Supporting information for

Efficient dehydrogenation of formic acid-ammonium formate mixture over Au$_3$Pd$_1$ catalyst

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S1. Calculation methods:

(1) The turnover of frequency (TOF) is calculated based on the amount of Pd and Au atoms in the catalyst using the following equation:

$$\text{TOF} = \frac{pV / RT}{n_{\text{Pd+Au}}t}$$

where p is the atmospheric pressure, V is the volume of H_2 measured at standard temperature and pressure (STP), R is the universal gas constant, T is the absolute temperature, $n_{\text{Pd+Au}}$ is the mole number of Pd and Au in the catalyst, and t is the reaction time.

(2) The content of NH_3 is calculated as follows:

$$x_{\text{NH}_3} = \frac{m \times 25 \times 22.4 \times 1000}{14.01 V_{\text{CO}_2 + \text{H}_2}}$$

Where x_{NH_3} is the NH_3 content in ppm, m (mg/L) *is* the concentration of N in the diluted H_2SO_4 solution, 14.01 is the relative atomic mass of N, 22.4 is the standard molar volume of ideal gases at STP.

The content of NH_3 reported in the text was based on three experimental results. The measurement of NH_3 content was based on the relevant standards (GB/T 18204. 25—2000, HJ 535—2009).
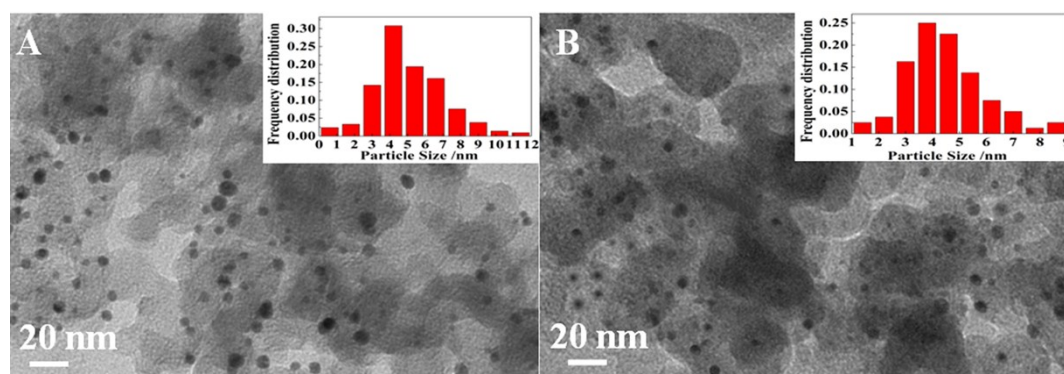
S2. TEM images for the AuPd/C catalysts.

Fig. S1 TEM images and particle size distribution of the newly prepared (A) $Au_{0.5}Pd_1/C$, (B) Au_1Pd_1/C, (C) Au_2Pd_1/C, (D) Au_4Pd_1/C and (E) Au_5Pd_1/C catalysts.
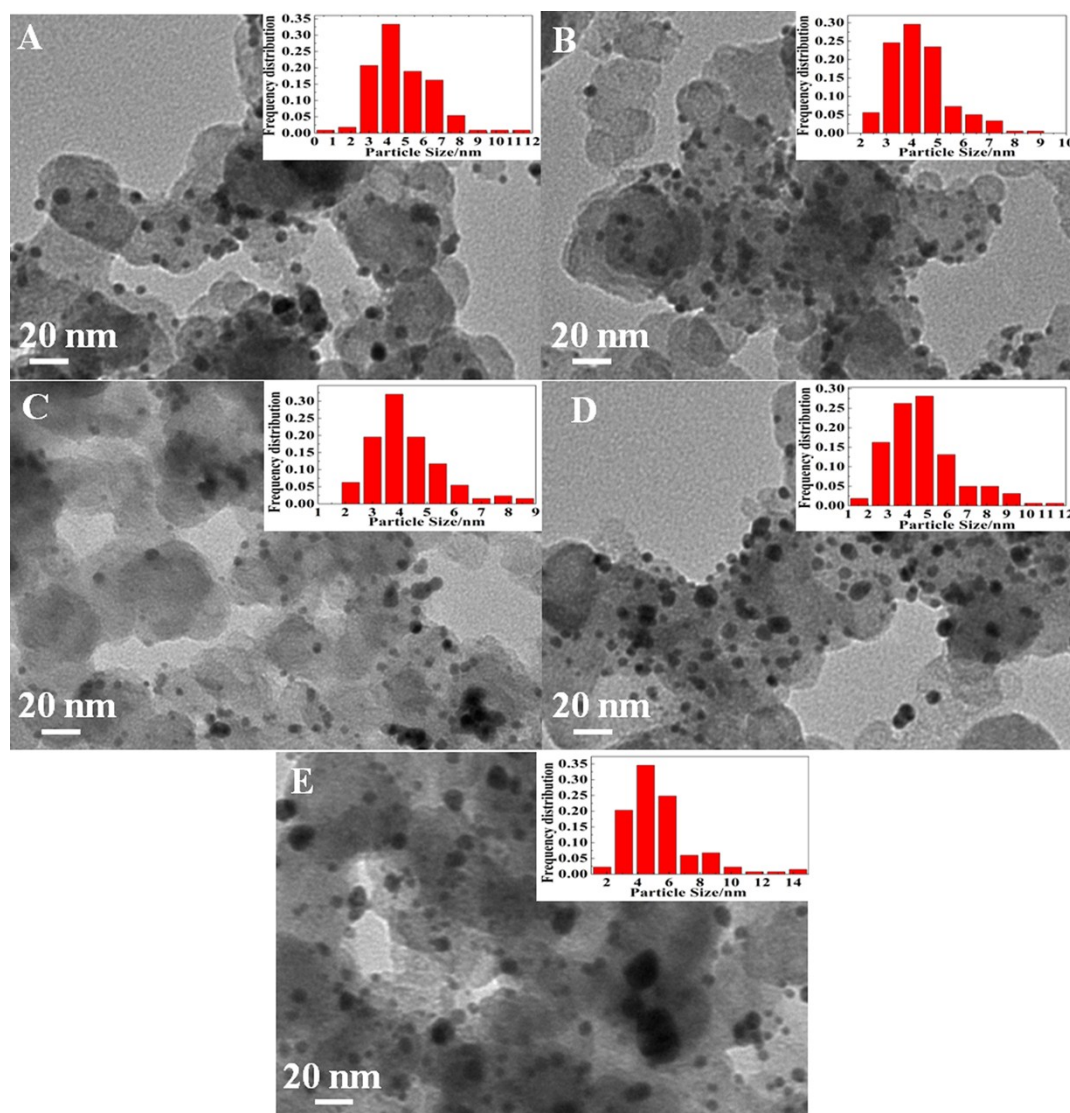
The mean particle sizes of the $Au_{0.5}Pd_1/C$, Au_1Pd_1/C, Au_2Pd_1/C, Au_4Pd_1/C and Au_5Pd_1/C catalysts were 4.86, 4.29, 4.25, 4.78 and 5.33 nm, respectively.

Fig. S2 TEM images and particle size distribution of the recovered Au_3Pd_1/C catalysts

after the 2nd run (A) and 4th run (B).

S3. Composition analysis for the AuPd/C catalysts.

Table S1. ICP results for the composition of the AuPd/C catalysts.

Catalyst	Metal content (wt%)	Atom ratio (Au/Pd)
$Au_{0.5}Pd_1/C$	Au, 22.37%; Pd, 25.70%	0.47
Au_1Pd_1/C	Au, 34.42%; Pd, 19.36%	0.96
Au_2Pd_1/C	Au, 43.30%; Pd, 12.14%	1.93
Au_3Pd_1/C	Au, 48.23%; Pd, 8.70%	2.99
Au_4Pd_1/C	Au, 50.47%; Pd, 7.06%	3.86
Au_5Pd_1/C	Au, 52.88%; Pd, 5.93%	4.82

Table S2. XPS results for the content of metal on the surface of AuPd/C catalysts.

Catalyst	Atomic %	Atom ratio (Au/Pd)
$Au_{0.5}Pd_1/C$	Au, 1.17%; Pd, 1.95%	0.6
Au_1Pd_1/C	Au, 1.85%; Pd, 1.89%	0.98
Au_2Pd_1/C	Au, 2.38%; Pd, 1.46%	1.63
Au_3Pd_1/C	Au, 0.74%; Pd, 0.31%	2.39
Au_4Pd_1/C	Au, 1.84%; Pd, 0.76%	2.42
Au_5Pd_1/C	Au, 2.23%; Pd, 0.85%	2.62

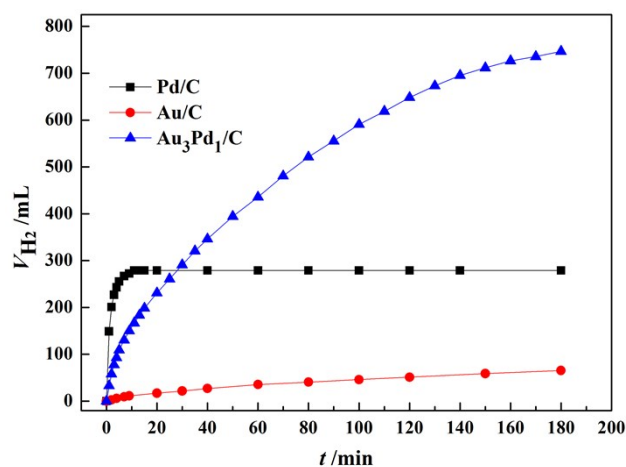## S4. Hydrogen generation over the Pd/C, Au/C, Au$_3$Pd$_1$/C catalysts.

Fig. S3 H$_2$ generation from 10 mL mixture with 3 mol/L FA and 3 mol/L AF over 60

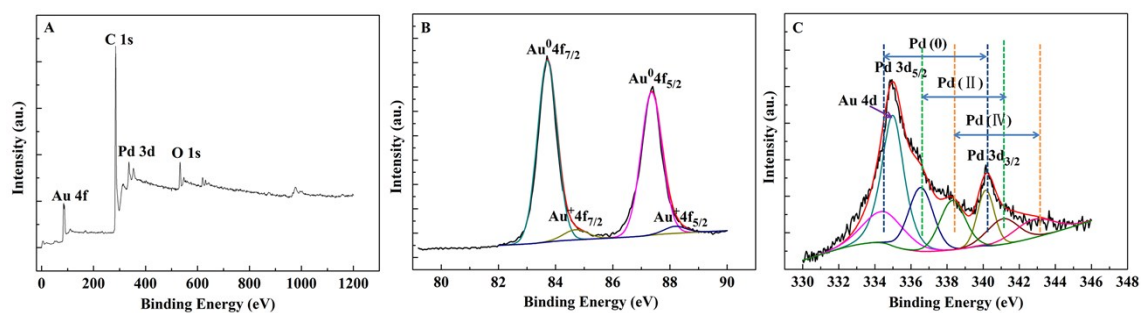mg of Pd/C, Au/C, Au$_3$Pd$_1$/C catalysts at 365 K.

S5. XPS spectrum of the Au$_3$Pd$_1$/C catalyst.

Fig. S4(A) XPS spectrum of the Au$_3$Pd$_1$/C catalyst; high-resolution XPS spectrum of

(B) Au 4f and (C) Pd 3d in the Au$_3$Pd$_1$/C catalyst.

S6. Detailed information for the dehydrogenation of FA-AF mixture.

Table S3. The maximum volume of H_2, initial TOF for the first 10 min, decomposition efficiency of FA (η_{FA}) and AF (η_{AF}) for 0.02 mol of FA-AF mixture at different concentrations.

c_{FA+AF}/mol/L	V_{H_2}/mL	Initial TOF/h^{-1}	η_{FA}/%	η_{AF}/%
2	310	145.1	100	38.4
4	330	227.8	100	47.3
6	330	269.6	100	47.3
8	307	293.1	100	37.1
10	315	312.2	100	40.6

S7. Comparison of activation energies of various catalysts.

Table S4. Comparison of activation energies of various catalysts for dehydrogenation of FA.

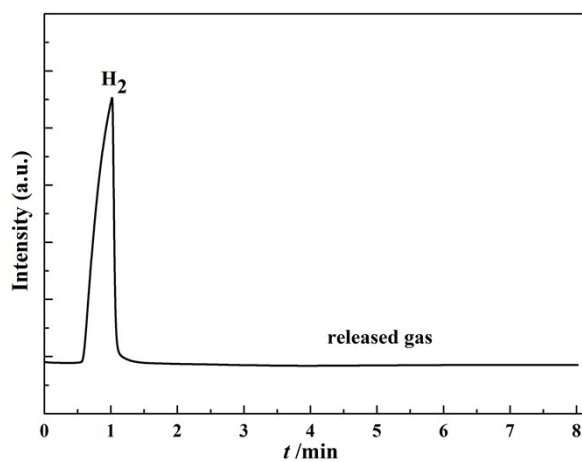| Catalysts	Ea (KJ/mol)	Ref
PtRuBiOx/C	37.3	[1]
Au/ZrO$_2$	49.3	[2]
Au$_{41}$Pd$_{59}$/C	28±2	[3]
(Co$_3$)$_E$Au$_{0.6}$Pd$_{0.4}$/rGO	39.77	[4]
Ag$_{10}$Pd$_{90}$/0.2CND/SBA-15	43.2	[5]
Pd$_{0.5}$Au$_{0.3}$Mn$_{0.2}$/N-SiO$_2$	26.2	[6]
Au$_{0.75}$Pd$_{0.25}$/C–L-7.5	42.23	[7]
5 wt% Pd/C	39	[8]
Au$_3$Pd$_1$/C	23.3±1.3	this study

S8. GC spectrum of the released gas.

Fig. S5 GC spectrum using TCD for the released gas from 5 mL mixture with 5 mol/L

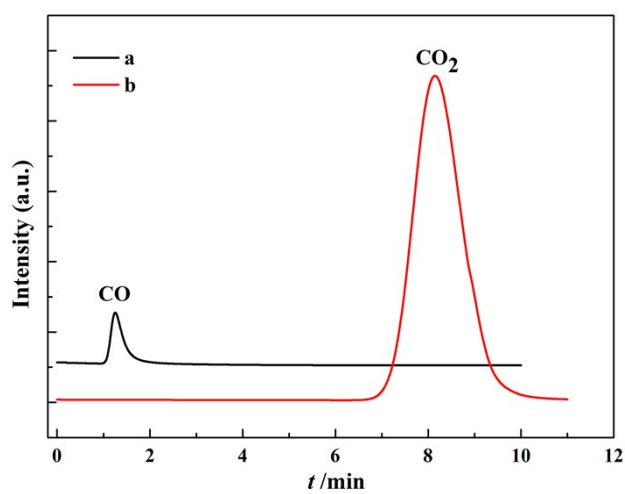FA and 7.5 mol/L AF over the Au_3Pd_1/C catalyst at 365 K.

Fig. S6 GC spectrum using FID-Methanator for the (a) pure CO and (b) released gas

from 5 mL mixture with 5 mol/L FA and 7.5 mol/L AF over the Au_3Pd_1/C catalyst at

365 K. The detection limit of CO is 5 ppm.
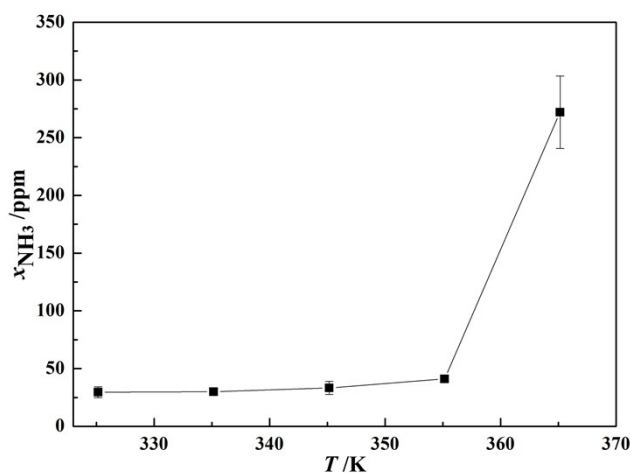
S9. The content of NH₃ from the released gas.

Fig. S7 The content of NH$_3$ from the released gas from 5 mL mixture with 5 mol/L FA and 7.5 mol/L AF at different temperatures over the Au$_3$Pd$_1$/C catalyst. The theoretical conversion of FA in each case is 10%.

S10 Notes and references

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