

## Electronic Supplementary Information

# Immobilization of highly active bimetallic PdAu nanoparticles to nanocarbons for dehydrogenation of formic acid

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## 1. Experimental Section

### 1.1 Chemicals

All chemicals have been used as received without any purifications. Vulcan XC-72R carbon (Cabot Corp., USA), maxsorb MSC-30 and MSP-20X carbons (Nanoporous Carbon, Kansai Coke and Chemicals Co. Ltd.), formic acid (FA, Sigma-Aldrich, >98%), sodium borohydride (Sigma-Aldrich), L-Arginine (LA) (Sigma-Aldrich), trisodium citrate (TSC) (Sigma-Aldrich), commercial Pd/C (5 wt% Pd, Sigma-Aldrich), sodium hydroxide (Wako Pure Chemical Industries, Ltd), Polyvinylpyrrolidone (PVP-K30) (Wako Pure Chemical Industries, Ltd),  $K_2PdCl_4$  (Wako Pure Chemical Industries, Ltd),  $HAuCl_4$  (Wako Pure Chemical Industries, Ltd), sodium formate dehydrate (SF) (Tokyo Chemical Industry Co. Ltd.), L-lysine (LL) (Tokyo Chemical Industry Co. Ltd.), Piperazine anhydrous (PA) (Tokyo Chemical Industry Co. Ltd.) and ethylenediamine (EG) (Tokyo Chemical Industry Co. Ltd.) were used as received. Deionized water with a resistance of 18.2  $M\Omega \cdot cm$  which was obtained by reverse osmosis followed by ion exchange and filtration (RFD 250NB, Toyo Seisakusho Kaisha, Ltd., Japan) has been used throughout the whole experiments.

## 1.2 Catalyst synthesis

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-LA:** An aqueous mixture containing 3 mL of LA (0.1 g mL<sup>-1</sup>), 0.3 mL of K<sub>2</sub>PdCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) and 0.3 mL of HAuCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) was diluted to a volume of 10 mL with water, then added into 0.1 g of MSC-30 carbon and sonicated for 30 min. Subsequently, 1 mL of freshly prepared NaBH<sub>4</sub> solution (2.64 mol L<sup>-1</sup>) was injected into the above mixture and was allowed to stir for another 30 min. Finally, the product was collected with centrifugation, washed with water for three times and collected for further use. For the structure and composition characterizations, the final samples were dried at room temperature in a vacuum oven after collected.

**Synthesis of PdAu/30-LA with different Pd/Au ratios:** The synthetic process was the same as the synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-LA, except for the use of following metal precursors: 0.2 mL of K<sub>2</sub>PdCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) and 0.4 mL of HAuCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) for Pd<sub>1</sub>Au<sub>2</sub>/30-LA; 0.4 mL of K<sub>2</sub>PdCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) and 0.2 mL of HAuCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) for Pd<sub>2</sub>Au<sub>1</sub>/30-LA; 0.6 mL of K<sub>2</sub>PdCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) for Pd/30-LA; 0.6 mL of HAuCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) for Au/30-LA.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-X (X= LL, PA, EG):** The synthetic process was the same as the synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-LA, except for the use of other small molecules X (X= LL, PA, EG) in place of LA.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-NaOH:** The synthetic process was the same as the synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-LA, except for the use of NaOH instead of LA.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-TSC:** The synthetic process was the same as the synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-LA, except for the use of 1 mL of aqueous TSC (0.2 mol L<sup>-1</sup>) instead of LA.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-SF:** The synthetic process was the same as the synthesis of MSC-30-Pd<sub>1</sub>Au<sub>1</sub>-LA, except for the use of 0.3 g of SF in place of LA.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-PVP:** The synthetic process was the same as the synthesis of MSC-30-Pd<sub>1</sub>Au<sub>1</sub>-LA, except for the use of 0.3 g of PVP (K 30) in place of LA.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-none:** The synthetic process was the same as the synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-LA without adding LA.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/20-LA:** The synthetic process was the same as the synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-LA, except for the use of MSP-20X carbon in place of MSC-30 carbon.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/72-X (X=LA, LL, PA, NaOH):** The synthetic process was the same as the synthesis of Pd<sub>1</sub>Au<sub>1</sub>/30-LA and Pd<sub>1</sub>Au<sub>1</sub>/30-X, except for the use of Vulcan XC-72R carbon instead of MSC-30 carbon.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/72-none:** The synthetic process was the same as the synthesis of Pd<sub>1</sub>Au<sub>1</sub>/72-LA except without adding LA.

**Synthesis of Pd<sub>1</sub>Au<sub>1</sub>/72-LA with different Pd/Au ratios:** The synthetic process was the same as the synthesis of Pd<sub>1</sub>Au<sub>1</sub>/72-LA, except for the use of the metal precursors as: 0.2 mL of K<sub>2</sub>PdCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) and 0.4 mL of HAuCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) for Pd<sub>1</sub>Au<sub>2</sub>/72-LA; 0.4 mL of K<sub>2</sub>PdCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) and 0.2 mL of HAuCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) for Pd<sub>2</sub>Au<sub>1</sub>/72-LA; 0.6 mL of K<sub>2</sub>PdCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) for Pd/72-LA; 0.6 mL of HAuCl<sub>4</sub> (0.1 mol L<sup>-1</sup>) for Au/72-LA.

### 1.3 Instruments

X-ray diffraction patterns were recorded on a Rigaku Ultima IV diffractometer with Cu- $K_{\alpha}$  radiation (scan rate: 10 / min). The N<sub>2</sub> adsorption/desorption isotherms were collected at liquid nitrogen temperature (77 K) using automatic volumetric adsorption equipment (Belsorp-max) after degassing at 60 °C. X-ray photoelectron spectrum (XPS) data were gained on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer with an Mg K  $\alpha$  source (10 kV, 10 mA). A Titan<sup>3</sup> G2 60-300 transmission electron microscope (FEI Company) equipped with energy-dispersive X-ray detector (super-x with Esprit, Bruker Company) was used to further characterize the structure and composition. The operating voltage for TEM and high-angle annular dark-field scanning TEM (HAADF-STEM) measurements was 300 kV. The Pd and Au metal contents of the resulted products were determined with an inductively coupled plasma (ICP) analysis system (Thermo Scientific iCAP6300). Elemental analysis was carried on CE EA1110 and Perkinelmer 2400II instruments. The gases were detected on SHIMADZU GC-8A, TCD.

#### **1.4 Dehydrogenation of formic acid (DOFA) measurements**

The apparatus for the measurements of H<sub>2</sub>/CO<sub>2</sub> generated from aqueous FA is the same as our previous reports.

**From aqueous FA:** In brief, the as-prepared catalyst suspended in 1 mL of water (for VXC-72 carbon supported catalyst 2 mL water was used) was transferred into a flask with capacity of 30 mL which was kept at a preset temperature with a water bath. To start the FA dehydrogenation reaction, 0.5 mL of FA (6 mol L<sup>-1</sup>) aqueous solution was injected with a pipette. Under ambient temperature, the volume of released gas was recorded by the displacement volume of water from a gas burette filled with water. The molar ratio of  $n_{Pd+Au} / n_{FA}$  was fixed at 0.02 during the whole measurements unless otherwise stated. For the durability test, 0.5 mL of FA (6 mol L<sup>-1</sup>) was consecutively added into the mixture without separation.

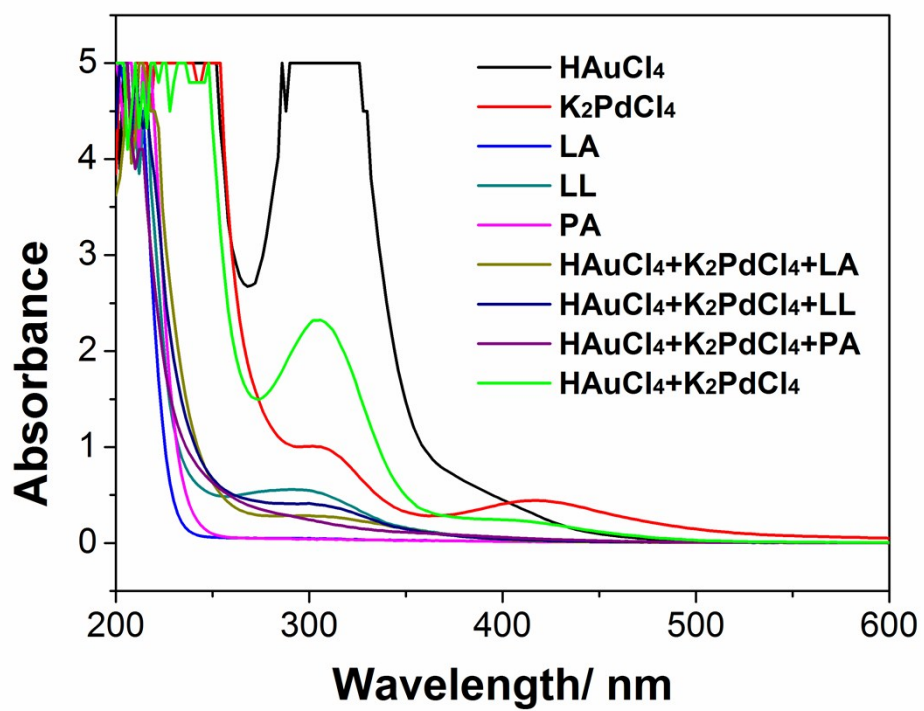
**From a mixture of aqueous FA/SF:** 1 mL of FA/SF mixture (FA : 3 mol L<sup>-1</sup>) with different FA/SF ratios was injected into the catalyst suspension. For each run of the durability test, the catalyst was separated from the mixture by centrifugation and washed with water several times, followed by drying in vacuum at room temperature.

**TOF Calculation methods:**

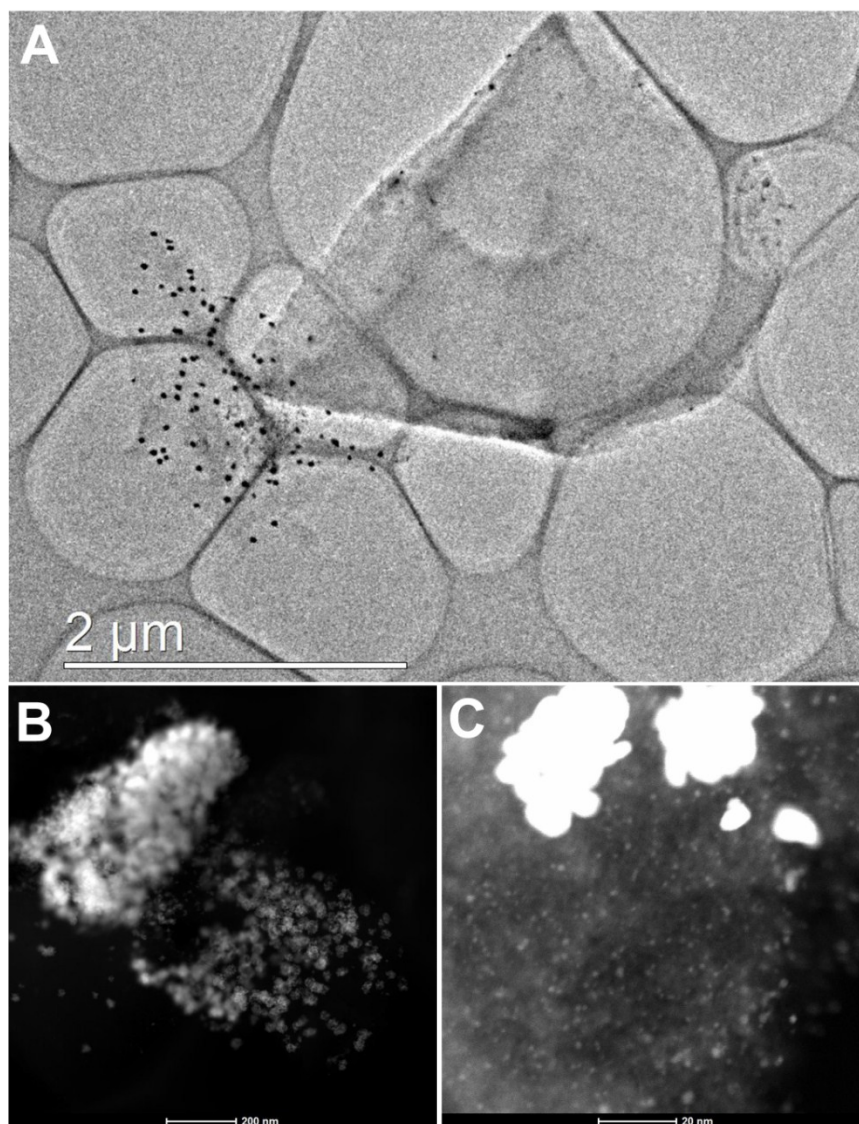
$$\text{TOF} = \frac{P_{atm} V/RT}{2 n_{metal} t}$$

TOF is turnover frequency,  $P_{atm}$  is the atmospheric pressure,  $V$  is the volume of gas generated during the reaction,  $R$  is the gas constant,  $T$  is the dehydrogenation reaction temperature (298-333 K),  $n_{metal}$  represents the molar amount of the noble metals: Pd, Au or Pd + Au, and  $t$  represents the time of completion of gas generation. Note: for the experiment using the sodium formate as the additive, the time represents the generated gas volume reached at 146 mL.

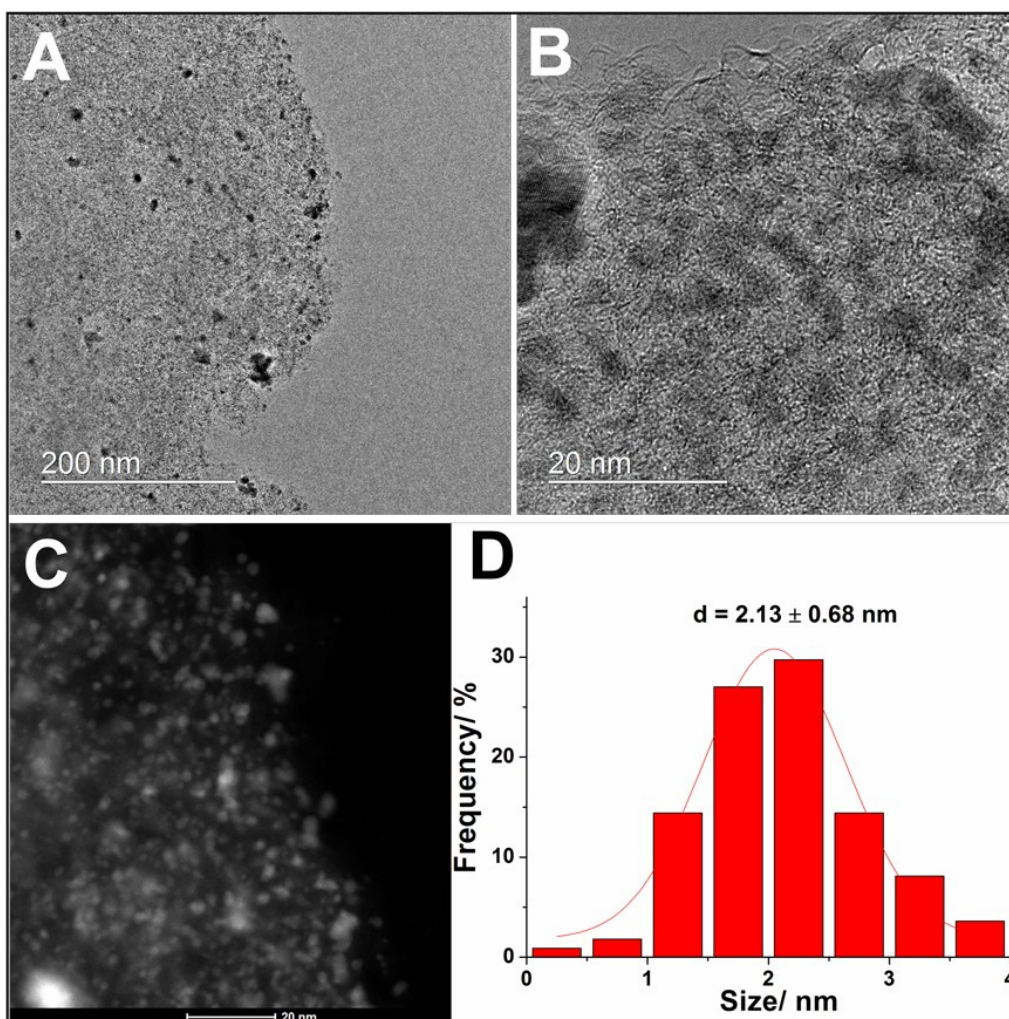




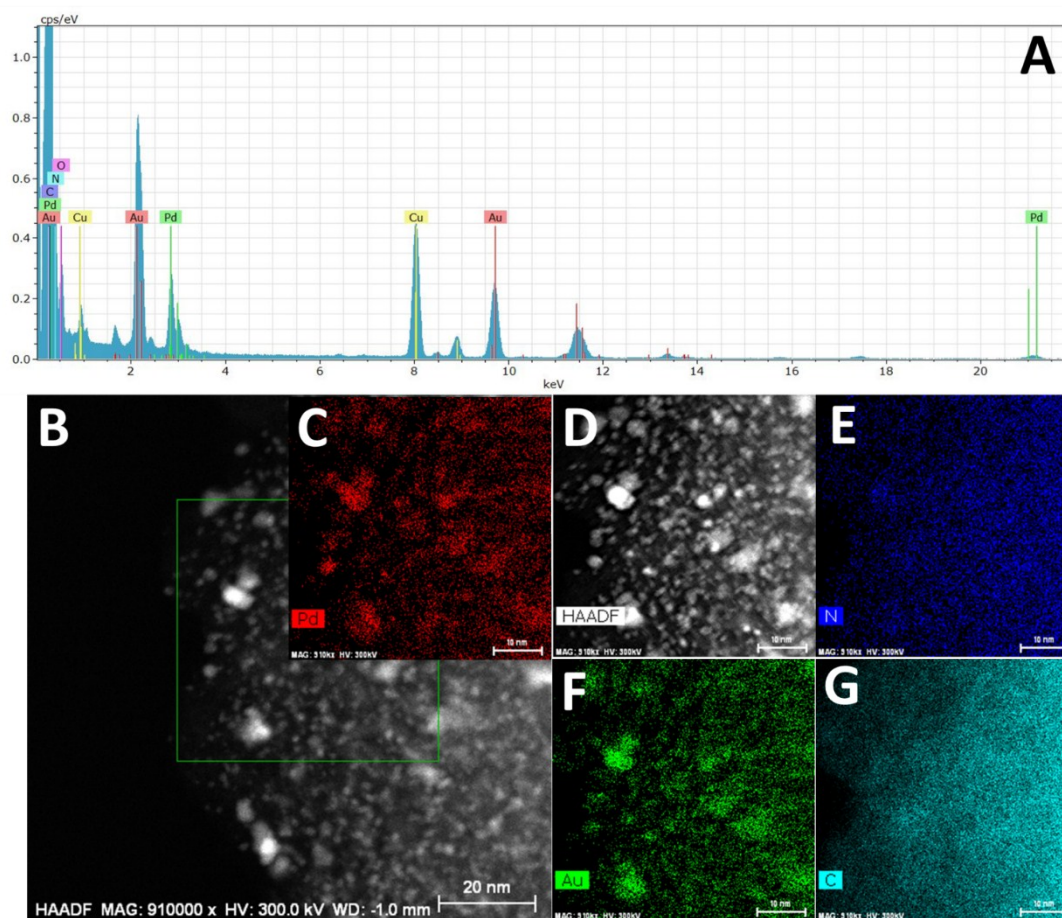
**Fig. S1** UV-Vis spectra of different aqueous solutions.



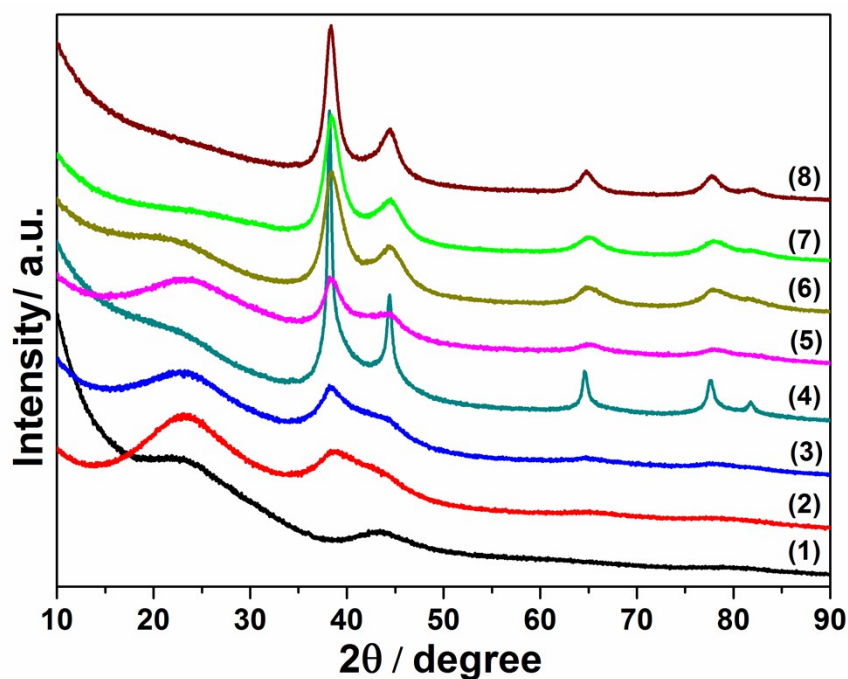
**Fig. S2** (A) TEM and (B, C) HAADF-STEM images of the as-prepared Pd<sub>1</sub>Au<sub>1</sub>/30-None catalyst.



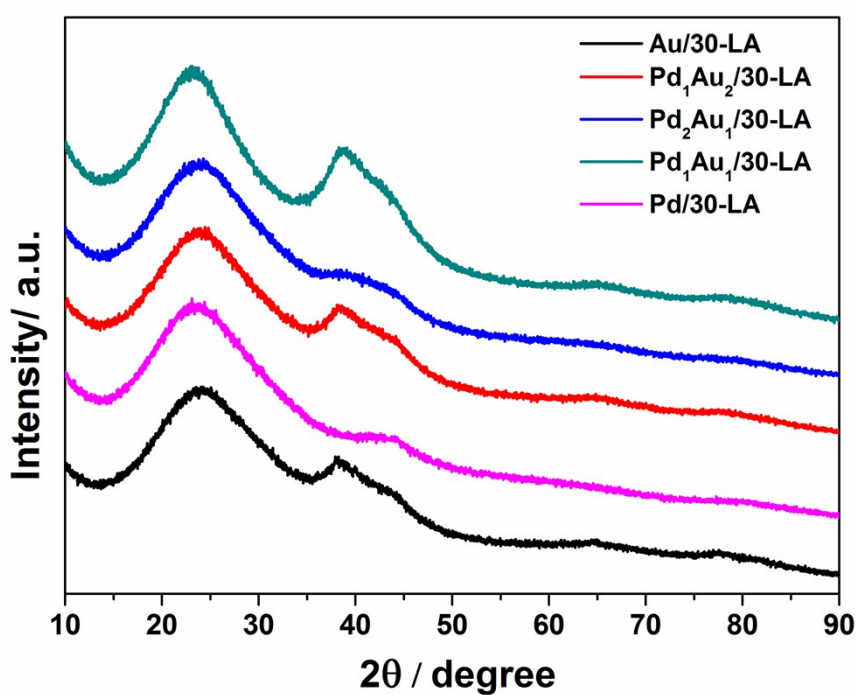
**Fig. S3** (A, B) TEM and (C) HAADF-STEM images of the as-prepared Pd<sub>1</sub>Au<sub>1/30</sub>-NaOH catalyst. (D) The size distribution of metallic PdAu NPs.



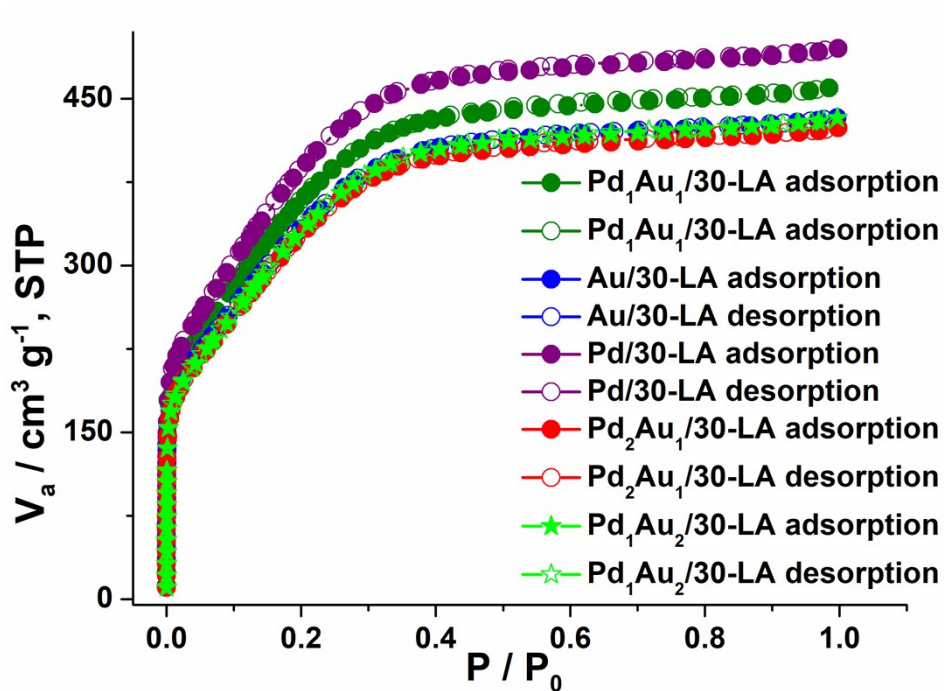
**Fig. S4** (A) EDS, (B, D) HAADF-STEM and (C, E, F, G) EDS elemental mapping images of the as-prepared Pd<sub>1</sub>Au<sub>1</sub>/30-LA catalyst. The signal of Cu in (A) was originated from the carbon coated copper grid.



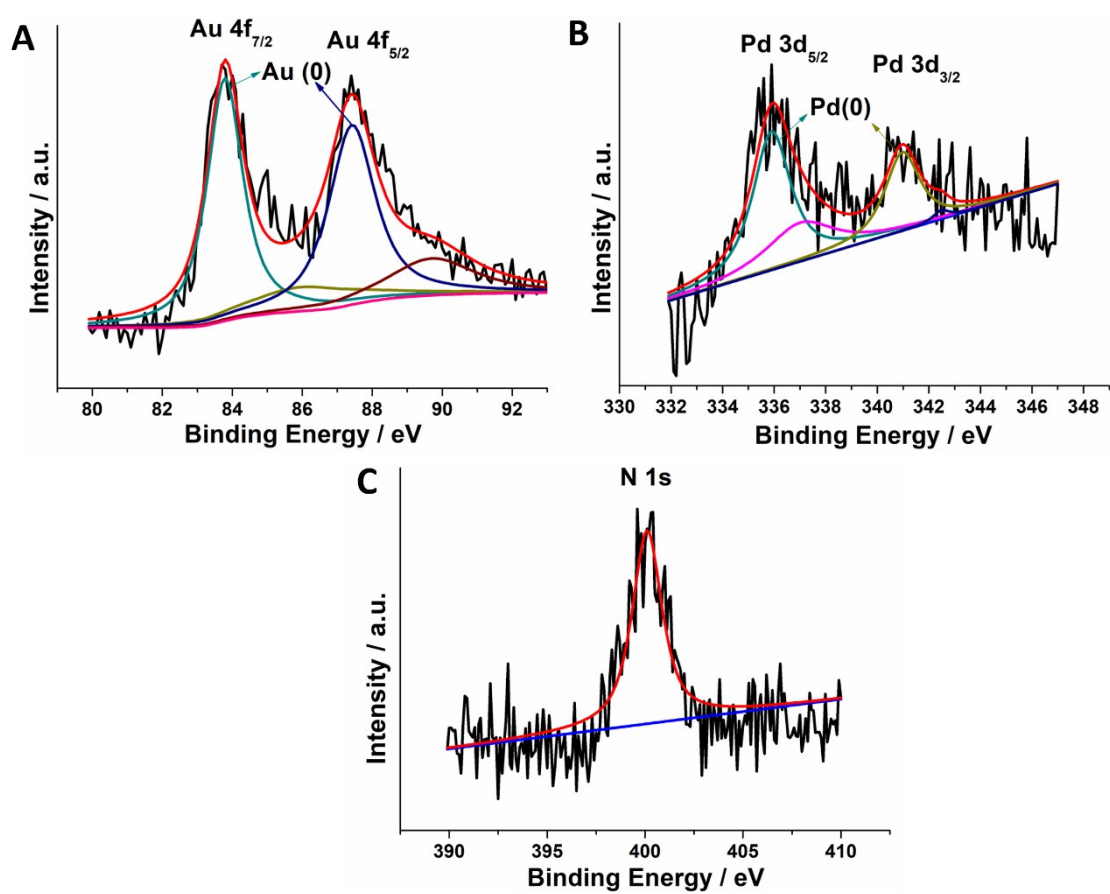
**Fig. S5** XRD patterns of (1) commercial MSC-30 carbon, (2) Pd<sub>1</sub>Au<sub>1</sub>/30-LA, (3) Pd<sub>1</sub>Au<sub>1</sub>/30-LL, (4) Pd<sub>1</sub>Au<sub>1</sub>/30-EG, (5) Pd<sub>1</sub>Au<sub>1</sub>/30-PA, (6) Pd<sub>1</sub>Au<sub>1</sub>/30-PVP, (7) Pd<sub>1</sub>Au<sub>1</sub>/30-SF and (8) Pd<sub>1</sub>Au<sub>1</sub>/30-TSC.



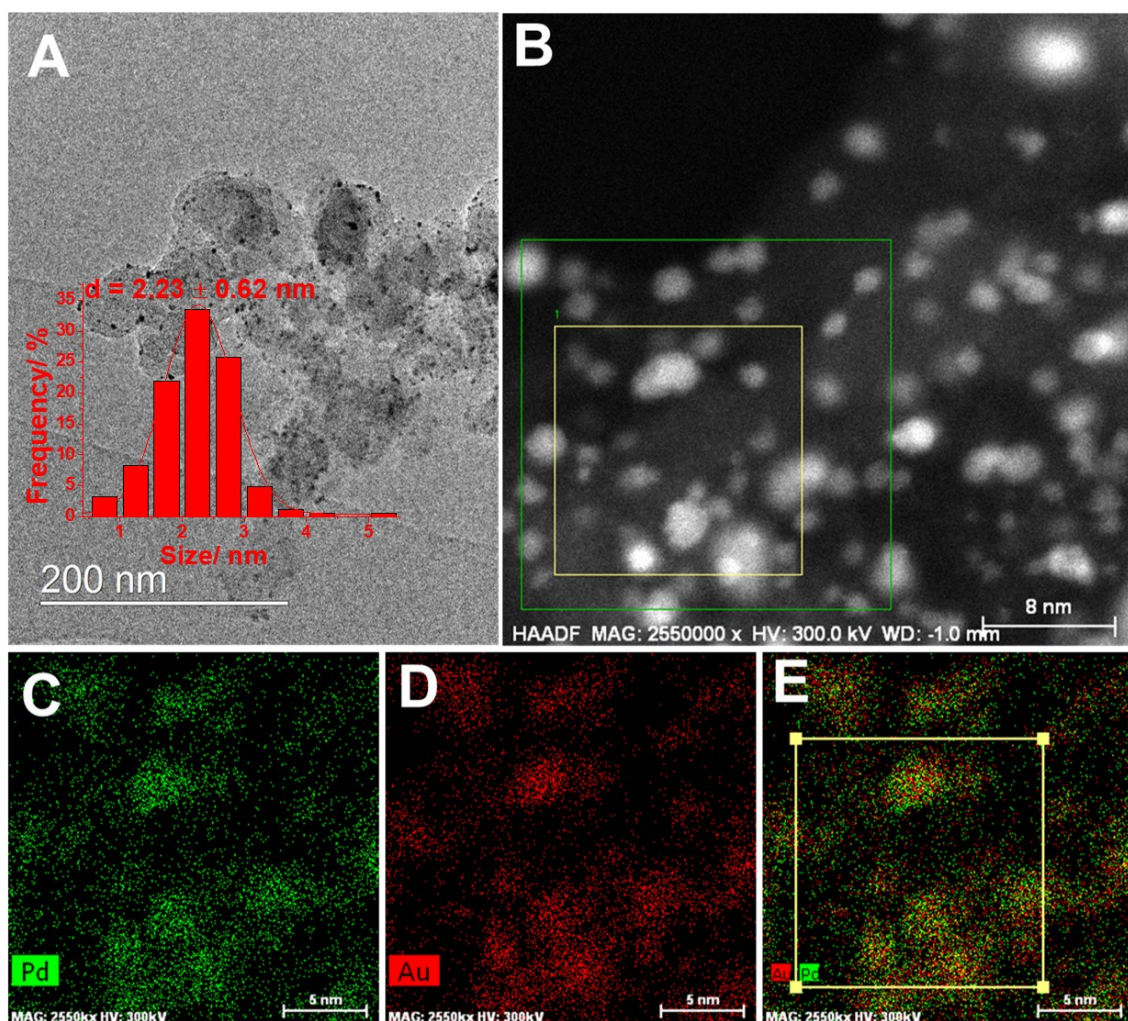
**Fig. S6** XRD patterns of the PdAu/30-LA catalysts with different Pd/Au ratios.



**Fig. S7** N<sub>2</sub> adsorption and desorption isotherms at 77 K for PdAu catalysts loaded on MSC-30 carbon with different Pd/Au ratios.

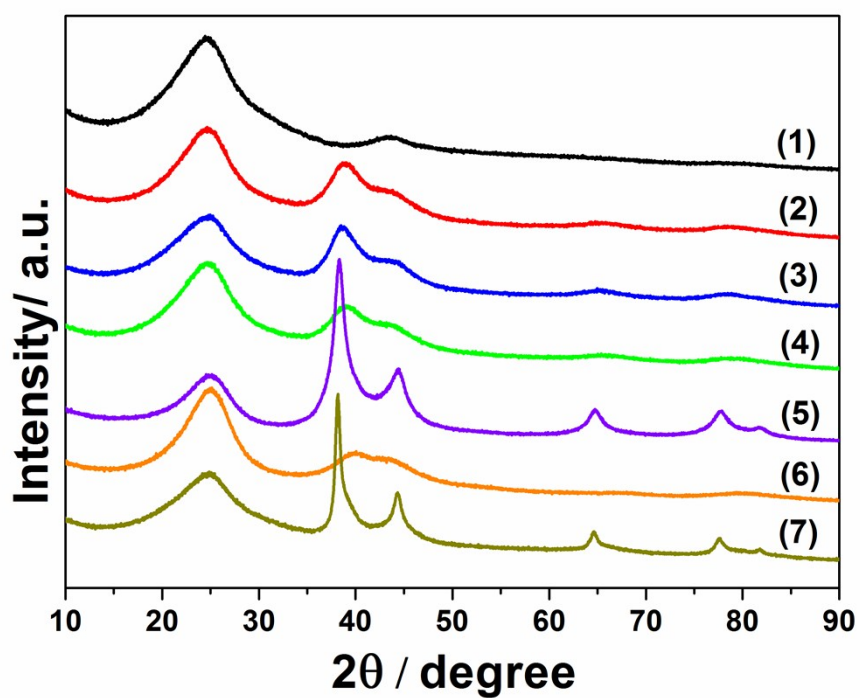


**Fig. S8** XPS spectra of the as-prepared Pd<sub>1</sub>Au<sub>1</sub>/30-LA catalyst: (A) Au 4f, (B) Pd 3d, (C) N1s.

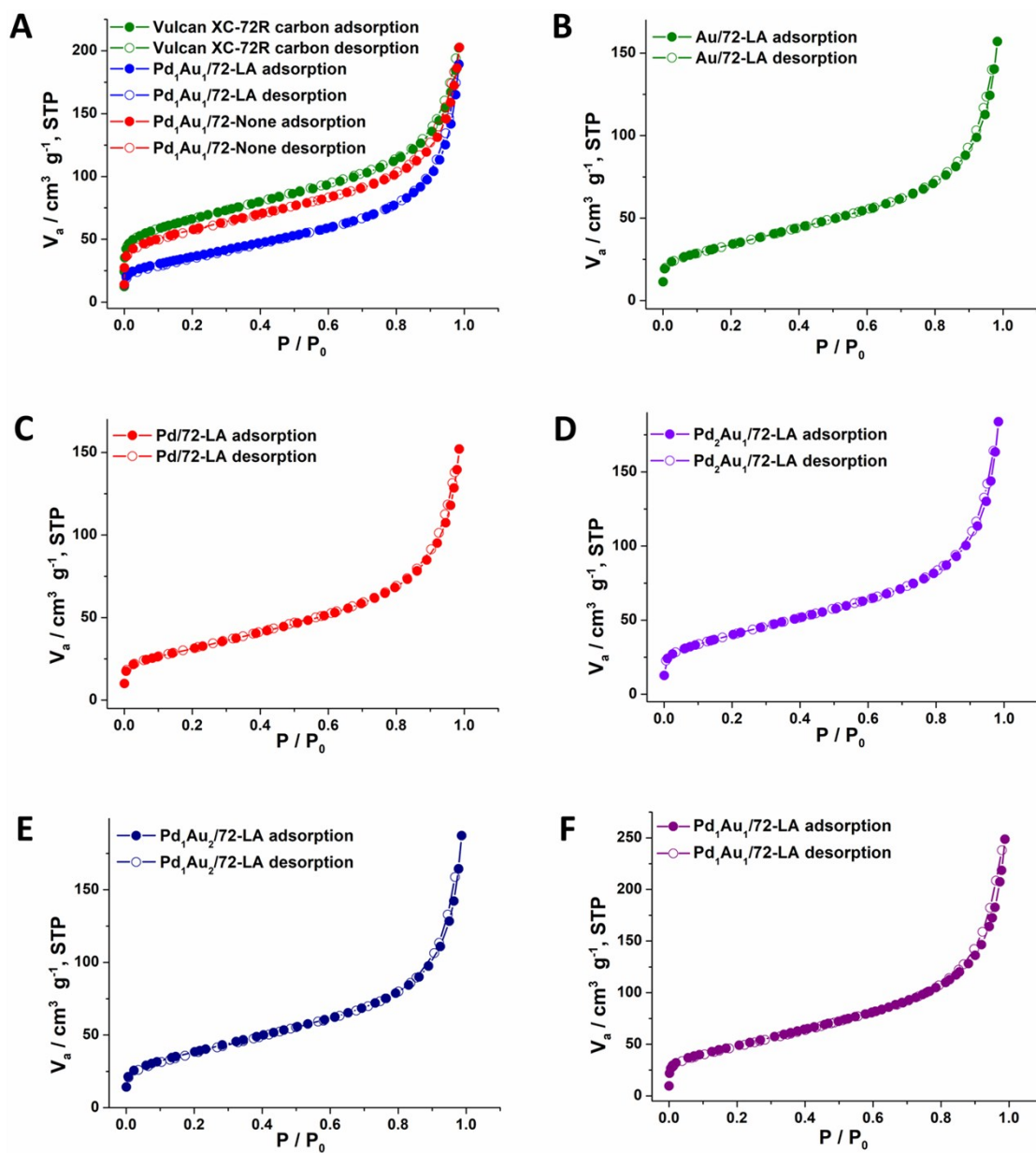


**Fig. S9** (A) TEM and the size distribution of PdAu NPs (inset), (B) HAADF-STEM and (C-E) EDS elemental mapping images of the as-prepared Pd<sub>1</sub>Au<sub>1/72</sub>-LA catalyst.

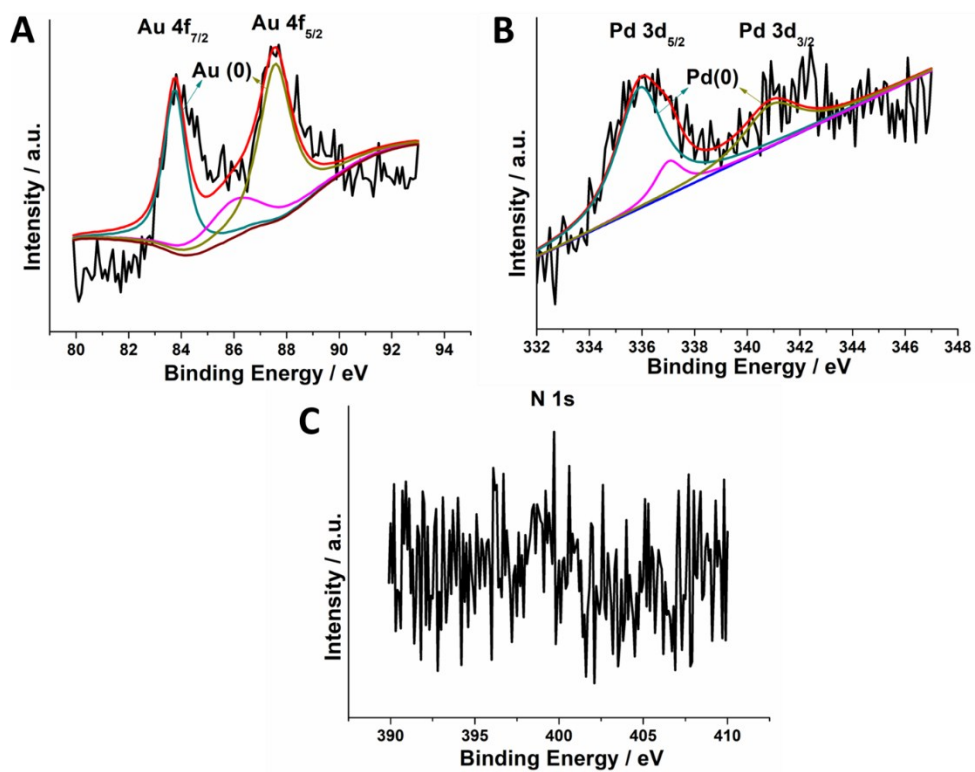




**Fig. S10** XRD patterns of the different products. (1) Vulcan XC-72R carbon, (2) Pd<sub>1</sub>Au<sub>1</sub>/72-LA, (3) Pd<sub>1</sub>Au<sub>2</sub>/72-LA, (4) Pd<sub>2</sub>Au<sub>1</sub>/72-LA, (5) Au/72-LA, (6) Pd/72-LA and (7) Pd<sub>1</sub>Au<sub>1</sub>/72-None.



**Fig. S11**  $N_2$  adsorption and desorption isotherms at 77 K of, (A) commercial Vulcan XC-72R carbon, Pd<sub>1</sub>Au<sub>1</sub>/72-LA and Pd<sub>1</sub>Au<sub>1</sub>/72-None, (B) Au/72-LA, (C) Pd/72-LA, (D) Pd<sub>2</sub>Au<sub>1</sub>/72-LA, (E) Pd<sub>1</sub>Au<sub>2</sub>/72-LA and (F) the Pd<sub>1</sub>Au<sub>1</sub>/72-LA after catalysis.



**Fig. S12** XPS spectra of the as-prepared Pd<sub>1</sub>Au<sub>1/72</sub>-LA catalyst: (A) Au 4f, (B) Pd 3d, (C) N1s.

**Table S1** ICP results of the as-prepared samples.

Element Sample	Au (mass ratio %)	Pd (mass ratio %)	Au : Pd (molar ratio)
<b>Pd<sub>1</sub>Au<sub>1</sub>/30-LA</b>	3.4	1.8	1.72 : 1.69
<b>Pd<sub>2</sub>Au<sub>1</sub>/30-LA</b>	1.7	1.9	0.863 : 1.78
<b>Pd<sub>1</sub>Au<sub>2</sub>/30-LA</b>	4.0	1.1	2.03 : 1.03
<b>Pd<sub>1</sub>Au<sub>1</sub>/72-LA</b>	4.7	2.7	2.39 : 2.54
<b>Pd<sub>2</sub>Au<sub>1</sub>/72-LA</b>	2.9	3.5	1.47 : 3.29
<b>Pd<sub>1</sub>Au<sub>2</sub>/72-LA</b>	6.4	1.8	3.25 : 1.69
<b>Pd<sub>1</sub>Au<sub>1</sub>/20-LA</b>	2.3	0.9	1.17 : 0.846

**Table S2** Elemental analysis results of the as-prepared samples.

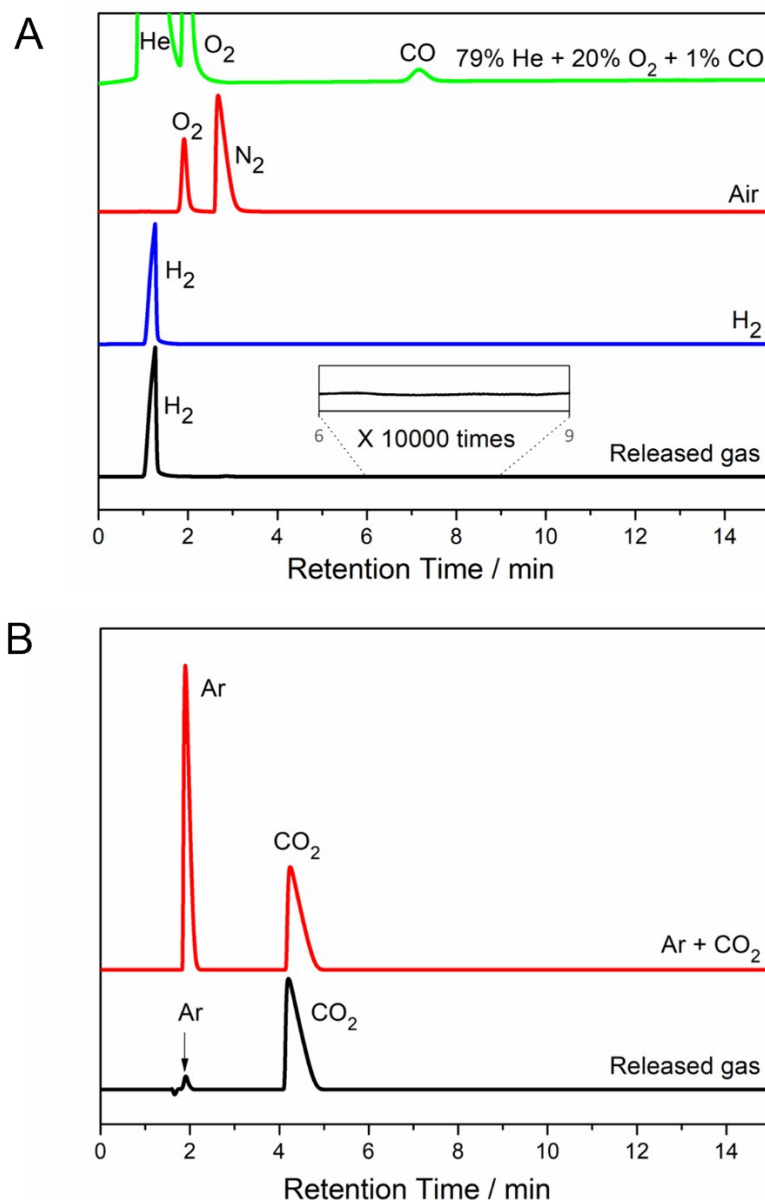
Element Sample	C (mass ratio %)	H (mass ratio %)	N (mass ratio %)
<b>Pd<sub>1</sub>Au<sub>1</sub>/30-LA</b>	68.6	2.83	8.76
<b>Pd<sub>1</sub>Au<sub>1</sub>/72-LA</b>	86.41	0.35	—
<b>Pd<sub>1</sub>Au<sub>1</sub>/20-LA</b>	71.93	2.65	7.53
<b>Pd<sub>1</sub>Au<sub>1</sub>/30-LA-after catalysis</b>	74.06	2.12	5.99

Note: For Pd<sub>1</sub>Au<sub>1</sub>/72-LA catalyst, there was no detectable N element.

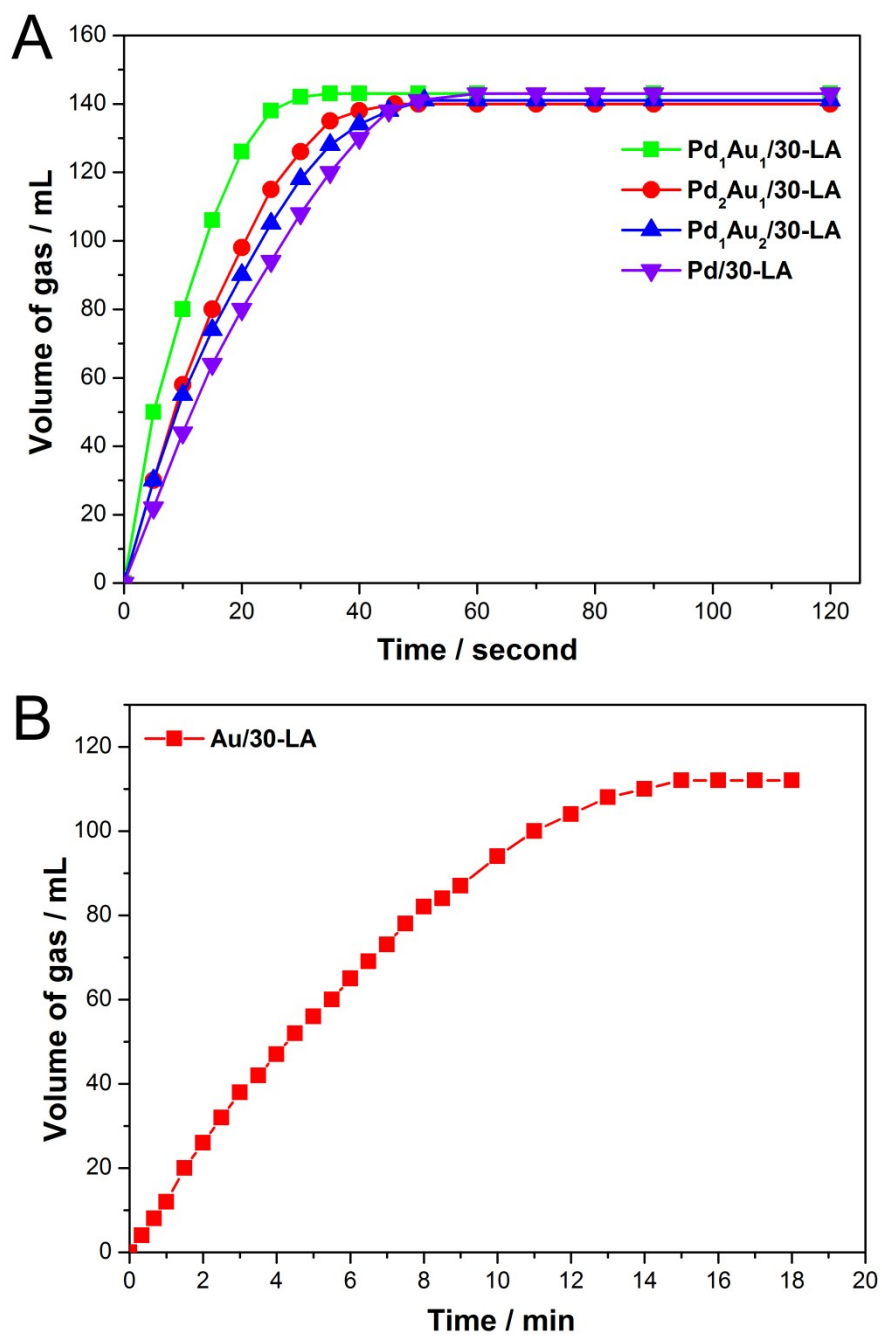
**Table S3** BET surface areas and pore volumes of different samples.

Sample	BET surface area / m <sup>2</sup> g <sup>-1</sup>	Pore volume cm <sup>-3</sup> g <sup>-1</sup>
MSC-30	3509.8	1.8448
Pd <sub>1</sub> Au <sub>1</sub> /30-LA	1372.3	0.7111
Pd <sub>2</sub> Au <sub>1</sub> /30-LA	1246.5	0.6544
Pd <sub>1</sub> Au <sub>2</sub> /30-LA	1281.5	0.668
Pd/30-LA	1456.2	0.7646
Au/30-LA	1264.0	0.6689
Pd <sub>1</sub> Au <sub>1</sub> /30-LA-after catalysis	2061.4	1.0775
Pd <sub>1</sub> Au <sub>1</sub> /30-None	2659.4	1.4081
Pd <sub>1</sub> Au <sub>1</sub> /30-None+LA	2100.0	1.0893
Pd <sub>1</sub> Au <sub>1</sub> /30-NaOH	2578.3	1.3407
Pd <sub>1</sub> Au <sub>1</sub> /30-LL	1998.1	1.0347
Pd <sub>1</sub> Au <sub>1</sub> /30-PA	2870.6	1.5385
Pd <sub>1</sub> Au <sub>1</sub> /30-EG	2792.7	1.4534
Pd <sub>1</sub> Au <sub>1</sub> /30-TSC	3459.6	1.8244
Commercial Pd/C	971.3	0.7850
Commercial Pd/C+LA	685.2	0.6115
MSP-20X	2142.6	1.0287
Pd <sub>1</sub> Au <sub>1</sub> /20-LA	726.8	0.3665
Vulcan XC-72R carbon	232.4	0.3129
Pd <sub>1</sub> Au <sub>1</sub> /72-LA	130.4	0.2928
Pd <sub>2</sub> Au <sub>1</sub> /72-LA	144.1	0.2843
Pd <sub>1</sub> Au <sub>2</sub> /72-LA	138.9	0.2896
Pd/72-LA	112.7	0.2350
Au/72-LA	122.2	0.2429
Pd <sub>1</sub> Au <sub>1</sub> /72-None	203.2	0.3136
Pd <sub>1</sub> Au <sub>1</sub> /72-LA-after catalysis	177.3	0.3847

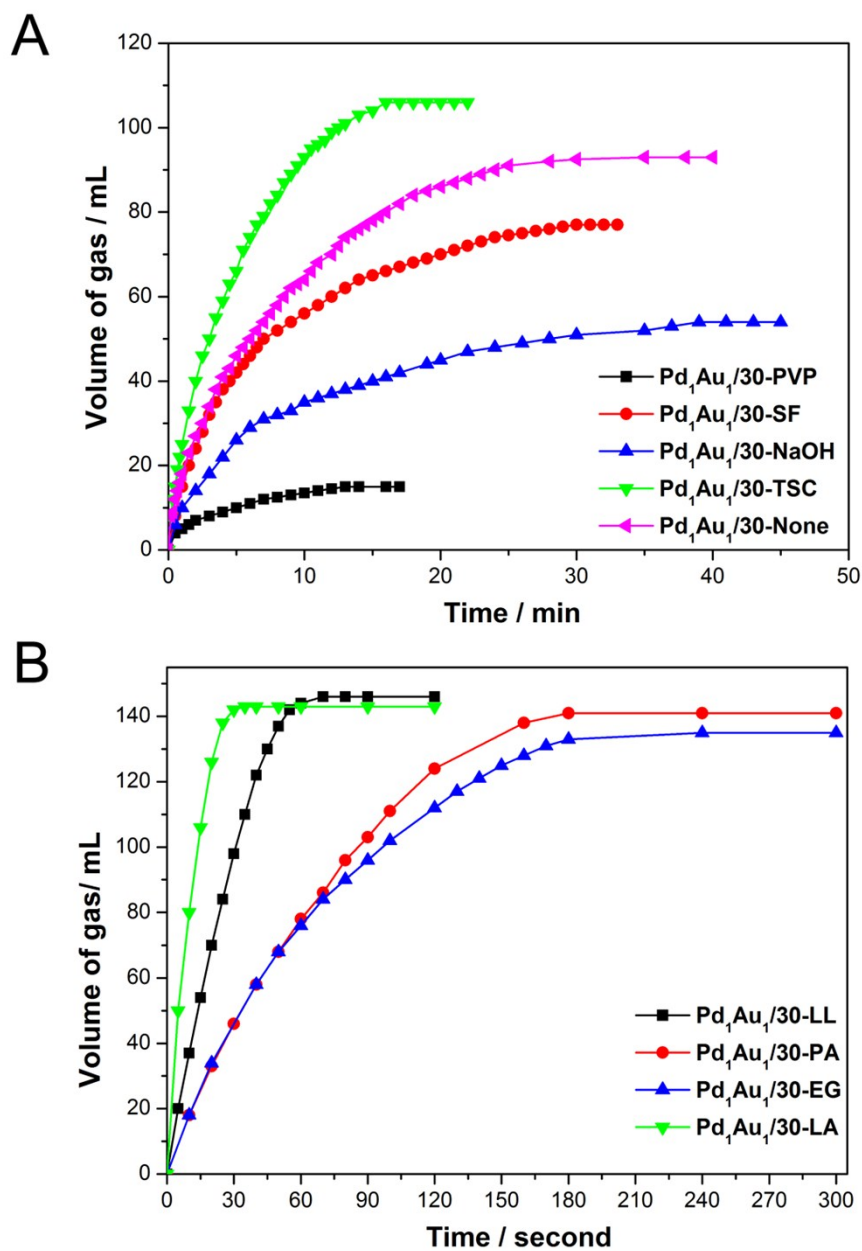
Note: The commercial Pd/C+LA catalyst was prepared as follows: 0.128 g of the commercial Pd/C catalyst was mixed with 3 mL of LA (0.1 g m L<sup>-1</sup>), then diluted to 45 mL with water. The mixture was shaken for one hour, then collected by centrifugation and washed for several times. Finally, the sample was dried at room temperature in vacuum.



**Fig. S13** Gas chromatograms of gas generated from FA dehydrogenation over the as-prepared Pd<sub>1</sub>Au<sub>1</sub>/30-LA catalyst at 50 °C, (A) with CO, air, H<sub>2</sub> and (B) CO<sub>2</sub> as the reference gases, respectively. The results demonstrate the presence of H<sub>2</sub> and CO<sub>2</sub> in the released gas, and no CO was observed at the detection limit. The analysis was performed using, (A) packed column Molecular Sieve 5A and carrier gas Ar and (B) packed column Porapak N and carrier gas He.

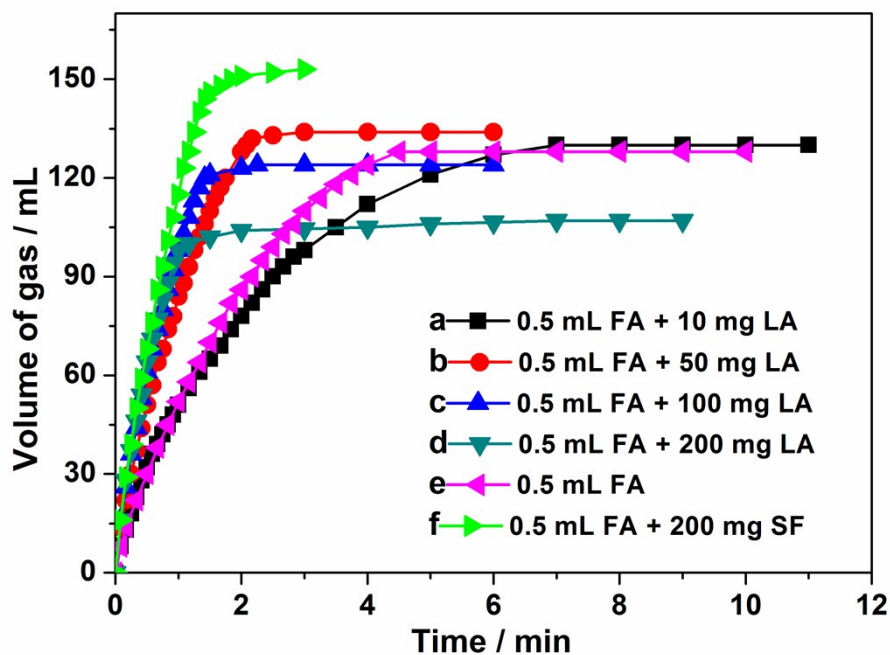


**Fig. S14** The volume of the generated gas ( $H_2 + CO_2$ ) from formic acid dehydrogenation versus time over the as-prepared PdAu/30-LA catalysts with different Au/Pd ratios at 50 °C ( $n_{FA} = 3 \text{ mmol}$ ,  $n_{metal} : n_{FA} = 0.02$ ).

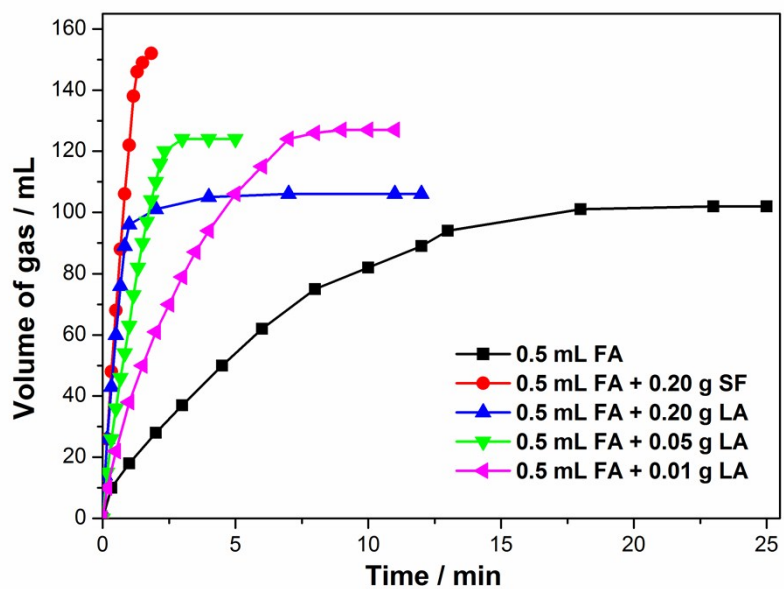


**Fig. S15** The volume of the generated gas ( $H_2 + CO_2$ ) from formic acid dehydrogenation versus time over the as-prepared Pd<sub>1</sub>Au<sub>1</sub>/30-X (X represents different mediate reagents) catalysts synthesized with different mediated molecules at 50 °C ( $n_{FA} = 3$  mmol,  $n_{metal} : n_{FA} = 0.02$ ).

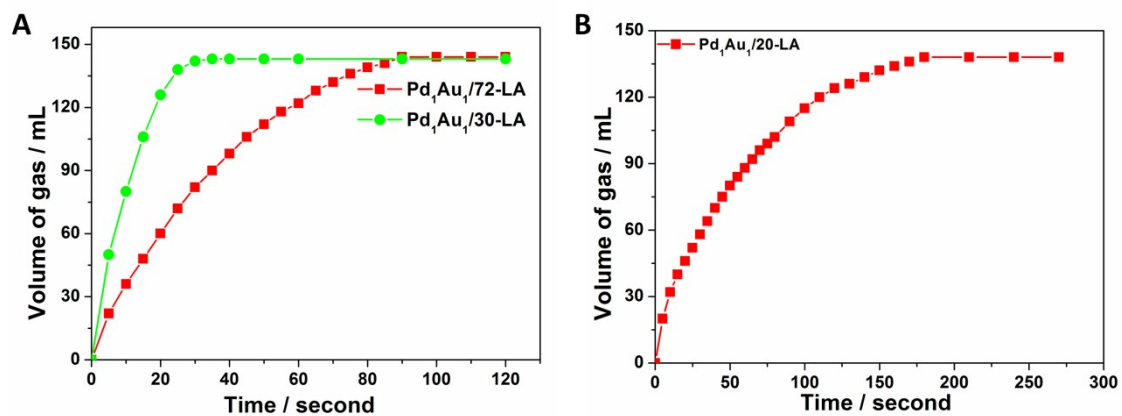




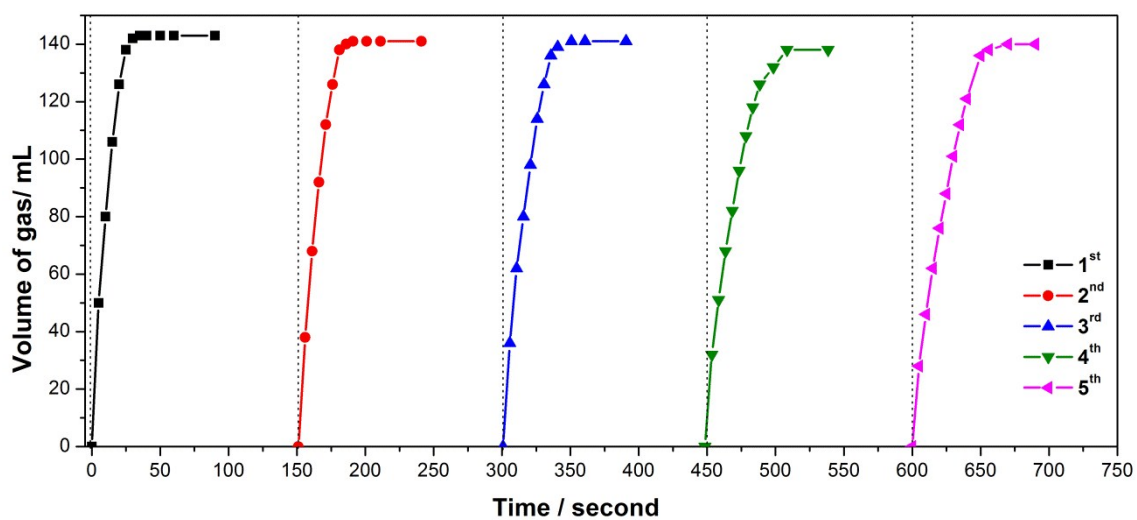
**Fig. S16** The volume of the generated gas ( $H_2 + CO_2$ ) from formic acid dehydrogenation versus time over the  $Pd_1Au_1/30$ -None catalyst in different solutions at  $50\text{ }^\circ\text{C}$  (FA:  $6\text{ mol L}^{-1}$ ,  $n_{metal} : n_{FA} = 0.02$ ). For curve (e) the  $Pd_1Au_1/30$ -None catalyst was treated as follows: the  $Pd_1Au_1/30$ -None catalyst was mixed with  $3\text{ mL}$  of LA ( $0.1\text{ g mL}^{-1}$ ), diluted to  $45\text{ mL}$  and shaken for  $5\text{ hours}$ . Then the catalyst was washed with water for several times and finally collected by centrifugation.



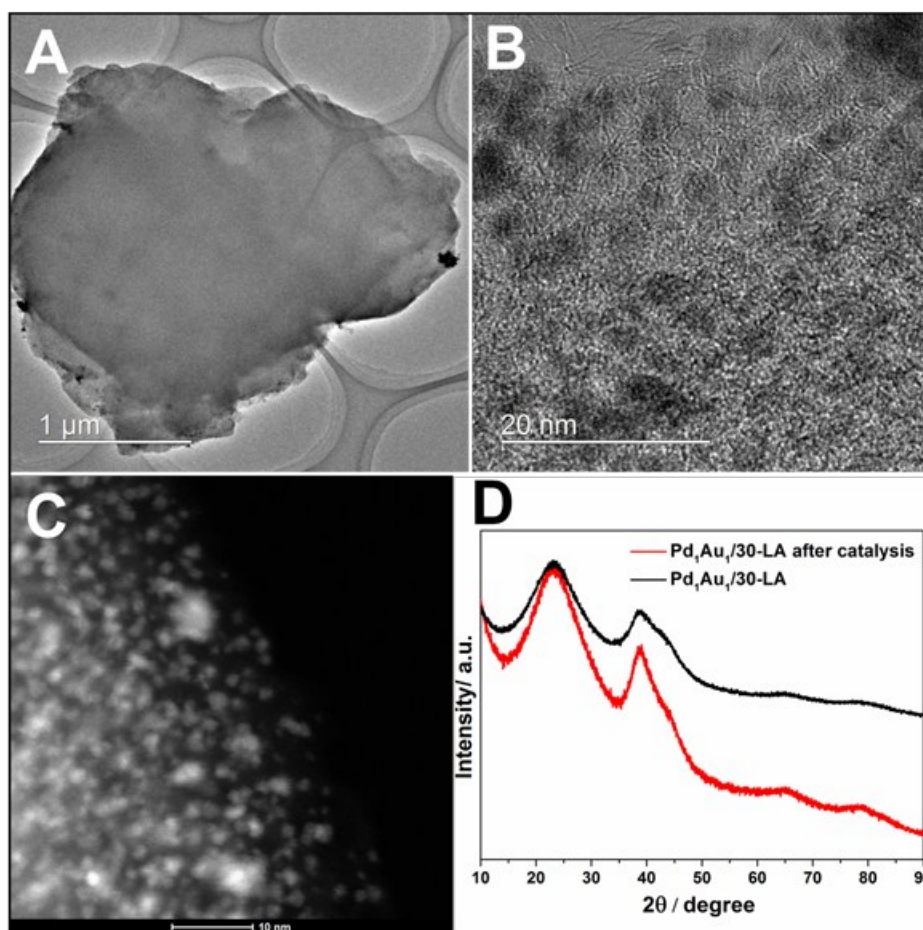
**Fig. S17** The volume of the generated gas ( $H_2 + CO_2$ ) from formic acid dehydrogenation versus time over the commercial Pd/C catalyst in different solutions at 50 °C (FA: 6 mol  $L^{-1}$ ,  $n_{metal} : n_{FA} = 0.02$ ).



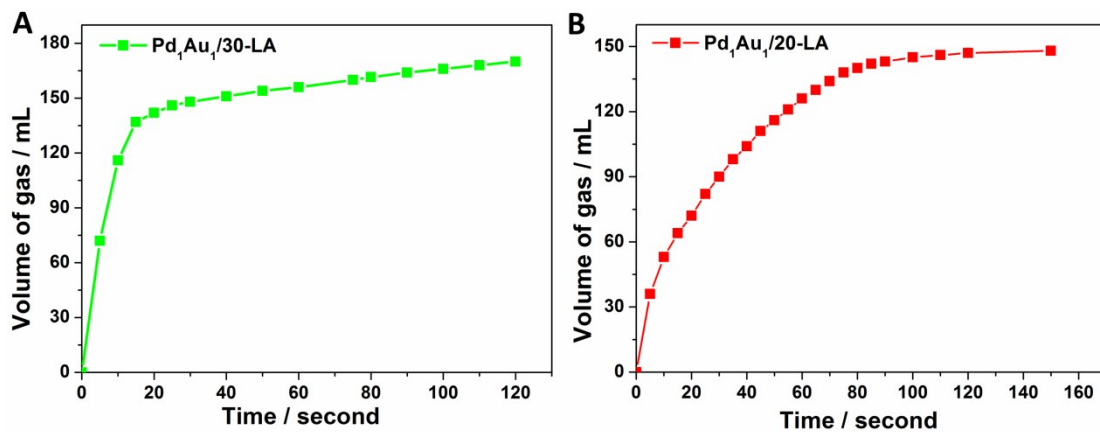
**Fig. S18** Volume of gas ( $H_2 + CO_2$ ) released from formic acid dehydrogenation versus time over (A)  $Pd_1Au_1/30-LA$  and  $Pd_1Au_1/72-LA$ , and (B)  $Pd_1Au_1/20-LA$  at  $50\text{ }^\circ C$  ( $n_{FA} = 3\text{ mmol}$ ,  $n_{metal} : n_{FA} = 0.02$ ).



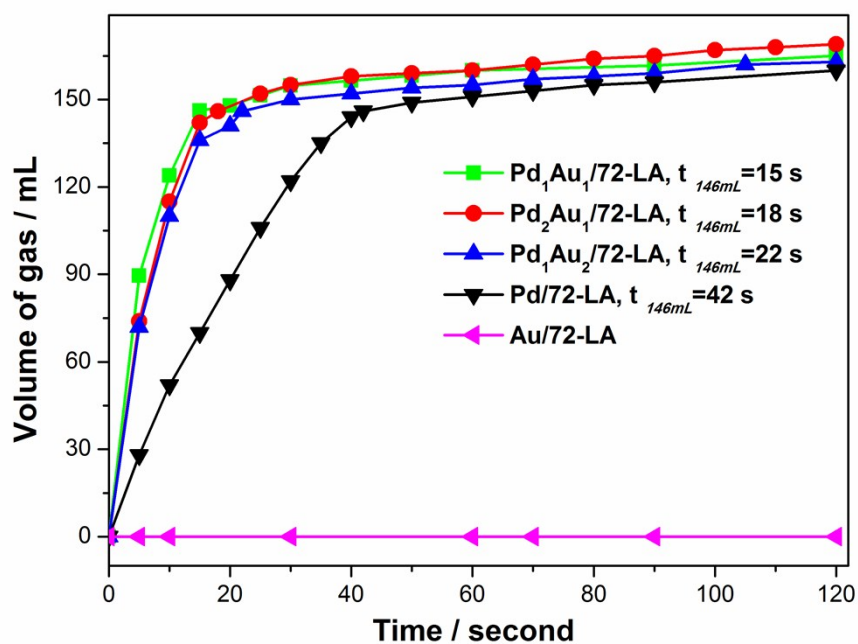
**Fig. S19** Durability test of the as-prepared Pd<sub>1</sub>Au<sub>1</sub>/30-LA catalyst for the dehydrogenation of FA at 50 °C by consecutively adding 0.5 mL of FA (FA: 6 mol L<sup>-1</sup>,  $n_{metal} : n_{FA} = 0.02$ ).



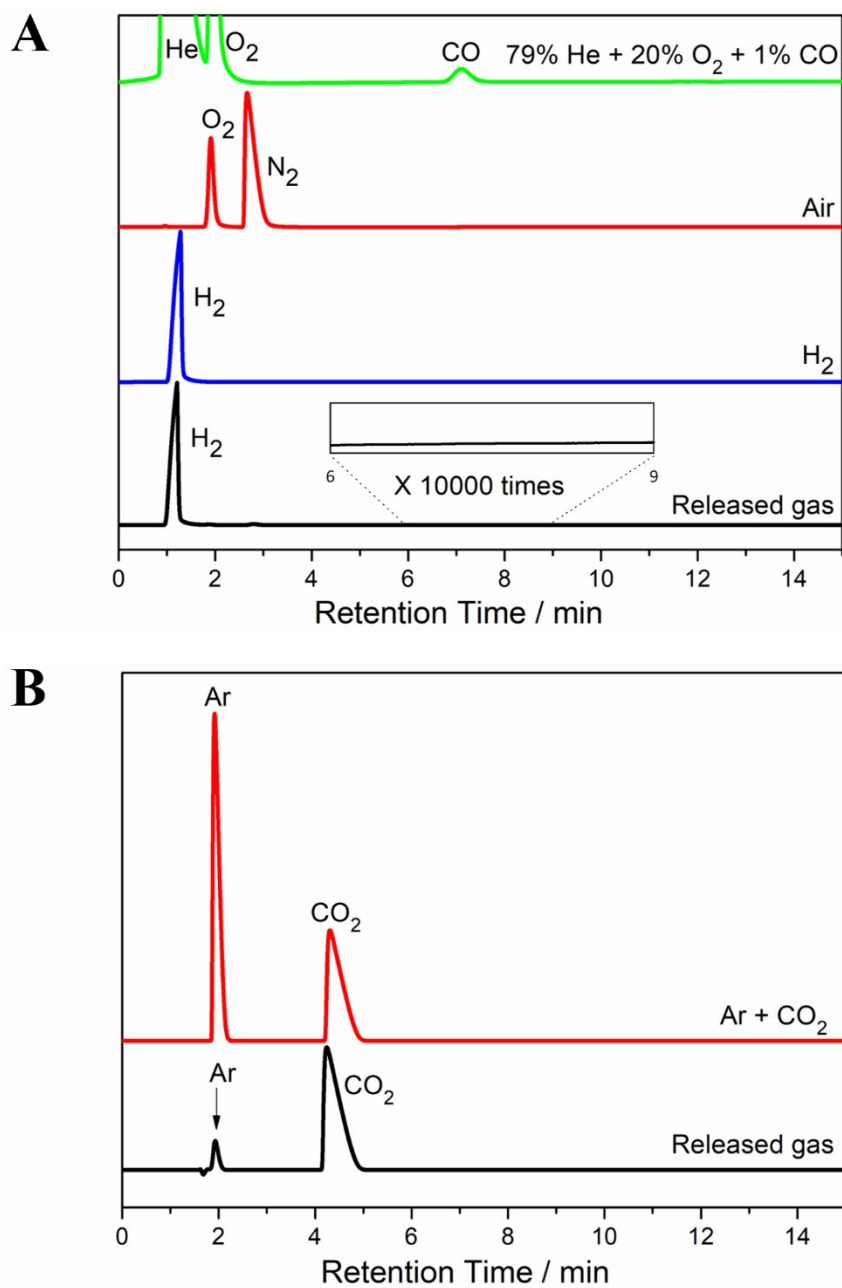
**Fig. S20** (A, B) TEM, (C) HAADF-STEM images and (D) XRD pattern of the as-prepared  $\text{Pd}_1\text{Au}_1/30\text{-LA}$  catalyst after 5 runs for the dehydrogenation of FA at 50 °C. XRD pattern of the  $\text{Pd}_1\text{Au}_1/30\text{-LA}$  catalyst before the catalysis was also provided in (D) for comparison.



**Fig. S21** Volume of gas ( $H_2 + CO_2$ ) released from formic acid dehydrogenation versus time over (A) Pd<sub>1</sub>Au<sub>1</sub>/30-LA and (B) Pd<sub>1</sub>Au<sub>1</sub>/20-LA at 60 °C ( $n_{FA} = 3$  mmol,  $n_{FA} / n_{SF} = 1 : 3$ ,  $n_{Pd+Au} : n_{FA} = 0.02$ ).

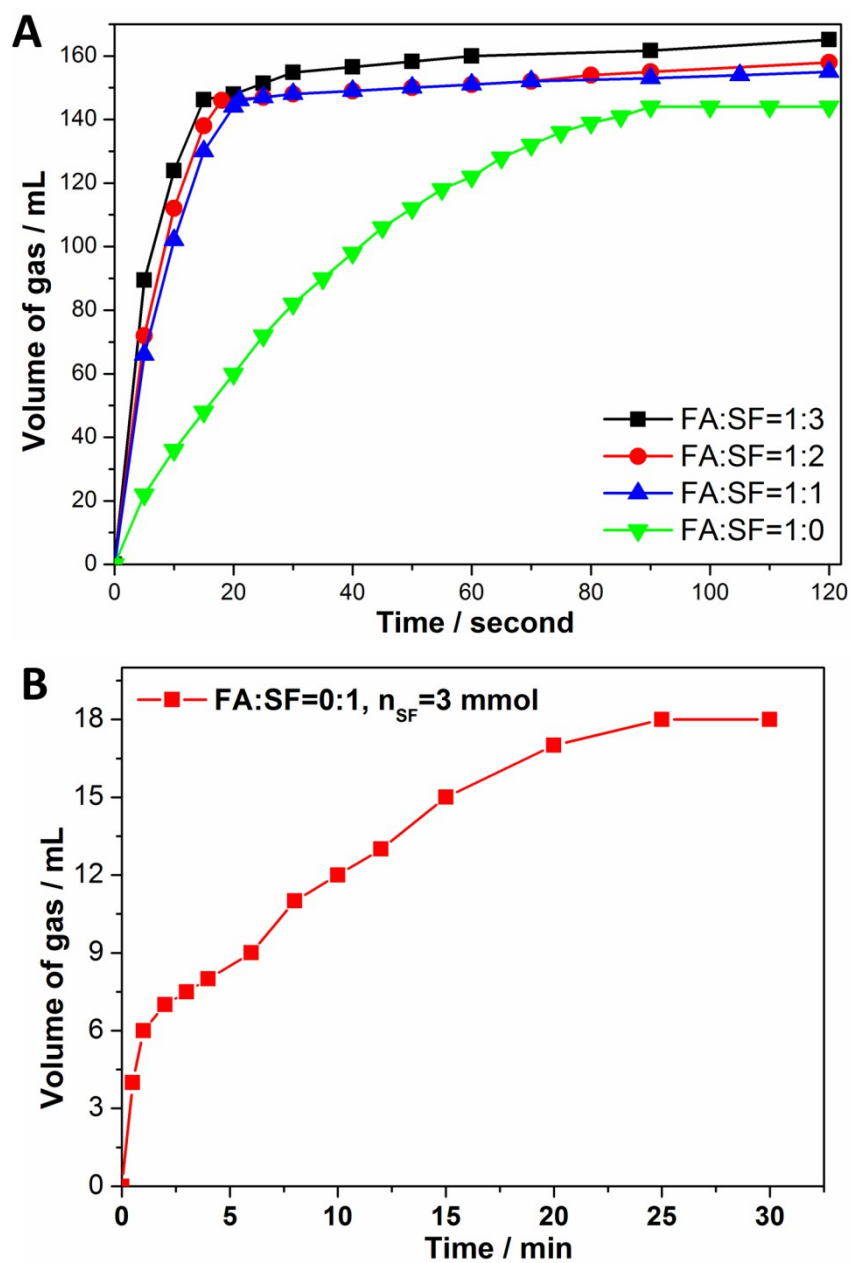


**Fig. S22** Volume of gas ( $H_2 + CO_2$ ) released from formic acid dehydrogenation versus the time over the as-prepared PdAu/72-LA catalysts with different Au/Pd ratios at 60 °C ( $n_{FA} = 3$  mmol,  $n_{FA} / n_{SF} = 1 : 3$ ,  $n_{metal} : n_{FA} = 0.02$ ).

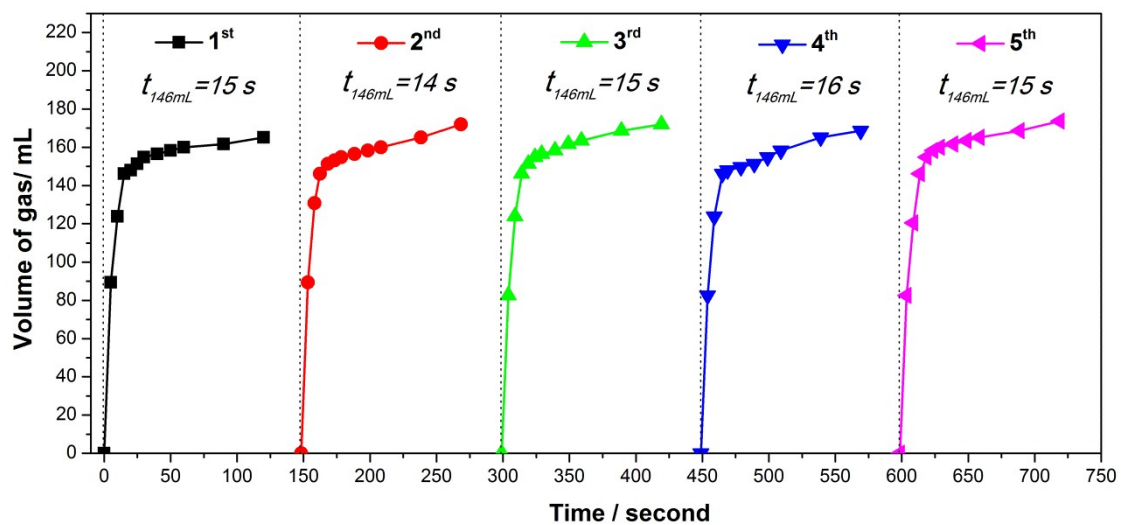


**Fig. S23** Gas chromatograms of gas generated from FA dehydrogenation over the as-prepared Pd<sub>1</sub>Au<sub>1</sub>/72-LA catalyst at 60 °C, with CO, air, H<sub>2</sub> (A) and CO<sub>2</sub> (B) as the reference gases respectively. The results demonstrate the presence of H<sub>2</sub> and CO<sub>2</sub> in the released gas, and no CO gas was observed at the detection limit.

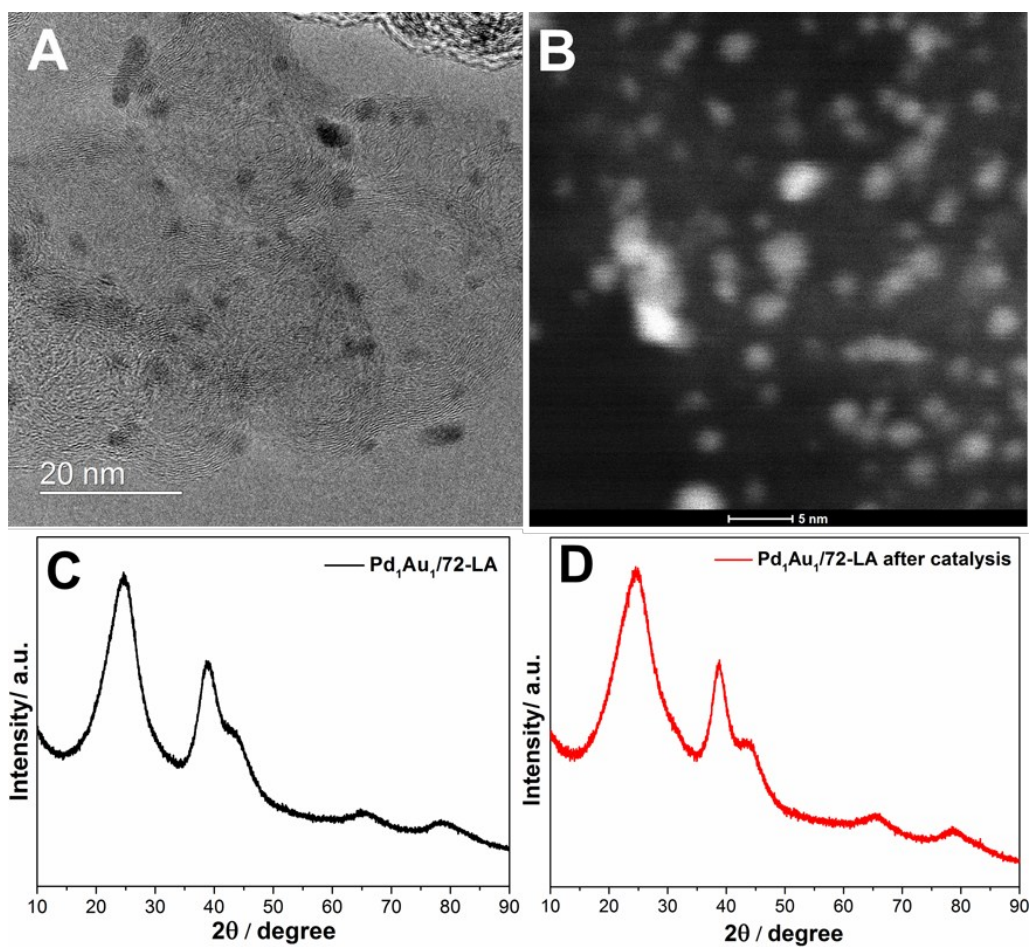




**Fig. S24** (A, B) Volume of gas ( $H_2 + CO_2$ ) released from formic acid dehydrogenation versus time over the as-prepared  $Pd_1Au_{1/72}$ -LA catalyst at  $60\text{ }^\circ\text{C}$ , with different FA/SF ratios ( $n_{FA} = 3\text{ mmol}$ ,  $n_{FA} / n_{SF} = 1 : 3$ ,  $n_{metal} : n_{FA} = 0.02$ ).



**Fig. S25** Durability test of the as-prepared Pd<sub>1</sub>Au<sub>1</sub>/72-LA catalyst for the dehydrogenation of FA at 60 °C, in an aqueous FA/SF solution ( $n_{FA} = 3$  mmol,  $n_{FA} / n_{SF} = 1 : 3$ ,  $n_{metal} : n_{FA} = 0.02$ ).



**Fig. S26** (A) TEM, (B) HAADF-STEM images and (D) XRD pattern of as-prepared Pd<sub>1</sub>Au<sub>1</sub>/72-LA catalyst. XRD pattern of the Pd<sub>1</sub>Au<sub>1</sub>/72-LA catalyst (C) before and (D) after catalysis.

**Table S4** Formic acid dehydrogenation performance over different state-of-art heterogeneous catalysts.

Catalyst	Medium	Temp. /K	CO evolution	TOF/ h <sup>-1</sup>	E <sub>a</sub> /kJ mol <sup>-1</sup>	Ref.
<b>Pd<sub>1</sub>Au<sub>1</sub>/30-LA</b>	FA	298		1881	38.9	This work
		303		2069		
		313		3168		
		323	no	5013		
		333		8355		
<b>Pd<sub>1</sub>Au<sub>1</sub>/72-LA</b>	FA/SF	303		3583	34.4	This work
		313		5268		
		323		8530		
<b>Au@Schiff-SiO<sub>2</sub></b>	FA	323	no	1633*	71.6	1
		333	no	11958		
		333	no	11958		
<b>Pd/CN<sub>0.25</sub></b>	FA	298	no	391*	48.8	2
<b>Co<sub>0.30</sub>Au<sub>0.35</sub>Pd<sub>0.35</sub>/C</b>	FA	298	no	4.6*	—	3
<b>AuPd-MnO<sub>x</sub>/ZIF-8-rGO</b>	FA	298	no	122*	—	4
<b>0.8Pd0.2Ni(OH)<sub>2</sub>@S-1</b>	FA	333	< 10 ppm	1876*	52.4	5
<b>Au/ZrO<sub>2</sub> NCs</b>	FA/NEt <sub>3</sub>	323	<5 ppm	1063*	—	6
<b>Pd/N-MSC-30</b>	FA/SF	333	no	8414	43.7	7
<b>Pd/C<sub>m</sub></b>	FA/SF	333	no	5842*	39.6	8
<b>(Co<sub>6</sub>)Ag<sub>0.1</sub>Pd<sub>0.9</sub>/RGO</b>	FA/SF	333	no	4711	43.1	9
<b>Pd/MSC-30</b>	FA/SF	323	no	2623	38.6	10
<b>Pd/S-1-in-K</b>	FA/SF	323	< 10 ppm	3027	39.2	11
<b>Pd/PDA-rGO</b>	FA/SF	323	no	3810	54.3	12

<b>Co<sub>48</sub>Au<sub>5</sub>Pd<sub>47</sub> @MIL-101-NH<sub>2</sub> Pd@CN900K</b>	FA/SF	323	no	361	67.1	13
	FA/SF	333	no	14400	46.9	14
<b>Catalyst</b>	<b>Medium</b>	<b>Temp. /K</b>	<b>CO evolution</b>	<b>TOF/ h<sup>-1</sup></b>	<b>E<sub>a</sub> /kJ mol<sup>-1</sup></b>	<b>Ref.</b>

FA = formic acid, SF = sodium formate. The TOF with a symbol of ‘\*’ was calculated by us from the reported results.

## References

- 1 Q. Liu, X. Yang, Y. Huang, S. Xu, X. Su, X. Pan, J. Xu, A. Wang, C. Liang, X. Wang, T. Zhang, *Energy Environ. Sci.*, 2015, **8**, 3204.
- 2 Q. Y. Bi, J. D. Lin, Y. M. Liu, H. Y. He, F. Q. Huang, Y. Cao, *Angew. Chem. Int. Ed.*, 2016, **55**, 11849.
- 3 Z. L. Wang, J. M. Yan, Y. Ping, H. L. Wang, W. T. Zheng, Q. Jiang, *Angew. Chem. Int. Ed.*, 2013, **52**, 4406.
- 4 J.-M. Yan, Z.-L. Wang, L. Gu, S.-J. Li, H.-L. Wang, W.-T. Zheng, Q. Jiang, *Adv. Energy Mater.*, 2015, **5**, 1500107.
- 5 Q. Sun, N. Wang, Q. Bing, R. Si, J. Liu, R. Bai, P. Zhang, M. Jia, J. Yu, *Chem*, 2017, **3**, 477.
- 6 Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *J. Am. Chem. Soc.*, 2012, **134**, 8926.

- 7 Z. Li, X. Yang, N. Tsumori, Z. Liu, Y. Himeda, T. Autrey, Q. Xu, *ACS Catal.*, 2017, **7**, 2720.
- 8 Q. L. Zhu, N. Tsumori, Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 11743.
- 9 Y. Chen, Q. L. Zhu, N. Tsumori, Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 106.
- 10 Q.-L. Zhu, N. Tsumori, Q. Xu, *Chem. Sci.*, 2014, **5**, 195.
- 11 N. Wang, Q. Sun, R. Bai, X. Li, G. Guo, J. Yu, *J. Am. Chem. Soc.*, 2016, **138**, 7484.
- 12 F.-Z. Song, Q.-L. Zhu, N. Tsumori, Q. Xu, *ACS Catal.*, 2015, **5**, 5141.
- 13 P. Zhao, W. Xu, D. Yang, W. Luo, G. Cheng, *ChemistrySelect*, 2016, **1**, 1400.
- 14 Q. Wang, N. Tsumori, M. Kitta and Q. Xu, *ACS Catal.*, 2018, **8**, 12041.