Appendix

Synthesis and Chemical Properties of a Earth-Abundant Bimetallic Nanoparticles

Supporting Information

By Jonathan F. Senn, Jr. and Bryan Eichhorn*

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742

General Experimental Details	
Synthetic Methods	
Characterization Methods	
Supporting Data	

A. Experimental Details. All reactions were pumped down under vacuum, backfilled and performed under N_2 atmosphere using Schlenk line techniques to ensure proper reaction conditions moisture-sensitive and air-sensitive reactants. Reactions were performed using a New Star Environmental Inc. hot plate stirrer equipped with a temperature control unit combined with a Teflon-coated K–type thermocouple or a Magnestir stir plate equipped with a Staco Inc. variac temperature control unit and a thermometer. The colloidal suspensions described below were diluted with solventmixture and centrifuged at 6000 rpm using a Hermle Z 300. The precipitate materials were washed with solvent-mixtures by sonication. The process of dilution, sonication, and centrifugation was repeated 3-4 times. The precipitates were dried in open air before characterization. Yields of unsupported NPs were recorded as molar values using mass of products as converted from reactant materials and final volume of as-prepared reaction solution, also assuming 100% reduction and no loss of NPs during centrifugation. Details of analytical methods can be found in characterization section of the appendix.

Chemicals used were the following: Ni(acac)₂ (Strem, 95%, acac = acetylacetonate), Co(acac)₂ (Aldrich, 97%), SnCl₄ (Aldrich, 1 M in heptane), PtCl₂ (Engelhard, Pt 73.07%), Pt(acac)₂ (Aldrich, 97%), polyvinylpyrrolidone (PVP, Sigma-Aldrich, typical MW = 55,000), NaBH₄ (granular, 10-40 mesh, 98%), NaEt₃BH (Aldrich, 1 M in toluene), trioctylphosphine (Aldrich, technical grade, 90%), 1,2-hexadecanediol (Aldrich, technical grade, 90%), 1-octadecene (Aldrich, technical grade, 90%), diethyl ether (Fischer, BHT stabilized), oleic acid (Fluka, technical GC grade, 70%), oleylamine (Aldrich, technical grade, 90%) hydrogen peroxide (Fischer, aqeous solution, 30%), 1,4-butanediol (Sigma-Aldrich, ReagentPlus*R, 99%), ethylene glycol (EG, Sigma-Aldrich,

ReagentPlus*R, 99%), acetone (Sigma-Aldrich, 99.5%), ethanol (Pharmco-Aaper, 200 proof), methanol (Sigma-Aldrich, HPLC grade, 99.9%), hexanes (Fischer, HPLC grade, 99.7%), diphenyl ether (Aldrich, ReagentPlus*R, 99%), carbon black (Cabot, Vulcan XC-72), γ -Al₂O₃ (Alfa Aesar, 99.97% metal basis), graphite powder (Sigma-Aldrich, synthetic), sulfuric acid, KMnO₄ (Sigma-Aldrich, 99%), and NaNO₃ (Sigma-Aldrich, 99%). Starting materials were purchased and used as received.

A1. Synthesis of 4.0 nm Pt NPs. In a typical reaction, 17.0 mg of PtCl₂ (63.9 μ mol) and 50.0 mg of polyvinylpyrrolidone (MW = 55,000) were added to a 50 mL three-necked round-bottom flask. 15 mL of ethylene glycol were then added to the flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum and heated to 80°C, then filled with N₂. The solution was ramped at 3°C/min until nanoparticle nucleation occurred at ~130°C accompanied by gas evolution. The reaction was held at this temperature for 1 h, then quenched in RT water. The black colloidal solution was washed with acetone four times, and separated by centrifugation.

A2. Synthesis of 2.3 nm PtSn NPs. In a typical synthesis, 20.0 mg of Pt(acac)₂ (50.9 μ mol) were dissolved in 500 μ L oleic acid, 500 μ L oleylamine, and 5 mL 1-octadecene in a 50 mL three-necked round-bottom flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The solution was stirred under vacuum for 10 minutes, then cycled between flowing N₂ and vacuum 5 times. Then, 1 mL of 47.6 mM SnCl₄ (47.6 μ mol) in heptane was added dropwise to the reaction flask. This PtSn precursor solution was stirred under flowing N₂ for 15 minutes, then heated to ~120°C, resulting in a clear, yellow solution. In a separate three-necked

round-bottom flask, 10 mL of 1-Octadecene were heated under vacuum at ~80°C, then ramped to 190°C under flowing N₂. While at 190°C, 4 mL of 1M NaEt₃BH in toluene were injected into 1-octadecene reaction flask below the solvent surface to instantly cause gas evolution. Immediately thereafter, the PtSn precursor solution was injected into the NaEt₃BH solution above the solution in a dropwise manner to produce a black nanoparticle solution. The reaction refluxed at 195°C for 1 h under flowing N₂. The heating source was removed, and the solution cooled to room temperature. The black nanoparticle solution was washed with ethanol twice, ethanol-ethylene glycol mix (2 drops of ethylene glycol) once, and ethanol-methanol mix (30:1 v/v) once, then separated by centrifugation.

A3. Synthesis of PtSn₂ NP's. In a typical synthesis, 14.0 mg of Pt(acac)₂ (33.9 μ mol) were dissolved in 500 μ L oleic acid, 500 μ L oleylamine, and 5 mL 1-octadecene in a 50 mL three-necked round-bottom flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The solution was stirred under vacuum for 10 minutes, then cycled between flowing N₂ and vacuum 5 times. Then, 1.5 mL of 47.6 mM SnCl₄ (71.4 μ mol) in heptane was added dropwise to the reaction flask. This PtSn precursor solution was stirred under flowing N₂ for 15 minutes, then heated to ~120°C. In a separate three-necked round-bottom flask, 10 mL of 1-Octadecene were heated under vacuum at ~80°C, then ramped to 190°C under flowing N₂. While at 190°C, 4 mL of 1M NaEt₃BH in toluene were injected into 1-octadecene reaction flask below the solvent surface. Immediately thereafter, the PtSn precursor solution was injected into the NaEt₃BH solution above the solution in a dropwise manner to produce a black nanoparticle solution. The reaction refluxed at 195°C for 1 h under flowing N₂. The

heating source was removed, and the solution cooled to room temperature. The black nanoparticle solution was washed with ethanol twice, ethanol-ethylene glycol mix (2 drops of ethylene glycol) once, and ethanol-methanol mix (30:1 v/v) once, then separated by centrifugation.

A4. Synthesis of 3.9 nm Pt₃Sn NPs. In a typical synthesis, 14.0 mg of Pt(acac)₂ (76.2 µmol) were dissolved in 500 µL oleic acid, 500 µL oleylamine, and 5 mL 1octadecene in a 50 mL three-necked round-bottom flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The solution was stirred under vacuum for 10 minutes, then cycled between flowing N₂ and vacuum 5 times. Then, 500 µL of 47.6 mM SnCl₄ (23.8 µmol) in heptane was added dropwise to the reaction flask. This PtSn precursor solution was stirred under flowing N2 for 15 minutes, then heated to ~120°C. In a separate three-necked round-bottom flask, 10 mL of 1-Octadecene were heated under vacuum at ~80°C, then ramped to 190°C under flowing N₂. While at 190°C, 4 mL of 1M NaEt₃BH in toluene were injected into 1-octadecene reaction flask below the solvent surface. Immediately thereafter, the PtSn precursor solution was injected into the NaEt₃BH solution above the solution in a dropwise manner to produce a black nanoparticle solution. The reaction refluxed at 195°C for 1 under flowing N₂. The heating source was removed, and the solution cooled to room temperature. The black nanoparticle solution was washed with ethanol twice, ethanolethylene glycol mix (2 drops of ethylene glycol) once, and ethanol-methanol mix (30:1 v/v) once, then separated by centrifugation.

A5. Synthesis of 9.1 nm Ni NP's using 1,2-hexadecanediol. In a typical synthesis, 50 mg of Ni $(acac)_2$ (195 µmol) and 100 mg of 1,2-hexadecanediol were added

28

to a 50 mL three-necked round-bottom flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum, then filled with N₂. Then, 10 mL of diphenyl ether, 120 μ L of trioctylphosphine, 50 μ L of oleic acid, and 50 μ L of oleylamine were injected into the reaction flask. Again, the flask was purged, then filled with N₂. The clear, green solution was first heated to 160°C, then upon transition from green to colorless, ramped at 3°C/min until nanoparticle nucleation occurred at ~210°C. The reaction was held at this temperature until the entire solution became an opaque black in appearance (~5 minutes), then the reaction was quenched in RT water. The black nanoparticle solution was washed with ethanol four times, and separated by centrifugation.

A6. Synthesis of 25.0 nm Ni NP's using 1,2-hexadecanediol in 1-Octadecene. In a typical synthesis, 50 mg of Ni(acac)₂ (195 μ mol) and 100 mg of 1,2-hexadecanediol were added to a 50 mL three-necked round-bottom flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum, then filled with N₂. Then, 10 mL of 1-octadecene, 120 μ L of trioctylphosphine, 50 μ L of oleic acid, and 50 μ L of oleylamine were injected into the reaction flask. Again, the flask was purged, then filled with N₂. The clear, green solution was first heated to 160°C, then upon transition from green to colorless, ramped at 3°C/min until nanoparticle nucleation occurred at ~220°C. The reaction was held at this temperature until the entire solution became an opaque black in appearance (~5 minutes), then the reaction was quenched in RT water. The black nanoparticle solution was washed with ethanol four times, and separated by centrifugation. A7. Synthesis of Ni 57.8 nm NP's using 1,4-butanediol. In a typical reaction, 50.0 mg of Ni(acac)₂ (194 μ mol), and 150.0 mg of polyvinylpyrrolidone (MW = 55,000) were added to a 50 mL three-necked round-bottom flask. 15 mL of 1,4-butanediol were then added to the flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum and heated to 80°C, then filled with N₂. The solution was heated to 200°C, and stirred for 1 hr. The nanoparticle solution was quenched in RT water. The black colloidal solution was washed with acetone four times, and separated by centrifugation.

A8. Synthesis of Co NP's using 1,2-hexadecanediol. In a typical synthesis, 100 mg of $Co(acac)_2$ (194 µmol), 300 mg of 1,2-hexadecanediol, and 400 mg of PVP were added to a 50 mL three-necked round-bottom flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum, then filled with N₂. The clear, purple solution was ramped at 3°C/min, then progressively became darker in appearance, culminating in reflux at 258°C for 45 minutes. The nanoparticle solution was quenched in RT water. The black colloidal solution was washed with ethanol-acetone mix (1:1 v/v) three times, and separated by centrifugation.

A9. Synthesis of Co NP's using 1,4-butanediol. In a typical reaction, 50.0 mg of $Co(acac)_2$ (194 µmol), and 150.0 mg of polyvinylpyrrolidone (MW = 55,000) were added to a 50 mL three-necked round-bottom flask. 15 mL of 1,4-butanediol were then added to the flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum and heated to 80°C, then filled with N₂. The solution was heated to 230°C, and refluxed for 1 hr. The nanoparticle

solution was quenched in RT water. The black colloidal solution was washed with acetone four times, and separated by centrifugation.

A10. Synthesis of CoNi NP's using 1,2-hexadecanediol and trioctylphosphine. In a typical synthesis, 25.0 mg of Ni(acac)₂ (97.3 μ mol), 25.0 mg of Co(acac)₂ (97.2 μ mol), and 100 mg of 1,2-hexadecanediol were added to a 50 mL three-necked roundbottom flask. The reaction solution contained Co and Ni in 1:1 molar ratio. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum, then filled with N₂. Then, 10 mL of diphenyl ether, 120 μ L of trioctylphosphine, 50 μ L of oleic acid, and 50 μ L of oleylamine were injected into the reaction flask. Again, the flask was purged of air, then filled with N₂. The clear, purple solution was heated to 240°C, then ramped at 3°C/min until nanoparticle nucleation occurred at 256°C. The reaction refluxed at 258°C for 1 h. The nanoparticle solution cooled to RT. The black colloidal solution was washed with ethanol four, and separated by centrifugation.

A11. Synthesis of Co@Ni NP's using 1,2-hexadecanediol and PVP. In a typical synthesis, Co NP were synthesized using 1,2-hexadecanediol, as described above. 25.0 mg of Ni(acac)₂ (97.3 μ mol) and 200 mg of 1,2-hexadecanediol were added to a separate 50 mL three-necked round-bottom flask. Reaction solution contained Co and Ni in 4:1 molar ratio. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum, then filled with N₂. Then, the black Co NP reaction solution was injected into the clear, light green Ni(acac)₂ reaction solution. Again, the flask was purged of air, then filled with N₂. The solution was ramped at 3°C/min to 220°C accompanied by minor gas evolution, and held at 220°C

for 10 minutes without noticeable color changes due to black Co colloidal solution. Subsequently, the nanoparticle solution was quenched in RT water and further cooled in an ice bath. The black colloidal solution was washed with an ethanol-acetone mix (1:1 v/v) four times, and separated by centrifugation.

A12. Synthesis of CoNi NP's using 1,2-hexadecanediol and PVP. In a typical synthesis, Co NP were synthesized using 1,2-hexadecanediol, as described above. 50.0 mg of Ni(acac)₂ (194.6 μ mol) and 400 mg of 1,2-hexadecanediol were added to a separate 50 mL three-necked round-bottom flask. Co and Ni were combined in 2:1 ratio. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum, then filled with N₂. Then, the Co NP reaction solution was injected into the Ni(acac)₂ reaction flask. Again, the flask was purged of air, then filled with N₂. The solution clear, light purple solution was ramped at 3°C/min to 240°C, and held at 240°C for 10 minutes. Subsequently, the nanoparticle solution was washed with an ethanol-acetone mix (1:1 v/v) four times, and separated by centrifugation.

A13. Synthesis of CoNi NP's using 1,4-butanediol. In a typical reaction, 25.0 mg of Ni(acac)₂ (97.3 μ mol), 25.0 mg of Co(acac)₂ (97.2 μ mol), and 400.0 mg of polyvinylpyrrolidone (MW = 55,000) were added to a 50 mL three-necked round-bottom flask. Reaction solution contained Co and Ni in 1:1 molar ratio. 15 mL of 1,4-butanediol were then added to the flask. The flask was equipped with a magnetic stir bar, thermometer, heating mantle, and reflux condenser. The flask was purged under vacuum and heated to 80°C, then filled with N₂. The solution was heated to 230°C, and refluxed

for 1 hr. The nanoparticle solution cooled to RT. The black colloidal solution was washed with acetone four times, and separated by centrifugation.

A14. Preparation of Vulcan Supported Catalysts. Carbon-supported catalysts with 30 wt% total metal loading were made by combining Vulcan XC-72 and dispersed as-prepared, washed NP colloidal suspension in hexanes, and sonicating for 1.5 h. The solution was centrifuged, then dried in air. The catalyst was then annealed at 400°C in 5% H₂/Ar for 1 hr with a temperature ramp of 5°C/min.

A15. Preparation of γ -Al₂O₃ Supported Catalysts. The NP catalysts were prepared by adding γ -Al₂O₃ to colloidal suspensions of NP's, with 1 wt% total metal loadings. For example, 10 mL of 5.49 μ M (8.62 mg) PtSn NP's were dispersed and sonicated in ethanol for 15 minutes, while 853.38 mg γ -Al₂O₃ were sonicated in ethanol for 15 minutes. The two solutions were combined and sonicated for 30 minutes, then centrifuged for catalyst isolation. The catalyst was re-dispersed and washed by centrifugation in ethanol and hexanes, diethyl ether, and diethyl ether and hexanes. The catalyst was dried at RT overnight, then annealed at 400°C for 1 hr with a ramp rate of 5°C/min.

A16. Evaluation of Catalytic Activity for PROX. Development and execution of catalytic studies were done in collaboration with Dr. Will Gibbons. Catalytic reactions used 100 mg of NP-supported material (ie. 1 wt% PtSn on γ -Al₂O₃) in a quartz fixed-bed flow-through reactor with an inner diameter of 6.8 mm. The reactor bed composition is the following: 600 mg quartz sand and 40 mg of quartz wool; evenly loaded catalyst material; then, additional quartz wool and quartz sand for support. Samples were loaded vertically into a cylindrical furnace, with K-type thermocouple inserted into reactor bed

for temperature monitoring and control in conjunction with Lab View software. Total flow rate and inlet velocities were calculated, observed, and ultimately chosen in accordance to previous studies that have used this catalysis rig.^{6,25} Gaseous reactants were introduced using Brooks 5850C series mass flow controllers. Gaseous products were monitored by a Varian Chrompack CP-3800 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

In a typical trial, the catalyst was pretreated by heating at 250°C for 30 minutes in flowing 50% H₂-He mixture. PROX reactions consisted of heating to 250°C at rates of 0.25°C/min and 1°C/min, depending on the study, in various gas mixtures. The gas mixture for the 500 ppm CO PROX reaction was composed of 0.05% CO (UHP Grade 5 H₂ – 1% CO mixture, 99.999% purity, Al tank), 0.65% O₂ (UHP Grade 5, 99.999% purity), 50% H₂ (UHP Grade 5, 99.9995% purity). The gas mixture for the 1000 ppm CO PROX reaction was composed of 0.1% CO (UHP Grade 5, 1% CO/H₂ mixture, 99.999% purity, Al tank), 0.65% O₂ (UHP Grade 5, 99.9995% purity), and balance He (UHP Grade 5, 99.9995% purity), 50% H₂ (UHP Grade 5, 99.9995% purity), and balance He (UHP Grade 5, 99.9995% purity), and balance He (UHP Grade 5, 99.9995% purity). The gas mixture for the 2000 ppm CO PROX reaction was composed of 0.2% CO (UHP Grade 5 H₂ – 1% CO mixture, 99.9999% purity, Al tank), 0.65% O₂ (UHP Grade 5, 99.9995% purity), and balance He (UHP Grade 5, 99.9995% purity), 50% H₂ (UHP Grade 5, 99.9995% purity).

B. Characterization

B1. Powder X-ray Diffraction (XRD). XRD analysis was performed on a Bruker C2 Discover (parallel beam) general area diffraction detection system (GADDS), equipped with a Bruker ACS High Star detector. X-rays were generated via a monochromatic Cu K_{α} radiation source biased at 40 mV and 40 mA. Dried samples were pressed on a glass slide, and analyzed in air to obtain XRD patterns.

B2. Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDX). Nanoparticles supported on XC-72: Dried catalyst was dispersed in hexanes by sonication. 10 μ L aliquot of dispersion was drop-cast on carbon coated copper TEM grids. Unsupported nanoparticles: Dried nanoparticles was dispersed in diethyl ether or hexanes by sonication. 10 μ L aliquot of dispersion was drop-cast on carbon coated copper TEM grids. Nanoparticles supported on γ -Al₂O₃: Dried catalyst was dispersed in ethanol by sonication. 10 μ L aliquot of dispersion was drop cast on carbon coated copper TEM grids. TEM images were acquired on a JEOL 2100F Field Emission TEM operating at 200 kV. EDS analysis was performed on a JEOL 2100F Field Emission TEM operating in STEM mode.



Figure S1. (a) TEM image of 4.0 nm as-prepared Pt NPs unsupported. (b) HRTEM image of Pt NP with visible lattice fringes. (c) Histogram of NP size distribution.



Figure S2. Powder XRD diffraction pattern of 4.0 nm as-prepared Pt NPs unsupported. JCPDS¹⁰⁸ peak positions for Pt are also displayed.



Figure S3. TEM image of 4.8 nm PtSn NPs supported on Vulcan; annealed at 450°C in 5% H₂/Ar for 1 hr. Insert is histogram of NP size distribution.



Figure S4. TEM image of 3.2 nm PtSn NPs supported on Vulcan; annealed at 400°C in 5% H₂/Ar for 1 hr. Insert is histogram of NP size distribution.



Figure S5. TEM image of 2.41 nm PtSn NPs supported on Vulcan; annealed at 350°C in 5% H₂/Ar for 1 hr. Insert is histogram of NP size distribution.



Figure S6. EDX analysis of PtSn NPs supported on XC-72 Vulcan (carbon black). Area scan indicates Pt at 49.84% and Sn at 50.16%.



Figure S7. (a) TEM image of 7.5 nm PtSn₂ NPs supported on γ -Al₂O₃; annealed at 400°C in 5% H₂/Ar for 1 hr. (b) HRTEM image of PtSn₂ NP supported on γ -Al₂O₃ with visible lattice fringes. (c) Histogram of NP size distribution.



Figure S8. EDX analysis of $PtSn_2$ NPs supported on γ -Al₂O₃. Area scan indicates 26 at% Pt and 74 at% Sn.



Figure S9. (a) TEM image of 3.9 nm Pt₃Sn NPs supported on γ -Al₂O₃; annealed at 400°C in 5% H₂/Ar for 1 hr. (b) HRTEM image of Pt₃Sn NP supported on γ -Al₂O₃ with visible lattice fringes. (c) Histogram of NP size distribution.



Figure S10. Powder XRD diffraction pattern of 3.9 nm intermetallic Pt_3Sn NPs supported on XC-72 vulcan (carbon black). JCPDS¹⁰⁸ peak positions for Pt_3Sn are also displayed.



Figure S11. PROX activity for Pt_3Sn supported on γ -Al₂O₃ at 500 ppm CO for various gases.



Figure S12. PROX activity for Pt_3Sn supported on γ -Al₂O₃ at 1000 ppm CO for various gases.



Figure S13. PROX activity for Pt_3Sn supported on γ -Al₂O₃ at 2000 ppm CO for various gases.



Figure S14. PROX activity for Pt_3Sn supported on γ -Al₂O₃ at 5000 ppm CO for various gases.



Figure S15. PROX activity for Pt₃Sn supported on γ -Al₂O₃ at various CO concentrations, showing CO concentrations as a function of temperature.



Figure S16. PROX activity for Pt₃Sn supported on γ -Al₂O₃ at various CO concentrations, showing H₂ concentrations as a function of temperature.



Figure S17. PROX activity for PtSn supported on γ -Al₂O₃ at 1000 ppm CO for various gases.



Figure S18. PROX activity for PtSn supported on γ -Al₂O₃ and Pt₃Sn supported on γ -Al₂O₃ using 1000 ppm CO, showing CO Concentration as a function of temperature.



Figure S19. (a) TEM image of 9.1 nm as-prepared Ni NPs unsupported, synthesized in DPE using 1,2-hexadecanediol. (b) HRTEM image of Ni NP with visible lattice fringes. (c) Histogram of NP size distribution.



Figure S20. Powder XRD diffraction pattern of Ni NPs synthesized in DPE using 1,2-hexadecanediol. JCPDS¹⁰⁸ peak positions for Ni are also displayed.



Figure S21. (a) TEM image of 25.0 nm as-prepared Ni NPs unsupported, synthesized in Octadecene using 1,2-hexadecanediol. (b) HRTEM image of Ni NP with visible lattice fringes. (c) Histogram of NP size distribution.



Figure S22. Powder XRD diffraction pattern of Ni NPs synthesized in 1,4-butanediol. JCPDS¹⁰⁸ peak positions for Ni are also displayed.



Figure S23. Powder XRD diffraction pattern of Ni NPs synthesized in Octadecene using 1,2-hexadecanediol. JCPDS¹⁰⁸ peak positions for Ni are also displayed.



Figure S24. (a) TEM image of unsupported Co NPs and agglomerates synthesized in DPE using 1,2-hexadecanediol. (b) Histogram of NP size distribution.



Figure S25. EDX analysis of unsupported Co NPs and agglomerates synthesized in DPE using 1,2-hexadecanediol. Area scan indicates 100 at% Co.



Figure S26. TEM image of unsupported Co NPs synthesized in 1,4-butanediol.



Figure S27. Powder XRD diffraction pattern of Co NPs synthesized in 1,4-butanediol. JCPDS¹⁰⁸ peak positions for Co are also displayed.



Figure S28. TEM image of unsupported CoNi (1:1 molar ratio) NPs synthesized in DPE using 1,2-hexadecanediol and trioctylphosphine.



Figure S29. (a) EDX line scan analysis of unsupported CoNi NPs (1:1 molar ratio) synthesized in DPE using 1,2-hexadecanediol and trioctylphosphine. (b) Composition mapped as 55.5 at% Co and 44.6 at% Ni.



Figure S30. Powder XRD diffraction pattern of unsupported CoNi NPs synthesized in DPE using 1,2-hexadecanediol and trioctylphosphine. JCPDS¹⁰⁸ peak positions for CoNi are also displayed.



Figure S31. TEM of unsupported Co@Ni NP synthesized in DPE using 1,2-hexadecanediol, illustrating visible core-shell boundary.



Figure S32. EDX analysis of unsupported Co@Ni NPs (4:1 molar ratio) synthesized in DPE using 1,2-hexadecanediol and PVP.



Figure S33. Powder XRD diffraction pattern of Co@Ni NPs synthesized in DPE using 1,2-hexadecanediol. Incident JCPDS¹⁰⁸ peak positions for Co andNi are also displayed.



Figure S34. (a) TEM image of 27.1 nm CoNi NPs (2:1 molar ratio) synthesized using 1,2-hexadecanediol and PVP. (b) HRTEM image of CoNi NP with visible lattice fringes. (c) Histogram of NP size distribution.



Figure S35. (a) EDX line scan profile of unsupported CoNi NP (2:1 molar ratio) synthesized in DPE using 1,2-hexadecanediol and PVP. (b) Qualitative compositional analysis of unsupported CoNi NP.



Figure S36. Powder XRD diffraction pattern of unsupported CoNi NPs (2:1 molar ratio) synthesized in DPE using 1,2-hexadecanediol andPVP. JCPDS¹⁰⁸ peak positions for CoNi are also displayed.



Figure S37. TEM image of CoNi NPs (1:1 molar ratio) synthesized using 1,4-butanediol and PVP.



Figure S38. EDX analysis of unsupported CoNi NPs (1:1 molar ratio) synthesized using 1,4-butanediol. Area scan shows 83 at% Co and 17 at% Ni. 1:1 ratio of Co to Ni



Figure S39. Powder XRD diffraction pattern of unsupported CoNi NPs (1:1 molar ratio) synthesized using 1,4-butanediol and PVP. JCPDS¹⁰⁸ peak positions for CoNi are also displayed.