Electronic Supplementary Information

Electrocatalytic Reduction of Furfural with High Selectivity to Furfuryl Alcohol Using AgPd Alloy Nanoparticles

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This file includes:

Experimental

Chemicals and Materials

All reagents were used without further purification. Silver acetate (Ag(Ac), 99%), oleylamine (70%), oleic acid (90%), and Nafion (5 wt%) perfluorinated resin solution were purchased from Sigma-Aldrich. Palladium acetylacetonate ($Pd(acac)_2$, 35% Pd) and 1-octadecene (90%) were purchased from Acros Organics. 2-propanol (>99.5%), hexane (>98.5%) and acetonitrile (HPLC grade) were purchased from Fisher Chemical. Ethanol (200 proof) was purchased from Decon Labs. Ammonium chloride (NH_4Cl) was purchased from VWR Chemicals, and sulfuric acid solution (H_2SO_4, 50 wt% in water) was purchased from Honeywell. Vulcan carbon (XC-72R), carbon paper (Toray paper 060), and the Nafion membrane (Nafion 212) used in our electrochemical cell were purchased from Fuel Cell Store.

Synthesis of AgPd Nanoparticles

We synthesized AgPd nanoparticles using a previously reported method which produces nanoparticles with different alloy compositions.[1] In a typical synthesis of $Ag_{60}Pd_{40}$ nanoparticles, 0.101 g of Ag(Ac) (0.6 mmol) and 0.121 g of $Pd(acac)_2$ (0.4 mmol) were dissolved in 0.5 mL of oleic acid, 4.5 mL of oleylamine, and 10 mL of 1-octadecene. The solution was kept under vacuum to remove the moisture, and then held under gentle N_2 flow for the entire reaction. Using a temperature-controlled heating mantle, the system was heated to 60 °C, held until a homogenous solution formed, and then the temperature was increased to 180 °C at about 4 °C / min. At 150 °C, the color of the solution changed from transparent yellow to opaque dark-brown, and the reaction was held at 180 °C for 20 minutes to ensure sufficient nanoparticle ripening. The solution was cooled to room temperature and the nanoparticles were collected by precipitation using 50 mL of 2-propanol and centrifugation at 9500 rpm for 8 minutes. The precipitated nanoparticles were then re-dispersed in hexane, washed with 40 mL of ethanol, and separated by another centrifugation (9500 rpm, 8 min). The nanoparticles were finally stored in hexane for later use. With the total moles of metal precursor held constant at 1 mmol metal, the masses of Ag(Ac) and $Pd(acac)_2$ were varied between experiments to make nanoparticles with different relative atomic compositions of Ag and Pd. For example, to prepare a sample of $Ag_{50}Pd_{50}$ nanoparticles, the synthesis would include 0.5 mmol of Ag(Ac), and 0.5 mmol of $Pd(acac)_2$. The atomic ratio of Ag/Pd in the resultant AgPd nanoparticles is consistent with the molar ratio of $Ag(Ac)/Pd(acac)_2$. The atomic ratio of Ag and Pd in each nanoparticle sample was determined using inductively coupled plasma – optical emission spectroscopy (ICP-OES).

Preparation of Carbon Supported Nanoparticle Catalysts

The nanoparticles were deposited onto conductive carbon support to prepare the electrocatalyst. Vulcan carbon was first dispersed in hexane by sonication for 20 minutes, and then metal nanoparticles, also in hexane, were added to the mixture under sonication for 1 hour. The mass composition for each catalyst material was 40% of Vulcan carbon and 60% of metal. The carbon supported nanoparticle catalyst was collected by centrifugation (8500 rpm, 8 min), and then washed with ethanol twice. To remove bulky organic ligands from the metal nanoparticle surfaces, the catalyst was stirred in 40 mL of acetic acid at 70 °C overnight under N_2 atmosphere. After this, the mixture was washed with 40 mL of ethanol and separated by centrifugation (8500 rpm, 8 min), and then the catalyst was washed twice more. Lastly, the catalyst was dried overnight under vacuum. The metal mass loading amount for carbon supported catalysts was confirmed by ICP-OES.

Fabrication of Working Electrodes

The catalyst, in the form of an ink, was air-brushed onto carbon paper to develop the working electrodes for our electrochemical tests. To make the ink, a measured amount of dried catalyst plus 10 wt% of Nafion were sonicated for one hour in ethanol. The homogenous dispersion was sprayed through an airbrush onto both sides of carbon paper (1 cm^2). The carbon paper was left to dry in ambient condition and used as the working electrode. The metal loading on carbon paper was kept at 0.6 mg_{metal} cm^{-2} for all catalysts.

Electrocatalytic Measurements and Analysis

All electrochemical experiments were performed in an H-type cell with two compartments separated by a Nafion 212 membrane. Each chamber contained 12 mL of aqueous electrolyte composed of 100 mM furfural. A stir plate was used at 700 rpm in the cathodic chamber, and there was no stirring for the anolyte. The counter electrode was Pt mesh in anodic chamber. The cathodic chamber was sealed with a customized rubber cap which used Teflon capillary tubes to bubble N_2 gas into the catholyte and collect gas from the cathodic chamber headspace, feeding it directly into a gas chromatographer. An external calibration curve was used to quantify the concentration of H_2 in the cathodic gas stream during constant potential electrolysis (CPE) experiments. The catholyte was purged of air under simultaneous stirring and N_2 bubbling at 100 sccm for 20 minutes before every experiment, and then the N_2 flow was lowered to 10 sccm for the duration of the experiment. The working electrode and the Ag/AgCl reference electrode were placed in the cathodic chamber.

The electrochemical study was conducted using an Autolab PGSTAT302N potentiostat. At the start of each experiment, a cyclic voltammogram (CV) tested the quality of the working electrode and the setup to ensure repeatability of the potential / current profile. A representative CV is displayed in Figure S3 for both pure nanoparticle catalysts and $Ag_{60}Pd_{40}$. Stirring was stopped to perform each CV experiment, then restarted before conducting the subsequent CPE experiment. CPE was performed at a desired potential for one hour, after which the catholyte was collected for product analysis. The electrolyte in both chambers was refreshed before each set of experiments. High-pressure liquid chromatography (HPLC, Shimadzu) was used for liquid product analysis.

The relevant equations for the calculations in this report are listed below. *F* is Faraday's constant. *C* is the amount of charge passed in Coulombs over the course of 1-hour CPE experiments. *n* is the number of electrons passed for each reduction reaction: it is equal to two for both the hydrogen evolution reaction, and furfural to furfuryl alcohol conversion. $[\text{Furfural}]_{\text{initial}}$ is the concentration of furfural calculated from HPLC analysis of each furfural-containing electrolyte without electrocatalytic testing. $[\text{Furfural}]_{\text{post-CPE}}$ and $[\text{furfuryl alcohol}]_{\text{post-CPE}}$ were determined from HPLC analysis of the catholyte after use in CPE experiments. The moles of furfuryl alcohol were calculated by multiplying $[\text{furfuryl alcohol}]_{\text{post-CPE}}$ by the volume of the catholyte (12 mL).

$$Furfural\ Conversion = \frac{[furfural]_{initial} - [furfural]_{post-CPE}}{[furfural]_{initial}} * 100\%$$

$$Carbon\ Balance = \frac{[furfuryl\ alcohol]_{post-CPE} + [furfural]_{post-CPE}}{[furfural]_{initial}} * 100\%$$

$$Faradaic\ Efficiency_{furfuryl\ alcohol} = \frac{moles_{furfuryl\ alcohol} nF}{C} * 100\%$$

$$Faradaic\ Efficiency_{H_2} = \frac{moles_{H_2} nF}{C} * 100\%$$

Other Physical Characterizations

Transmission electron microscopy (TEM) images were obtained on a Tecnai Spirit at 120 kV equipped with a tungsten filament. Compositional characterizations of our catalysts were conducted by inductively coupled plasma – optical emission spectroscopy (ICP-OES) using a Perkin Elmer Avio 200. All electrolytes were prepared using Ultrapure (Type I) water dispensed through a Millipore Synergy purification system, and pH measurements were made using a Mettler Toledo FiveEasy pH meter. Liquid products were analyzed on a Shimadzu HPLC equipped with two LC-20AD pumps, using a Phenomenex Luna Omega C18 column for separation. The aqueous mobile phase contained 15% acetonitrile with a gradient flow method in which the acetonitrile concentration is gradually increased to 60%, and then lowered back to 15%. A diode array detector (Shimadzu SPD-M20A) and external calibration curves were used to determine the concentration of furfural and furfuryl alcohol. The gaseous product (H_2) was quantified by feeding the cathodic headspace directly into a Shimadzu GC-2014 gas chromatographer equipped with thermal conductivity detector (TCD).

Figures S1-S6

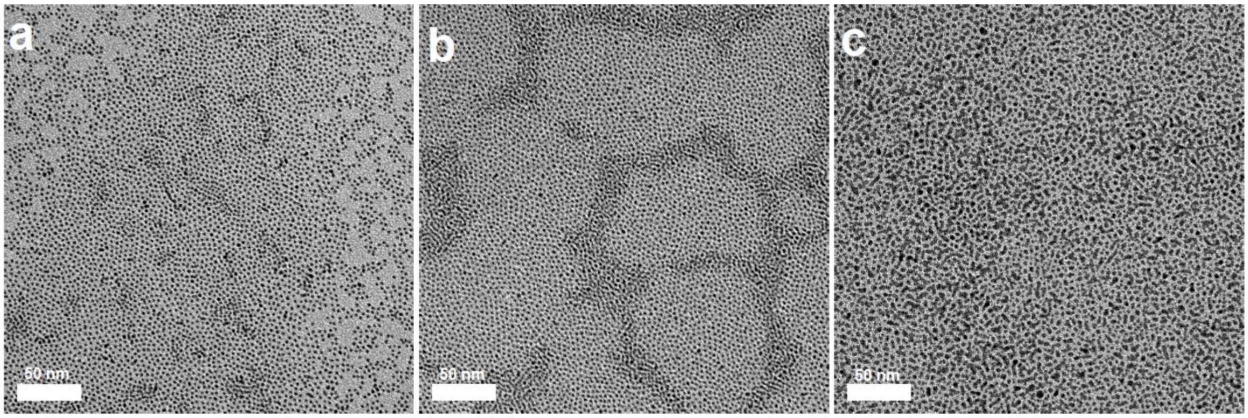

Figure S1. TEM images of as-synthesized (a) $Ag_{30}Pd_{70}$, (b) $Ag_{50}Pd_{50}$, and (c) $Ag_{75}Pd_{25}$ nanoparticles.

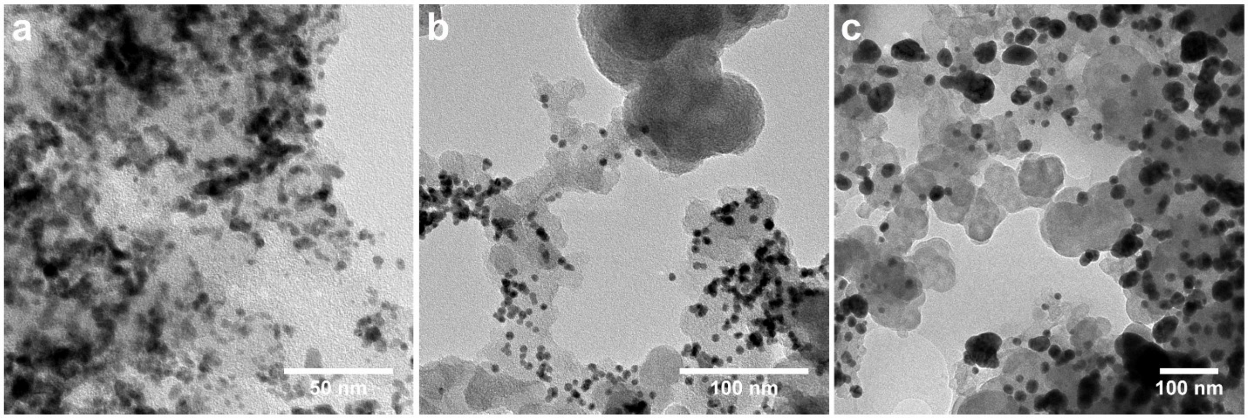

Figure S2. TEM images of carbon supported (a) $Ag_{60}Pd_{40}$, (b) Pd, and (c) Ag catalysts after CPE experiments.

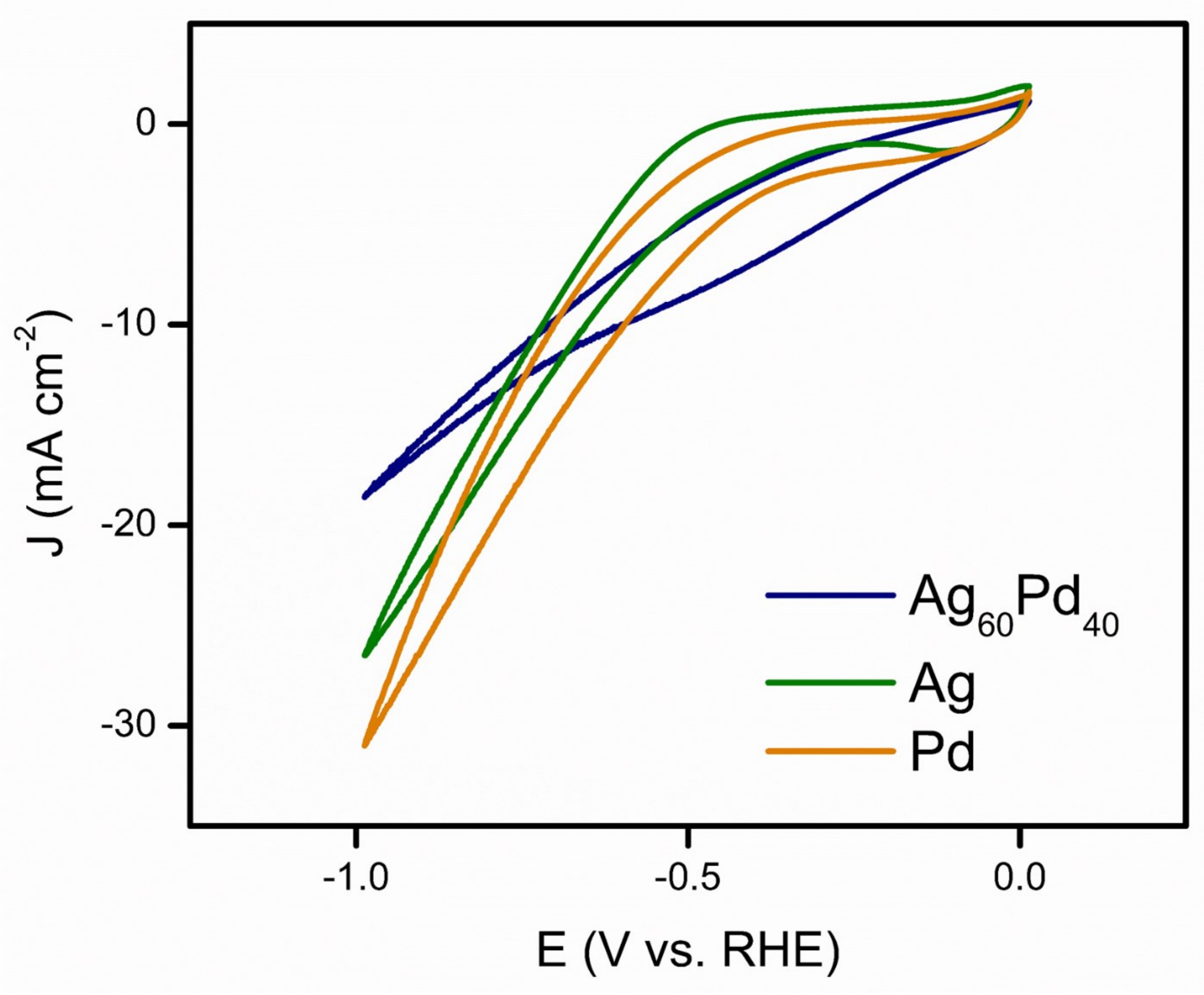

Figure S3. CVs of Ag, Pd and $Ag_{60}Pd_{40}$ nanoparticle catalysts in 0.1 M sodium phosphate buffer solution containing 100 mM furfural.

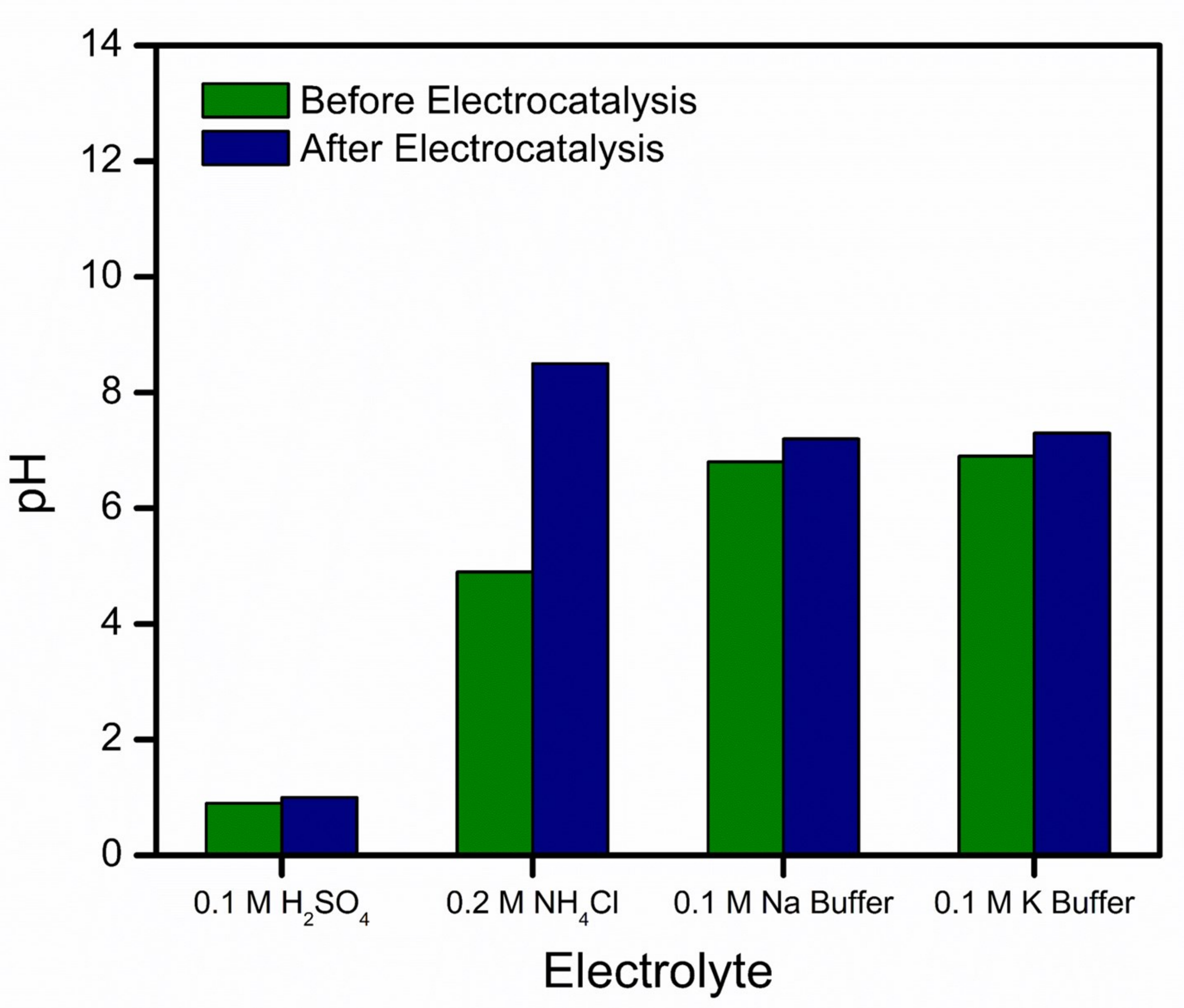

Figure S4. Measured pH of different electrolytes before and after CPE tests. CPE was performed using identical working electrodes ($Ag_{60}Pd_{40}$) held at -0.5 V vs. RHE for 1 hour in 12 mL of electrolyte containing 100 mM furfural.

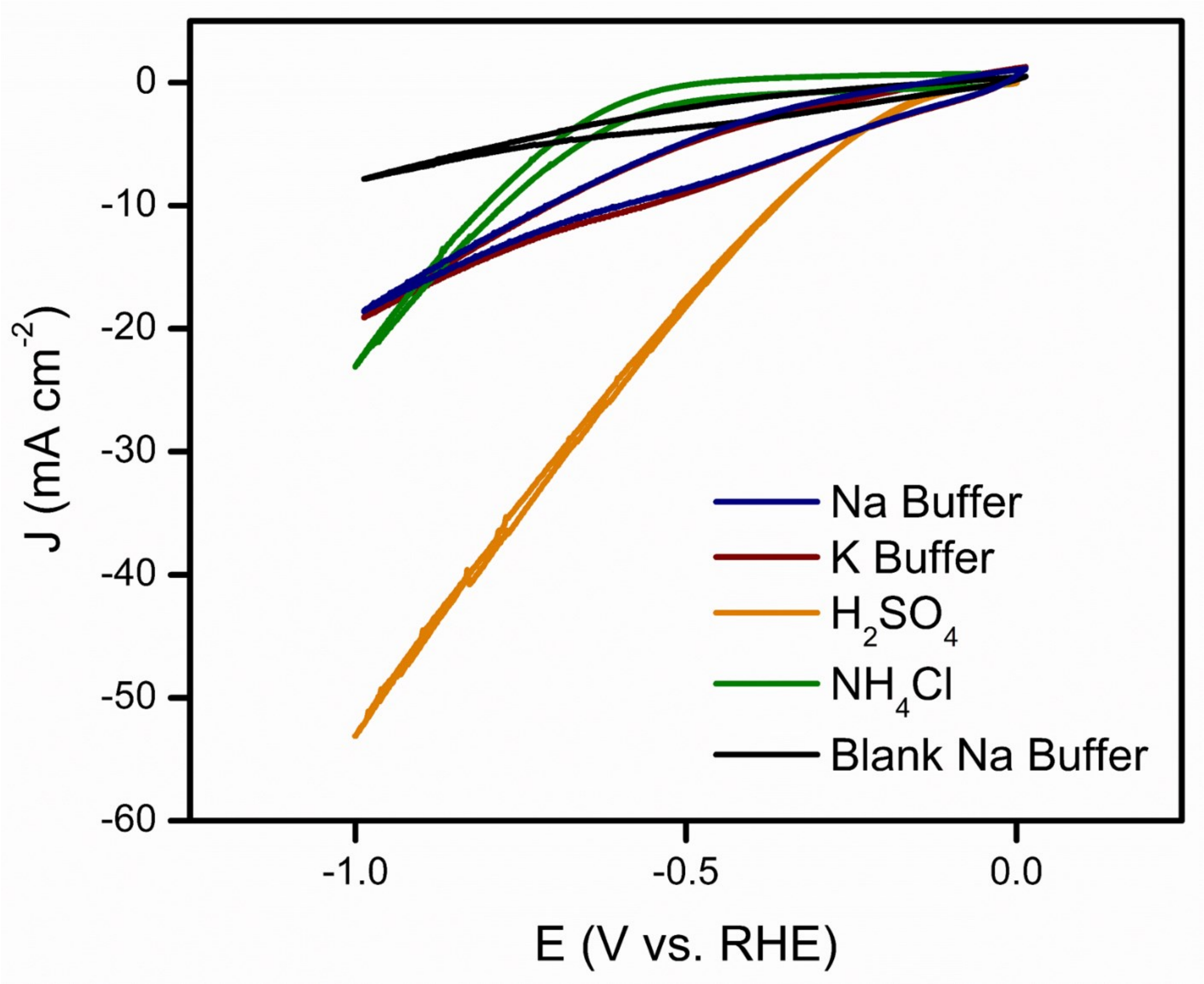

Figure S5. CVs of $Ag_{60}Pd_{40}$ catalyst in different aqueous electrolytes containing 100 mM furfural. The experiment labeled “blank Na buffer” did not contain any furfural.

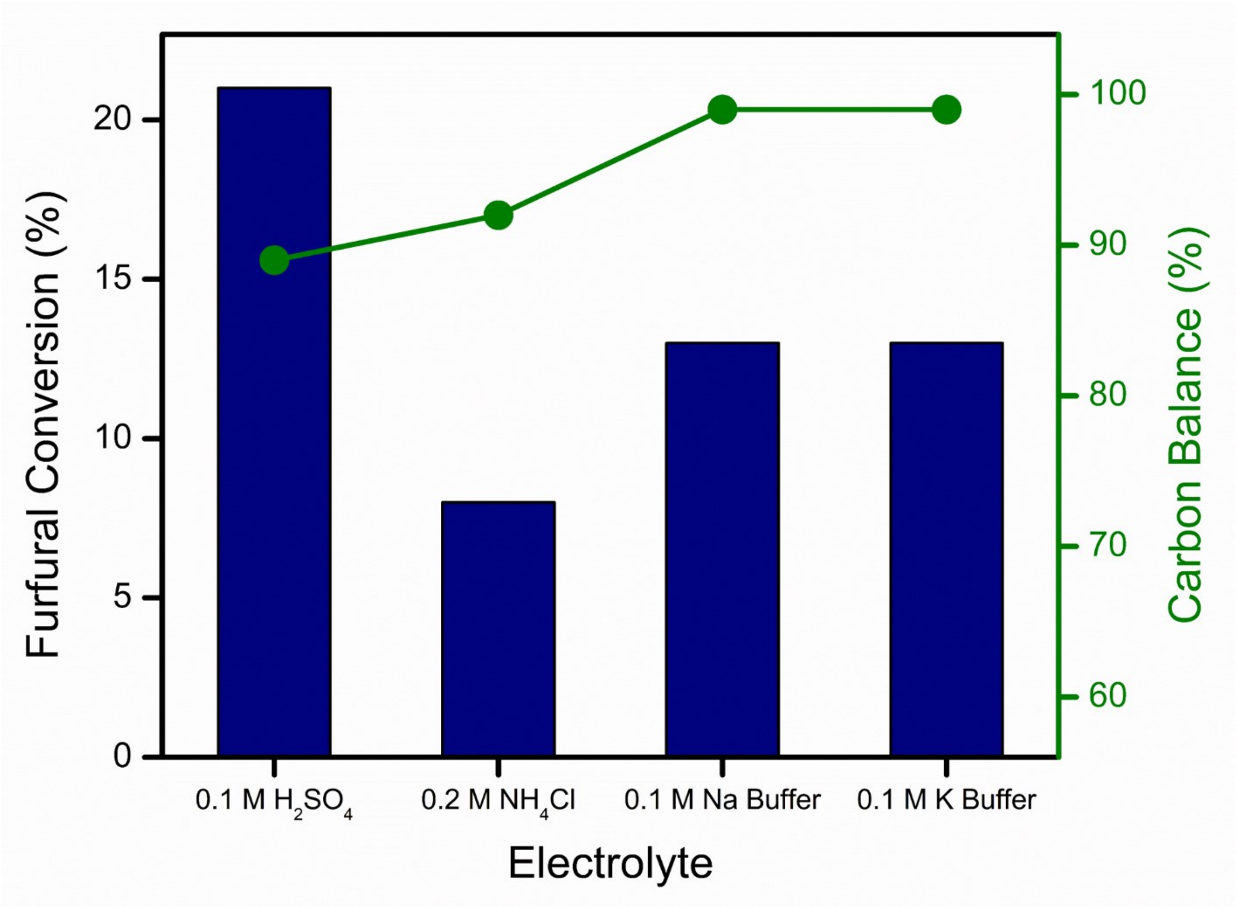

Figure S6. Catalytic activity results of $Ag_{60}Pd_{40}$ catalyst for the electrocatalytic reduction of furfural in different electrolytes. CPE was performed using identical working electrodes held at -0.5 V vs. RHE for 1 hour in 12 mL of electrolyte containing 100 mM furfural.

Table S1. Literature Reports of Furfuryl Alcohol Production from Electrocatalytic Reduction of Furfural

Catalyst	Aqueous Electrolyte (pH)	Furfuryl Alcohol Yield	Faradaic Efficiency to Furfuryl Alcohol (%)	Ref.
Cu-graphite	phosphate buffer (6.6)	N/A	95%	2
Cu foil	0.5 M sulfate (3)	65 umol h^{-1}	40%	3
Cu	0.2 M NH_4Cl	N/A	25%	4
Cu-DHP	0.5 M C_2H_5OK	N/A	60%	5
Pt	0.5 M H_2SO_4	N/A	60%	6
Pd	5wt% acetic acid; 47.5wt% isopropanol	4600 umol h^{-1}	N/A	7
Pd	0.5 M H_2SO_4	110 umol h^{-1}	30%	8
$Ag_{60}Pd_{40}$ nanoparticles	phosphate buffer (6.8)	160 umol h^{-1}	96%	This work

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