Electronic Supplementary Information for:

Surface Pd-Rich PdAg Nanowires as Highly Efficient Catalysts for Dehydrogenation of Formic Acid and Subsequent Hydrogenation of Adiponitrile

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1. Supplementary Materials and Methods

1.1 Chemicals and Materials: Silver nitrate ($AgNO_3$), palladium (II) nitrate dihydrate ($Pd(NO_3)_2 \cdot 2H_2O$), 1,6-hexanedinitrile, formic acid (HCOOH) and poly-*n*-vinylpyrrolidone (PVP, M_w = 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 (Na_2S, A. R. grade, Tianjin Chemical Reagent), 1, 3-butylene glycol (1, 3-BG, A. R. grade, Tianjin Chemical Reagent), ethylene glycol (EG, A. R. grade, Tianjin Chemical Reagent) were used as received without further purification.

1.2 Synthesis of diffused-induced PdAg NWs(D-PdAg NWs): In a typical polyol process, PVP (1.2 mmol, 133.2 mg, M_W = 58,000, as calculated in terms of the repeating unit) and 10 mL 1, 3-BG were added into a 50 mL two-neck flask heated with an oil bath at 170 °C for 10 min. Then 0.5 mL ammonium hydroxide (25 %) was then quickly added into the above 1, 3-BG solution using a pipette with immediately sealing the exit of two-neck flask and reflux pipe. After refluxing for 2 h, the clear solution turns yellow, and opened above reaction system with refluxing for 0.5 h at 170 °C to remove ammonium hydroxide and water. Then 0.5 mL Na_2S solution (1 mM in EG) was then quickly added into the 1, 3-BG solution. After 5 min, $AgNO_3$ (0.1 mmol, 16.99 mg) were dissolved into 2 mL of distilled water at room temperature, and then the solution was rapidly quickly added into the stirring 1, 3-BG solution using a syringe. When above solution was refluxing for 0.5 h, the 2 mL aqueous solution including $Pd(NO_3)_2 \cdot 2H_2O$ (0.1 mmol, 26.64 mg) were rapidly quickly added into the stirring above solution and was refluxing for another 2 h. Refluxing and stirring was always continuing during throughout the synthesis process. After the reaction system was cooled to room temperature, the black production was washed by 60 mL acetone for the first centrifugal process at a rate of 8500 rpm for 3 min. The as-synthesized D-Ag_5Pd_5 NWs were was 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. For the other composition networked D-AgPd NWs were synthesized by same mothod by controlling metal Ag and Pd precursor ratios (7:3 and 3:7) respectively. Ag NPs were prepared by same mothod with refluxing for 0.5 h. The co-reducing Pd_5Ag_5 NWs (C-Pd_5Ag_5 NWs) were synthesized by our reported method. [1]

1.3 D-PdAg NWs Characterizations: X-ray diffraction (XRD) characterization was carried out on a Bruker AXS D8-Advanced diffractometer with Cu *K*α radiation (λ =1.5418 Å). The composition analyses of the samples were carried on FEI Nova Nano SEM450 with energy dispersive spectro-scopy (EDS). Samples for TEM analysis were prepared by depositing a single drop of diluted networked D-PdAg 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 the 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*α X-ray radiation as the X-ray source for excitation. The UV/Vis spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. Infrared spectra were recorded on a Bruker Tensor 27 FTIR spectrometer. Detailed analyses for CO_2, H_2, N_2 and CO were performed on GC-6890 with thermal conductivity detector (TCD) and flame ionization detector (FID)-Methanator (detection limit for CO: ~ 2 ppm). The progress of the reaction and the yield of the 1, 6-hexanediamine were determined by GC-MS with benzyl ether as the internal standard. The sample solution (0.2 ML) was directly injected into the GC for quantitative analysis. ^1H NMR spectra were performed on an INOVA-400 NMR spectrometer with $CDCl_3$-d^6 as solvent.

1.4 D-PdAg NWs Catalyst Evaluation: 1) The catalytic activity of the composition D-PdAg NWs and Ag NPs 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 and 9.6 mL aqueous dispersed catalyst (0.1 mmol) were placed on a magnetic stirrer and thermostated to a desired temperature value. One neck of the flask was connected to a gas burette, and the other neck was sealed rubber stopper. Next, the aqueous dispersion of D-PdAg NWs catalyst was stirred with magnetic stirring (600 r/min) at least 15 min in the reaction flask for keeping a constant temperature condition. Finally, when the desired amount of FA was rapidly injected into the flask using a syringe from the rubber stopper neck under a 600 rpm stirring rate, the gas volume generated was recorded at certain time intervals.

2) The reduction experiments of 1, 6-hexanedinitrile were conducted in a two-neck round bottom flask (25 mL) at 25 °C. In the setup, before the test, a two-neck round bottom flask (25 mL) containing a teflon-coated stir bar and 9.3 mL aqueous dispersed catalyst (0.1 mmol) were placed on a magnetic stirrer and thermostated to a desired temperature value under magnetic stirring (600 r/min) at least 15 min. One neck of the flask was connected to a balloon, and the other neck was sealed rubber stopper. Then, 0.2 mL FA and 0.5 mL 1, 6-hexanedinitrile ethanol solution (5 mol/L) were rapidly rejected into the flask using a syringe from the rubber stopper neck, respectively. During the experiment, we extracted 0.5 mL suspension from catalytic system at the regular time interval. The D-AgPd NWs catalyst was separated from the suspension by centrifugation, and the yield of the 1, 6-hexanedinitrile were determined by GC-MS with benzyl ether as the internal standard. The sample solution (0.2 ML) was directly injected into the GC for quantitative analysis. The CO_2 and H_2 were performed on GC-6890.

1.5 CO_2 Removal from H_2/CO_2 Mixture: The molar ratio of CO_2/H_2 was tested through a NaOH trap and the CO_2 was absorbed.[2] In the experiment, the gas burette system was modified by placing a trap (10 M NaOH solution) between the reaction flask and gas burette. The generated gas mixture was passed the NaOH trap and the CO_2 was captured. The volume of gas generated from 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.

2. Supplementary figures and tables

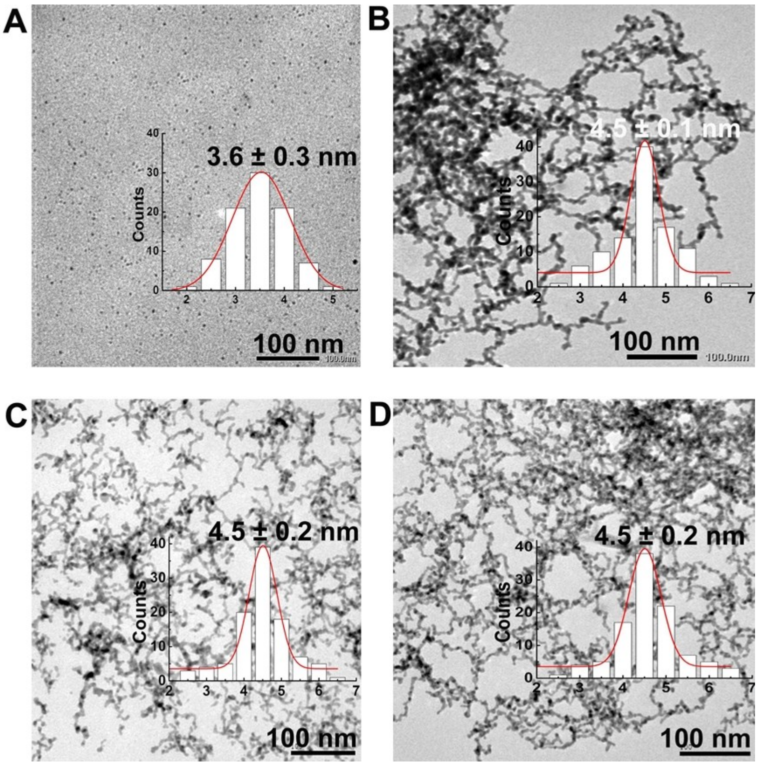

Figure S1 TEM images of **(A)** Ag NPs, **(B)** Pd-NWs, **(C)** D-Pd_7Ag_3 NWs, **(D)** D-Pd_3Ag_7 NWs.

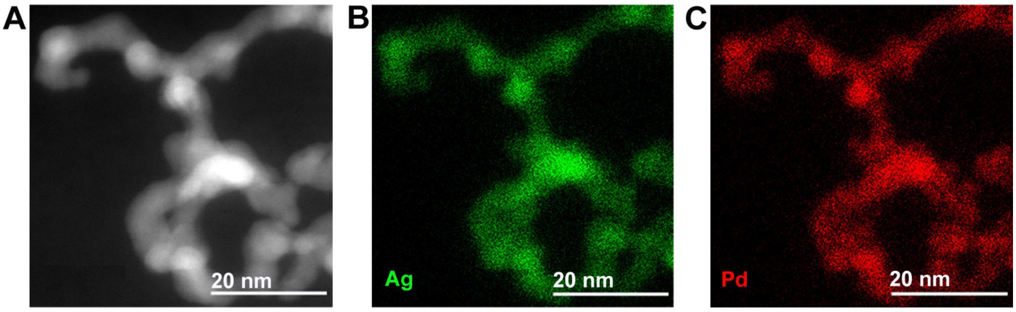

Figure S2 (**A-C**) HAADF-STEM and elemental mapping of the networked D-Pd_5Ag_5 NWs.

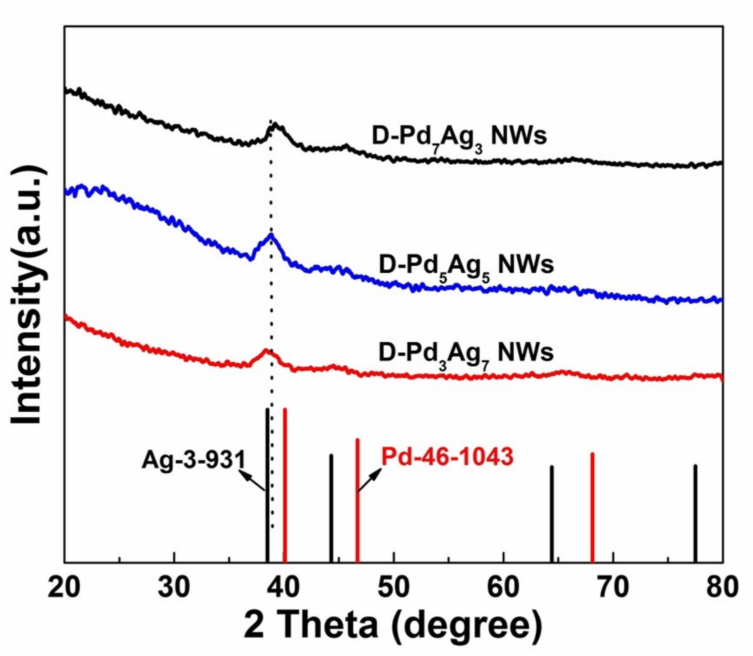

Figure S3 XRD patterns of D-Pd_7Ag_3 NWs, D-Pd_5Ag_5 NWs and D-Pd_3Ag_7 NWs.

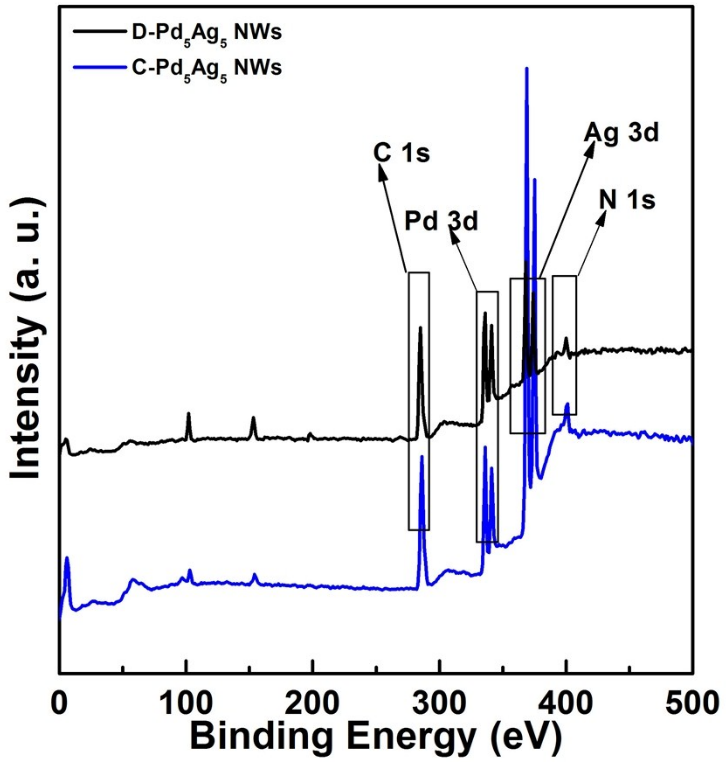

Figure S4 XPS spectrum of D-Pd_5Ag_5 NWs and C-Pd_5Ag_5 NWs.

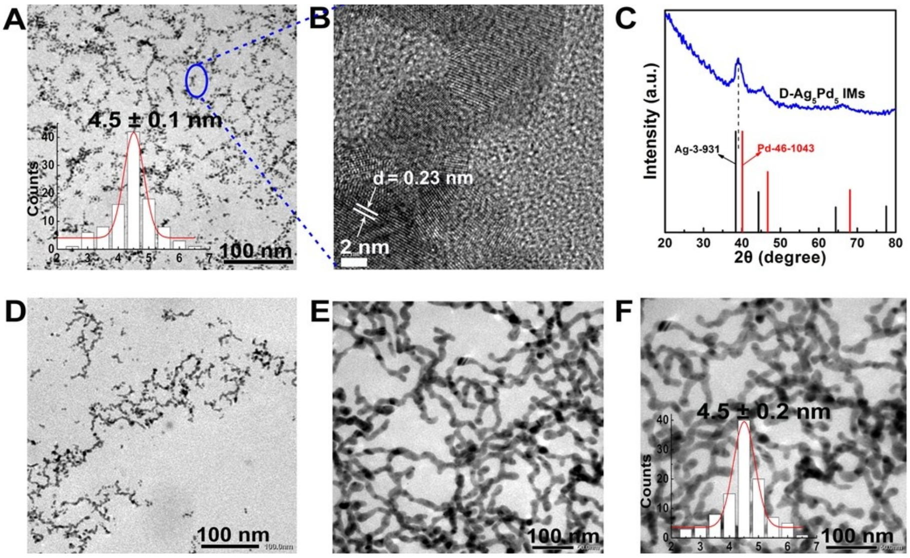

Figure S5 Typical TEM images of intermediates for synthesizing the networked D-Pd_5Ag_5 NWs at different reaction time: (**A**) 15 s, (**D**) 1 min, (**E**) 20 min and (**F**) 3 h. (**B**) HRTEM image and diffraction profile of the D-Pd_5Ag_5 IMs (the growth intermediates of D-Pd_5Ag_5 NWs) at 15 s. (**C**) XRD patterns of D-Pd_5Ag_5 IMs at 15 s.

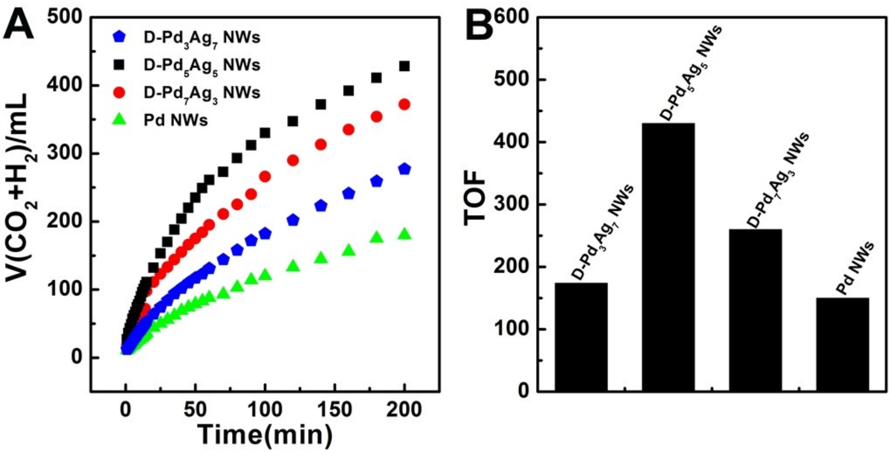

Figure S6 (**A**) The volume of CO_2+H_2 generated *vs.* time from FA hydrogengeneration system in the presence of the different D-PdAg NWs and Pd NWs in water at 25 °C and (**B**) TOF of the different D-PdAg NWs and Pd NWs.

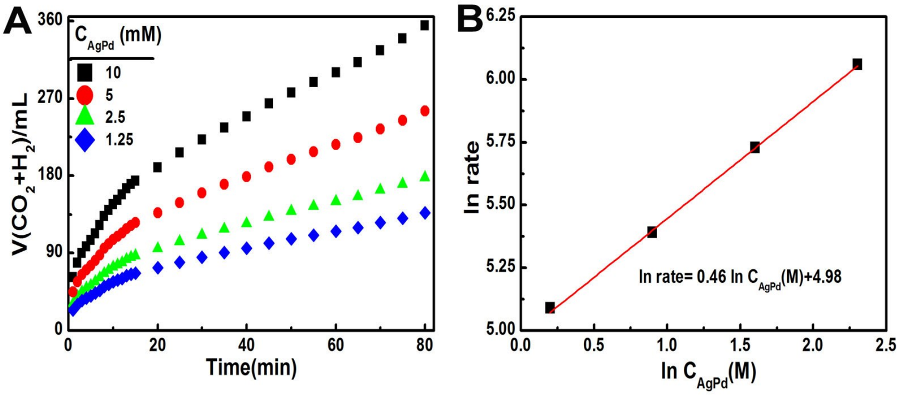

Figure S7 (**A**) Gas generated *vs.* time during the dehydrogenation of aqueous FA solution (10 mL, 1 M) in the presence of different catalyst concentration at 25 ℃, and (**B**) plot of hydrogen generation rate *vs.* D-Pd_5Ag_5 NWs concentration.

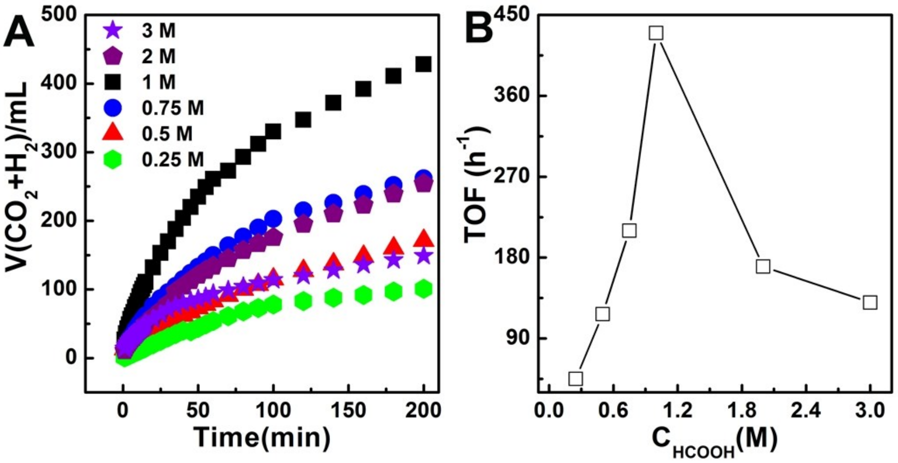

Figure S8 A) The plots of generated gas (CO_2 + H_2) *vs.* time for the FA dehydrogenation catalyzed by D-Pd_5Ag_5 NWs at different FA concentrations and **B**) the plot of gas generation rate *vs.* FA concentration (both in logarithmic scale).

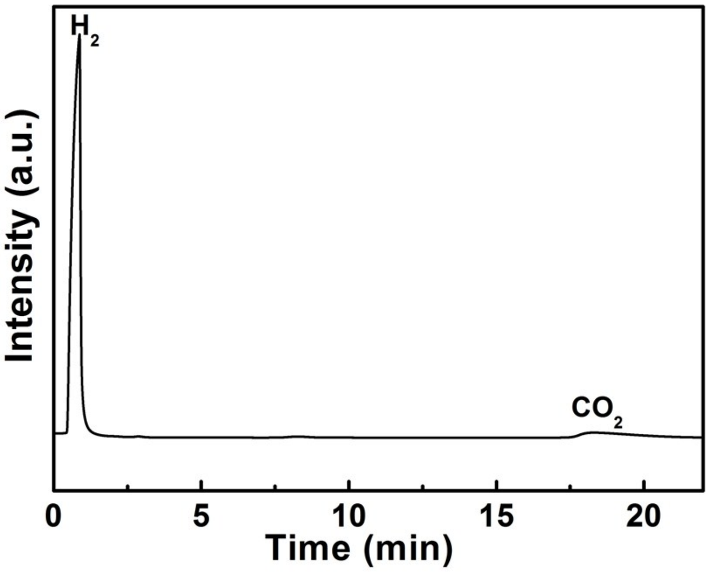

Figure S9 GC spectrum using TCD for the evolved gas from FA (1 M, 10 mL) over D-Pd$_5$Ag$_5$ NWs.

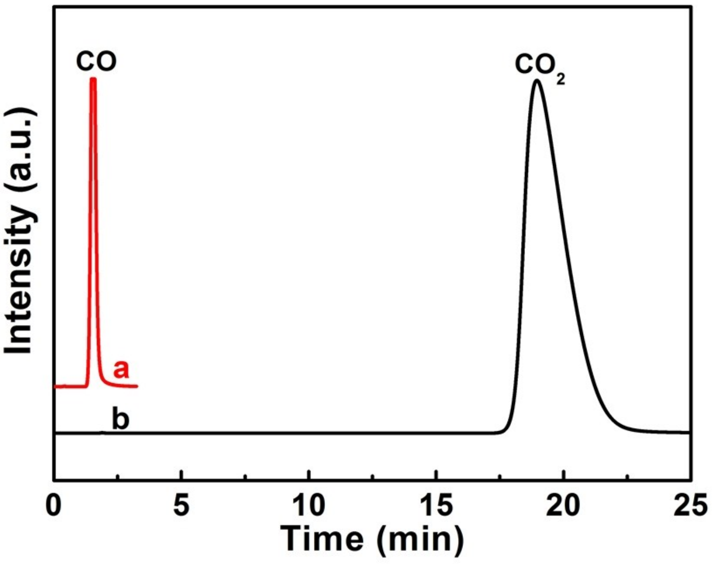

Figure S10 GC spectrum using FID-Methanator for **(a)** commercial pure CO and **(b)** the evolved gas from FA (1 M, 10 mL) over D-Pd$_5$Ag$_5$ NWs.

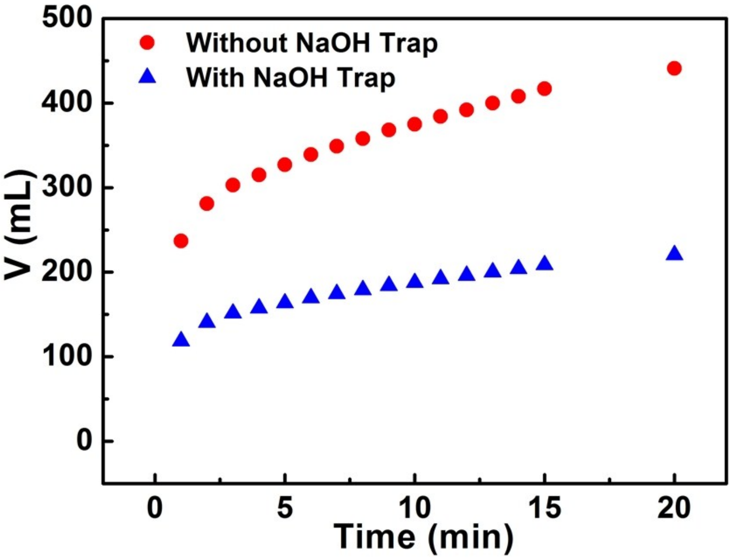

Figure S11 The comparison of the volume of gas generated during D-Pd_5Ag_5 NWs catalyzed dehydrogenation of aqueous FA solution (10 mL, 1 M) with and without NaOH trap.

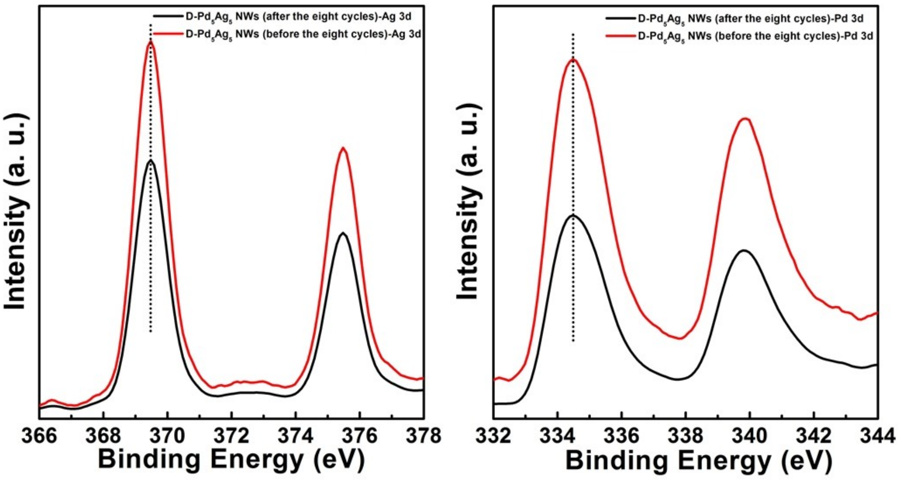

Figure S12 The XPS data of the networked D-PdAg NWs before and after 8 cycles.

Table S1 Elemental analysis result of the catalysts characterized by inductively coupled plasma-atomic emission spectroscopy (ICP-OES).

Entry	$AgNO_3/Pd(NO_3)_2$ molar ratio	$AgNO_3/Pd(NO_3)_2$ molar ratio of D-PdAg NWs
D-Pd_3Ag_7 NWs	3.0:7.0	3.0:6.95
D-Pd_5Ag_5 NWs	5.0:5.0	5.0:4.96
D-Pd_7Ag_3 NWs	7.0:3.0	7.0:2.98

Table S2 Initial TOF ($mol_{H2}\cdot molcatalyst^{-1}\cdot h^{-1}$) values for the decomposition of FA over various heterogeneous catalysts.

Catalyst	FA(mmol)	Additive(mmol)	Tem.(K)	$n_{Catalyst}$(mmol)	TOF$_{initia}$	Recycle times	Ref.
			Without support				
C-Pd_5Ag_5 NWs	10.0	None	298	0.100	245	6	[1]
D-Pd_5Ag_5 NWs	10.0	None	298	0.100	430	8	This work
D-Pd_5Ag_5 NWs	10.0	None	323	0.100	1600	8	This work
PdAg Nanosheets	10.0	HCOONa(5.0)	298	0.100	156.0	—	[5]
			With support				
$Ag_{42}Pd_{58}$/C	10.0	None	323	0.100	**382.0**	**4**	[3]
Ag@Pd/C	10.0	None	293	0.200	**192.0**	**2**	[4]
$Ag_{0.1}$-$Pd_{0.9}$/rGO	5.0	HCOONa (3.35)	298	0.100	**105.2**	—	[6]

“**—, —**”For comparison, the cycle property of catalyst was not tested.

Table S3. Elemental analysis result of the networked D-Pd_5Ag_5 NWs catalysts characterized by inductively coupled plasma-atomic emission spectroscopy (ICP-OES).

Entry	Before the four catalytic run	After the four catalytic run
1	Ag:Pd = 5.0:5.0	Ag:Pd = 5.0:4.95

Table S4. Pd content analysis result by inductively coupled plasma-atomic emission spectroscopy (ICP-OES) in our catalytic system of liquid phase.

Entry	Before the four catalytic run	After the four catalytic run
1	0.0 ppm	0.0 ppm

$\text{TOF}_{\text{initial}}$ Calculation methods:

$$x_a = \frac{\text{Patm V'H2/ RT}}{\text{nFA}} \qquad \text{S1}^{\text{f}}$$

Where x_a is conversion, P_{atm} is the atmospheric pressure, V'_{H2} is the final generated volume of H_2, R is the universal gas constant, T is room temperature (298 K), and n_{FA} is the mole number of FA.

$$\text{TOF}_{\text{initial}} = \frac{\text{Patm V'H2/ RT}}{\text{nAg + Pd t}} \qquad \text{S2}$$

Where $\text{TOF}_{\text{initial}}$ is initial turnover frequency, V'_{H2} is the generated volume of H_2 during the first 20 min of the reaction, n_{Ag+Pd} is the mole number of the Ag and Pd, and *t* is the reaction time of 20 min.

3. Supplementary references

[1] Liu, H., Huang B. L., Zhou J. H., Wang K., Yu, Y. Y., Yang, W. W., Guo, S. J., *J. Mater. Chem. A*, 2018, **6**, 1979-1984.

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