Electronic Supplementary Information for:

Photocatalytic Dehydrogenation of Formic Acid Promoted by Superior PdAg@g-C_3N_4 Mott-Schottky Heterojunction

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1. Supplementary Materials and Methods

1.1 Chemicals and Materials: Silver nitrate ($AgNO_3$), Palladium (II) nitrate dihydrate ($Pd(NO_3)_2 \cdot 2H_2O$), formic acid (HCOOH) and poly-*n*-vinylpyrrolidone (PVP, $M_w \approx 58{,}000$), melamine was 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), ammonium hydroxide (25 %), concentrated nitric acid (12 M), 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 The synthesis of the Graphitic Carbon Nitride (g-C_3N_4**):** For a typical synthesis process of g-C_3N_4[1], 10 g melamine powder went through one heating stage at 550 °C for 4 h. After naturally cooling down to room temperature, the final product was obtained for further characterization and catalytic reaction (abbreviated g-C_3N_4).

1.3 Synthesis of Pd_5Ag_5 NWs@g-C_3N_4: In a typical polyol process, the 10 mL 1, 3-BG, the PVP (0.6 mmol, 66.6 mg, M_W = 58,000, as calculated in terms of the repeating unit) and 60 mg g-C_3N_4 were added into a 50 mL two-neck flask, which was sonicated at room temperature for 0.5 h and heated by an oil bath at 170 ^oC for 10 min. Following 0.5 mL Na_2S solution (1 mM in EG) was quickly added into the 1, 3-BG mixture solution using a pipette. After 5 min, the 4 mL water solution containing

$AgNO_3$ (0.1 mmol, 16.99 mg) and $Pd(NO_3)_2·2H_2O$ (0.1 mmol, 26.64 mg) was rapidly added into the above solution refluxed for another 2 h. Refluxing and stirring was always continuing during the whole synthesis process. After the reaction system was cooled to room temperature, the black production was washed by 60 mL acetone for centrifugal process at a rate of 8000 rpm for 6 min. The synthesized Pd_5Ag_5 NWs@g-C_3N_4 was further purified at least three times with 50 mL acetone and 10 mL water. The final black precipitation was redispersed into 9.6 mL distilled water for further catalyst evaluation.

For the other composition, PdAg NWs@g-C_3N_4 (Pd, Pd_7Ag_3, Pd_3Ag_7) were synthesized by the same method by controlling metal precursors at the Ag/Pd ratios of 0:10, 3: 7 and 7:3, respectively.

1.4 PdAg NWs@g-C_3N_4 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 PdAg NWs@g-C_3N_4 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. Diffuse reflectance spectra (DRS) were measured using a Cary 5000 spectrophotometer fitted with an integrating sphere attachment from 220-850 nm with $BaSO_4$ as the reference. Infrared spectra were recorded on a Bruker Tensor 27 FTIR spectrometer. Solid-state ^{13}C MAS NMR spectra were recorded on a Bruker AVANCE III 400 MHz WB solid-state NMR spectrometer at room temperature. Detailed analyses for CO_2, H_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 specific surface areas of the g-C_3N_4 samples were calculated using the Brunauer-Emmett-Teller (BET) method. Photoluminescence data were collected on a Hitachi F4600 Luminescence Spectrometer. A photocatalytic equipment bought from BiLong company of Shang Hai was used as the visible light source to trigger the photocatalytic reaction.

1.5 PdAg NWs@g-C_3N_4 **Catalyst Evaluation:** The photocatalysis evaluation of PdAg NWs@g-C_3N_4 (Pd, Pd_7Ag_3, Pd_5Ag_5, Pd_3Ag_7)were carried out in a top-irradiation-type photoreactor connected to a gas burette system under visible light ($\lambda >$ 400 nm). 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 neck was connected to a gas burette, and the other neck was sealed rubber stopper, after 20 mg of PdAg NWs@g-C_3N_4 catalyst was dispersed in 9.6 mL of water via sonication and transferred into the reaction flask. Next, the aqueous dispersion of PdAg NWs@g-C_3N_4 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.

1.6 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

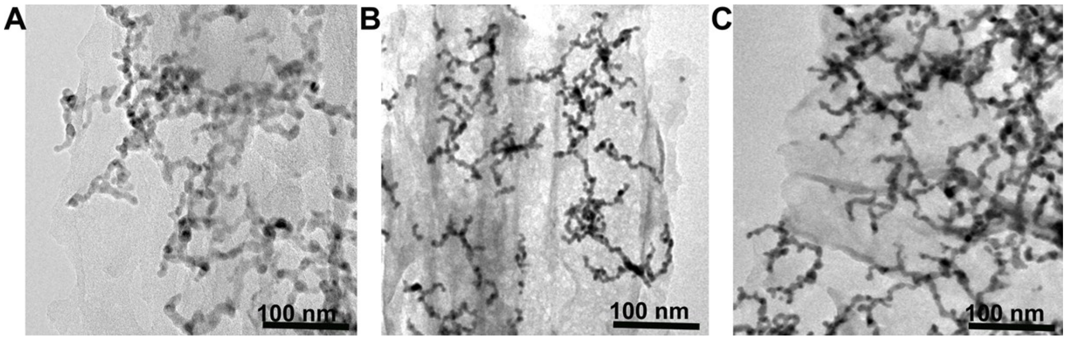

Figure S1. (**A-C**) TEM images of the Pd NWs@g-C_3N_4, Pd_7Ag_3 NWs@g-C_3N_4, and Pd_3Ag_7 NWs@g-C_3N_4, respectively.

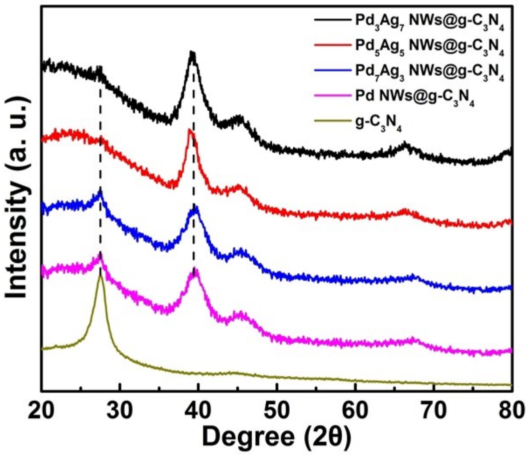

Figure S2. XRD patterns of corresponding different PdAg NWs@g-C_3N_4, Pd NWs@g-C_3N_4 and g-C_3N_4.

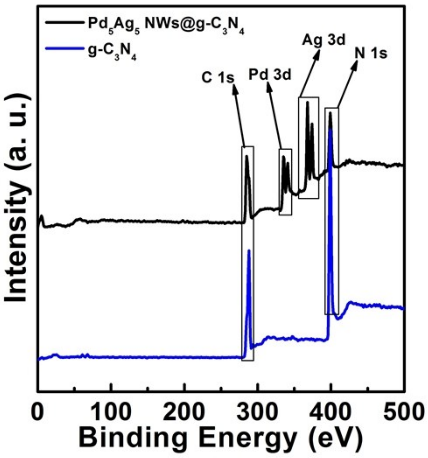

Figure S3. XPS spectrum of g-C_3N_4 and Pd_5Ag_5 NWs@g-C_3N_4.

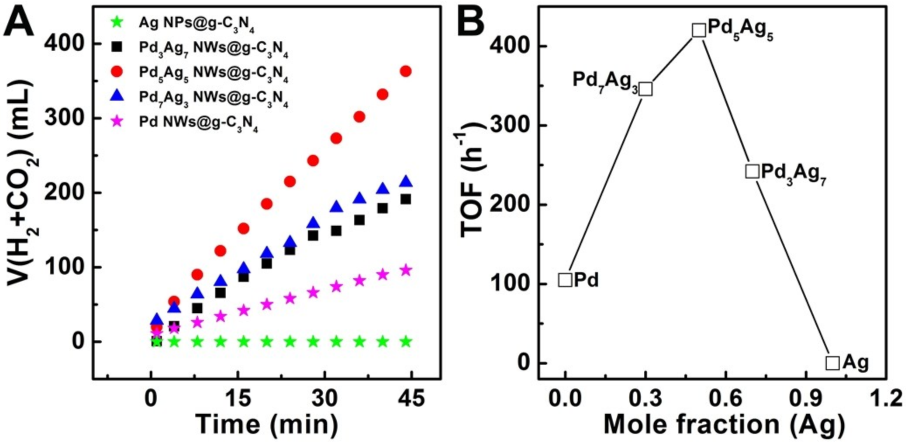

Figure S4. (**A**) The plots of generated gas (CO_2 + H_2) vs. time for the FA dehydrogenation catalyzed by different PdAg NWs@g-C_3N_4 catalysts in FA aqueous solution (10 mL of 1 M) under visible light (λ > 400 nm) at 25 °C and (**B**) TOF *vs.* mole fraction of Ag for PdAg NWs@g-C_3N_4 catalysts at different Ag and Pd compositions.

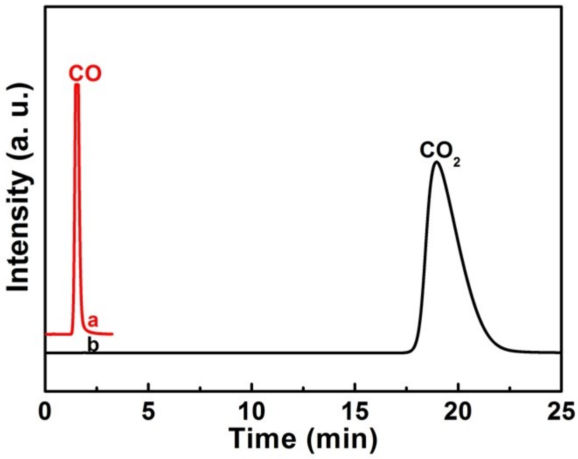

Figure S5. GC spectrum using FID-Methanator for (**a**) pure gas CO and (**b**) the evolved gas from FA (1 M, 10 mL) over Pd_5Ag_5 NWs@SBR^2-g-C_3N_4 under visible light (λ > 400 nm) at 25 °C.

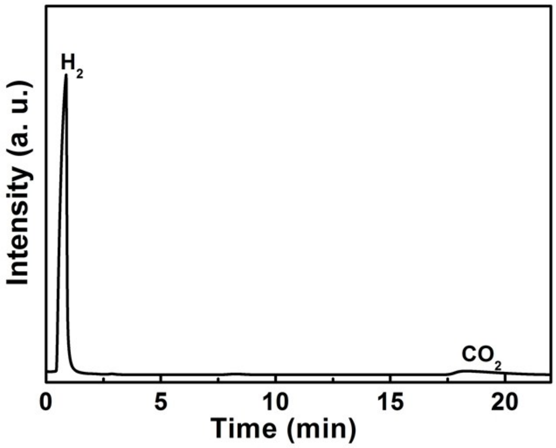

Figure S6. GC spectrum using TCD for the evolved gas from FA (1 M, 10 mL) over Pd_5Ag_5 NWs@SBR^2-g-C_3N_4 under visible light (λ > 400 nm) at 25 °C.

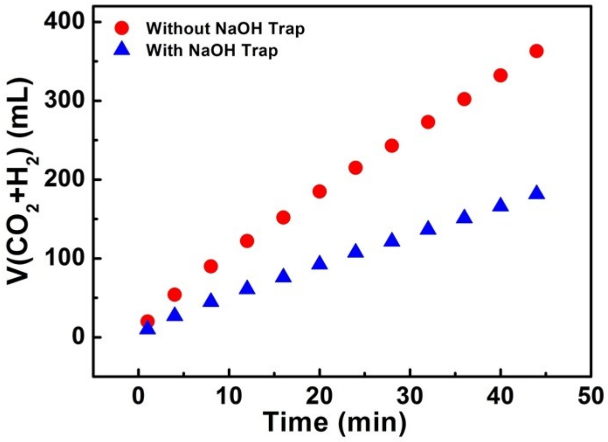

Figure S7. The comparison of the volume of gas generated during Pd_5Ag_5 NWs@SBR^2-g-C_3N_4 catalyzed dehydrogenation of aqueous FA solution (10 mL, 1 M) with and without NaOH trap under visible light (λ > 400 nm) at 25 ^oC.

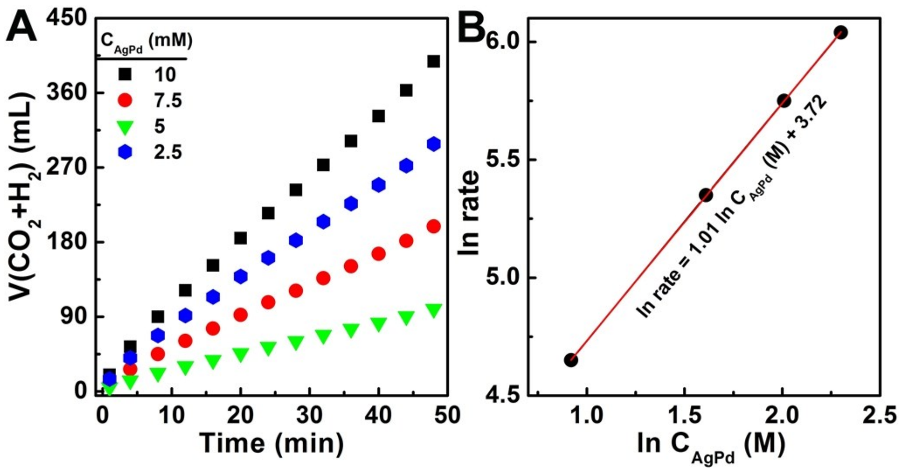

Figure S8. (**A**) Gas generated *vs.* time during the dehydrogenation of aqueous FA solution (10 mL, 1 M) in the presence of different catalyst concentration under visible light (λ > 400 nm) at 25 ^oC, and (**B**) plot of hydrogen generation rate *vs.* Pd_5Ag_5 NWs@g-C_3N_4.

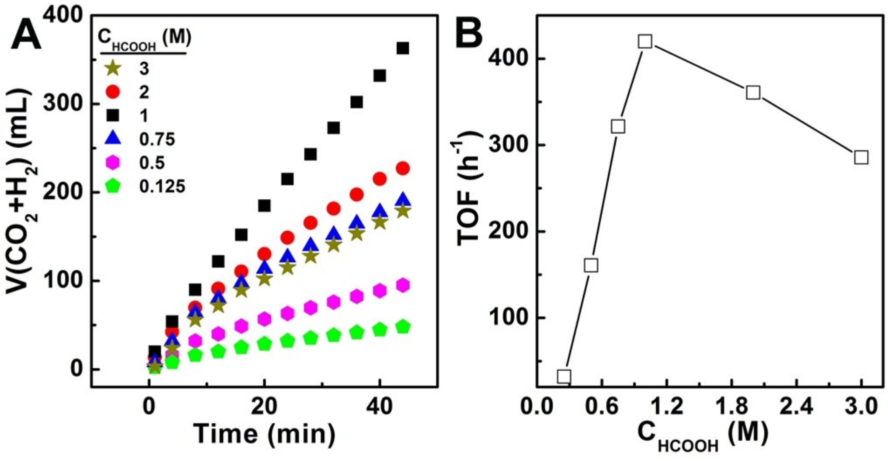

Figure S9. (**A**) CO_2 + H_2 volum generated *vs*. time for the catalytic the dehydrogenation of FA at different FA concentrations and (**B**) the plot of gas generation rate *vs*. FA concentration.

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

Entry	$Pd(NO_3)_2$/ $AgNO_3$ molar ratio	As-synthesized Networked NWs
1	3:7	$Pd_{3.10}Ag_7$ NWs@g-C_3N_4
2	5:5	$Pd_{5.08}Ag_5$ NWs@g-C_3N_4
3	7:3	$Pd_{6.91}Ag_3$ NWs@g-C_3N_4

Table S2. Initial TOF values for the decomposition of FA catalyzed by various Pd-based catalysts.

Catalyst	FA(mmol)	Note	Tem.(K)	n_{Catalyst}(mmol)	$\text{TOF}_{\text{initia}}$	Recycle times	Ref.
With Light							
Pd_5Ag_5 NWs@g-C_3N_4	10.0	Visible Light	298	0.100	420	4	This work
Pd_5Ag_5 NWs@g-C_3N_4	10.0	Visible Light	323	0.100	1180	4	This work
PVPI- Pd_5Ag_5 NWs	10.0	365 nm	323	0.100	312	6	[3]
Pd_5Ag_5 NPs@CN	10.0	Visible Light	303	0.100	254	—	[4]
Ligand-capped CdS	10.0	Visible Light	298	0.100	116	—	[5]
Pd@CN	10.0	Visible Light	288	0.100	71	—	[6]
Without Light							
Pd_5Ag_5 NWs@g-C_3N_4	10.0	None	298	0.100	260	4	This work
$Pd_{58}Ag_{42}$/C	10.0	None	323	0.100	382.0	4	[7]
Ag@Pd/C	10.0	None	293	0.200	192.0	2	[8]
$Ag_{0.1}Pd_{0.9}$/rGO	5.0	HCOONa (Additive)	298	0.100	105.2	—	[9]
AgAuPd/rGO	5.0	None	298	0.100	73.6	—	[10]
CoAuPd/DNA-rGO	5.0	None	298	0.100	85.0	3	[11]
$Au_{42}Pd_{58}$@C	10.0	None	323	0.100	60	—	[12]

"—" For comparison, the cycle property of catalyst was not tested.

Table S3. Elemental analysis result of the Pd_5Ag_5 NWs@g-C_3N_4 characterized by XPS spectrum.

Entry	Before the four catalytic run	After the four catalytic run
1	Ag:Pd = 5:5, C:N = 10:4	Ag:Pd = 5:4.98, C:N = 10:4

Table S4. Elemental analysis result of the 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 = 5:5.05	Ag:Pd = 5:5

$\mathrm{TOF_{initial}}$ Calculation methods:

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

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.

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

Where $\mathrm{TOF_{initial}}$ is initial turnover frequency, V'_{H2} is the generated volume of H_2 during the first 10 min of the reaction, n_{Ag+Pd} is the mole number of the Ag and Pd, and *t* is the reaction time of 10 min.

3. Supplementary References

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