SUPPORTING INFORMATION

Monodisperse Gold-Palladium Alloy Nanoparticles and Their Composition-Controlled Catalysis in Formic Acid Dehydrogenation Under Mild Conditions

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Materials and Methods

The nanoparticles (NPs) synthesis was carried out using standard airless procedures and commercially available reagents.

Synthesis of AuPd alloy NPs. Under a gentle argon flow, 0.20 g of borane-morpholine complex (BM, 1.9 mmol, Sigma-Aldrich 95%) was mixed with 10.0 mL oleylamine (OAm, Acros 80-90%) in a four-necked glass reactor. The formed solution was magnetically stirred and heated to 75 °C. Next, 0.07 g of palladium (II) acetylacetonate ($Pd(acac)_2$, 0.23 mmol, Sigma-Aldrich 99%) and 0.06 g of hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4.xH_2O$, 0.15 mmol Au, Strem Chemicals 99.9%) was mixed in 4.0 mL of OAm in a glass vial and injected into the solution in reactor *(Note: Gental heating and sonication were necessary to dissolve $HAuCl_4.xH_2O$ in OAm)*. The resulted solution was heated to 220 °C at a rate of 5-7 °C/min and kept at this temperature for 30 min before it was cooled down to 70 °C. The NPs were separated by adding isopropanol (40 mL), followed by centrifugation (8500 rpm, 10 min). The NPs were dispersed in hexane (15 mL), and centrifugated (9000 rpm, 12 min) after addition of ethanol (35 mL). The separated NPs were re-dispersed in hexane. The synthesis yielded $Au_{41}Pd_{59}$ NPs.

Under the same reaction condition, 0.042 g of $Pd(acac)_2$ (0.14 mmol) and 0.08 g of $HAuCl_4.xH_2O$ (0.2 mmol Au) led to the formation of $Au_{59}Pt_{41}$ NPs. 0.032 g of $Pd(acac)_2$ (0.1 mmol) and 0.08 g of $HAuCl_4.xH_2O$ (0. 2 mmol Au) yielded $Au_{67}Pd_{33}$ NPs and 0.078 g of $Pd(acac)_2$ (0.25 mmol), and 0.044g of $HAuCl_4.xH_2O$ gave $Au_{32}Pd_{68}$ NPs.

Synthesis of 5 nm Au NPs. The synthesis of 5 nm Au NPs was conducted according to a procudure published elsewhere, with some minor modifications.[1] Under a argon flow, 0.2 g of $HAuCl_4.xH_2O$, 10.0 mL of OAm and 10.0 mL of 1,2,3,4-tetrahydronaphthalene (tetralin, Acros 95-98%) were mixed in a four-necked 100 mL glass-reactor at room temperature (~20 °C). A reducing agent solution containing *tert*-butylamineborane complex (1.0 mmol, TBB, Sigma-Aldrich 97%), tetralin (1.0 mL) and OAm (1.0 mL) was prepared by sonication and injected into the precursor solution. The mixture was allowed to react at rt for 2 h before acetone (60 mL) was added to precipitate the NPs. The Au NPs were collected by centrifugation (9000 rpm, 10 min), washed with ethanol and redispersed in hexane.

Synthesis of 4.5 nm Pd NPs. The synthesis of 4.5 nm Au NPs was conducted according to the procedure published elsewhere, with some modifications.[2] Under a nitrogen flow, 78.0 mg of $Pd(acac)_2$ was mixed with 15.0 mL of OAm. The formed solution was heated to 60 °C, resulting in a near colorless solution. 150 mg of TBB was solvated in minimum amount of OAm (~3-4 mL) and quickly injected into the Pd-OAm solution. The temperature was raised to 80°C and kept at this temperature for 60 min. The solution was cooled down to room temperature. 30 mL of ethanol was added and the product was separated by centrifugation (8500 rpm for 8 min). The product was then re-dispersed in hexane and precipitated with ethanol. The NP product was separated by centrifugation (9000 rpm, 16 min) and redispersed in hexane.

Preparation of C-NP Catalysts. In a typical procedure, 50 mg of Ketjen carbon was dispersed in 10 mL of hexane and sonicated with a Fischer Scientific FS 110 for 15 min. Next, ~25 mg of NPs in hexane was added dropwise into the carbon suspension under sonication. The mixture was sonicated for 1 h to ensure complete adsorption of NPs onto the carbon support. The C-NP catalyst was separated by centrifugation and washed with ethanol. Next, the C-NPs were suspended in 30 mL of acetic acid and the mixture was heated for 10 h at 70 ^{o}C. The reaction mixture was cooled down to room temperature. 30 mL of ethanol was added and the mixture was centrifuged at 8500 rpm for 6 min. The product was washed with ethanol for two more times and dried under vacuum.

NP Characterization

Samples for TEM analysis were prepared by depositing a single drop of diluted NP dispersion in hexane on amorphous carbon coated copper grids. The low resolution TEM images were obtained using a Philips CM 20 (200 kV) and HRTEM images were obtained by a JEOL 2010 TEM (200 kV). The ICP-AES measurements were carried on a JY2000 Ultrace ICP Atomic Emission Spectrometer equipped with a JY AS 421 autosampler and 2400g/mm holographic grating. XRD characterizations were carried out on a Bruker AXS D8-Advanced diffractometer with CuKα radiation (λ =1.5418 Å). The UV/Vis spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. Infrared spectra were recorded on a Bruker Tensor 27 FTIR spectrometer.

NP Catalyst Evaluation

The catalytic activity of the C-NP catalysts for FA dehydrogenation in water was determined by measuring the rate of gas (CO_2 + H_2) evolved in a typical gas burette system. Before the test, a jacketed reaction flask (25 mL) containing a teflon-coated stir bar was placed on a magnetic stirrer (VWR) and thermostated to a desired temperature level by circulating water through its jacket from a constant temperature bath. Next, 25 mg of C-NP catalyst was suspended in 9.6 mL of water via sonication and transferred into the reaction flask. The aqueous dispersion of C-NP catalysts was stirred vigorously at least 15 min in the reaction flask to reach a steady temperature level. Finally, the desired amount of FA was injected into the catalyst suspension under a 1200 rpm stirring rate. Then, the gas burette was connected to the reaction flask to measure the volume of the gas generated from the reaction at certain time intervals.

CO_2 Removal from H_2/CO_2 Mixture. We obtained the CO_2 to H_2 molar ratio in the gas mixture by removing CO_2 from the gas mixture through a NaOH trap.[3] In these experiments, the gas burette system was modified by placing a trap (10 M NaOH solution) between the jacketed reactor and gas burette. The generated gas during the reaction was passed through the NaOH trap and CO_2 was captured. Next, the volume of the gas generated from catalytic FA dehydrogenation with and without NaOH trap was compared.

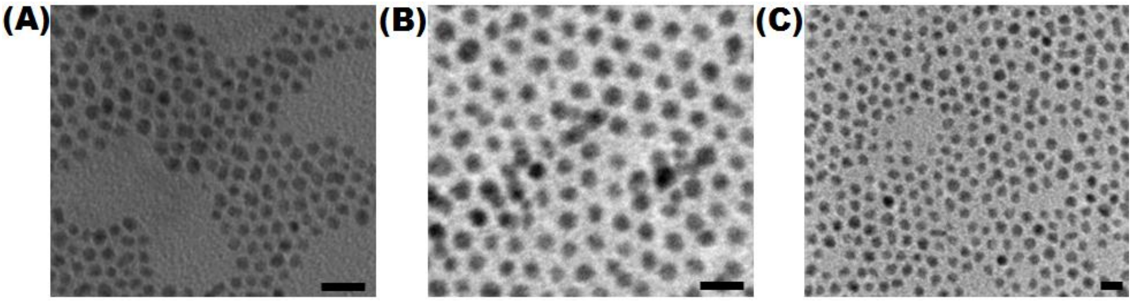

Figure S1. TEM images of **(A)** $Au_{67}Pd_{33}$ **(B)** $Au_{59}Pd_{41}$ and **(C)** $Au_{32}Pd_{68}$ NPs (Scale bars = 10 nm).

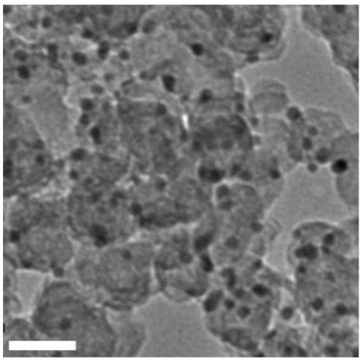

Figure S2. TEM image of the C-$Au_{41}Pd_{59}$ (Scale bar = 20 nm). The image was taken after the catalyst was treated with acetic acid.

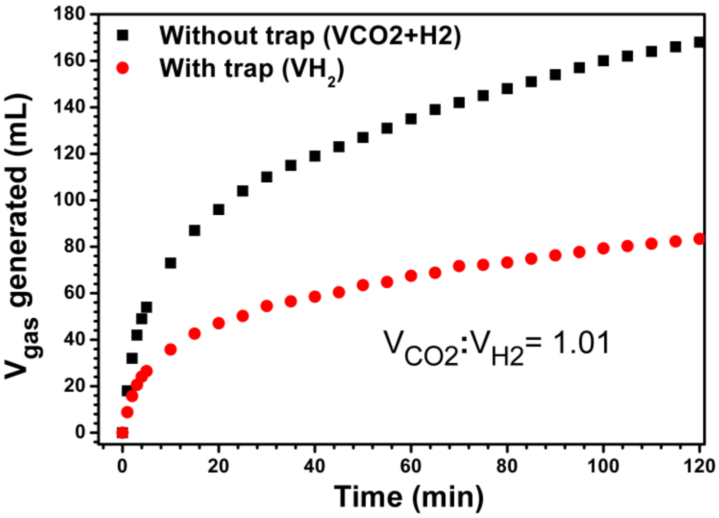

Figure S3. The comparison of the volume of gas generated during the C-$Au_{41}Pd_{59}$ catalyzed dehydrogenation of 1 M FA aqueous solution with and without NaOH trap.

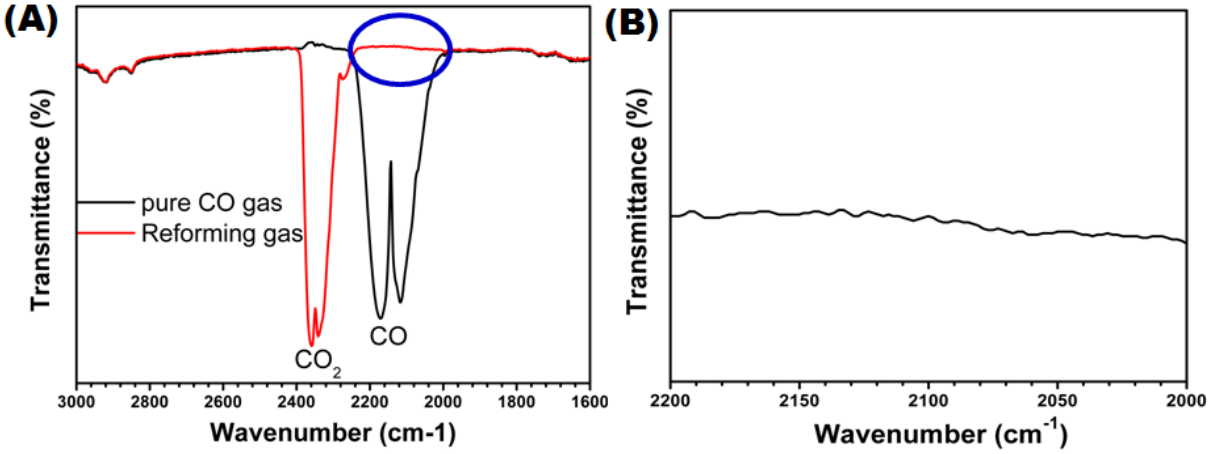

Figure S4. FTIR spectra of pure CO gas and reforming gas generated during the C-$Au_{41}Pd_{59}$ catalyzed FA dehydrogenation in water at 50 °C for 1 h **(A)** and **(B)** the focus on the blue circled range, which corresponds to CO strecthings.

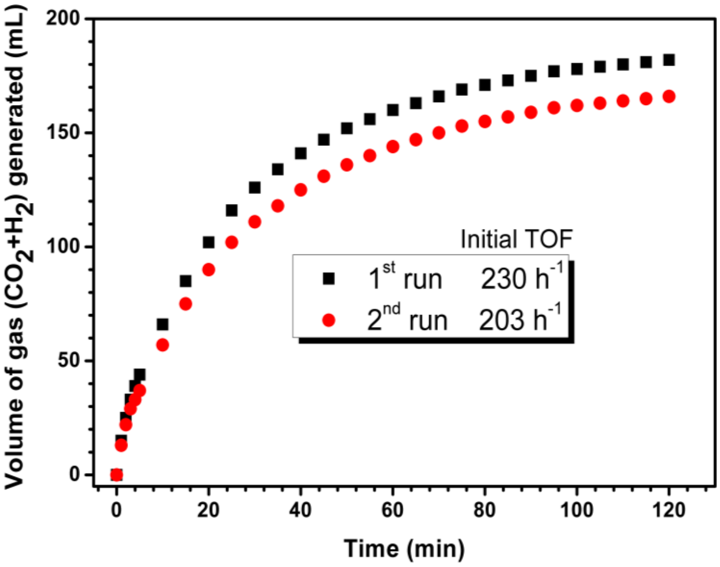

Figure S5. Stability test on the C-$Au_{41}Pd_{59}$ catalyst in the dehydrogenation of 1 M FA aqueous solution (10 mL) at 50 °C

References

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