

Electronic Supplementary Information

Activating Pd Nanoparticles on Sol-Gel Prepared Porous g-C₃N₄/SiO₂ via Enlarging the Schottky Barrier for Efficient Dehydrogenation of Formic Acid

Characterization

The Powder X-ray diffraction (**PXRD**) measurements were performed on a Bruker D8 Advance diffractometer with Cu K α 1 radiation. Fourier transformed infrared (**FT-IR**) spectra were recorded using a Spectrum 100 FTIR spectrometer (Perkin Elmer, Inc., USA). The thermal gravity analysis (TGA) experiments were carried out on a Thermogravimetric Analyzer TGA 7 (Perkin Elmer, Inc., USA). The UV-Visible absorption spectra were collected on a Lambda 35 UV/Vis Spectrometer (Perkin Elmer, Inc., USA). The transmission electron microscopy (**TEM**) measurements were performed on a JEOL JEM-2100 instrument (JEOL Ltd., Japan). **Nitrogen adsorption-desorption** isotherms were performed at 77K using Micromeritics ASAP 2010 equipment. The UV-visible (**UV-Vis**) absorption spectra were recorded using Lambda 35 UV/Vis Spectrometer (Perkin Elmer, Inc., USA). The **Mott-Schottky** plots were recorded on an electrochemical workstation (AUTOLAB PGSTAT, 302N) by using the Impedance-Potential technique. Measurements were performed on a conventional three-electrode cell in dark: cleaned fluoride-tin oxide (FTO) deposited with a sample film as the working electrode, graphite electrode as the counter electrode and SCE electrode as the reference electrode, respectively. The aqueous solution of 0.2 M Na₂SO₄ purged with nitrogen gas was used as the electrolyte.

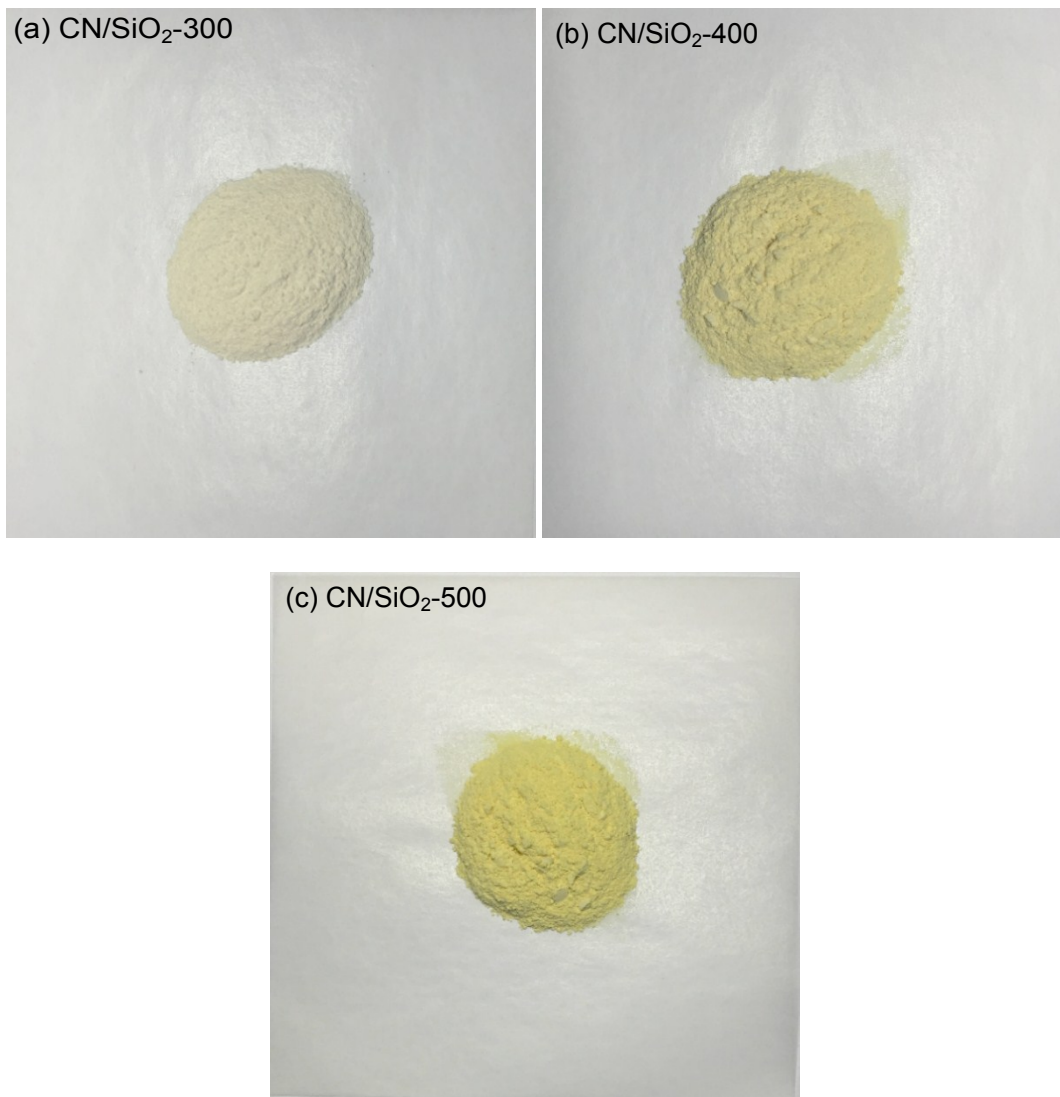


Figure S1. Photographs of typical CN/SiO₂ samples synthesized at different temperatures: (a) 300 °C, (b) 400 °C and (c) 500 °C.

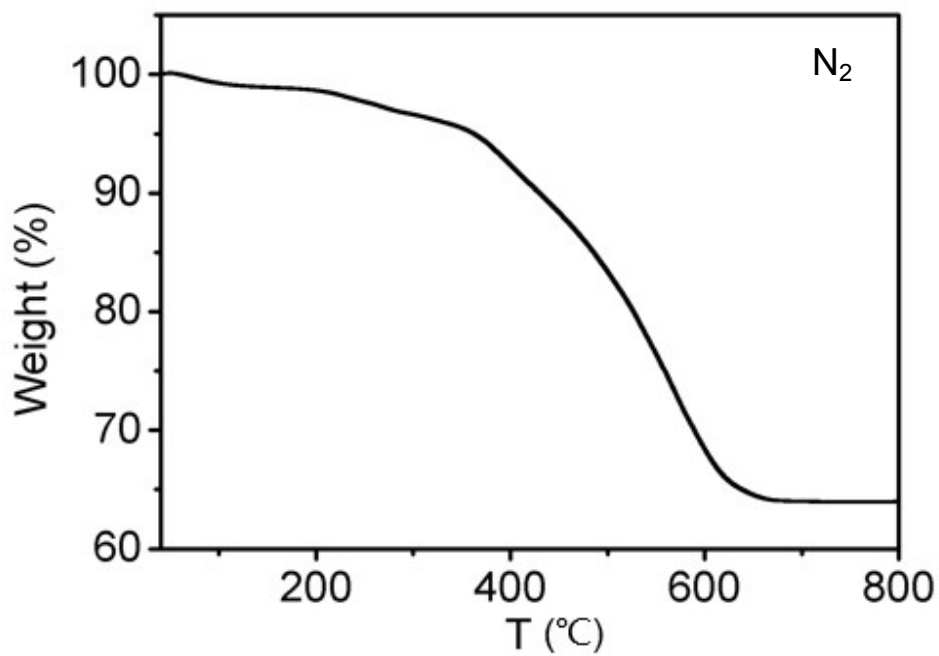


Figure S2. TGA curves of CN/SiO₂-300 under N₂ (TGA heating rate: 20 °C/min). The result indicates that the weight percentage of SiO₂ in the sample CN/SiO₂-300 was 64%.

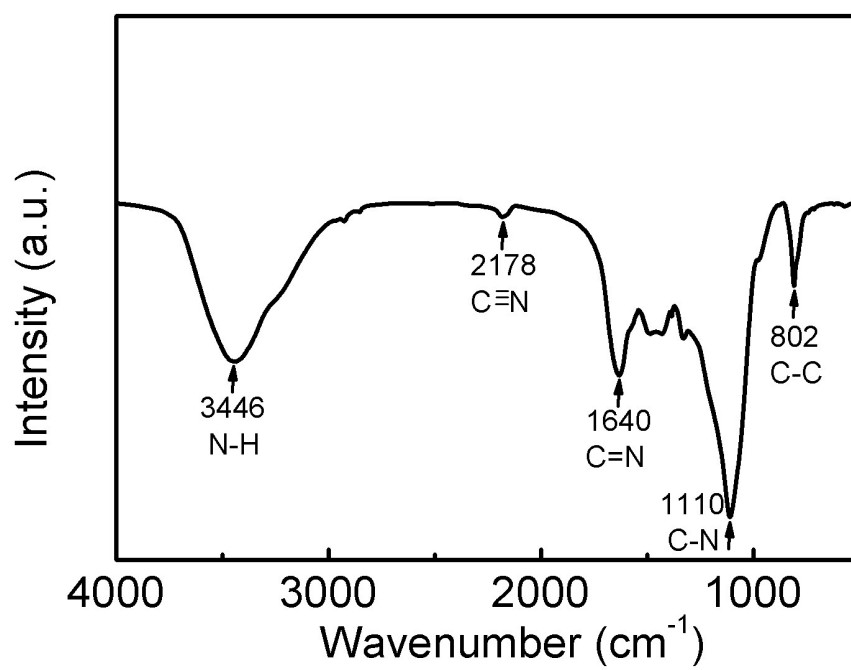


Figure S3. FT-IR spectrum of CN/SiO₂-300

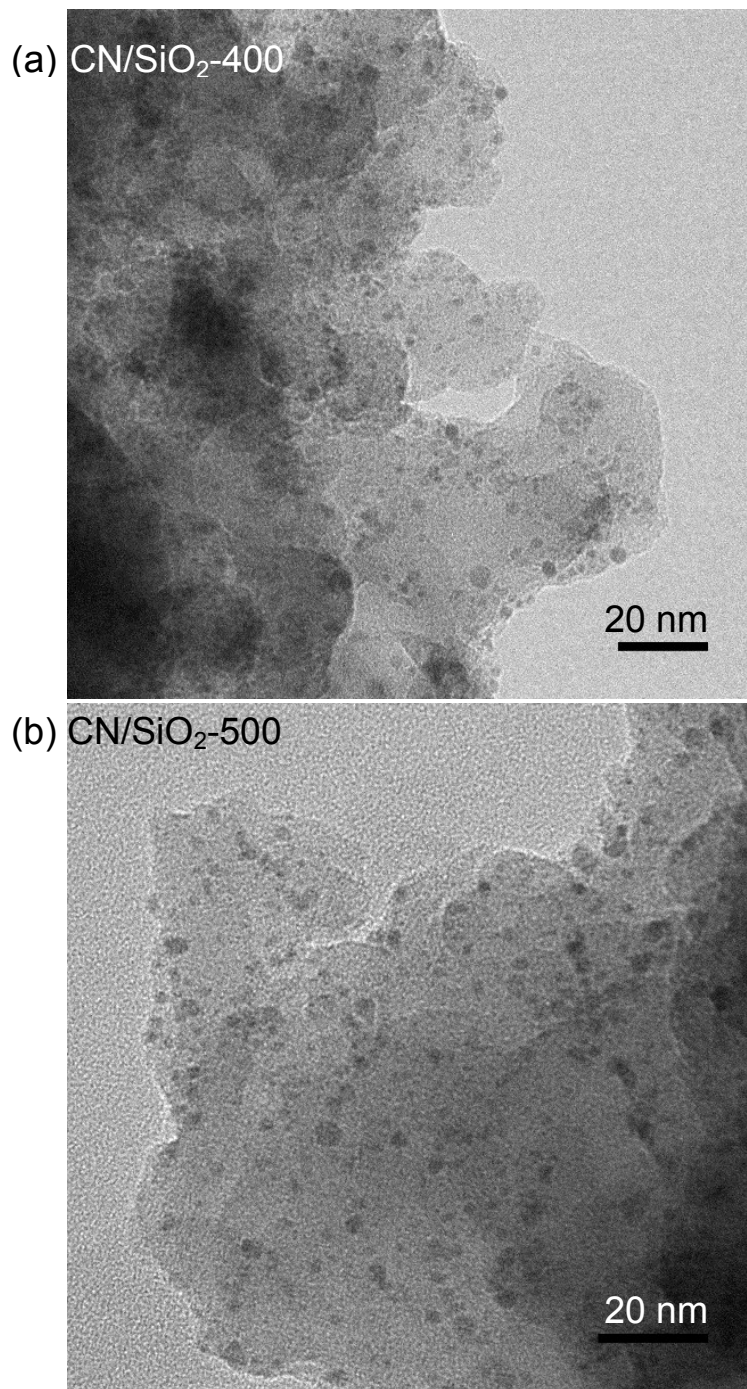


Figure S4. TEM images of Pd@CN/SiO₂-400 a) and Pd@CN/SiO₂-500 b) of which the Pd load is 9%.

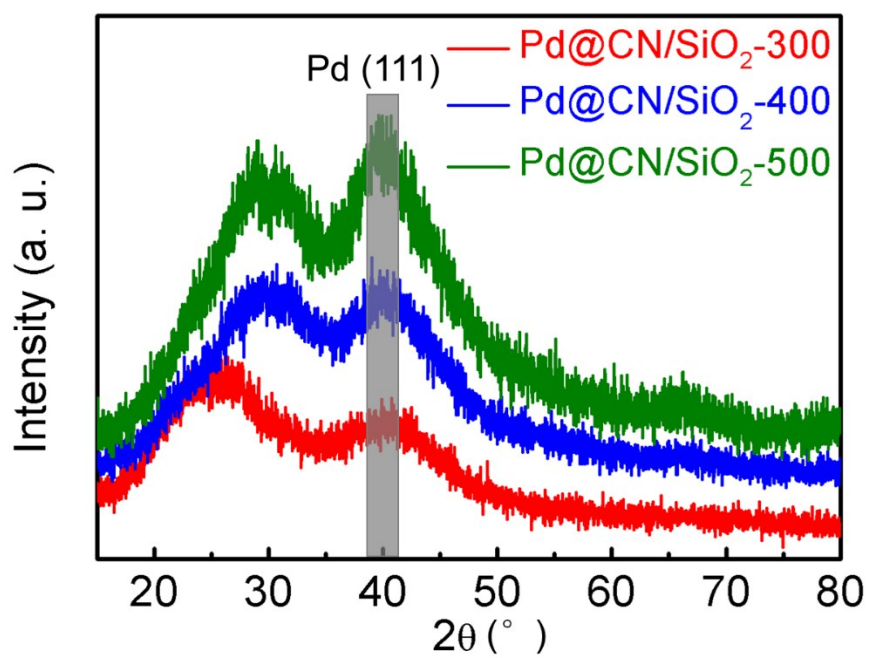
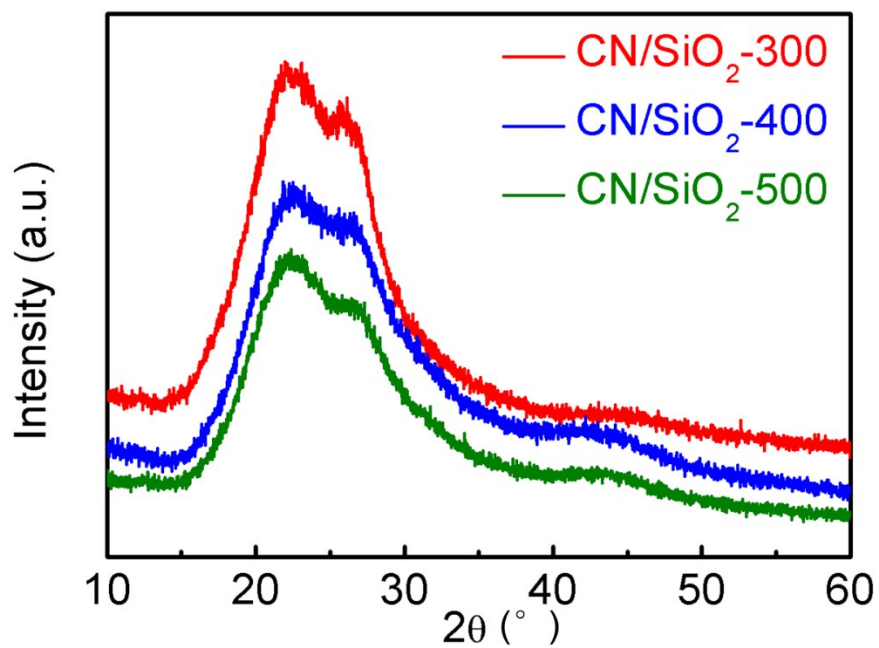


Figure S5. PXRD patterns of CN/SiO₂ (a) and 9% Pd@CN/SiO₂ (b) samples. The weight percentages of Pd in the nanocomposite catalyst are all 9 wt.%.

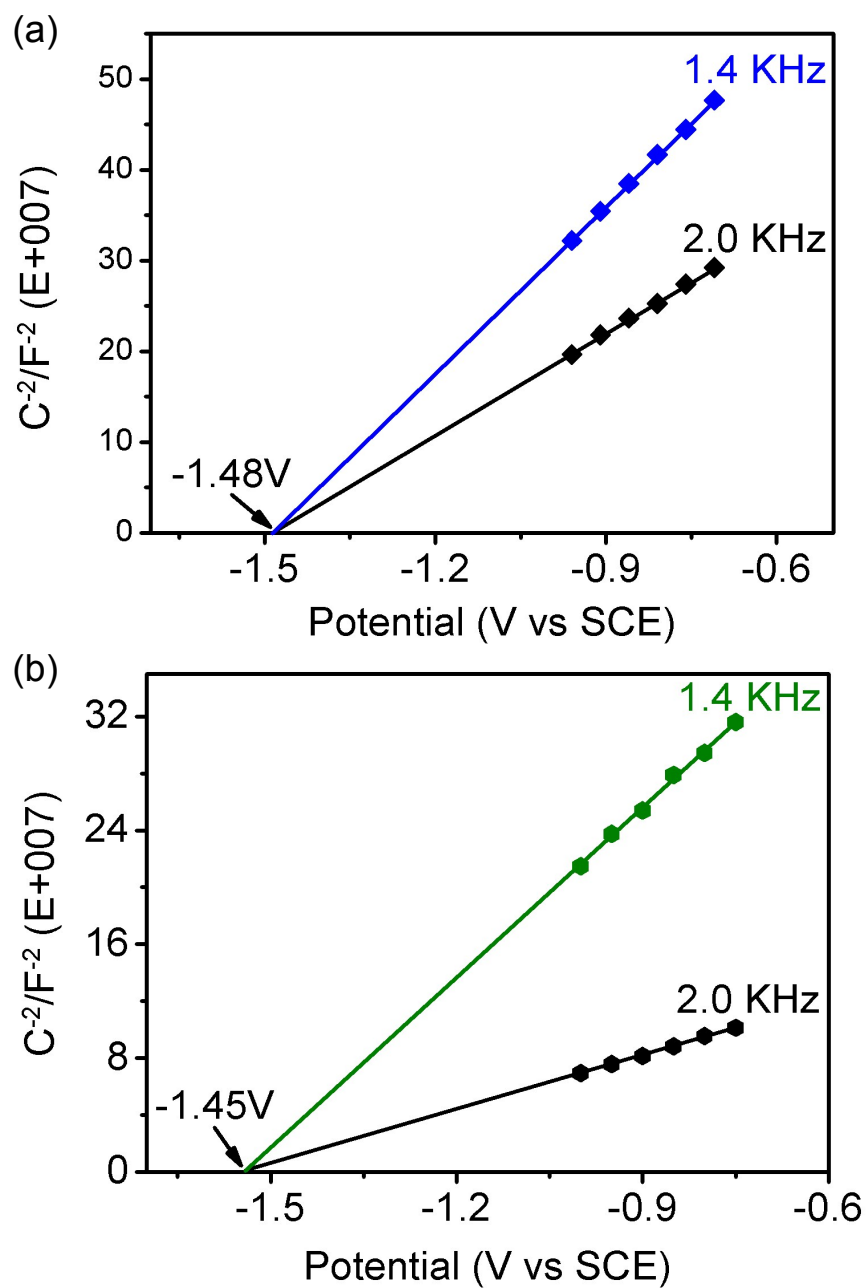


Figure S6. Mott-Schottky plots of CN/SiO₂-400 (a) and CN/SiO₂-500 (b) at selected frequencies of 1.4 and 2.0 kHz. The derived flat-band potentials for CN/SiO₂-400 and CN/SiO₂-500 are -1.48 V and -1.45 V *versus* SCE, respectively.

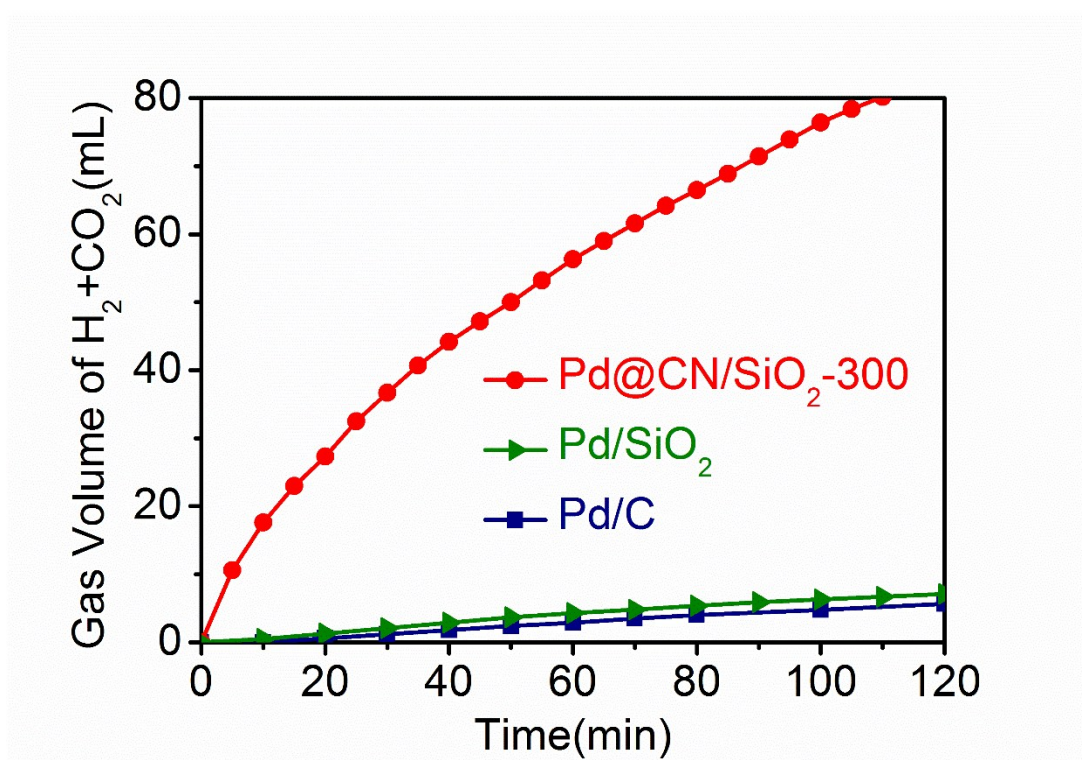


Figure S7. Decomposition of FA over different catalysts. Typical conditions: 1 M aqueous FA solution (5 mL), catalyst (10 mg), 273 K.

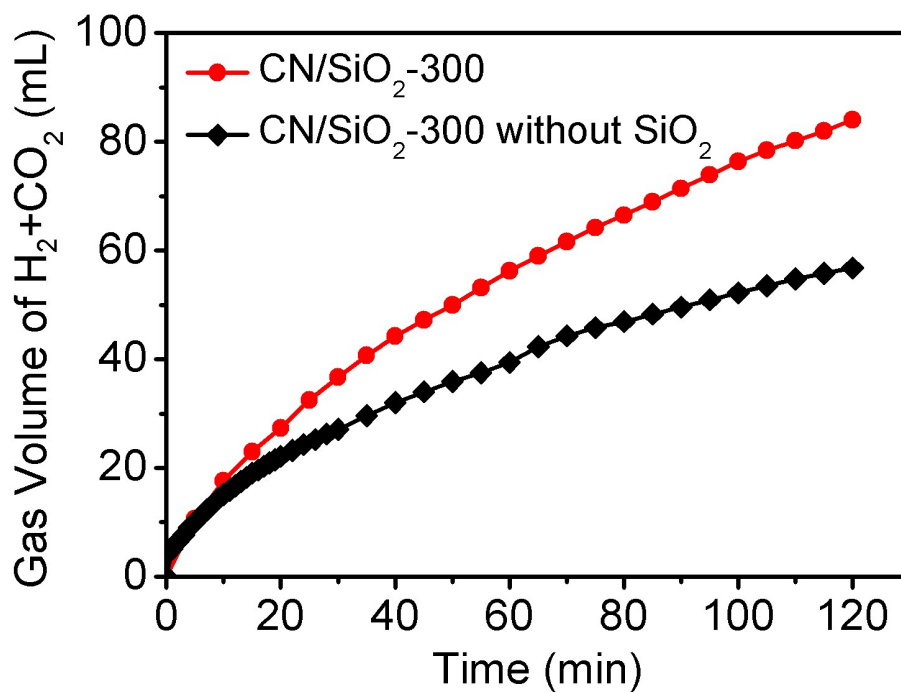


Figure S8. Volume of the produced gas ($\text{H}_2 + \text{CO}_2$) versus time for the dehydrogenation of FA/SF (1:4) over $\text{CN/SiO}_2\text{-300}+9\%\text{Pd}$ and $\text{CN-300}+9\%\text{Pd}$ from which SiO_2 was chemically etched by HF respectively. Typical reaction conditions: 1 M of aqueous FA solution (5 mL), catalyst (10 mg), 278 K.

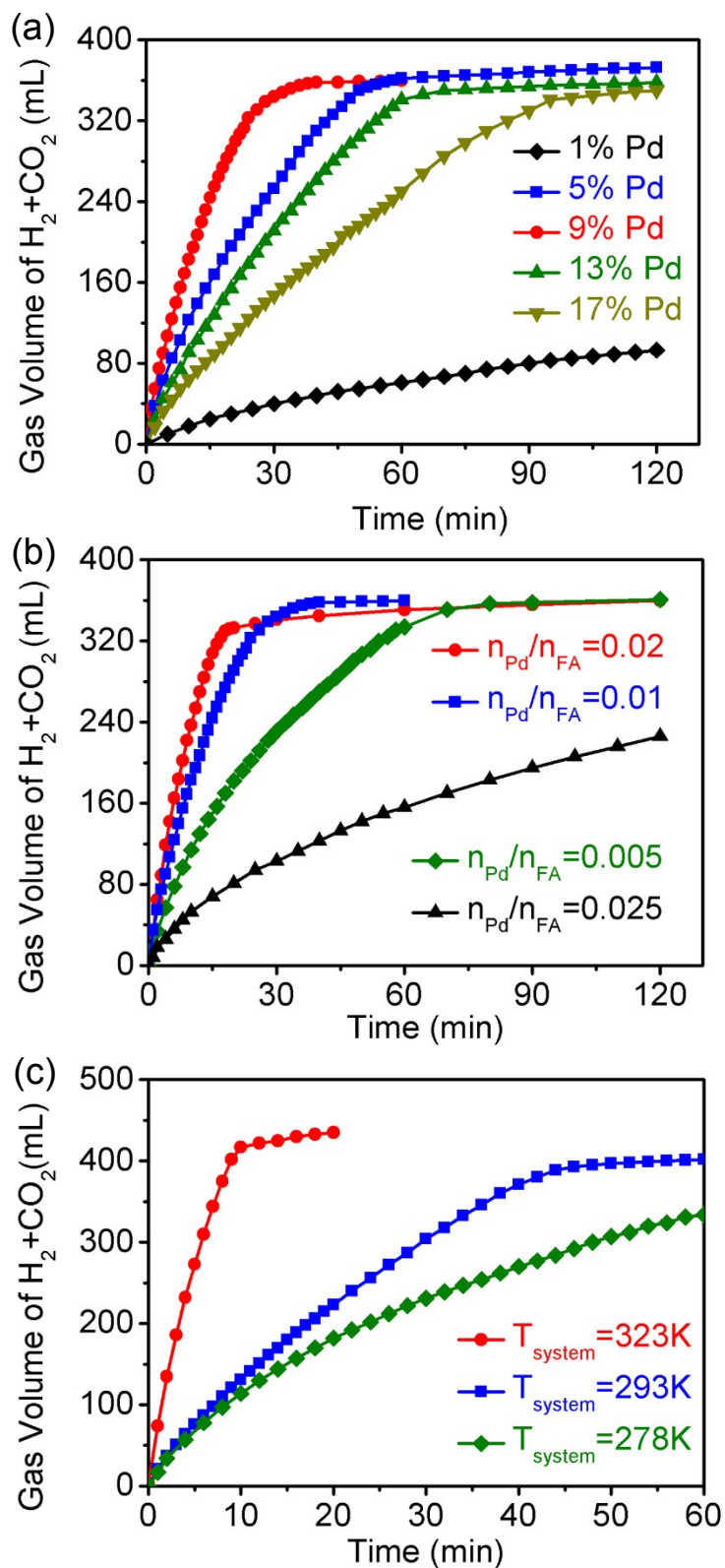


Figure S9. The volume of gas mixture ($CO_2 + H_2$) versus the reaction time over Pd@CN/SiO₂-300 with different Pd loadings (a), different ratios of n_{Pd}/n_{FA} (b) and at different reaction temperatures (c). Typical conditions: 1.5 mL of 6 M aqueous FA solution, $n_{FA}/n_{SF}=1$. The reaction temperatures is 278K for (a) & (b); n_{Pd}/n_{FA} is 0.01 and 0.005 for (a) and (c), respectively.

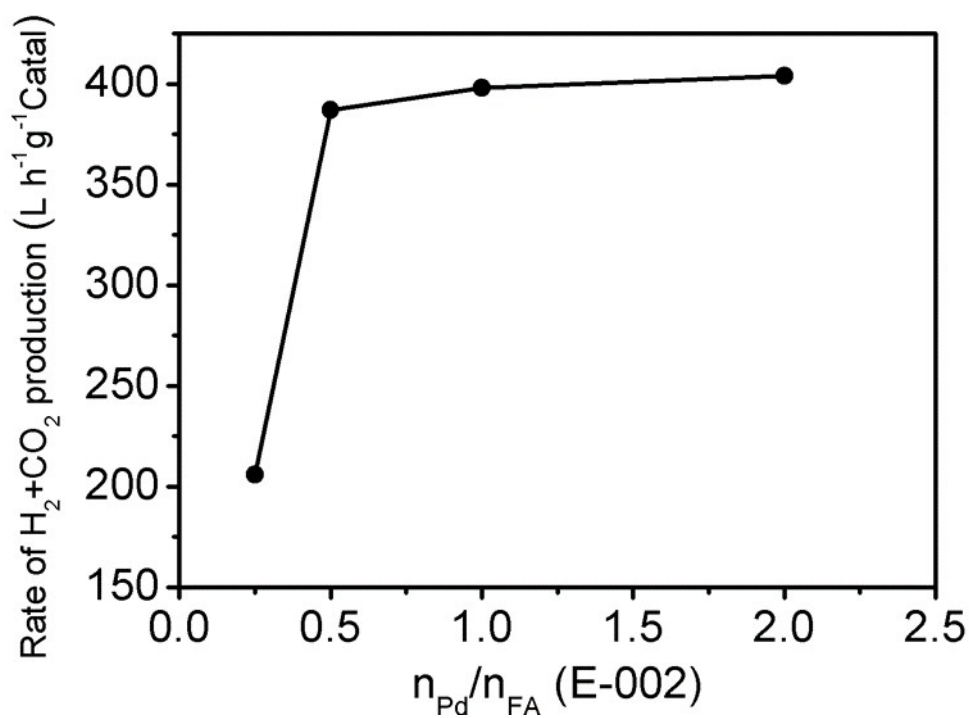


Figure S10. The output rate of gas mixture versus the molecular ratio of n_{FA}/n_{Pd} in the reaction system. It is obvious that with the concentration of Pd@CN/SiO₂-300 catalyst increasing, the reaction rate of dehydrogenation of FA reaches saturation. Typical conditions: 1.5 mL of 6 M aqueous FA solution, $n_{FA}/n_{SF}=1$, $n_{Pd}/n_{FA}=0.01$, $T_{system}=278K$.

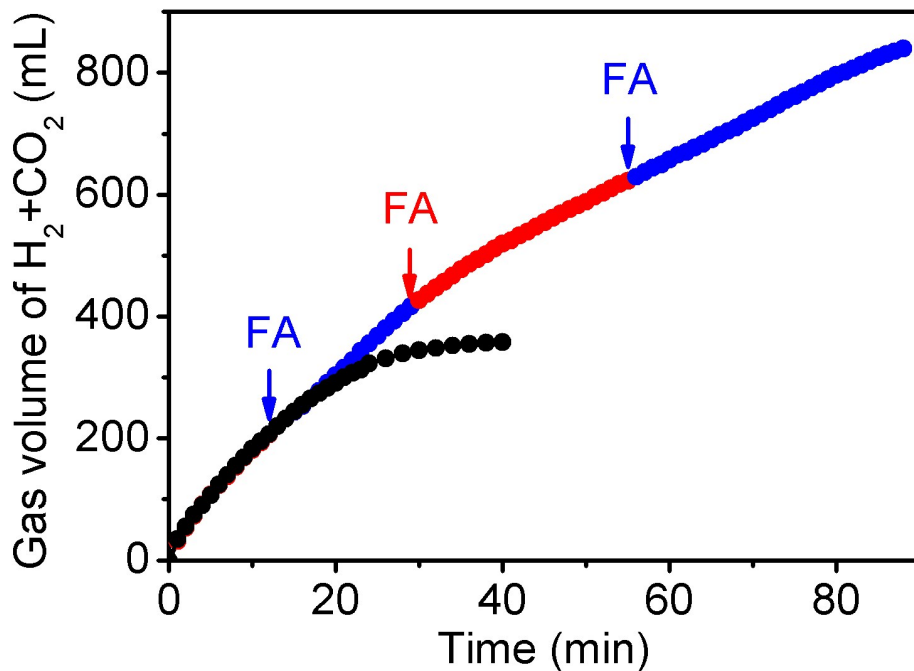


Figure S11. Recycle test of decomposition of FA over Pd@CN/SiO₂-300 by adding a certain amount of pure FA to keep the FA's concentration of around the initial value at the time when half amount of FA was consumed. Typical reaction conditions: 1.5 mL of 6M aqueous FA solution, $n_{\text{Pd}}/n_{\text{FA}}=0.01$, $n_{\text{FA}}/n_{\text{SF}}=1$, the corresponding amount of catalyst dispersed in 2 mL DI water.

Table S1. Features of a series of catalyst supports.

Sample	BET Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)
CN/SiO ₂ -300	49.0786	0.347946
CN/SiO ₂ -400	53.8768	0.360732
CN/SiO ₂ -500	63.5086	0.372239

Table S2. TOF values for decomposition of FA catalyzed by various Pd NPs based catalysts.

Catalyst	[FA] (M)	T (K)	TOF	Note	Reference
Pd@CN/SiO ₂	2.57	323	1119^a	2.57 M sodium formate	This work
Pd@CN/SiO ₂	2.57	293	351^a	2.57 M sodium formate	This work
Pd@MSC	2.57	323	2623	2.57 M sodium formate	13
Pd@MSC	2.57	298	750	2.57 M sodium formate	13
Au/ZrO ₂ NCs	10.6	323	1593 ^b	4.24 M NEt ₃	14
Au/ZrO ₂ NCs	10.6	298	252 ^b	4.24 M NEt ₃	14
Ag ₄₂ Pd ₅₈ @C	1	323	60		S1
Co ₃₀ Au ₃₅ Pd ₃₅ /C	0.5	298	80 ^b		S2
Pd@CN	1	288	71	Visible light	3
Pd@CN	1	288	50		3
Pd@ED-MIL-101	3.04	363	57	1.02 M sodium formate	9
AuPd@ED-MIL-101	3.04	363	106	1.02 M sodium formate	9
PdAu@C-CeO ₂	9.94	365	113	3.33 M sodium formate	7
Pd-S-SiO ₂	4	318	16	0.44 M sodium formate	S3
Pd@C	1	323	9		S4
Pd@C	1.06	298	64	0.84 M sodium formate, 0.03 M citric acid	S5
Ag@Pd	1	293	17	Core-shell NPs	8
Ag@Pd/C	1	293	20	Core-shell NPs	8

^aTOF values were calculated based on the amount of released H₂ at 10 min, ^bTOF values were calculated at the initial stages of the reactions. (unit: mol H₂ mol Pd⁻¹ h⁻¹)

References

- [S1] S. Zhang, Ö. Metin, D. Su and S. Sun, *Angew. Chem. Int. Ed.*, 2013, **52**, 3681.
- [S2] Z.-L. Wang, J.-M. Yan, Y. Ping, H.-L. Wang, W.-T. Zheng and Q. Jiang, *Angew. Chem. Int. Ed.* 2013, **52**, 4406.
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- [S4] O. Metin, X. Sun and S. Sun, *Nanoscale*, 2013, **5**, 910.
- [S5] Z.-L. Wang, J.-M. Yan, H.-L. Wang, Y. Ping and Q. Jiang, *Sci. Rep.* 2012, **2**, 598.