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Electronic Supplementary Information for:

Bifunctional Networked Ag/AgPd Core/Shell Nanowires for Highly Efficient Dehydrogenation of Formic Acid and Subsequent Reduction of Nitrate and Nitrite in Water

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1. Supplementary Materials and Methods

1.1 Chemicals and Materials: Silver nitrate ($AgNO_3$), palladium (II) nitrate dihydrate ($Pd(NO_3)_2 \cdot 2H_2O$), sodium nitrite ($NaNO_2$), formic acid (HCOOH) and poly-*n*-vinylpyrrolidone (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 (Na_2S, A. R. grade, Tianjin Chemical Reagent), sodium nitrate ($NaNO_3$, 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 networked Ag/AgPd CS-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 2h, the clear solution turns yellow, and opened above reaction system with refluxing for 0.5 h at 170 ^{o}C to remove ammonium hydroxide and water[1]. 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) and $AgNO_3$ (0.1 mmol, 16.99 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 Ag/AgPd CS-0.9 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.

The other composition networked Ag/AgPd CS-NWs were synthesized in same method by controlling the amount of Pd and Ag precursor (0.05 mmol, 0.075 mmol and 0.125 mmol), respectively.

In addition, PVPI-capped networked Pd_5Ag_5 NWs were also prepared by our previous work[1].

1.3 Networked Ag/AgPd CS-NWs Characterizations: X-ray diffraction (XRD) characterization was carried out on a Bruker AXS D8-Advanced diffractometer with CuKα 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 Ag@AgPd 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 concentrations of NH_4^+, NO_3^-, NO_2^-, and $HCOO^-$ by the ion chromatograph (Dionex 4500i Ion Chromatography with a conductivity cell). The concentration of ammonia nitrogen concentration was detected by Nessler's reagent dectrophotometry.

1.4 Networked Ag/AgPd CS-NWs Catalyst Evaluation: 1) The catalytic activity of the composition networked Ag/AgPd CS-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 networked Ag/AgPd CS-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 NO_3^- and NO_2^- 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 9.1 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 $NaNO_3$ solution (3.2 g NO_3^-/L) were rapidly rejected into the flask using a syringe from the rubber stopper neck, respectively. The final NO_3^- concentration is 160 mg/L and FA concentration is 0.5 M. During the experiment, we extracted 0.5 mL suspension from catalytic system at the regular time interval. The networked Ag/AgPd CS-NWs catalyst was separated from the suspension by centrifugation, and the concentrations of NH_4^+, NO_3^-, NO_2^-, and $HCOO^-$ in the clear solution were detected by the ion chromatograph (Dionex 4500i). The ammonia nitrogen concentration were detected by Nessler's reagent dectrophotometry. The CO_2, H_2, N_2 and CO were performed on GC-6890. Before the test, the reaction system was refilled with argon for 5-6 times, and then the Ag/AgPd CS-0.9 catalyst (20 mg) dispersed 9.1 mL water was rejected into the reaction vessel, the thermostat was heated to the setting temperature. 0.2 mL FA and 0.5 mL $NaNO_3$ solution (3.2 g NO_3^-/L) were rejected to the vessel. After running the reaction during the desired time, a GC sample was taken to determine the identity of the gas components. The initial NO_3^- and NO_2^- reduction rate (V_{NO3-} and V_{NO2-}) was calculated by changing concentration of NO_3^- and NO_2^- in the initial 10 min by Eq. (1) and (2) [2]:

$$V_{NO3-} = \textbf{Error!} \qquad (1)$$

$$V_{NO2-} = \textbf{Error!} \qquad (2)^{f}$$

f

The nitrate and nitrite conversion (X_{NO3-} and X_{NO2-}) used to evaluate the catalyst activity and the selectivity of nitrate converted to NO_3^- (S_{NO3-}) was calculated by Eqs. (3), (4), (5) and (6), respectively [2].

$$X_{NO3-} = \frac{CNO3i - \ - \ CNO3t -}{CNO3i -} \qquad (3)$$

$$X_{NO2-} = \frac{\text{CNO2i - - CNO2t -}}{\text{CNO2i -}} \quad (4)$$

$$S_{NO_3^-} = \frac{\text{nNO3t +}}{\text{nNO3i - - nNO3t - - nNO2t -}} \quad (5)$$

$$S_{NO_2^-} = \frac{\text{nNO2t +}}{\text{nNO2i - - nNO2t -}} \quad (6)^f$$

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.[3] 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

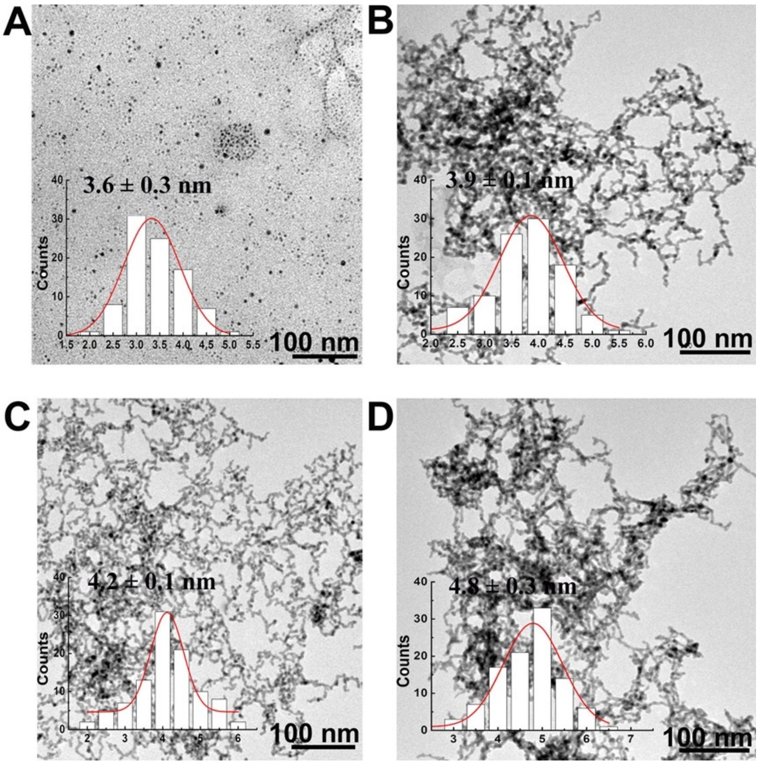

Figure S1 TEM images of **(A)** Ag NPs, **(B)** Ag/AgPd CS-0.3, **(C)** Ag/AgPd CS-0.6, **(D)** Ag/AgPd CS-1.2. The insert shows the diameter distribution of CS-NWs catalyst.

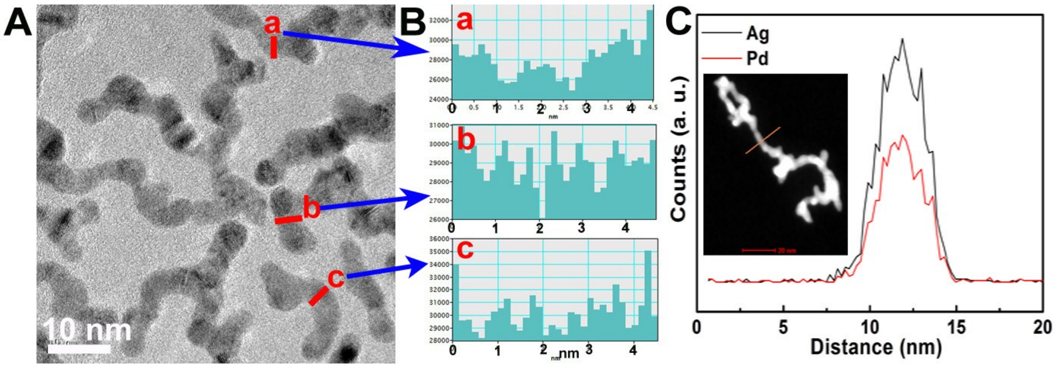

Figure S2 (**A and B**) HR-TEM images and diffraction profiles of the Ag/AgPd CS-0.9. The insert **a, b**＆**c** of **Figture S2B** shows three sets of lattice profile of the Ag/AgPd CS-0.9. (**C**) HAADF-STEM image and line scan analysis spectrum of the Ag/AgPd CS-0.9.

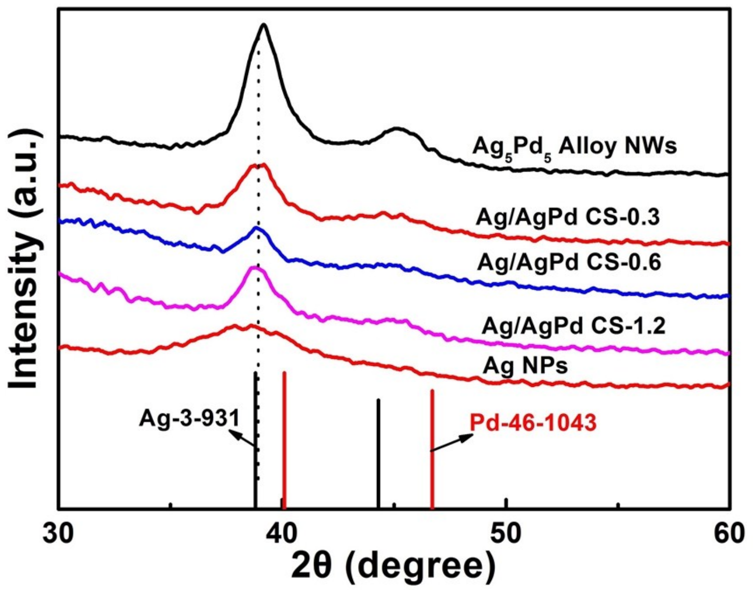

Figure S3 XRD patterns of the the CS-NWs, Ag NPs and AgPd alloy NWs.

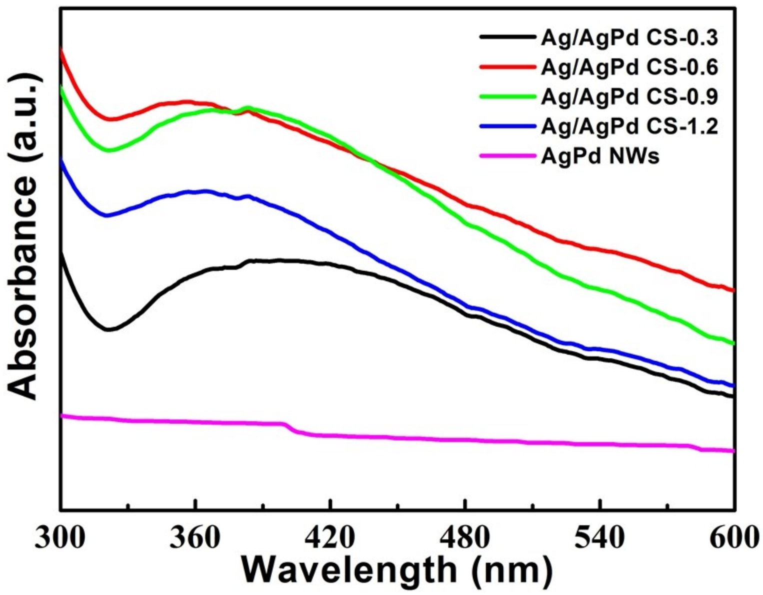

Figure S4 UV-vis spectra from water suspensions containing the CS-NWs and AgPd alloy nanowires.

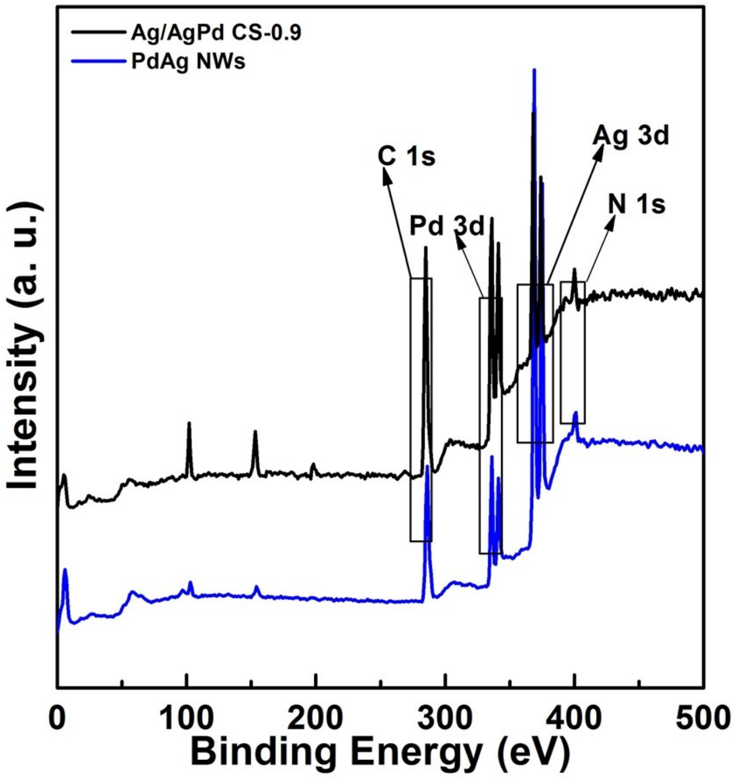

Figure S5 XPS spectrum of Pd_5Ag_5 NWs and Ag/AgPd CS-0.9.

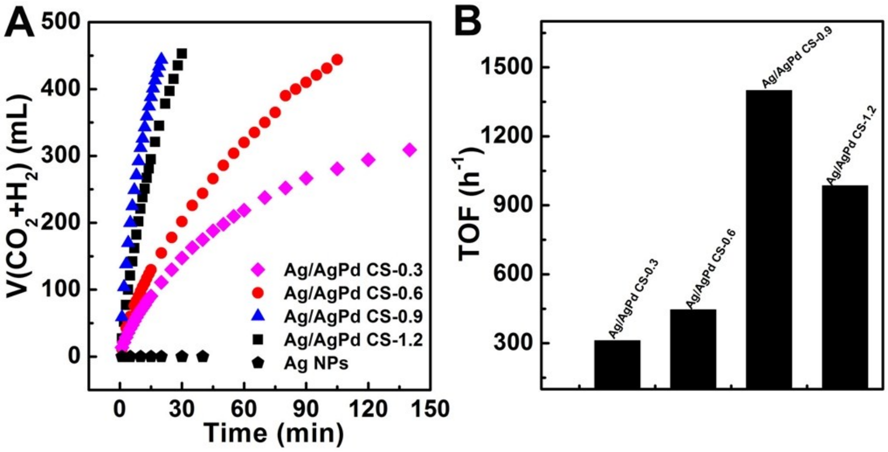

Figure S6 (**A**) The volume of CO_2 + H_2 generated *vs.* time from FA hydrogengeneration system in the presence of the different CS-NWs and Ag NPs in water at 50 °C and (**B**) TOF of the CS-NWs.

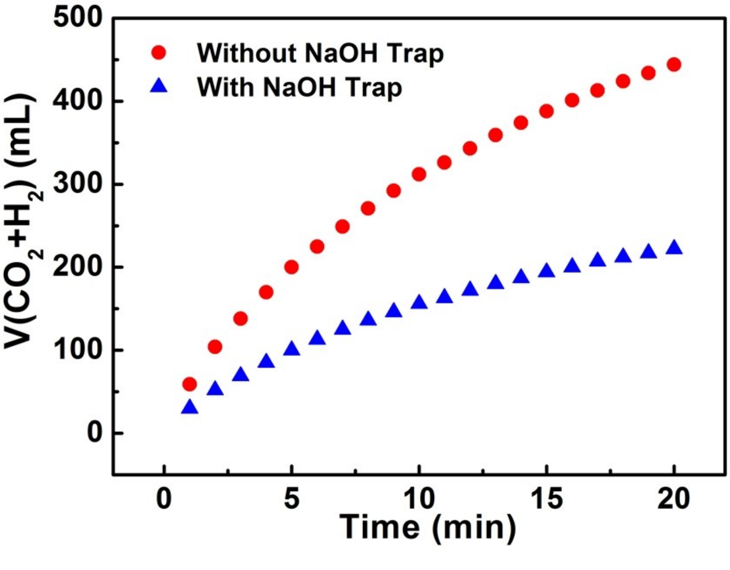

Figure S7 The comparison of the volume of gas generated during Ag/AgPd CS-0.9 catalyzed dehydrogenation of aqueous FA solution (10 mL, 1 M) with and without NaOH trap.

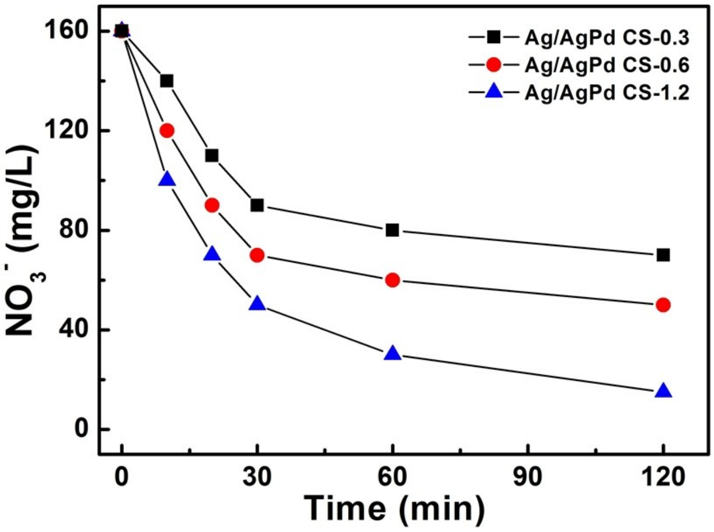

Figure S8 The catalytic NO_3^- reduction of the Ag/AgPd CS-NWs catalyst *vs.* the reaction time in 0.5 M FA aqueous at 25 °C.

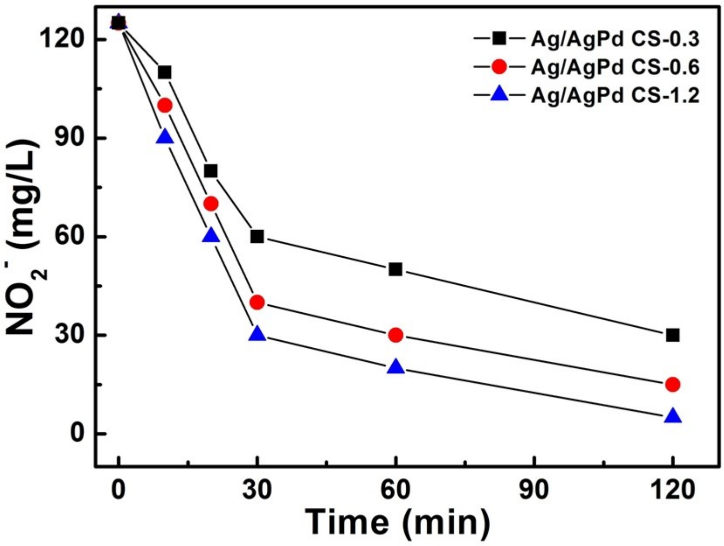

Figure S9 The catalytic NO_2^- reduction of the Ag/AgPd CS-NWs catalyst *vs.* the reaction time in 0.5 M FA aqueous at 25 °C.

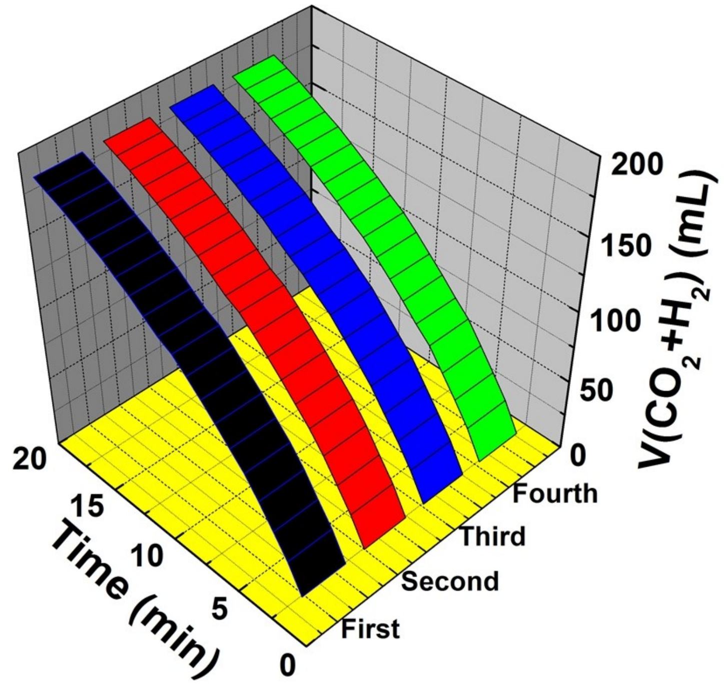

Figure S10 The stability of Ag/AgPd CS-0.9 was tested in aqueous FA solution (10 mL, 0.5 M) at 25 °C.

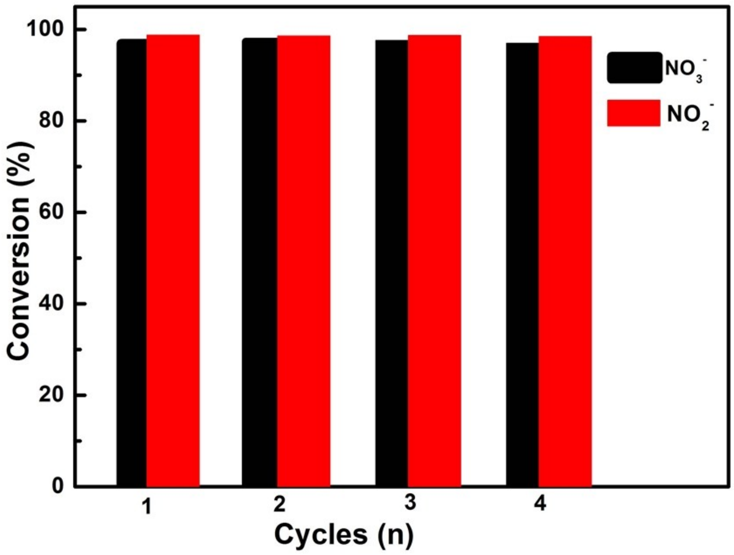

Figure S11 The stability of Ag/AgPd CS-0.9 was tested in aqueous FA solution (10 mL, 0.5 M) with NO_3^- and NO_2^- at 25 °C.

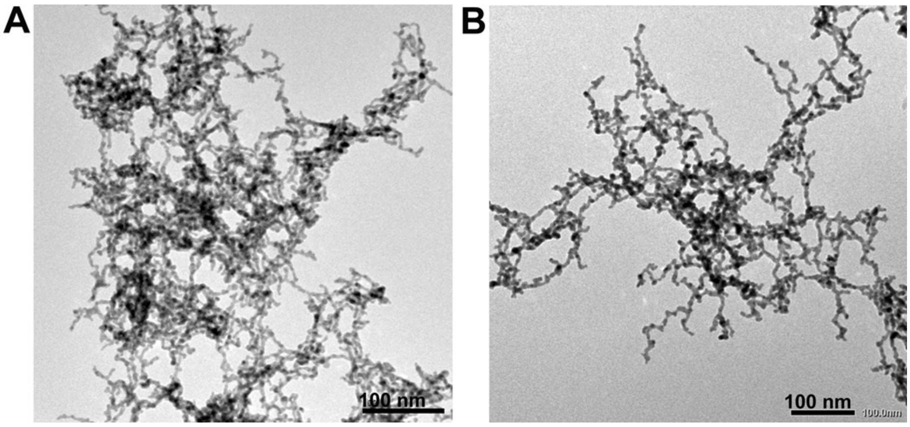

Figure S12. TEM image of the Ag/AgPd CS-0.9 catalyst (**A**) before and (**B**) after the four catalytic run.

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 CS-NWs
Ag/AgPd CS-0.3	0.15:0.05	2.92:1
Ag/AgPd CS-0.6	0.175:0.075	2.30:1
Ag/AgPd CS-0.9	0.2:0.1	2.01:1
Ag/AgPd CS-1.2	0.225:0.125	1.79:1

Table S2 Initial TOF ($mol_{H2}\cdot molcatalyst^{-1}\ h^{-1}$) 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							
PVP-networked Pd_5Ag_5 NWs	10.0	None	303	0.100	120	**6**	[4]
PVPI-networked Pd_5Ag_5 NWs	10.0	None	298	0.100	245	**6**	[1]
Ag/AgPd CS-0.9	10.0	None	298	0.100	370	**4**	This work
Ag/AgPd CS-0.9	10.0	None	323	0.100	1400	**4**	This work
AgPd (1:1) NPs	10.0	None	323	0.200	**144.0**	—	[5]
Ag@Pd core-shell NPs	10.0	None	293	0.200	**15.5**	—	[6]
PdAg Nanosheets	10.0	HCOONa (5.0)	298	0.100	**156.0**	—	[7]
AgPd (41:59) NPs	10.0	None	298	0.100	**150.0**	—	[5]
With support							
$Ag_{42}Pd_{58}$/C	10.0	None	323	0.100	**382.0**	**4**	[5]
Ag@Pd/C	10.0	None	293	0.200	**192.0**	**2**	[6]
$Ag_{0.1}$-$Pd_{0.9}$/rGO	5.0	HCOONa (3.35)	298	0.100	**105.2**	—	[8]
AgAuPd/rGO	5.0	None	298	0.100	**73.6**	—	[9]

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

Table S3. Elemental analysis result of the Ag/AgPd CS-0.9 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 = 2.0:1.0	Ag:Pd = 1.96:1

$TOF_{initial}$ Calculation methods:

$$x_a = \frac{Patm\ V'H2/\ RT}{nFA} \qquad S1f$$

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.

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

Where $TOF_{initial}$ 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

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