Supplementary Information (SI) for Catalysis Science & Technology.

Supporting Information

Exploiting Tripeptide in Pd/C for Boosting Hydrogen Production from Formic Acid Dehydrogenation

Yan Gu[a], Hongli Wang[b], Yaohao Zhang[b], Lu Yang[a], Xiaoshan Liu[a], Xuesong Li[b*]*

[a] Chongqing Key Laboratory of Extraordinary Bond Engineering and Advanced Materials Technologies (EBEAM), Yangtze Normal University, Chongqing 408100, China

[b] College of Material Science and Engineering, Key Laboratory of Advanced Structural Materials , Ministry of Education, Changchun University of Technology, Changchun, 130012, China

[*]Corresponding Authors' e-mail addresses: wanghongli@ccut.edu.cn, lixuesong@ccut.edu.cn

Chemicals: Vulcan XC-72 carbon (C, Sinopharm Chemical Reagent Co., Ltd), tripeptide ($C_{14}H_{24}N_6O_4$, TPT, Macklin Biochemical Co., Ltd, ≥98%), hexadecyl trimethyl ammonium bromide ($C_{19}H_{42}BrN$, CTAB, Aladdin Chemistry Co., Ltd, ≥99%), polyvinylpyrrolidone($(C_6H_9NO)_n$, PVP, Sinopharm Chemical Reagent Co., Ltd, GR), L-Histidine ($C_6H_9N_3O_2$, Sinopharm Chemical Reagent Co., Ltd, BR), L-Lysine ($C_6H_{14}N_2O_2$, Sinopharm Chemical Reagent Co., Ltd, BR), palladium chloride ($PdCl_2$, Sinopharm Chemical Reagent Co., Ltd, ≥59%), sodium chloride (NaCl, Sinopharm Chemical Reagent Co., Ltd, ≥99.5%), formic acid (HCOOH, FA, Aladdin Chemistry Co., Ltd, ≥99.0%), 1,4-phenylenediamine (PDA, Aladdin Chemistry Co., Ltd, ≥99.0%), urea (H_2NCONH_2, Aladdin Chemistry Co., Ltd, ≥99.0%) sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd,≥98%), De-ionized water with the specific resistance of 18.2 MΩ cm was obtained by reversed osmosis followed by ion-exchange and filtration.

Synthesis of catalysts: All the catalysts were synthesized by impregnation-reduction processes. The Na_2PdCl_4 (0.025 M) solution was obtained by dissolving 2.5 mmol NaCl and 1.25 mmol $PdCl_2$ into 50.0 mL H_2O under magnetic stirring for 10 h. Typically, for the synthesis of Pd/C-TPT, 80 mg C was dispersed into distilled water (10 mL) by ultrasonicating for 15 min. Then, 20 mg TPT was added to the suspension as above and ultrasonicated for 30 min. After that, the Na_2PdCl_4 (0.025 M, 4.0 mL) solution was added to the mixed solution mentioned above with magnetic stirring for 3 h. The resulting suspension was reduced by $NaBH_4$ (40.0 mg) for stirring 30 min. Finally, the catalyst was centrifuged and washed with distilled water. For comparison, Pd-TPT was synthesized using the above method, except for not adding C. Pd^{2+}/C-TPT was prepared without the $NaBH_4$ reduction and centrifugal process.

Catalyst characterization: X-ray powder diffraction X-ray powder diffraction (XRD) was conducted on a Rigaku RINT-2000 X-ray diffractometer operated at 30 kV and 20 mA, using a Cu-Kα radiation source (λ=1.54056Å). The transmission electron microscope (TEM), energy-dispersive X-ray spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM) images were obtained with a FEI-Talos-F200S microscope. Fourier transform infrared (FT-IR) spectra were performed on a Thermo IS50 FT-IR with the wave number range of 800-4000 cm^{-1}. The actual metal contents in this work were determined by the inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Jarrell Ash (TJA) Atom scan Advantage). X-ray photoelectron spectroscopy (XPS) spectra were conducted on an ESCALABMKLL (Vacuum Generators) spectrometer employing an Al Kα X-rays source. UV-visible absorption spectra were recorded using a UV-visible spectrophotometer (Cary-5000) to monitor the absorption process.

H_2 from FA aqueous solution: The catalysts were placed into a flask with double neck, which one of them was attached to a gas burette, and another was connected to a partial pressure funnel to introduce FA aqueous solution (1.0 M, 5 mL). The reaction started as the FA solution was added into the flask with magnetic stirring. The reduced gases were detected by the gas burette. A series of catalytic reactions were executed at different temperatures (303 K, 313 K, 323 K and 333K) under ambient atmosphere.

After the catalytic reaction by Pd/C-TPT was totally finished, another equivalent amount of FA aqueous solution (1.0 M, 5 mL) was added into the flask to generated hydrogen with magnetic stirring. The production of gas was monitored by the gas burette. Such recycle experiments were repeated 3 times at 323 K under ambient atmosphere. The methodology for the durability tests of Pd/C-H and Pd/C-L is the same as Pd/C-TPT.

In order to investigate the effects of different amino acids on the functionalization of metal NPs on the FA dehydrogenation reaction, lysine and histidine were tested respectively under ambient atmosphere at 323 K, where FA was kept at 5 mmol. In addition, in order to study the modification effect of TPT on the surface of the catalyst, CTAB, PVP, PDA and urea were used under the same conditions as above.

Calculation methods:

$$\mathrm{TOF} = \frac{P_{atm}V_{H_2}/\mathrm{R}T}{n_{Pd}t} \qquad (1)$$

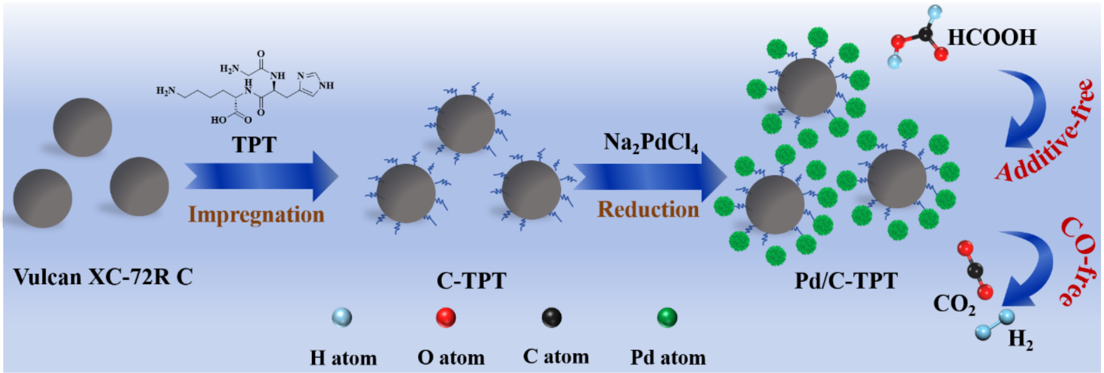
Where TOF is the initial turnover frequency (mol H_2 mol Pd^{-1} h^{-1}), P_{atm} is the atmospheric pressure, V_{H2} is the volume of the generated H_2 when the conversion reaches 50%. R is the ideal gas constant 8.314 kJ/mol, T is the room temperature (298 K), n_{Pd} is the measured mole number of Pd catalyst by ICP-OES, and t is the reaction time when the conversion reaches 50%.

The relationship between initial TOF values and temperatures was followed Arrhenius behavior. The Arrhenius' reaction rate equation can be written as follow:

$$\ln\mathrm{TOF} = \ln\mathrm{A} - E_{\mathrm{a}} / \mathrm{R}T \qquad (2)$$

where A is preexponential factor.

Supplementary Figures



Scheme S1 Schematic diagram of the synthetic procedure of Pd/C-TPT.

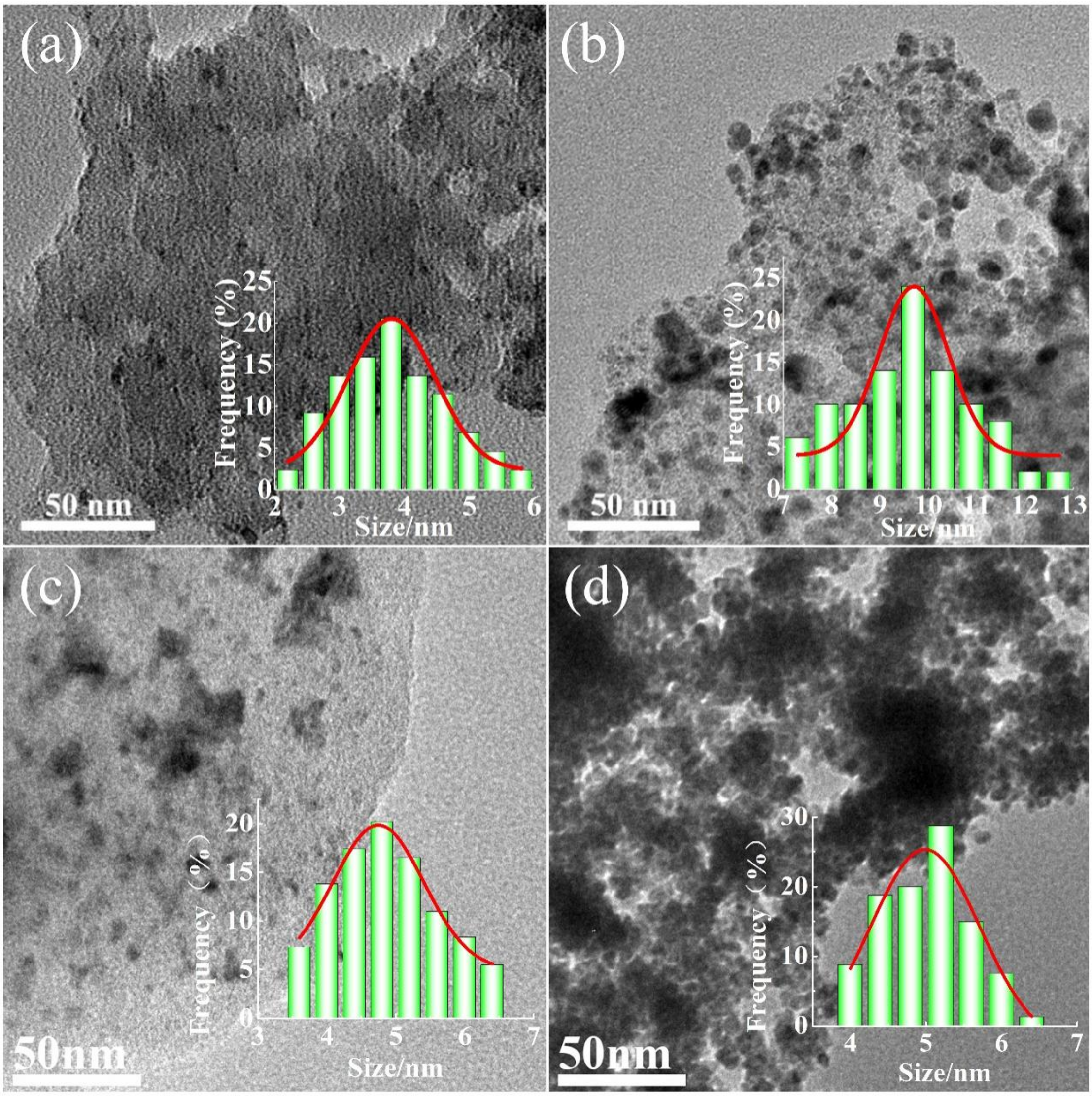


Fig. S1 TEM images and the histogram of particle size distributions (inset) of (a) Pd/C-TPT, (b) Pd/C, (c) Pd/C-L and (d) Pd/C-H.

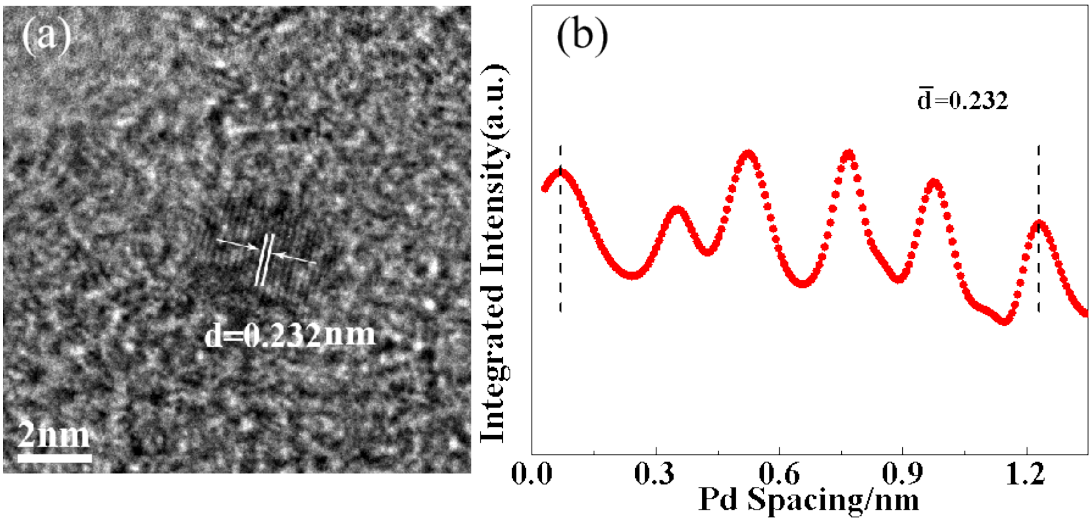


Fig. S2 (a) HRTEM image and (b) the integrated pixel intensities of Pd/C-L catalyst along Pd (111) spacing directions (which is perpendicular to the facets).

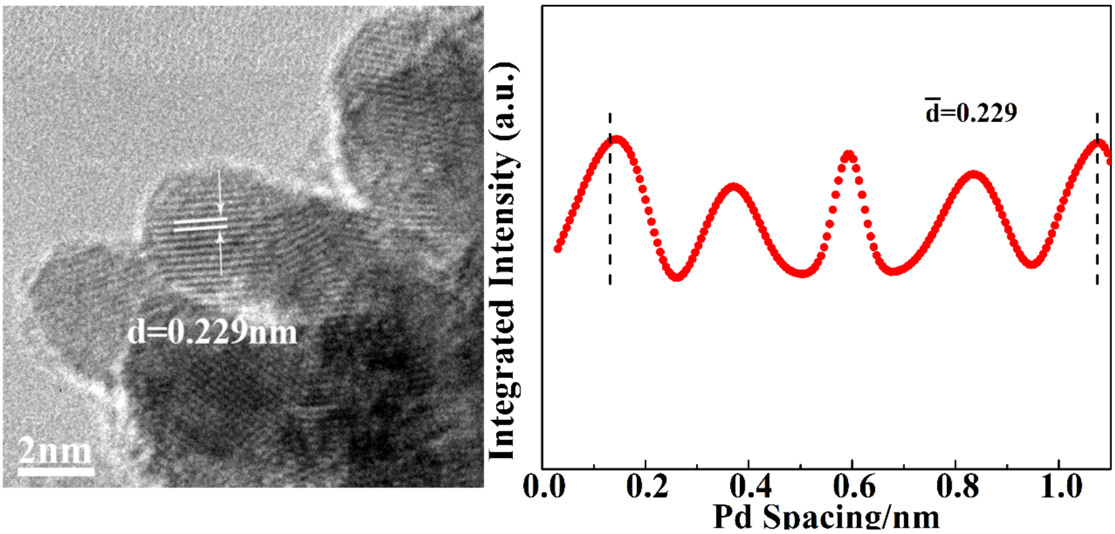


Fig. S3 (a) HRTEM image and (b) the integrated pixel intensities of Pd/C-H catalyst along Pd (111) spacing directions (which is perpendicular to the facets).

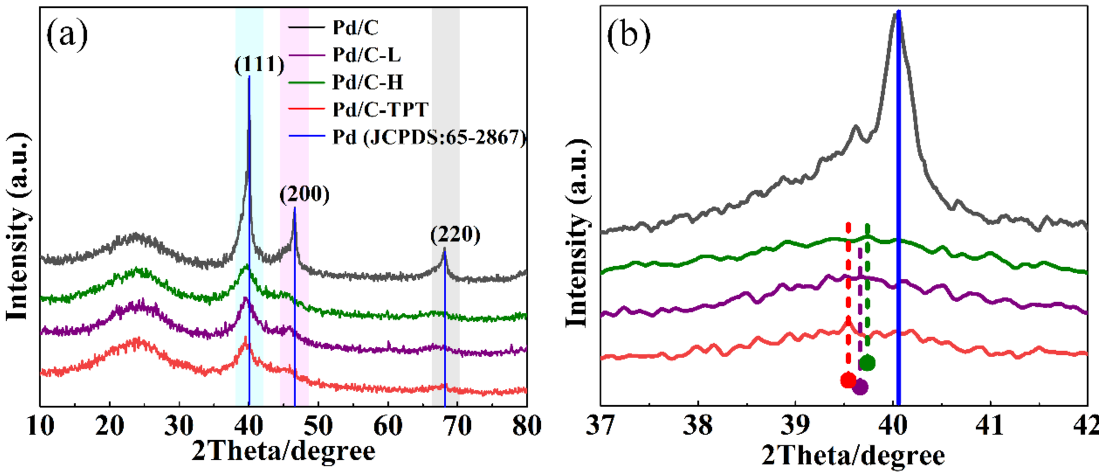


Fig. S4 (a) XRD spectra of Pd/C-TPT, Pd/C-L, Pd/C-H and Pd/C and (b) the corresponding magnified patterns of the selected area in (a).

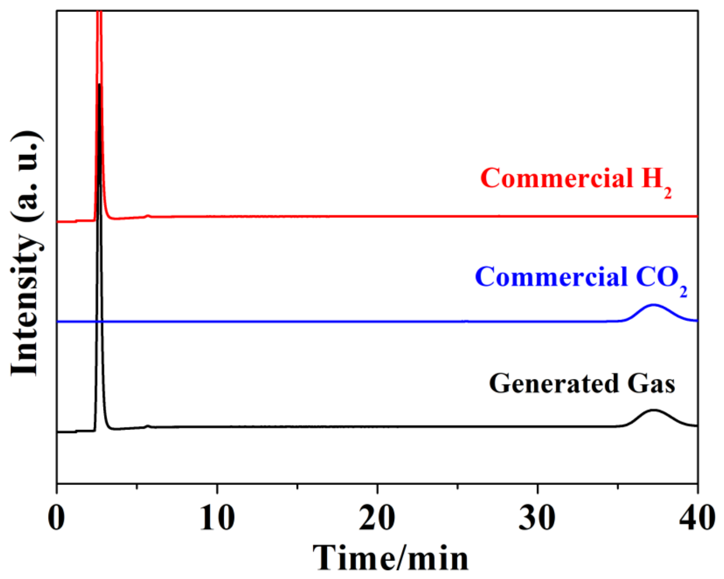


Fig. S5 GC spectra using TCD for the commercial gas and the evolved gas from FA aqueous solution (1.0 M, 5.0 mL) over Pd/C-TPT at 323 K.

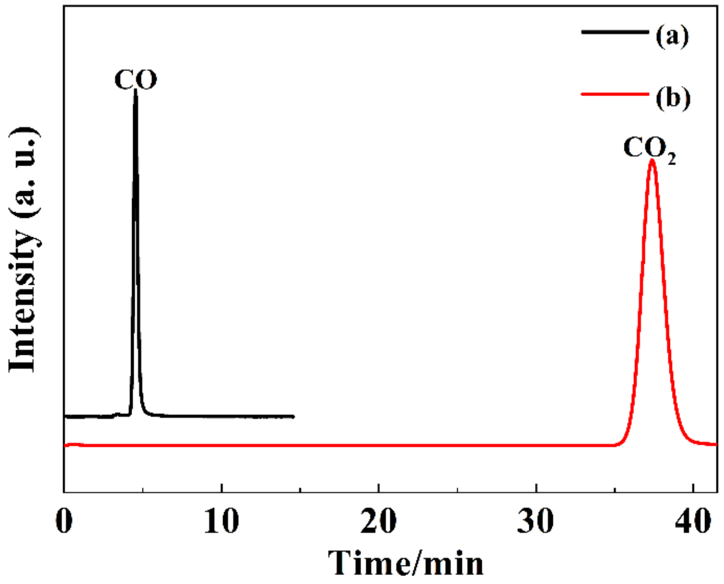


Fig. S6 GC spectrum using FID-Methanator for the (a) commercial pure CO, and (b) evolved gas from FA aqueous solution (1.0 M, 5.0 mL) over Pd/C-TPT at 323 K.

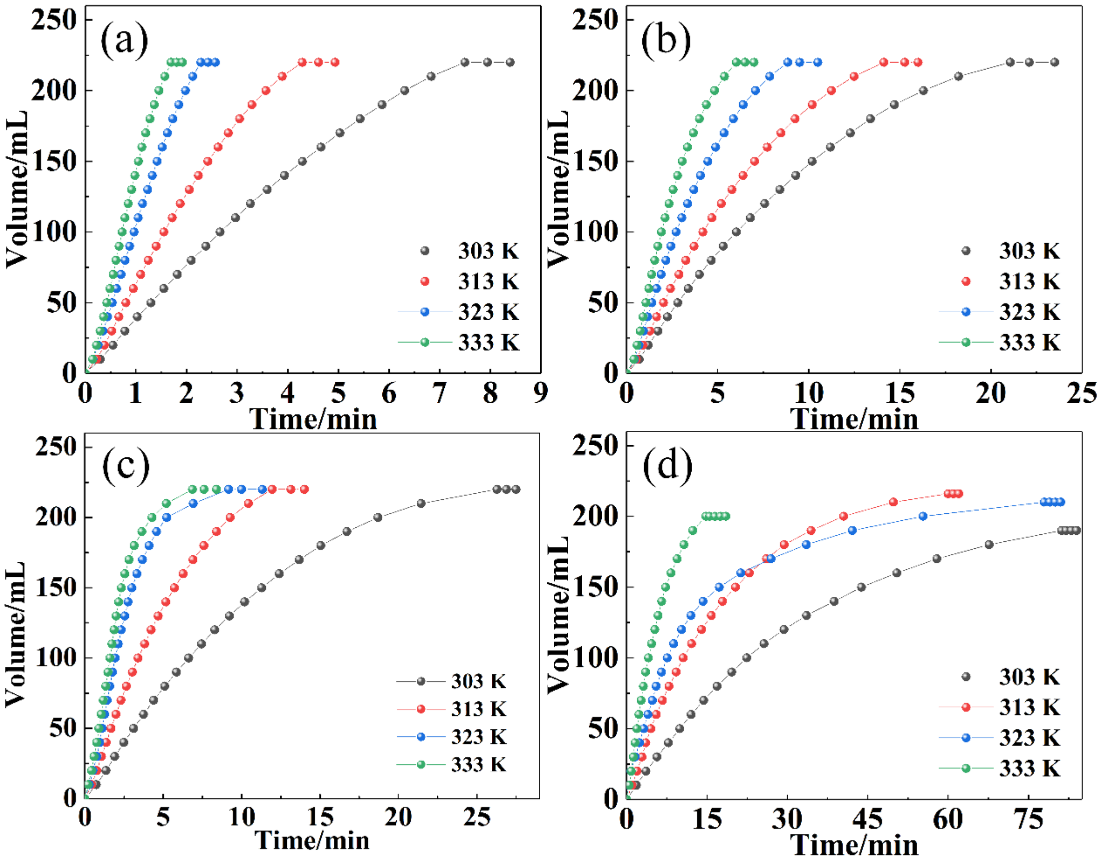


Fig. S7 Volume of gas generation from the dehydrogenation of FA (1.0 M, 5.0 mL) versus time for (a) Pd/C-TPT, (b) Pd/C-L, (c) Pd/C-H and (d) Pd/C at different temperatures (303 K, 313 K, 323 K and 333K).

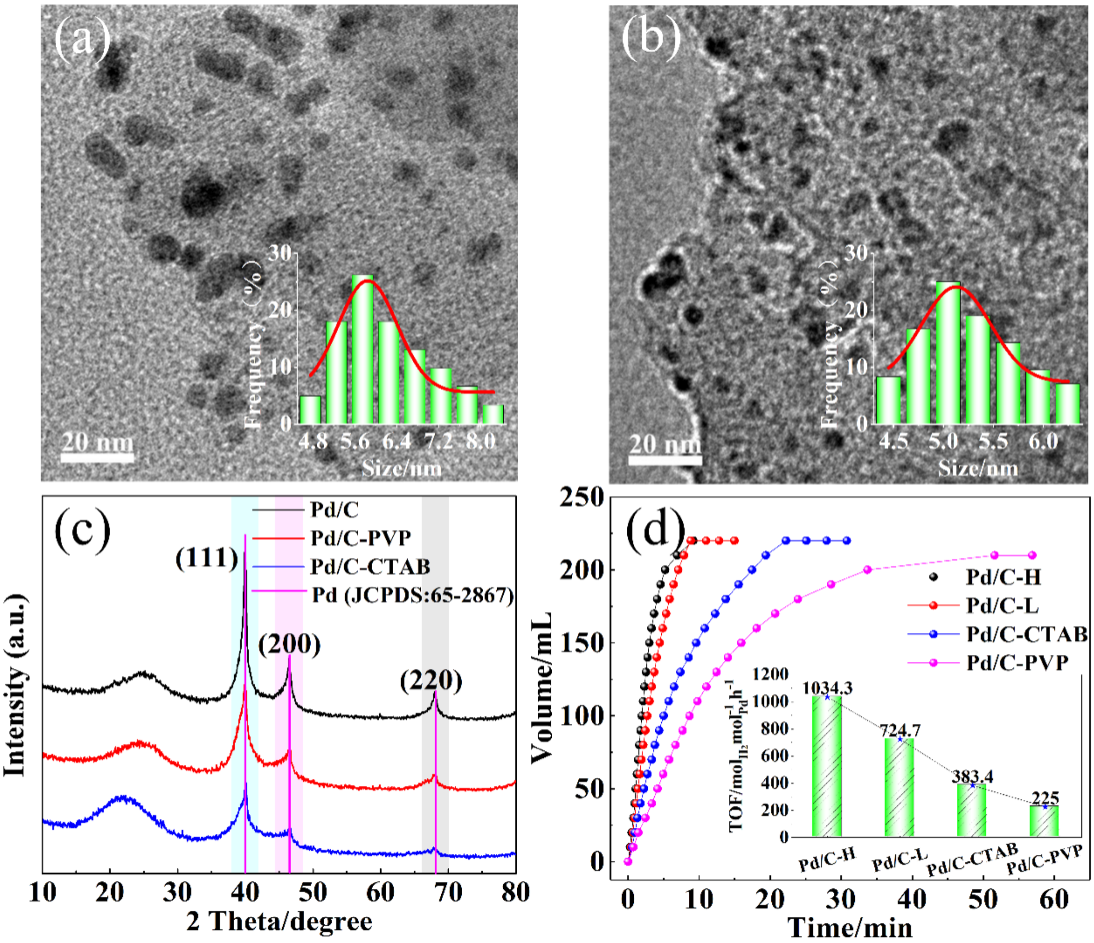


Fig. S8 TEM images and their histograms of particle size distribution (a-b inset) of (a) Pd/C-PVP and (b) Pd/C-CTAB. (c) XRD patterns for Pd/C, Pd/C-PVP and Pd/C-CTAB. (d) Volume of gas generation from the dehydrogenation of FA (1.0 M, 5.0 mL) versus time and the corresponding TOF values (inset) of Pd/C-H, Pd/C-L, Pd/C-CTAB, Pd/C-PVP.

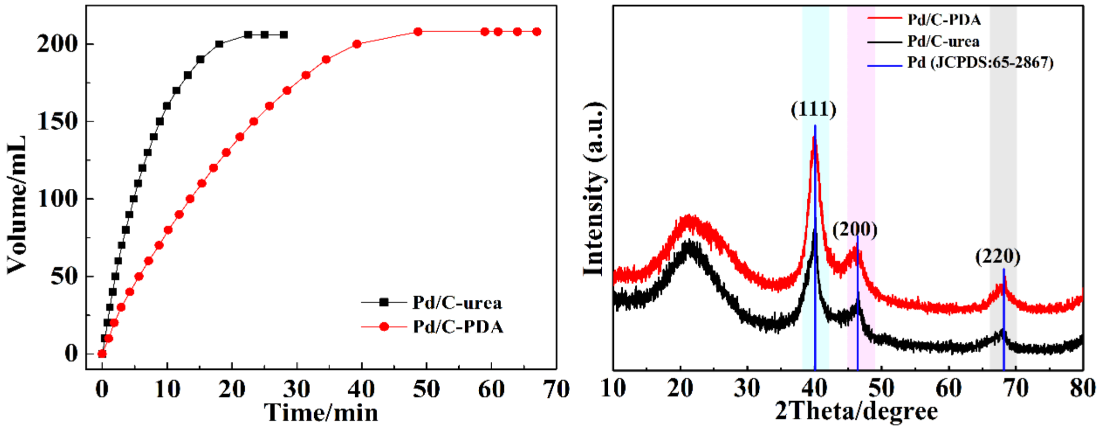


Fig. S9 Volume of gas generation from the dehydrogenation of FA (1.0 M, 5.0 mL) versus time for Pd/C-Urea and Pd/C-PDA.

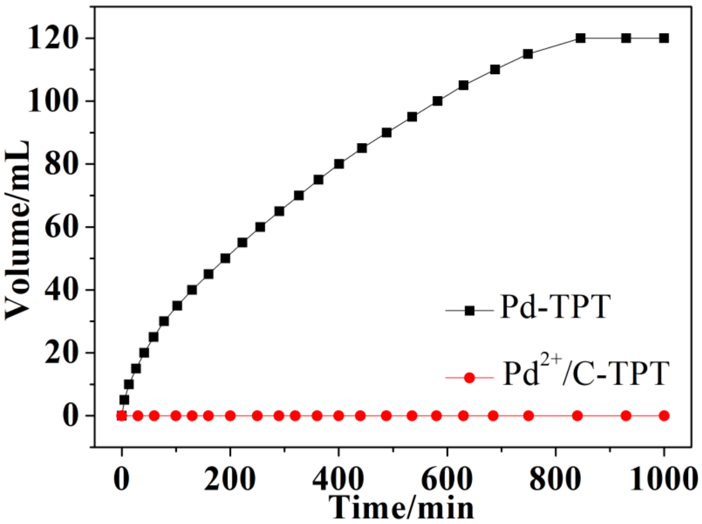


Fig. S10 Volume of gas generation from the dehydrogenation of FA (1.0 M, 5.0 mL) versus time for Pd-TPT and Pd^{2+}/C-TPT.

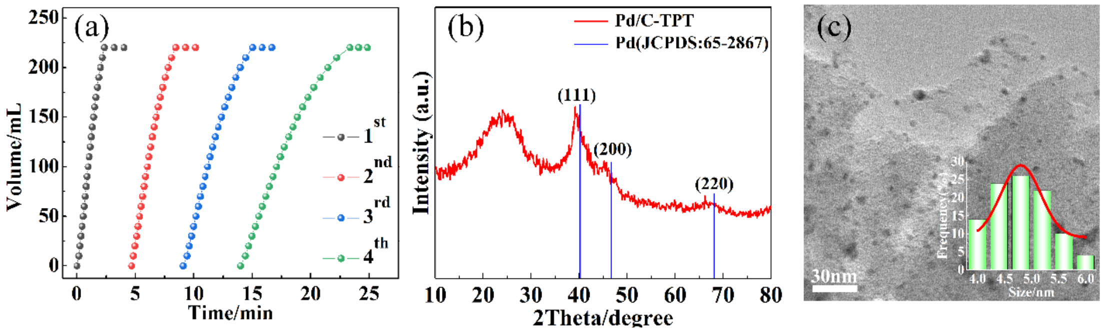


Fig. S11 (a) Durability tests of Pd/C-TPT towards the decomposition of FA (1.0 M, 5.0 mL). (b) XRD spectrum, (c) TEM image and the corresponding particle size distribution (inset) of Pd/C-TPT after the 4th run.

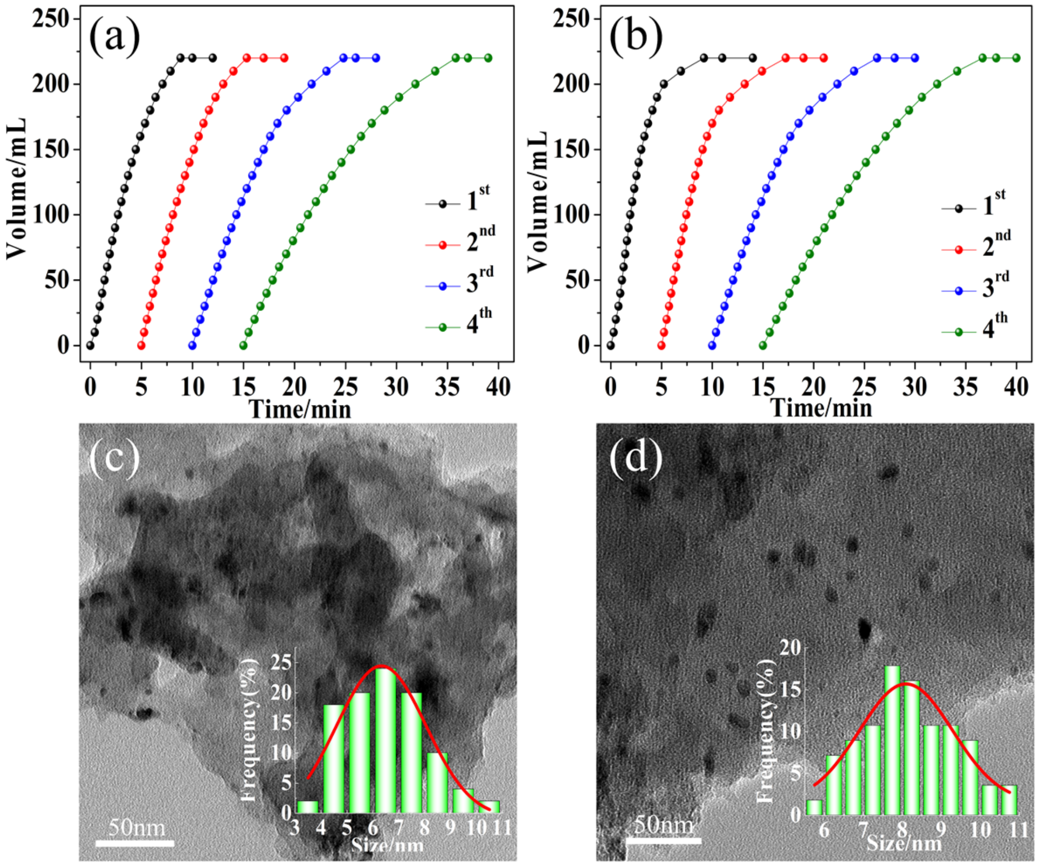


Fig. S12 Durability tests of (a) Pd/C-L and (b) Pd/C-H toward the decomposition of FA (1.0 M, 5.0 mL), TEM images and the corresponding particle size distribution (inset) of (c) Pd/C-L and (d) Pd/C-H after the 4th run.

Supplementary Table

Table S1 ICP analyses for the samples.

Sample	Pd content (wt%)
Pd/C-TPT	8.17
Pd/C-H	8.31
Pd/C-L	8.33
Pd/C	8.78
Recycled Pd/C-TPT	8.15

Table S2 Comparisons of catalytic activities for the dehydrogenation of FA catalyzed by previously reported heterogeneous Pd monometallic catalysts with the as-synthesized in this work.

Catalyst	T/K	$n_{Catalyst}/n_{FA}$	TOF/ mol H_2 mol Pd^{-1} h^{-1}	E_α/kJ mol^{-1}	Ref.
Without additive					
Pd-NPs@TA-CoP	328	0.0130	233.2	29.0	28
Pd/D201	323	---	547.6	42.9	29
Pd_{IMP}/CNF	303	0.0188	563.2	27.5	30
Pd/$CN_{0.25}$	298	0.0080	752.0	48.8	31
Pd@TB-POP	323	0.1000	1344.0	41.8	32
Pd/ImIP-2	323	0.0080	1593.0	46.5	33
Pd_3@S-2	303	0.0050	2009.0	29.6	34
Pd/C-TPT	323	0.0134	2101.8	37.5	This work
PdAu/ArGO	298	0.0400	10699.5	15.1	35
With additive (HCOONa)					
Pd@ED/Cr-MIL-101	328	0.0030	583.0	29.3	36
Pd/NH_2-rGO	298	0.0200	767.0	30.7	37
Pd@MC(2)-P	303	0.0090	971.0	42.9	38
Pd-B/C	303	0.0140	1184.0	---	39
Pd/NC400@WO3	323	0.0040	1225.0	37.0	40
Pd/NTNC-950	303	0.0020	1631.0	33.7	41
Pd/APC	323	0.0110	2230.0	46.3	42
Pd/C	323	0.0100	3440.0	42.0	4
Pd/PDA-rGO	323	0.0150	3810.0	54.3	10
Pd-WO_x/(P)NPCC	323	0.0400	6135.0	35.9	44
Pd/FeNC	323	0.0200	7361.0	47.3	43
Pd-La$(OH)_3$/N-PCB-NH_2	323	0.0400	9585.0	40.4	45