Electronic Supplementary Information for

High-density Defects on PdAg Nanowire Networks as Catalytic Hot Spots for

Efficient Dehydrogenation Catalysis of Formic Acid and Reduction of Nitrate

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Experiments

Chemicals and Materials. Silver nitrate (AgNO₃), palladium (II) nitrate dihydrate (Pd(NO₃)₂·2H₂O), formic acid (HCOOH) and poly(vinyl pyrrolidone) (PVP, $M_w \approx 58,000$) were purchased from Aldrich Company, USA. The distilled water (18 MΩ/cm) was supplied by a Water Purifier Nanopure water system. Sodium hydroxide (NaOH, A. R. grade, Tianjin Chemical Reagent), sodium sulphide (Na₂S, A. R. grade, Tianjin Chemical Reagent), 1, 3-butylene glycol (1, 3-BG, A. R. grade, Tianjin Chemical Reagent) and ethylene glycol (EG, A. R. grade, Tianjin Chemical Reagent) were used as received without further purification.

Synthesis of Networked Pd₅Ag₅ NWs. In a typical polyol process, 1.2 mmol of poly(vinyl pyrrolidone) (133.2 mg, $M_W = 58000$, as calculated in terms of the repeating unit) was added into 10 mL of BG solution in 50 mL two-neck flask, and then heated at 170 °C for 1 h. Then, 0.5 mL of Na₂S solution (1 mM in EG) was then quickly added into the 1, 3-BG solution using a pipette. After 5 min, AgNO₃ (0.1 mmol, 16.99 mg) and Pd(NO₃)₂·2H₂O (0.1 mmol, 26.64 mg) codissolved in 4 mL of distilled water at room temperature, were quickly added into the stirred 1, 3-BG solution using a syringe. Refluxing and stirring were continued throughout the synthesis for 2 h. After the reaction system was cooled to room temperature, the black production was washed by 60 mL acetone. The synthesized networked Pd₅Ag₅ NWs were further purified at least three times with 60 mL acetone and 3 mL water. The final black precipitation was redispersed into 9.6 mL water for further catalyst evaluation. The Pd and PdAg NWs networks were synthesized by the same method through controlling metal precursors at Pd/Ag precusor ratios of 10:0, 7:3 and 3:7, respectively. And Ag NWs were prepared by same method without refluxing.

The Characterizations of Networked Pd_5Ag_5 NWs. X-ray diffraction (XRD) was carried out on a Bruker AXS D8-Advanced diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The composition analyses of the samples were carried on FEI Nova Nano SEM450 with energy dispersive spectroscopy (EDS). Samples for TEM analysis were prepared by depositing a single drop of diluted networked Pd₅Ag₅ NWs catalyst dispersion in ethanol on amorphous carbon coated copper grids. TEM images were obtained with a Philips CM 20 operating at 120 kV. High-resolution TEM (HRTEM) and high-angle annular dark field (HAADF) images were obtained on a FEI Tecnai Osiris with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII spectrometer (Thermo Fisher Scientific) with Al $K\alpha$ X-ray radiation as the X-ray source for excitation. The UV/Vis spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. NO₃⁻ was tested by the ion chromatograph (Dionex ICS 1100 Ion Chromatogragh). N₂, CO₂ and H₂ were measured by GC-6890B with thermal conductivity detector (TCD) and flame ionization detector (FID)-Methanator (detection limit: \sim 2 ppm). The exact composition of the as-prepared the networked Pd₅Ag₅ NWs was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin Elmer, Model Optima 5300DV, USA).

The Networked PdAg NWs Catalyst Evaluation for FA dehydrogenation. The catalytic activity of the composition-controlled networked PdAg NWs (Pd, Pd₇Ag₃, Pd₅Ag₅, Pd₃Ag₇) and Ag NWs 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 two-neck round bottom flask (25 mL) containing a Teflon-coated stir bar was placed on a magnetic stirrer and thermostated to a desired temperature value. One the neck was connected to a gas burette, and the other neck was sealed. After the networked Pd₅Ag₅ NWs catalyst (0.1 mmol) was dispersed by sonication in water (9.6 mL) and then transferred into the reaction flask. Next, the aqueous dispersion of networked Pd₅Ag₅ NWs catalyst was stirred with magnetic stirring for 15 min in the reaction flask. Finally, when the desired amount of FA was rapidly injected into the flask using a syringe from the rubber stopper neck at a stirring rate of 600 rpm, the gas volume generated was recorded at certain time intervals.

The Networked PdAg NWs Catalyst Evaluation for Reduction of Nitrate. The catalytic activity of networked Pd₅Ag₅ NWs catalyst for reduction of nitrate was determined by the ion chromatograph (IC) and gas chromatograph (GC). During the synthesis of networked Pd₅Ag₅ NWs, we separately extracted 0.5 mL of the black reaction solution using a pipette at different reaction stage. After cooling down to room temperature quickly, the black reaction solution was washed with 20 mL acetone, and the solution that we got by centrifugation was used to test the nitrate concentration by the IC. In addition, we also tested reduction product of nitrate using the GC, which was found that the nitrate ion (NO₃⁻) of the AgNO₃ and Pd(NO₃)₂·2H₂O was reduced to nitrogen in the reaction.

CO₂ Removal from H_2/CO_2 Mixture. We tested the molar ratio of CO₂ to H_2 in gas mixture by removing CO₂ from the gas mixture through a NaOH trap (Gu X.; Lu Z. H.; Jiang H. L.; Akita T.; Xu Q. J. Am. Chem. Soc. 2011, 133, 11822-11825.). In the experiment, the gas burette system was modified by placing a trap (10 M NaOH solution) between the reaction flask and gas burette. When the generated gas mixture passed the NaOH trap, the CO₂ was captured. The volume of gas generated with NaOH trap was compared with the volume of gas generated from without NaOH trap in FA (1 M, 10 mL) hydrogen generation system in water.



Supplementary Figures and Tables

Figure S1. The photographs of networked Pd_5Ag_5 NWs catalyst dispersed in aqueous solution (a) before and (b) after 6 cycles.



Figure S2. XRD patterns of the Ag NWs, networked Pd and Pd₅Ag₅ NWs.



Figure S3. UV-Vis spectra of the Ag NWs and networked Pd₇Ag₃, Pd₅Ag₅, Pd₇Ag₃ and Pd NWs dispersed in water.



Figure S4. TEM images of (a) networked Pd₇Ag₃, (b) Pd₃Ag₇, (c) Pd NWs and (d) Ag NWs.

Table S1 Elemental analysis of the catalysts by the inductively coupled plasma optical emission spectrometer (ICP-OES).

Entry	$AgNO_3/Pd(NO_3)$ 2 molar ratio	As-synthesized Networked NWs	
1	7:3	Networked Ag ₇ Pd ₃ NWs	
2	5:5	Networked Ag ₅ Pd ₅ NWs	
3	3:7	Networked Ag ₃ Pd ₇ NWs	

Table S2 Elemental analysis of the catalysts by energy dispersive X-ray spectroscopy (EDS).

Entry	Catalyst	C Atom%	N Atom%	O Atom%	Ag Atom%	Pd Atom%
1	Networked Ag ₇ Pd ₃ NWs	43.0	9.0	2.94	14.4	5.9
2	Networked Ag ₅ Pd ₅ NWs	42.4	7.6	7.6	8.0	7.9
3	Networked Ag ₃ Pd ₇ NWs	46.7	15.6	6.7	4.2	9.8



Figure S5. XPS spectrum of Ag NWs, networked Pd and Pd_5Ag_5 NWs.



Figure S6. TEM images of networked PdAg NWs intermediates at different reaction time: (**a**) 5 s, (**b**) 20 s, (**c**) 30 s, (**d**) 30 min and (**e**) the schematic illustration on nucleation and oriented attachment of PdAg NPs for the growth mechanism of networked PdAg NWs.



Figure S7. GC spectrum using TCD for the evolved gas from FA (1 M, 10 mL), over networked Pd_5Ag_5 NWs at 60 °C.



Figure S8. GC spectrum using FID-Methanator for (a) the evolved gas from FA (1 M, 10 mL) over networked Pd_5Ag_5NWs at 60 °C, and (b) commercial pure CO.



Figure S9. The comparison of the volume of gas generated by catalyzing the dehydrogenation of aqueous FA solution (10 mL, 1 M) with and without NaOH trap.



Figure S10. TEM images of Pd₃Ag₇ NPs.



Figure S11. Gas generated vs. time during the dehydrogenation of aqueous FA solution (10 mL, 1 M) in the presence of networked Pd_3Ag_7 NWs and Pd_3Ag_7 NPs at 60 °C.



Figure S12. (a) Gas generated vs. time during the dehydrogenation of aqueous FA solution (10 mL, 1 M) in the presence of different catalyst concentration at 60 °C, and (b) plot of hydrogen generation rate vs. networked Pd_5Ag_5 NWs concentration.



Figure S13. The plots of generated gas (CO_2+H_2) vs. time for the FA dehydrogenation catalyzed by networked Pd₅Ag₅ NWs in aqueous FA solution (10 mL, 1 M) at 60 °C.



Figure S14. Every other week, the stability of networked Pd_5Ag_5 NWs catalyst was tested in aqueous FA solution (10 mL, 1 M) at 60 °C.

Methods for the TOF_{initial} Calculation:

$$x_{a} = \frac{Patm V'H2/RT}{nFA}$$
 S1f

Where x_a is conversion, P_{atm} is the atmospheric pressure, V'_{H2} is the final generated volume of H₂, R is the universal gas constant, T is room temperature (298 K), and n_{FA} is the mole number of FA. Patm V'H2/ RT

$$TOF_{initial} = \frac{Patm V H2/RT}{nAg + Pd t}$$
 S2

Where $\text{TOF}_{\text{initial}}$ is initial turnover frequency, V'_{H2} is the generated volume of H₂ during the first 20 min of the reaction, $n_{\text{Ag+Pd}}$ is the mole number of the Ag and Pd, and *t* is the reaction time of 20 min.