

Electronic Supplementary Information

A Facile Route to Monodisperse MPd (M = Co or Cu) Alloy Nanoparticles and Their Catalysis for Electrooxidation of Formic Acid

Sally Fae Ho,^a Adriana Mendoza-Garcia,^a Shaojun Guo,^a Kai He,^b Dong Su,^b Sheng Liu,^a Önder Metin,^{a,c} and Shouheng Sun^{a,*}

^aDepartment of Chemistry, Brown University, Providence, RI 02912

^bBrookhaven National Laboratory, Center for Functional Nanomaterials, Upton, NY 11973-5000, USA

^cDepartment of Chemistry, Faculty of Science, Atatürk University, 25240 Erzurum, Turkey

*To whom correspondence should be addressed. E-mail: ssun@brown.edu

Experimental Section

The synthesis was carried out using standard airless procedures and commercially available reagents. All reagents were used as received. 1-Octadecene (ODE), oleylamine (OAm) (> 70%), morpholine borane (MB) (95%), borane *tert*-butylamine (BBA), palladium acetylacetonate (Pd(acac)₂, 99%), copper acetylacetonate (Cu(acac)₂), cobalt acetylacetonate (Co(acac)₂, > 97%), carbon monoxide (≥ 99%) and Nafion 117 were purchased from Sigma Aldrich. Nickel (II) acetate tetrahydrate (NiAc₂•4H₂O, 98%) was obtained from Strem chemicals. Ketjen Black (800m²/g) was obtained from Tanaka Precious Metals. ACS Grade formic acid (98%) was purchased from EMD.

Synthesis of 3.5 nm Co₃₀Pd₇₀ NPs

0.2 g of BBA was mixed with 3 mL of OAm and 7 mL of ODE and heated to 100°C. Separately, 0.3 mmol Co(acac)₂ and 0.3 mmol Pd(acac)₂ were dissolved in 3 mL of OAm at room temperature and injected into the 100 °C solution. The reaction was maintained at 100°C for 1 h and subsequently cooled to room temperature. The NPs were separated from the solution by adding acetone and centrifugation. The NPs were dispersed in hexane and precipitated by ethanol and centrifugation. The purified NPs were then dispersed in hexane for further use.

Composition Control of CoPd NPs.

In similar conditions described in the synthesis of CoPd NPs, changing the composition of the starting metal precursor ratio leads to different composition CoPd NPs. For instance, reaction of 0.45 mmol or 0.25 mmol of Co(acac)₂ with 0.11 mmol Pd(acac)₂ yielded Co₇₀Pd₃₀ or Co₅₅Pd₄₅ NPs respectively.

Synthesis of Cu₃₀Pd₇₀ NPs

0.2 g of MB was mixed with 3 mL of OAm and 7 mL of ODE and heated to 80°C. Separately, 0.15 mmol Cu(acac)₂ and 0.35 mmol Pd(acac)₂ were dissolved in 3 mL of OAm at room temperature and injected into the 80 °C mixture. The reaction was raised to 100°C for 1 h and subsequently cooled to room temperature. The NPs were separated from the solution with a similar process described in the synthesis of CoPd NPs. Cu₇₅Pd₂₅ or Cu₆₂Pd₃₈ NPs could be produced by changing the starting Cu:Pd molar precursor ratios to 0.35:0.1 or 0.3:0.3, respectively.

Synthesis of 3.5 nm Pd NPs

These NPs were synthesized in similar conditions as the CoPd NPs, using 0.25 mmol of Pd(acac)₂.

NP Characterization

Samples for transmission electron microscopy (TEM) analysis were prepared by depositing a single drop of the diluted NP dispersion in hexane on amorphous carbon coated copper grids. Images were obtained on a Philips CM20 at 200 kV. High resolution TEM (HRTEM) images were obtained on a JEOL 2100F with an accelerating voltage of 200 kV. XRD patterns were recorded on a Bruker D8 Discover (Cu K α). Inductively coupled plasma (ICP) elemental analysis measurements were carried out on a JY2000 Ultrace ICP Atomic Emission Spectrometer equipped with a JY AS 421 autosampler and 2400g/mm holographic grating. For ICP analysis, an aliquot of the NPs in hexane was dried and subsequently dissolved in warm (~75°C) aqua regia for 30 min to ensure complete dissolution of metal into the acid. The solution was then diluted with 2% HNO₃ solution for analysis.

NP Preparation for Electrocatalytic Evaluation.

The NPs were supported onto Ketjen carbon in a 1:2 wt. ratio. An appropriate amount of the Ketjen Carbon was measured and sonicated (Fischer Scientific FS 110) in a 20 mL of hexane and 5 mL of acetone for 30 minutes. Then, an appropriate wt. amount of NPs dispersed in 20 mL of hexane was added dropwise to the Ketjen carbon solution and kept for 1 h under sonication. The C-NP was recovered by centrifuging the mixture at 8000 rpm for 8 min. The colorless supernatant was discarded and the C-NP product was washed with hexane and dried under nitrogen. The C-NPs were annealed in air at 165 °C overnight. An appropriate amount of product was weighed and dispersed in deionized water, isopropanol, and Nafion in a 4:1: 0.025 to yield a suspension of 4 mg/mL C-NPs. All C-NP catalysts were prepared in the same manner.

Electrochemical Evaluation of NPs/C for FAOR

5 μ L of the 4 mg/mL C-NP suspension prepared above was dropped onto a rotating disk electrode (RDE) with a glassy carbon surface (5 mm in diameter). The electrochemical measurements were performed on an Autolab Potentiostat from Metrohm Instrument Company (Autolab 302) by a cyclic voltammetry technique. Ag/AgCl and a Pt mesh wire were used as the reference and counter electrodes, respectively. The NP catalysts were evaluated for the FAOR in nitrogen saturated 0.1 M HClO₄ + 0.2 M HCOOH solution at 25°C. The C-NP was first electrochemically cleaned by scanning the potential from -0.2 V to 0.9 V for 30 cycles at 100 mV/s. All subsequent measurements were then scanned at a rate of 50 mV/s. The mass current was normalized to mA/cm² by dividing the measured electrode currents over the electrochemically active surface area of the C-NP catalyst.

Supplemental Figures

Figure S1 – TEM image of the as-synthesized Pd NPs

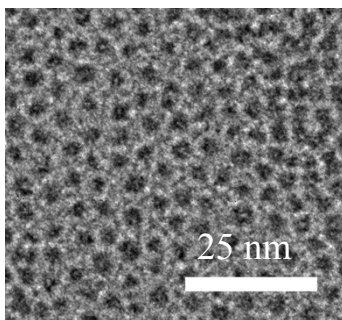


Figure S-2 : TEM images of the CoPd NPs synthesized at (A) 75 °C and (B) 125 °C

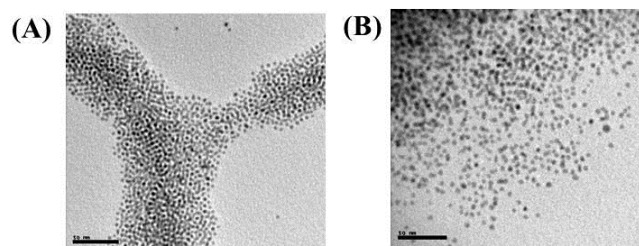


Figure S-3 : TEM image of the annealed C-CoPd catalysts

