; Zhao, J.; Yang, K.; Liang, J.; Liu, D.; Hu, W.; Liu, D.; Liu, Y.; Liu, C. Monodispersed Nickel Phosphide Nanocrystals with Different Phases: Synthesis, Characterization and Electrocatalytic Properties for Hydrogen Evolution. *J. Mater. Chem. A* **2015**, *3*, 1656–1665.

^{S7} Prüsse U.; Vorlop, K.-D. Supported Bimetallic Palladium Catalysts for Water-Phase Nitrate Reduction. *J. Mol. Catal. A* **2001**, *173*, 313–328.