Selective and controlled H_2 generation upon additive-free HCOOH dehydrogenation over Pd/NCS nanocatalyst

Qing Zhang,[a] *Yanlan Wang,*[b] *Xiaotao Jin*[a] and *Xiang Liu*[a]*

[a]Engineering Research Center of Eco-Environment in Three Gorges Reservoir Region of Ministry of Education, College of Materials and Chemical Engineering, China Three Gorges University, Yichang, Hubei 443002, China. Email: xiang.liu@ctgu.edu.cn

[b]Department of chemistry and chemical engineering, Liaocheng University, 252059 Liaocheng, China.

Table of Content

1. Chemicals and reagents

The chemicals are used without further purification. D(+)-Glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$, AR, Sinopharm Group Chemical Reagent Co., Ltd), Sodium bicarbonate ($NaHCO_3$, 99.8%, Shanghai Macklin Biochemical Co., Ltd.), Melamine ($C_3H_6N_6$, AR, 99%, Shanghai Macklin Biochemical Co., Ltd.), Formate (HCOOH, ≥98%, Aladdin), Potassium chloropalladite (K_2PdCl_4, 99.99%, Shanghai Bide Pharmaceutical Technology Co., Ltd.), 1,1-Diphenylethylene ($C_{14}H_{12}$, 97%, Shanghai Jiuding Chemical Technology Co., Ltd.), Methanol anhydrous (CH_3OH, AR, Sinopharm Group Chemical Reagent Co., Ltd), Sodium borohydride ($NaBH_4$, 97%, Shanghai Lingfeng Chemical Reagent Co., Ltd.), Sulfuric acid and Hydrochloric acid was supplied from Chengdu Chron Chemicals Co., Ltd. Sodium hydroxide (AR, 500g) was provided from Tianjin Komiou Chemical Reagent Co., Ltd. Deionized water (DI water, H_2O) was used throughout the experiments.

2. Characterization

Transmission electron microscopy (TEM) was measured by a United States-FEI-Talos F200S operated at 200 kV. Energy Dispersive Spectrometer (EDS) Mapping was performed with a United States-FEI-Talos F200S operated at 200 kV. X-ray diffraction (XRD) analyses were performed on a Germany-Bruker-D8 Advanced. X-ray photoelectron spectrometry (XPS) was performed on a Thermo SCIENTIFIC ESCALAB 250Xi system spectrometer in an ultra-high vacuum (UHV) chamber. GC spectra of generated gas (H_2, CO_2) were detected using GC-6890 with thermal conductivity detector (TCD) and flame ionization detector (FID)-Methanator. The element contents of samples were determined by ICP-MS United States-Agilent-7800(MS). Raman spectra the of catalysts were measured on a Thermo Scientific DXR. The Brunner-Emmet-Teller (BET) specific area, pore volume and pore size of Pd/CNS-800 was measured by a NOVAtouch HCOOHst. Fourier Transform Infrared Spectrometer (FTIR) of the catalysts was recorded on a United States -Thermo Fisher, Nicolet-iS50.

3. Synthesis of N-doped carbon nanospheres

N-doped carbon nanospheres had been obtained by a solvent-free method.[50] First, α-D-Glucose

hydrochar had been obtained from the hydrothermal reaction of glucose solution (1M) for 5 h at 180 °C. Then melamine, α-D-glucose hydrochar and $NaHCO_3$, with the mass ratio of 1.0 : 1.0 : 1.0, had been fully mixed and ground in agate mortar for 30 minutes. Next, the mixtures were calcination at 700 °C, 800 °C and 900 °C under N_2 atmosphere for 1 h, respectively. Finally, the residual had been washed by 2 M HCl, EtOH and H_2O, and dried at 60 °C for overnight. These products were denoted as NCS-700, NCS-800 and NCS-900, respectively.

4. Synthesis of Pd/NCSs

First, potassium tetrachloropalladate (0.02 mmol), NCSs (30 mg) and deionized H_2O (9 mL) had ben put into the flask (50 mL). Then, 0.2 M $NaBH_4$ solution was quickly injected into the mixture. Finally, Pd/NCS-700, Pd/NCS-800 and Pd/NCS-900 were successfully gained by centrifugation, and washed with H_2O, respectively.

5. H_2 generation upon additive-free HCOOH dehydrogenation

In general, 0.2 mol% of Pd/NCS-800 and 4 mL of water had been added into a Schlenk flask (10 mL) at 60 ℃. This Schlenk flask had been connected to a H_2O-filled glass column *via* a gas outlet. Once 1 mL of HCOOH (1 M) was injected into Schlenk flask, the corresponding H_2's volume was reported as time flies. The corresponding H_2's volume was confirmed by H_2O's variation in glass column periodically.

6. **Cycle experiment**

The Pd/CNS-800 was collected by filtration and washed twice with deionized water, and used for the next cycle. Reaction conditions: 1 mmol of HCOOH, 0.03 mmol of Pd/CNS-800 and 5 mL of deionized water at 60 °C.

All the data above are presented as a mean value with an error bar, while each experiment was run three times in parallel. The error bar is the standard error of the mean (SEM), which is the standard deviation of the sample-mean's estimate of a population mean. (It can also be viewed as the standard deviation of the error in the sample mean with respect to the true mean, since the sample mean is an unbiased estimator.) SEM is usually estimated by the sample estimate of the population standard deviation (sample standard deviation) divided by the square root of the

sample size (assuming statistical independence of the values in the sample): $\mathrm{SE}_{\bar{x}} = \frac{s}{\sqrt{n}}$

Where： **s** is the sample standard deviation (i.e., the sample-based estimate of the standard deviation of the population), and **n** is the size (number of observations) of the sample.

7. “On-off” switch

0.02 mmol of Pd/CNS-800 and 4 mL of deionized water were added into a 10 mL round-bottom flask. 1 mL solution of HCOOH (1 mmol of HCOOH) was added into the flask with stirring. The “on-off” control of H_2 generation was achieved by addition of an equimolar amount of NaOH and H_2SO_4 aqueous solution into the reaction media. After reacting for 30 s, 0.14 mL of a NaOH (6 M) solution was slowly added into the flask and the HCOOH dehydrogenation stopped. After 1 min, 0.14 mL H_2SO_4 (3 M) solution was added into the flask, and the HCOOH dehydrogenation was switched on again.

8. Physical characterization of nanocatalysts (Fig S1-S12 and Table S1)

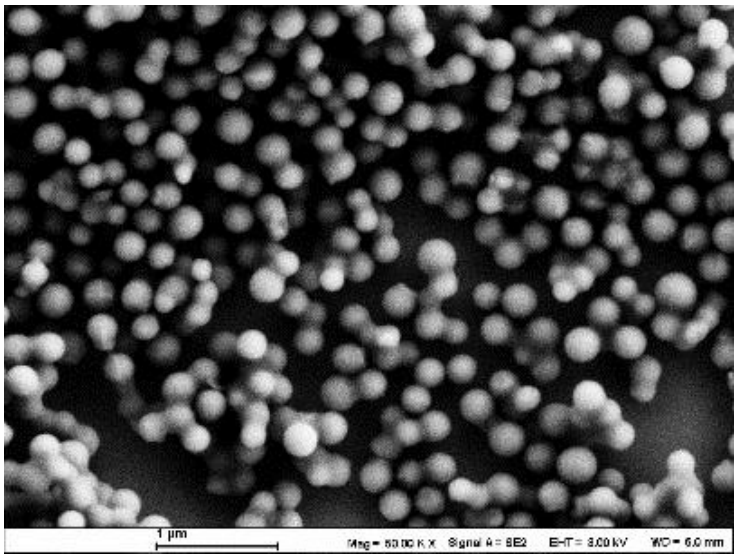

Figure S1. SEM of NCS

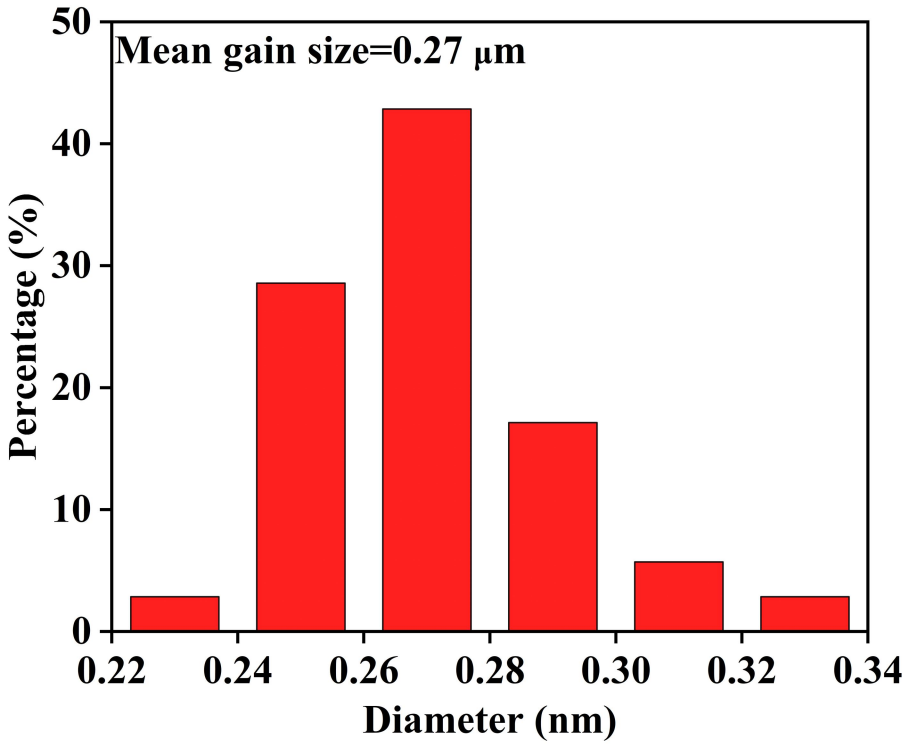

Figure S2. Distribution diagram of NCS

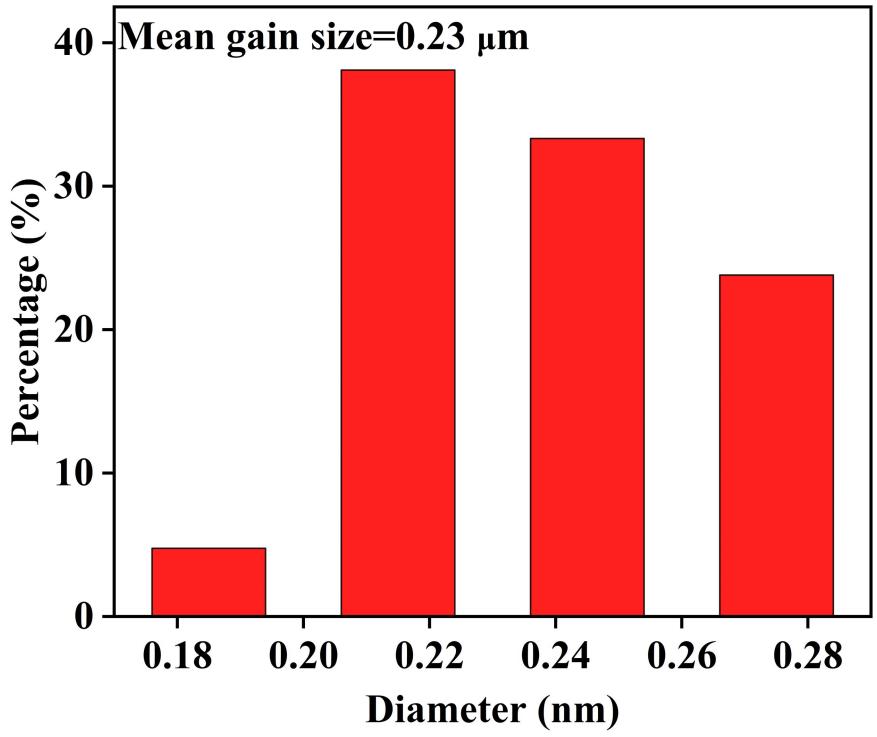

Figure S3. Distribution diagram of Pd/NCS-700

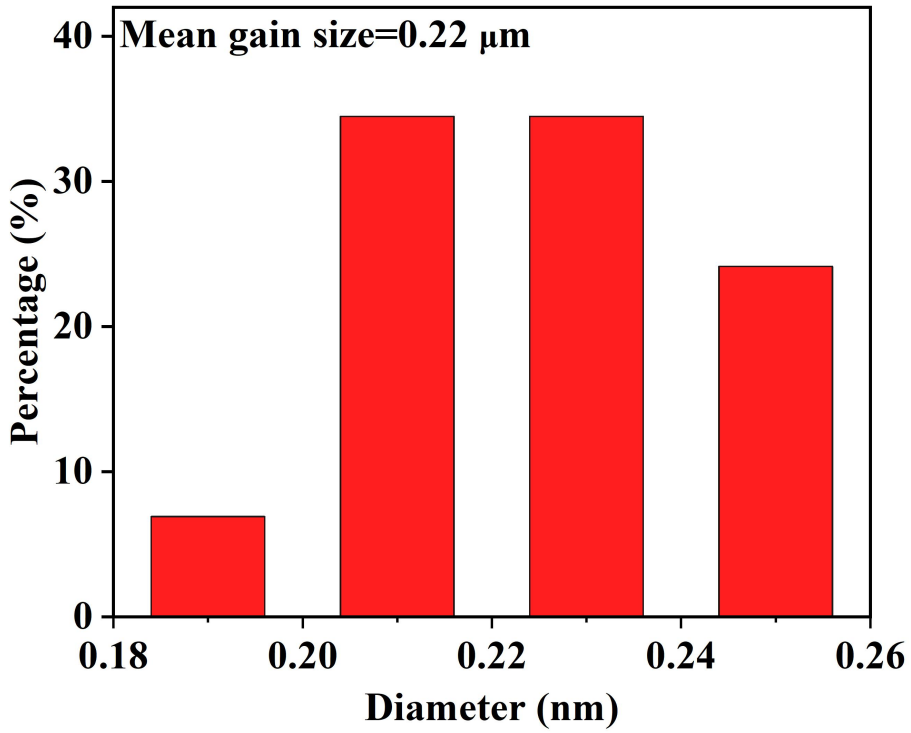

Figure S4. Distribution diagram of Pd/NCS-800

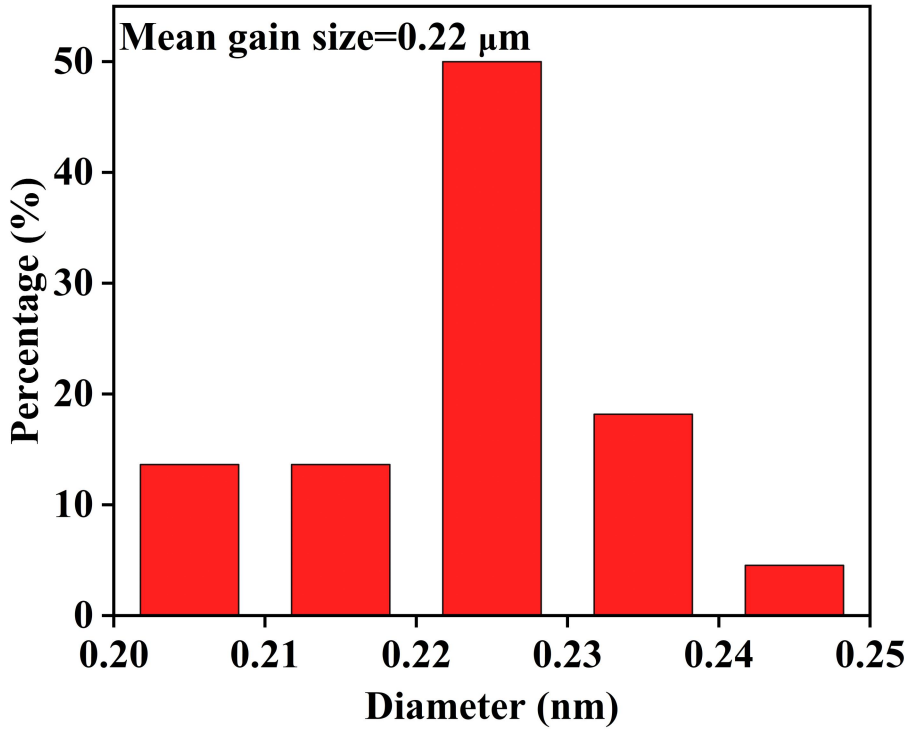

Figure S5. Distribution diagram of Pd/NCS-900

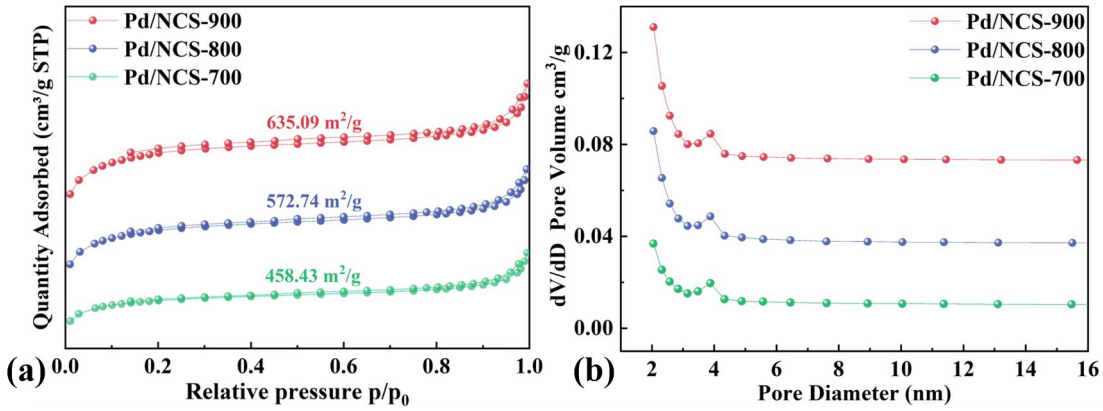

Figure S6. (a) BET SurHCOOHce area and (b) Pore volume of Pd/NCS-700, Pd/NCS-800 and Pd/NCS-900

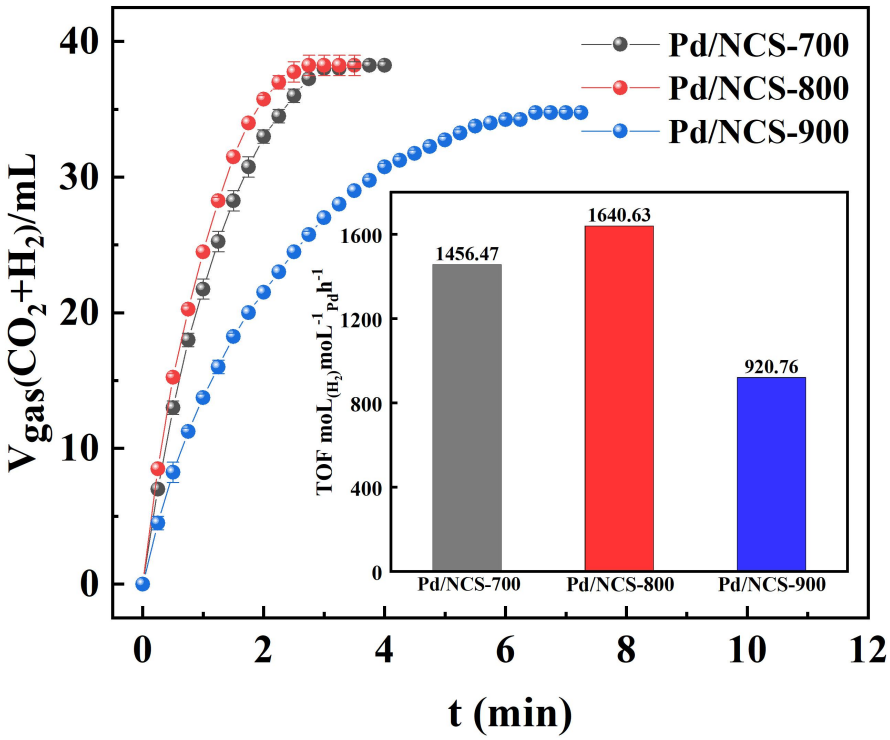

Figure S7. Comparison of H_2 evolution from HCOOH catalyzed by Pd/NCS-700, Pd/NCS-800 and Pd/NCS-900;

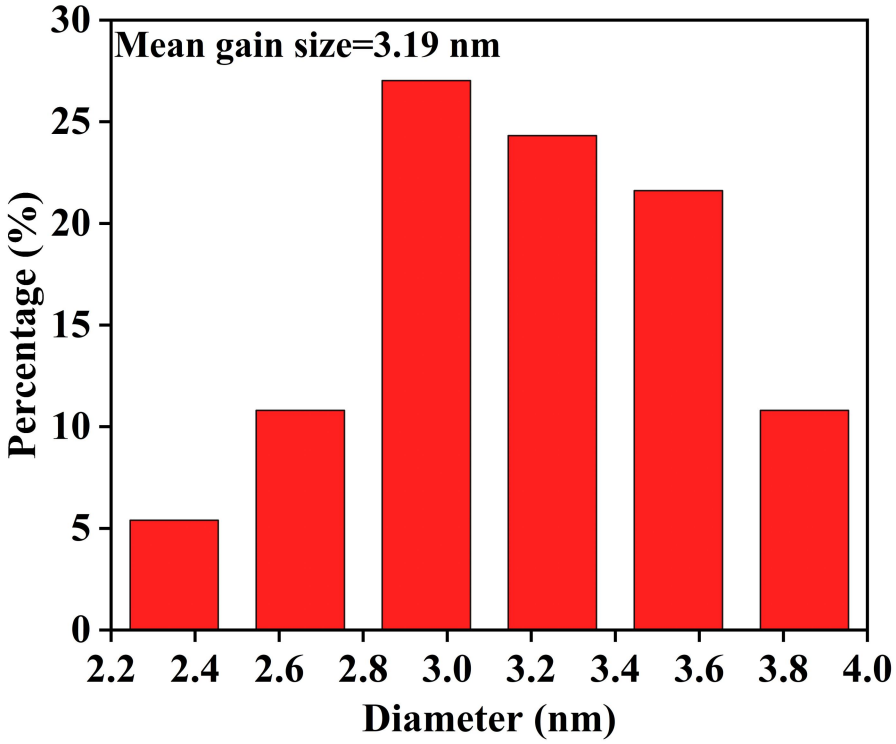

Figure S8. Distribution diagram of PdNPs in Pd/NCS-800

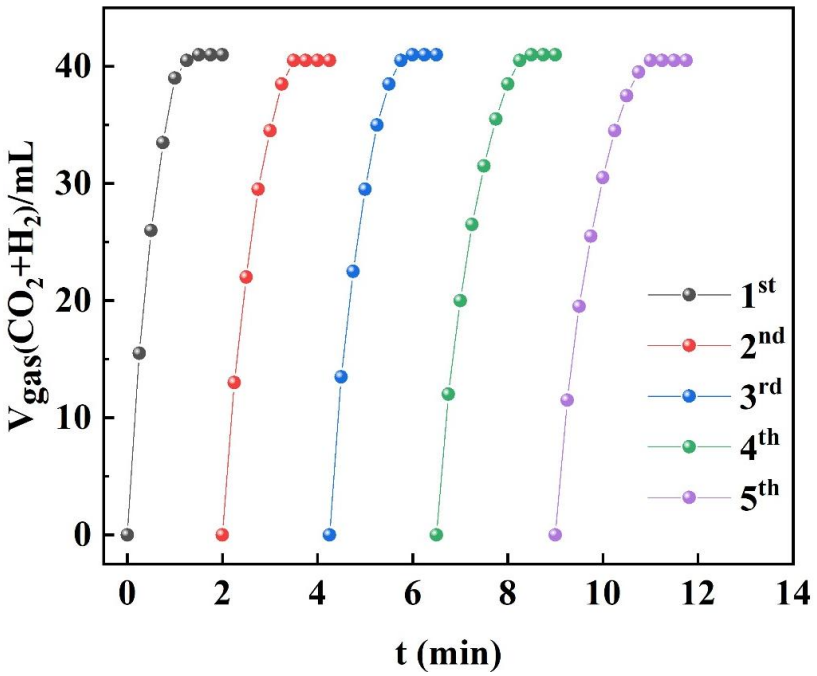

Figure S9. Stability test on the Pd/NCS-800 catalyst

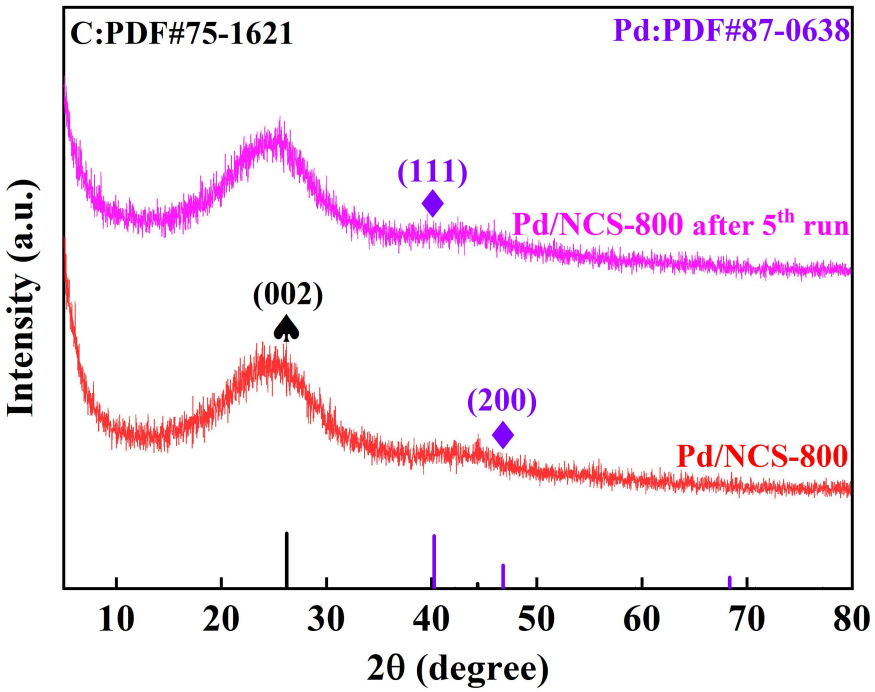

Figure S10. XRD of fresh and 5th reused Pd/NCS-800.

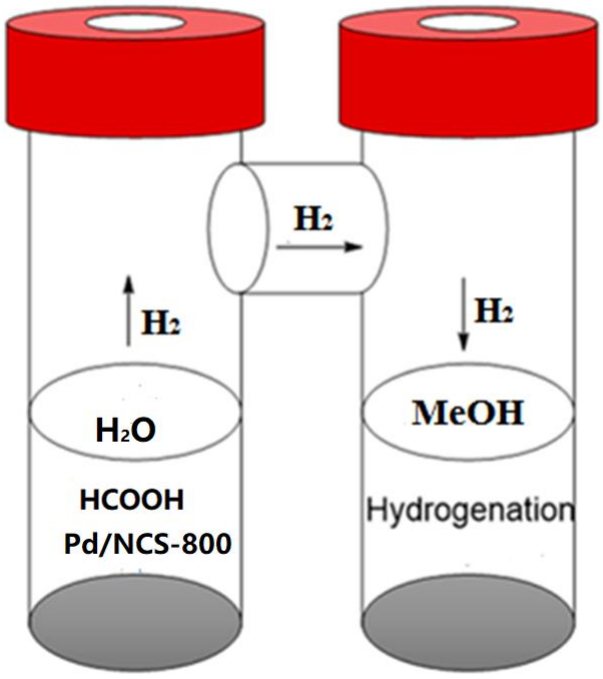

Figure S11. Sealed two-chamber system for 1,1-diphenylethylene hydrogenation with H_2. Following H_2 evolution, 1-diphenylethylene hydrogenation with generated H_2 occurred completely (99% yield) after 12 h at 30 °C.

The tandem reaction was reacted in the sealed two-chamber system. The left tube was used for

hydrogen generation, and the right one was used for hydrogenation with H_2 generated in the left tube. The generated hydrogen in the left tube transported to the hydrogenation reaction into the right tube through the connecting glass tube.

Hydrogenation of 1,1-diphenylethylene: 2 mol% Pd/NCS-800 was added into the left tube. Meanwhile, 10.6 mg (5 mmol % per styrene) Pd/C catalyst was added to the right tube. Air was removed *in vacuo*, and 2 mL methanol included 36 μL (0.1 mmol) 1,1-diphenylethylene was injected into the right tube. Then 4 mmol of HCOOH dissolved in 5 mL water was injected into the left tube. After 5 min, reaction was conducted at 60 °C for 12 h. The resulting product was filtered by 0.22 μ m organic needle barrel filter, and then vacuum dried at 60℃ under anhydrous conditions to obtain light yellow 1, 1-diphenethane.

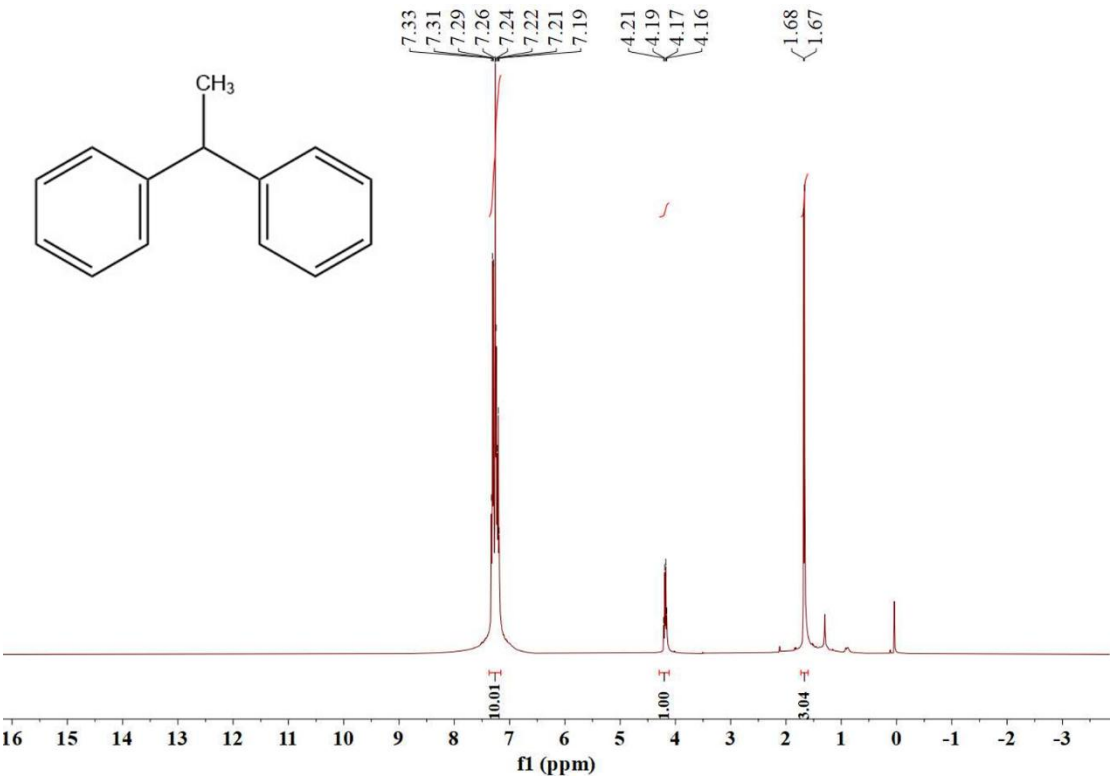

Figure S12. ^{1}H NMR (600 MHz, CD_3OD) δ 7.19-7.23 (m, 10 H), 4.16-4.21 (dd, 1H), 1.67-1.68 (m, 3H).

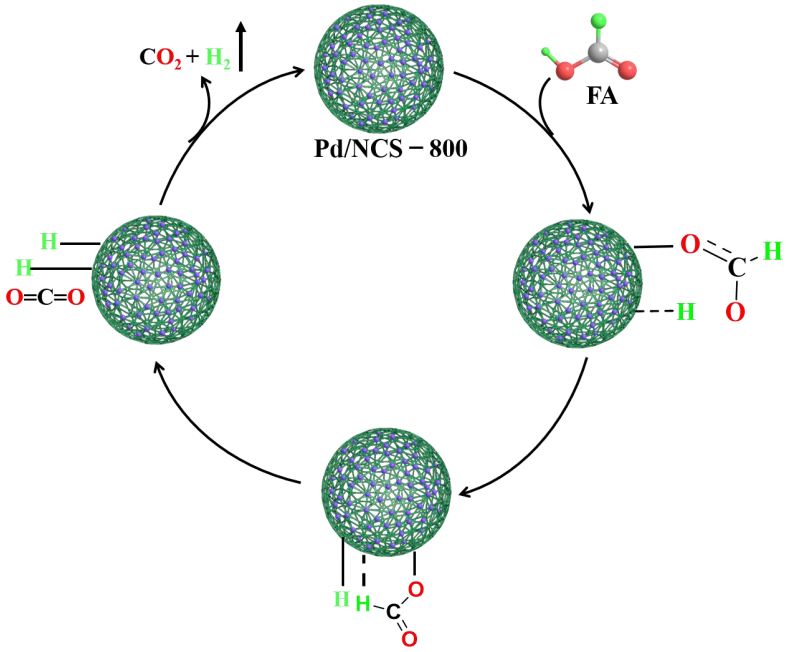

Figure S13. Mechanism of H_2 production from HCOOH dehydrogenation.

Table S1. Comparison of Pd/NCS-800 with other reported catalysts in H_2 generation upon additive-free HCOOH dehydrogenation.

Catalysts	TOF (h^{-1})	T/K	Ref.
Pd/CNS-800	1641	333	**This work**
Pd-MnO_X/SiO_2-NH_2	1300	323	[63]
$Pd_{60}Au_{40}$/HPC-NH_2	3763	298	[64]
$Pd_{90}Rh_{10}$/HHT	1793	303	[65]
Pd-sCeO_2/C	2691	303	[19]
Pd*CeO_2	807.7	313	[66]
PdAu-MnO_X/N-SiO_2	785	298	[67]
AuPd-CeO_2/N-rGO	52.9	298	[68]
Pd_8Ag_1/NH_2-TNS-rGO	1090	298	[69]
CoAuPd/DNA-rGO	85	298	[70]
Pd-WO_x/(P)NPCC	655	323	[71]
2wt.% Pd/KCC-1-PDETA	332	323	[72]
Pd/AFMS	862	323	[38]