Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Efficient dehydrogenation of high concentration formic acid over PdAu/AC-NH_2 catalyst without additives under ambient conditions

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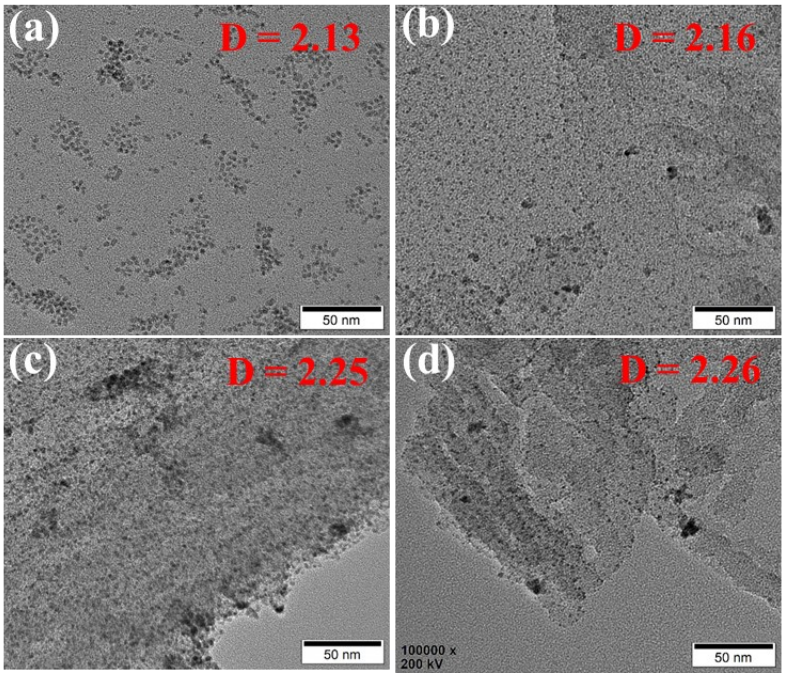

Fig. S1 TEM imagines of (a) Pd/AC-NH_2, (b) Pd_4Au_1/AC-NH_2, (c) Pd_2Au_3/AC-NH_2 and (d) Pd_1Au_4/AC-NH_2.

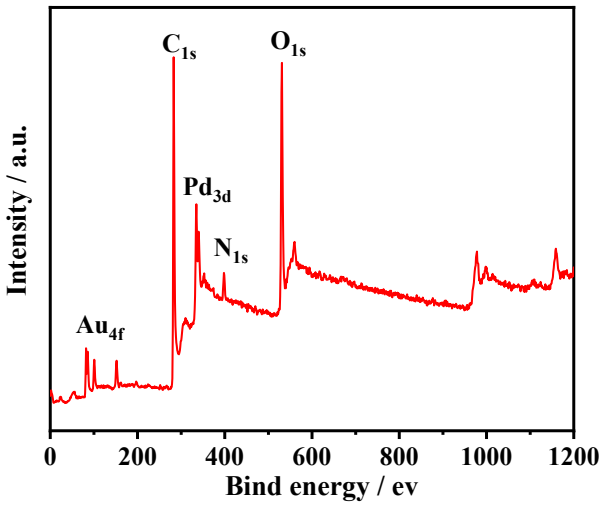

Fig. S2 Survey XPS characterization of Pd_3Au_2/AC-NH_2.

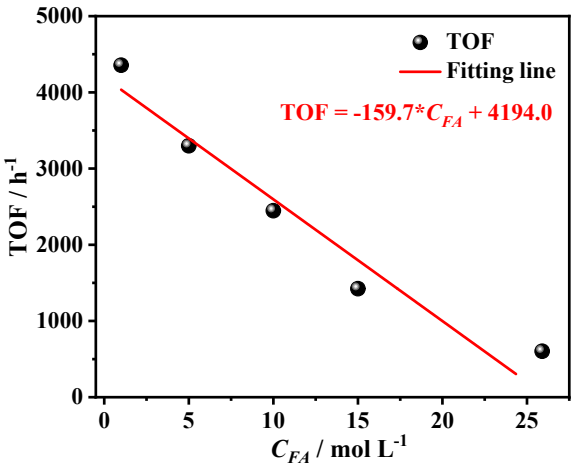

Fig. S3 TOF values' change with the concentration of FA at 303 K.

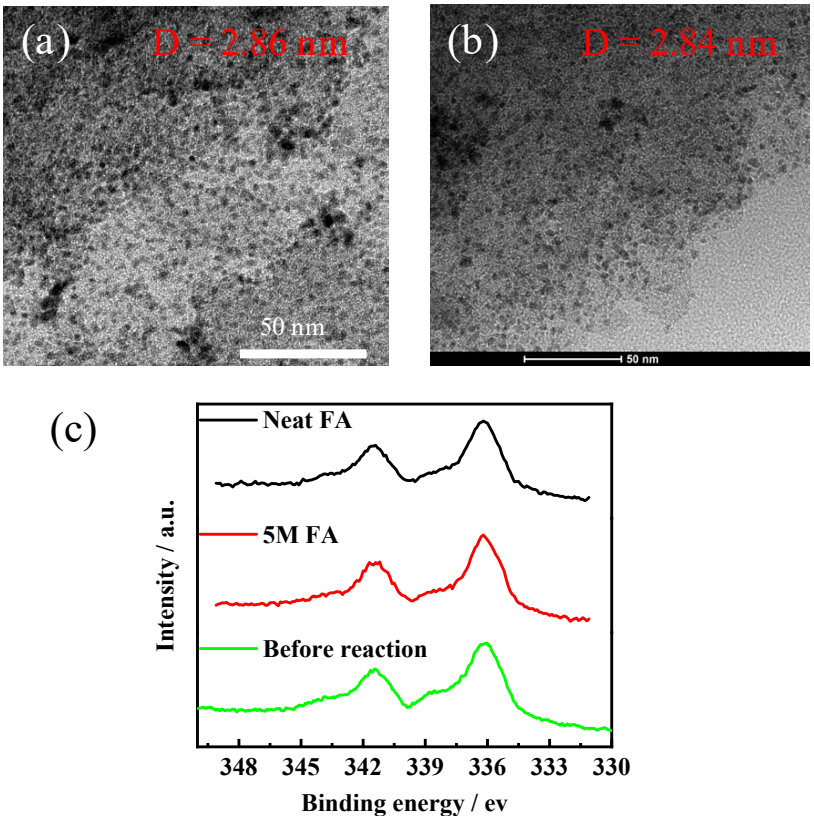

Fig. S4 TEM image of Pd_3Au_2/AC-NH_2 after 3 cycles of 5 M FA dehydrogenation (a) and neat FA (b). XPS spectra of Pd_3Au_2/AC-NH_2 before reaction and after 3 cycles of 5 M FA dehydrogenation and neat FA at 303 K.

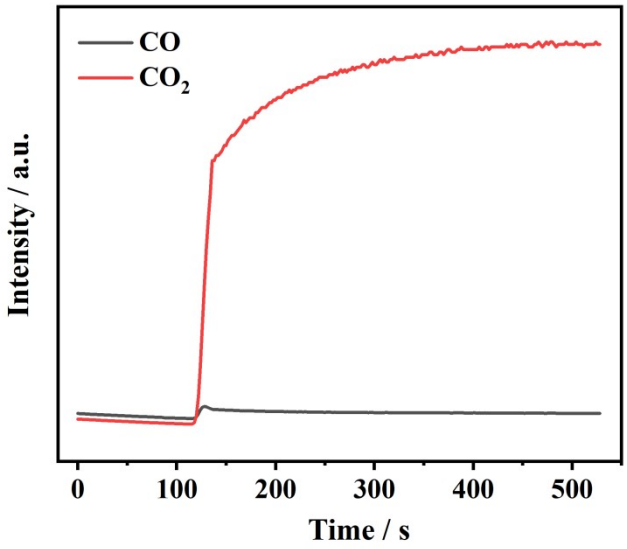

Fig. S5 Mass spectrum (MS) of gas products over Pd_3Au_2/AC-NH_2 using He carrier gas (Neat FA, 1 mL, 303 K).

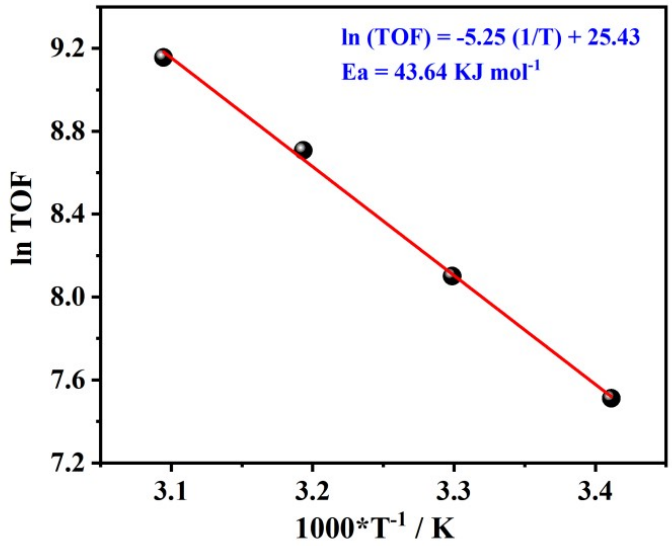

Fig. S6 Arrhenius plot (ln (TOF) vs. 1000*1/T of Pd_3Au_2/AC-NH_2 catalyst.

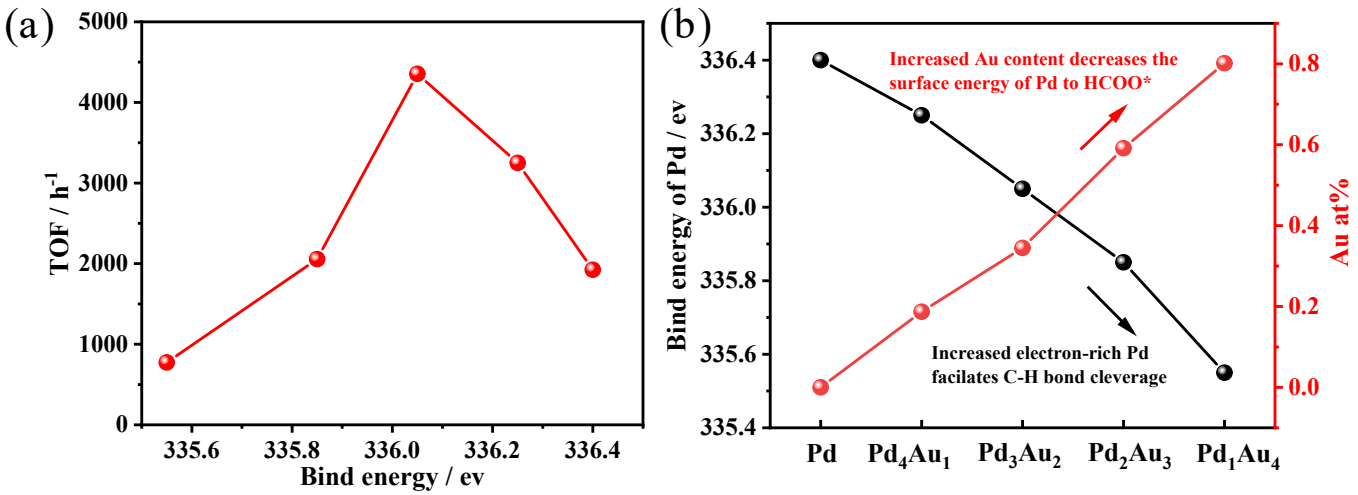

Fig. S7 (a) The relationship between TOF values and Pd binding energy. (b) A trade-off relation between Pd bind energy and surface energy as a function of Au content.

Table S1 ICP results of the as prepared catalysts.

Catalyst	Pd / *wt.*%	Au / *wt.*%	Mole ratio of Pd/Au
$Pd/AC\text{-}NH_2$	3.39	/	/
$Pd_4Au_1/AC\text{-}NH_2$	2.95	1.26	4.35
$Pd_3Au_2/AC\text{-}NH_2$	2.26	2.21	1.90
$Pd_2Au_3/AC\text{-}NH_2$	1.57	4.22	0.69
$Pd_1Au_4/AC\text{-}NH_2$	0.75	5.62	0.24
Pd_3Au_2/AC	2.41	2.38	1.88
Used $Pd_3Au_2/AC\text{-}NH_2$[a]	2.13	2.11	1.78

a ICP results of $Pd_3Au_2/AC\text{-}NH_2$ after three cycles of neat FA dehydrogenation at 303 K.

Table S2 The textural properties of various samples measured by N_2 adsorption/desorption isotherms.

Different stages	S_{BET} / m^2 g^{-1}	Pore volume / cm^{-3} g^{-1}	Pore size / nm
AC	939	0.66	5.34
Pd_3Au_2/AC	877	0.63	5.34
AC-NH_2	421	0.50	5.22
Pd_3Au_2/AC-NH_2	399	0.43	5.75

Table S3 Elemental content analysis of Pd_3Au_2/AC-NH_2.

Samples	C / *wt.*%	H / *wt.*%	N[a] / *wt.*%	N[b] / *wt.*%
Fresh Pd_3Au_2/AC-NH_2	63.57	3.52	2.88	5.23
Used Pd_3Au_2/AC-NH_2[c]	64.15	2.44	2.44	/

a Determined by Element Analysis (EA). *b* Determined by survey XPS. *c* Elemental content analysis of Pd_3Au_2/AC-NH_2 after three cycles of neat FA dehydrogenation at 303 K.

Table S4 Catalytic activities of reported catalysts for the dehydrogenation of formic acid.

Catalyst	Temp. / K	Additives	TOF / h^{-1}	Ref.
$Pd_3Au_2/AC\text{-}NH_2$	293	5 M FA	1830[b]	this work
	303	5 M FA	3300[b]	
	313	5 M FA	5730[b]	
	323	5 M FA	8710[b]	
	303	1 M FA	4355[a]	
	303	Neat FA	603[b]	
$Pd_{0.85}Ir_{0.15}/SBA\text{-}15\text{-}NH_2$	298	1 M FA	1500[b]	34
$PdMn_{0.6}@S\text{-}1$	298	1 M FA	610[b]	6
$Ni_{0.4}Pd_{0.6}/NH_2\text{-}N\text{-}rGO$	298	1 M FA	954[b]	16
$Au_1Pd_{1.5}/MIL\text{-}101\text{-}NH_2$	298	1 M FA / SF	526[b]	33
$Pd_1Au_1/72\text{-}LA$	303	1 M FA / SF	3583[a]	37
$Au_2Pd_3@(P)N\text{-}C$	303	1 M FA	358[a]	32
Pd@SS-CNR	303	1 M FA / SF	1878[b]	30
Pd/CZIF-8-950	303	1 M FA / SF	1166[b]	49
$Pd@Bi_{0.11}/C$	313	1 M FA / SF	4100[b]	31
Pd@CN900K	323	1 M FA / SF	8000[a]	14
$0.8Pd\text{-}0.2Ni(OH)_2@S\text{-}1$	333	1 M FA / SF	5803[b]	39
$(Co_6)Ag_{0.1}Pd_{0.9}/rGO$	333	1 M FA / SF	2739[b]	15
$Pd_{0.6}Ag_{0.4}@ZrO_2/C/rGO$	333	1 M FA / SF	4300[b]	38
$Au@SiO_2$	403	1 M FA	403[b]	45
Pd/C	293	6.6 M	87[b]	29

CoAgPd/MIL-101	323	1.5 M FA / SF	98[b]	40
AgPd/0.2CND/SBA-15	323	1.5 M FA / SF	893[b]	35
Pd/XC-72R	333	2.6 M FA / SF	7256[b]	30
Au/m-ZrO_2	353	10.5 M FA	660[b]	46
Au/SiO_2-Schiff	323	10 M FA	4683[b]	47
$Pd_{60}Au_{40}$/HPC-NH_2	298	1 M FA	3763[b]	57
$Au_{0.5}Pd_{0.5}$/NH_2-N-rGO	298	1 M FA	4446[b]	43
$Pd_{60}Au_{40}$/ZrSBA-15-AP	298	2 M FA	1185[b]	41
$Au_{0.4}Pd_{0.6}$/CBH-A	298	1 M FA	5625[b]	42

a: TOF value was calculated based on the completion time of gas releasing.

b: Initial TOF was calculated based on the initial conversion of FA.

SF: Sodium Formate.