Supplementary Information

Ultrafine AuPd Nanoparticles Supported on Amine Functionalized Monochlortriazinyl β-Cyclodextrin as Highly Active Catalysts for Hydrogen Evolution from Formic Acid Dehydrogenation

Xue Liu[a], Dawei Gao[a], Yue Chi[a], Hongli Wang[a,], Zhili Wang[b,*] and Zhankui Zhao[a]*

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

[b] Key Laboratory of Automobile Materials Ministry of Education, Department of Materials Science and Engineering, Jilin University, Changchun 130022, China

[*]***Corresponding Authors' e-mail addresses: wanghongli@ccut.edu.cn (H. Wang); zhiliwang@jlu.edu.cn (Z. Wang);***

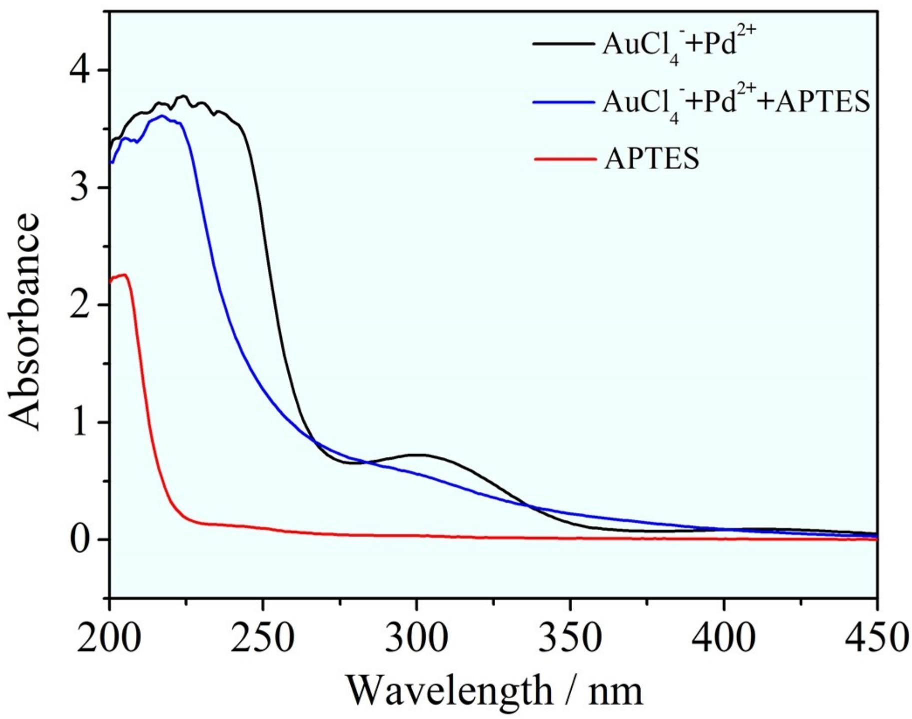

Fig. S1 UV-vis spectra of aqueous solutions containing various species.

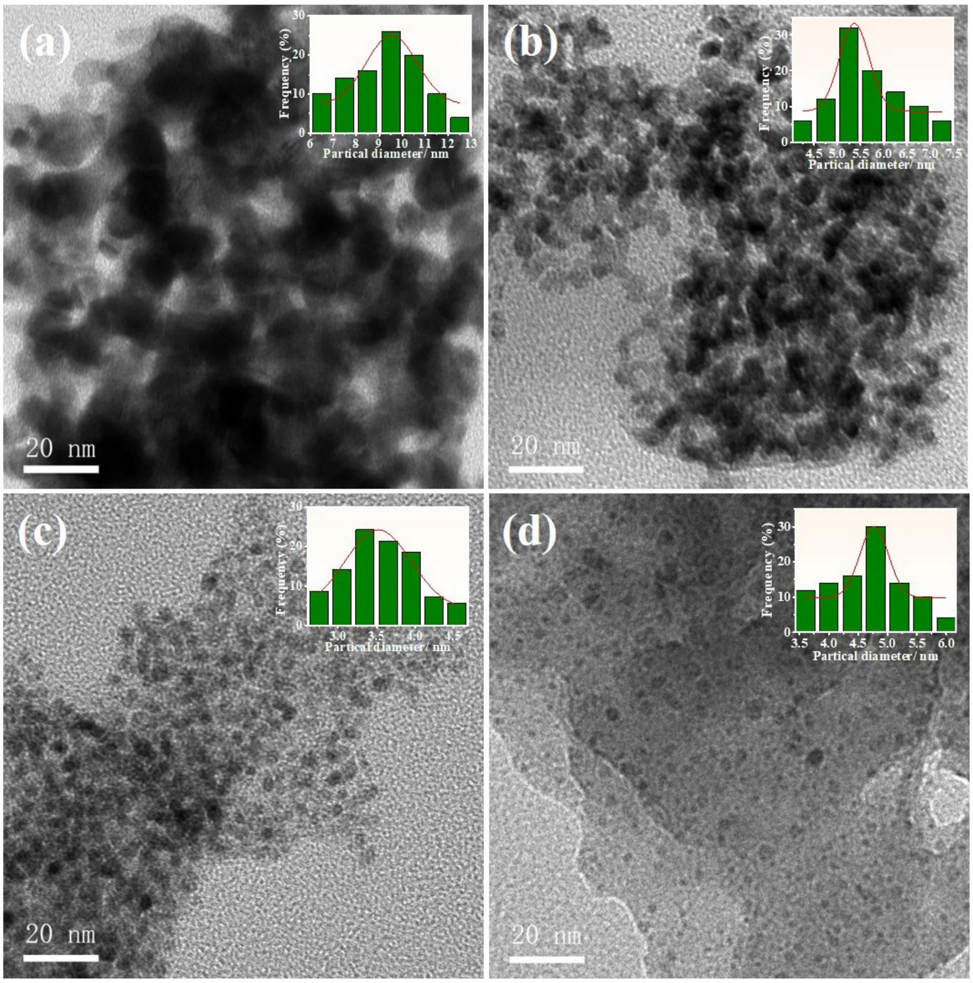

Fig. S2 TEM images and corresponding particle size distribution of (a) $Au_{0.3}Pd_{0.7}$, (b) $Au_{0.3}Pd_{0.7}$/M-β-CD, (c) $Au_{0.3}Pd_{0.7}$-A, (d) $Au_{0.3}Pd_{0.7}$/C.

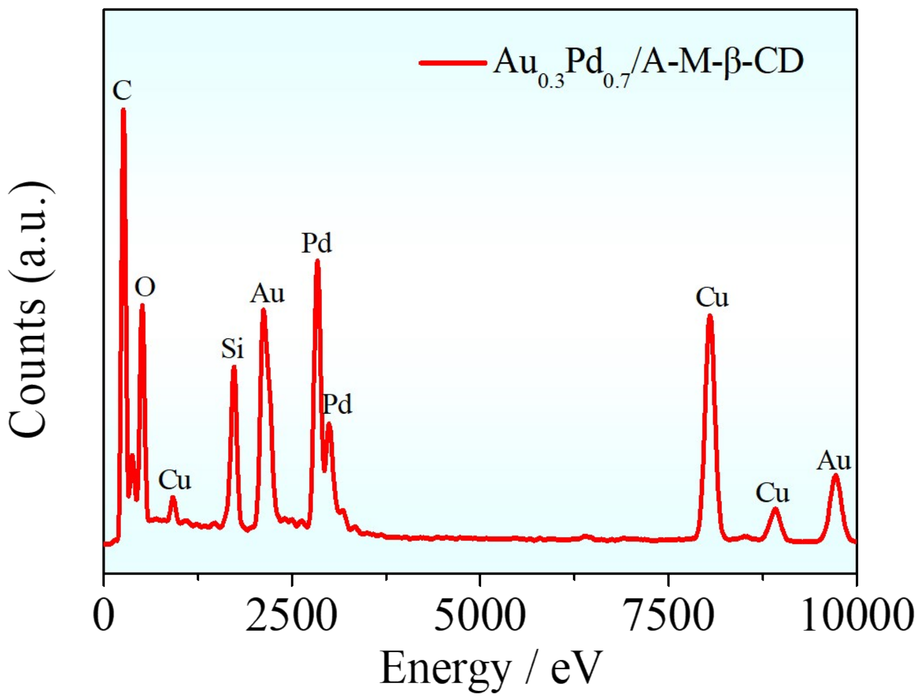

Fig. S3 EDX spectrum of $Au_{0.3}Pd_{0.7}$/A-M-β-CD.

Table S1. The metal loading amounts and the molar ratios of Au/Pd of $Au_{0.3}Pd_{0.7}$/A-M-β-CD before and after cyclic tests for dehydrogenation of FA reaction.

Sample	Au loading (mg)	Pd loading (mg)	Ratio of Au/Pd (mol/mol)
$Au_{0.3}Pd_{0.7}$/A-M-β-CD before cyclic tests	3.215	4.070	0.298:0.702
$Au_{0.3}Pd_{0.7}$/A-M-β-CD after cyclic tests	3.210	4.052	0.299:0.701

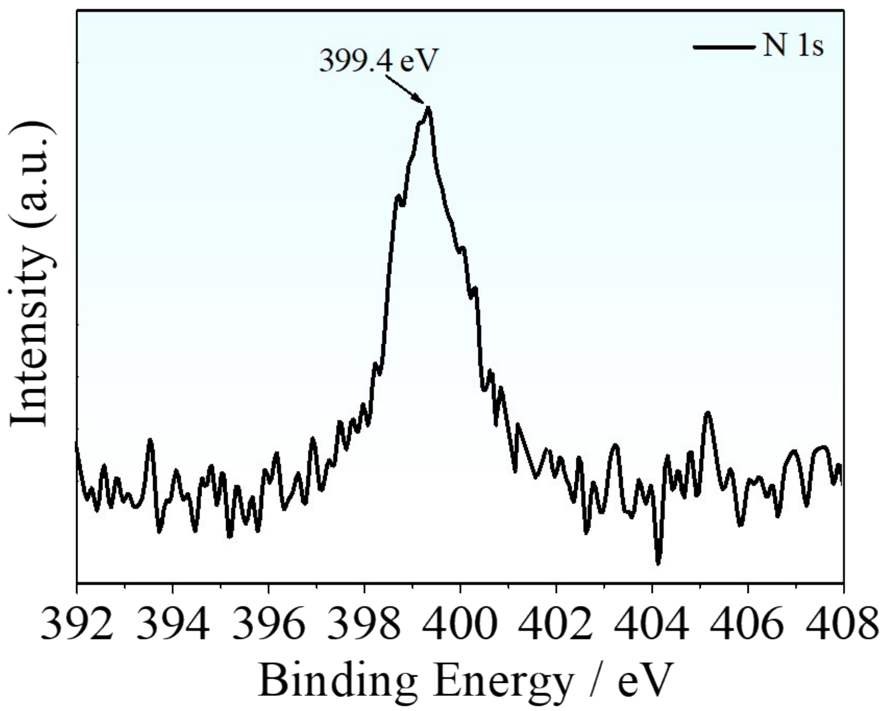

Fig. S4 High-resolution XPS spectrum of N1s for $Au_{0.3}Pd_{0.7}$-A.

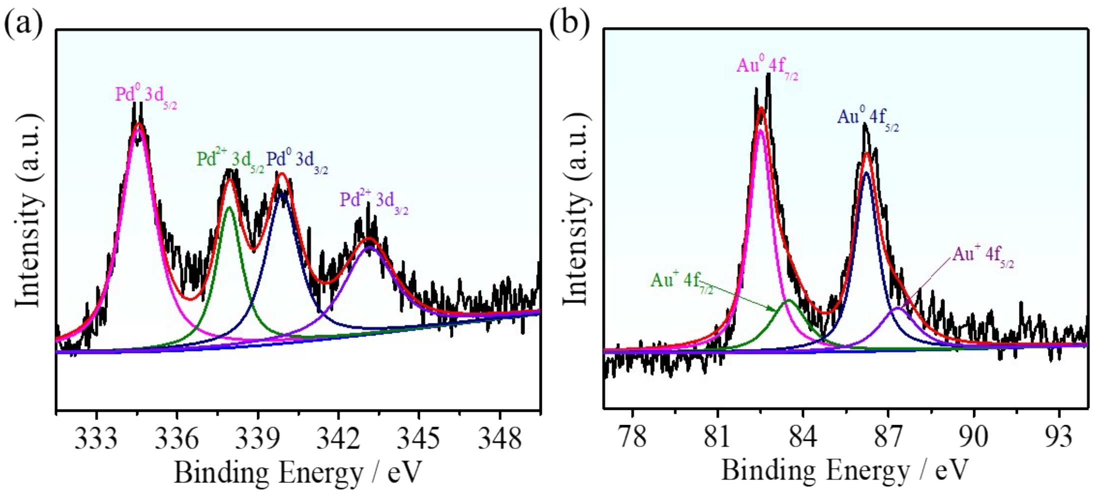

Fig. S5 High-resolution XPS spectra of (a) Pd 3d and (b) Au 4f for $Au_{0.3}Pd_{0.7}$/A-M-β-CD.

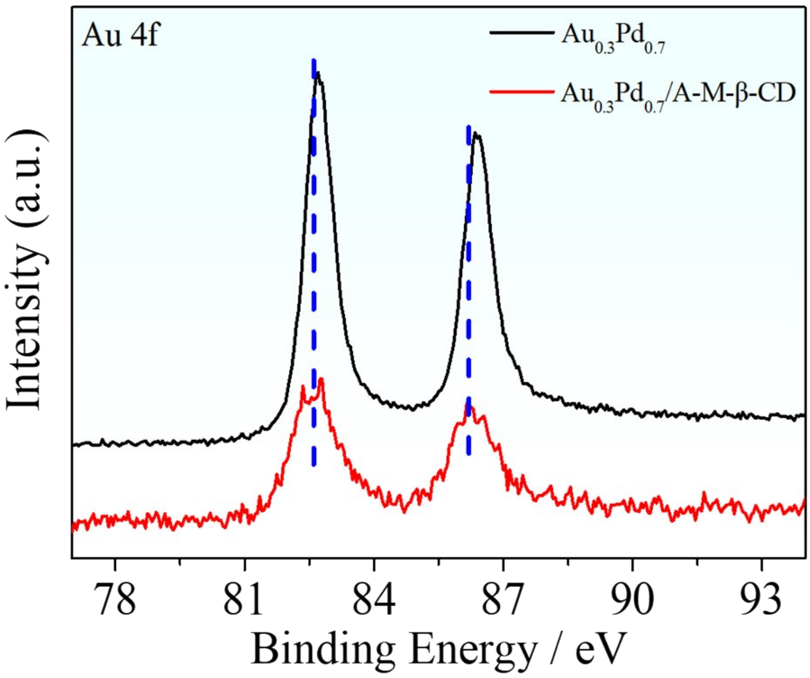

Fig. S6 High-resolution XPS spectra of Au 4f for $Au_{0.3}Pd_{0.7}$/A-M-β-CD and $Au_{0.3}Pd_{0.7}$ NPs.

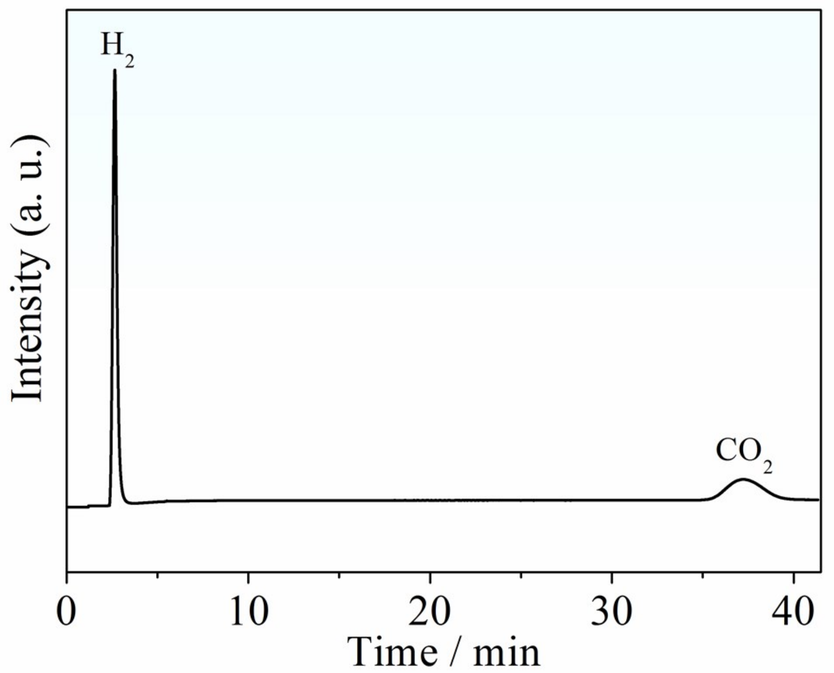

Fig. S7 GC spectrum using TCD for the evolved gas from FA aqueous solution (1.0 M, 5.0 mL) over $Au_{0.3}Pd_{0.7}$/A-M-β-CD at 323 K.

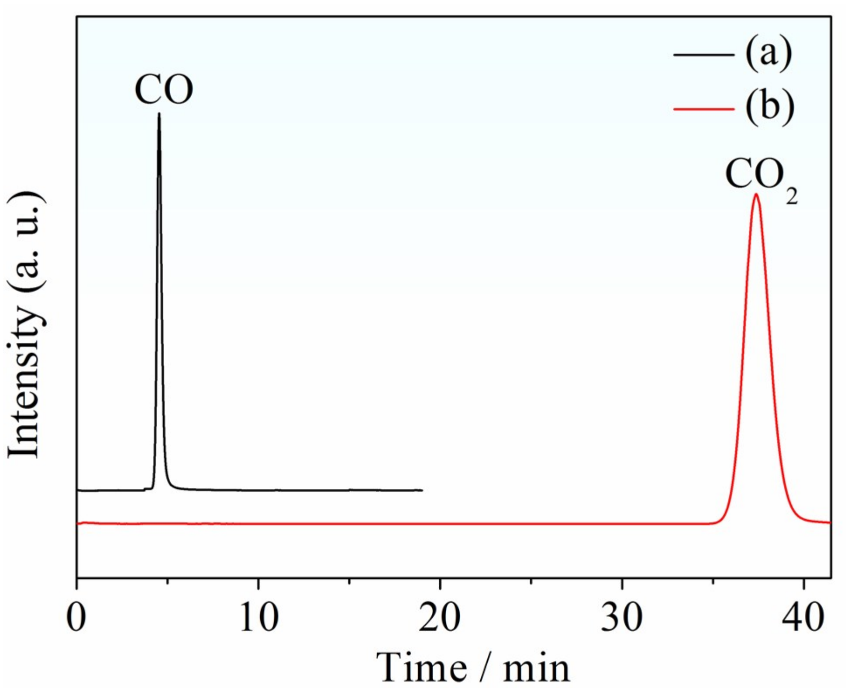

Fig. S8 GC spectrum using FID-Methanator for the (a) commercial pure CO, and (b) evolved gas from FA aqueous solution (1.0 M, 5.0 mL) over $Au_{0.3}Pd_{0.7}$/A-M-β-CD at 323 K.

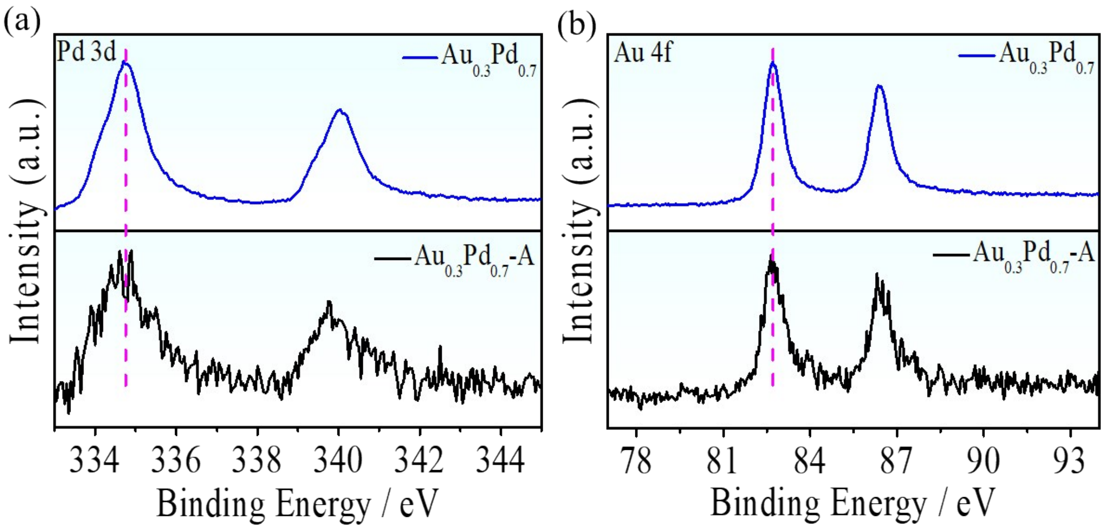

Fig. S9 High resolution XPS spectra of (a) Pd 3d and (b) Au 4f for $Au_{0.3}Pd_{0.7}$-A and $Au_{0.3}Pd_{0.7}$ NPs.

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

Catalyst	Temp. (K)	$n_{catalyst}/n_{FA}$	Additive	TOF (h^{-1})	*Ea* (kJ/mol)	Ref.
Without additive						
Au@Pd/N-mrGO	298	0.0200	None	89.1[a]	---	12
$Au_{42}Pd_{58}$	323	0.0100	None	382[a]	22±1	46
Pd_{IMP}/CNF	303	0.0188	None	563.2[b]	27.50	47
$Pd/CN_{0.25}$	298	0.0075	None	752[b]	48.80	48
$Ni_{0.4}Pd_{0.6}/NH_2$-N-rGO	298	0.0200	None	954.3[a]	---	41
Pd-MnO_x/SiO_2-NH_2	323	0.1068	None	1300[a]	61.9	49
$Cr_{0.4}Pd_{0.6}$/MIL-101-NH_2	323	0.0200	None	2009[a]	43.50	27
Pd/A-SEP-$NH_{2(0.9)}$	333	0.0315	None	5587[b]	44.5	50
$Au_{0.3}Pd_{0.7}$/A-M-β-CD	323	0.0200	None	7352[b]	39.50	This work
With Additive						
Pd-CNTs-in	303	0.0214	HCOONa	1135.8[a]	36.60	51
Pd-B/C	303	0.0143	HCOONa	1184[b]	---	7
Co_5Pd_5/CTF-600	323	0.0070	HCOOK	2129[a]	35.94	52
$(Co_6)Ag_{0.1}Pd_{0.4}$/RGO	323	0.0200	HCOONa	2739[b]	43.10	53
Pd/S-1-in-K	323	0.0100	HCOONa	3027[b]	39.2	54
Pd/PDA-rGO	323	0.0150	HCOONa	3810[b]	54.30	55
$(Co_3)_E Au_{0.6}Pd_{0.4}$/rGO	323	0.0200	HCOONa	4840[a]	---	16
Au_2Pd_3@(P)N-C	303	0.0170	HCOONa	5400[a]	---	56

a. Initial TOF values calculated based on total metal.

b. Initial TOF values calculated based on total Pd atoms.

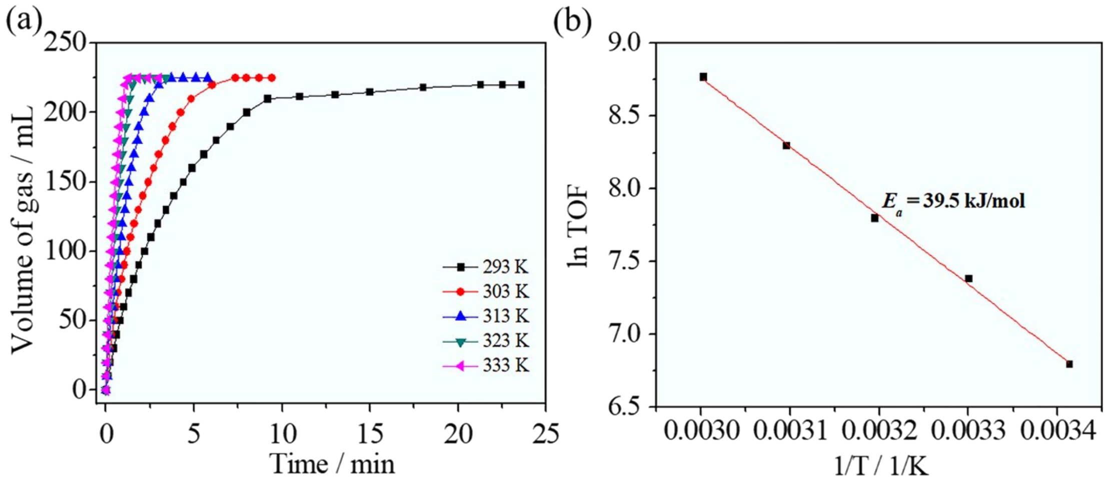

Fig. S10 (a) Plot of volume of gas over time for the dehydrogenation of FA catalyzed by $Au_{0.3}Pd_{0.7}$/A-M-β-CD at different temperatures; (b) Arrhenius plot of ln TOF vs. 1/T for $Au_{0.3}Pd_{0.7}$/A-M-β-CD.

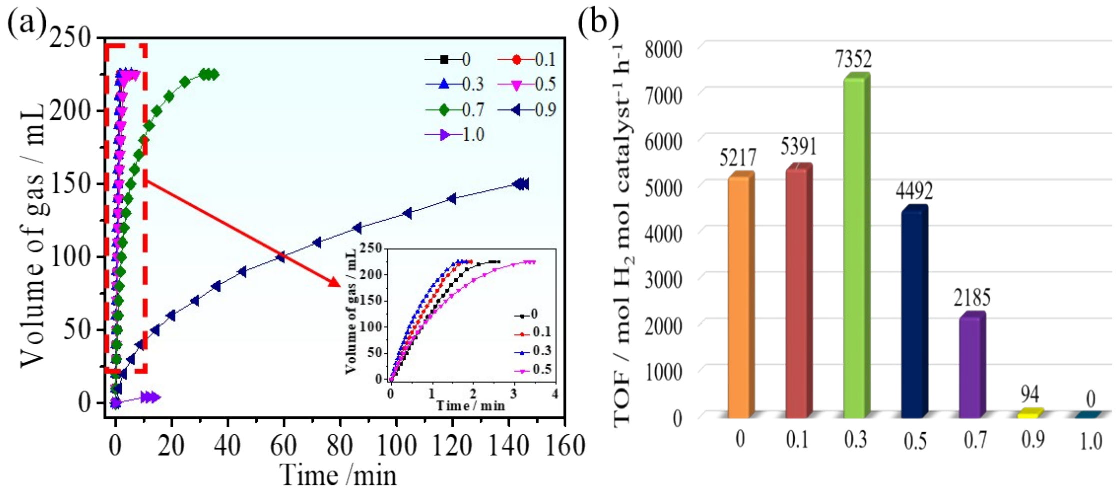

Fig. S11 (a) Time-course plots for the dehydrogenation of FA (1.0 M, 5.0 mL) catalyze by Au_xPd_{1-x}/A-M-β-CD (x= 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) at 323 K and the inset shows the corresponding larger plots; (b) their related initial TOF values.

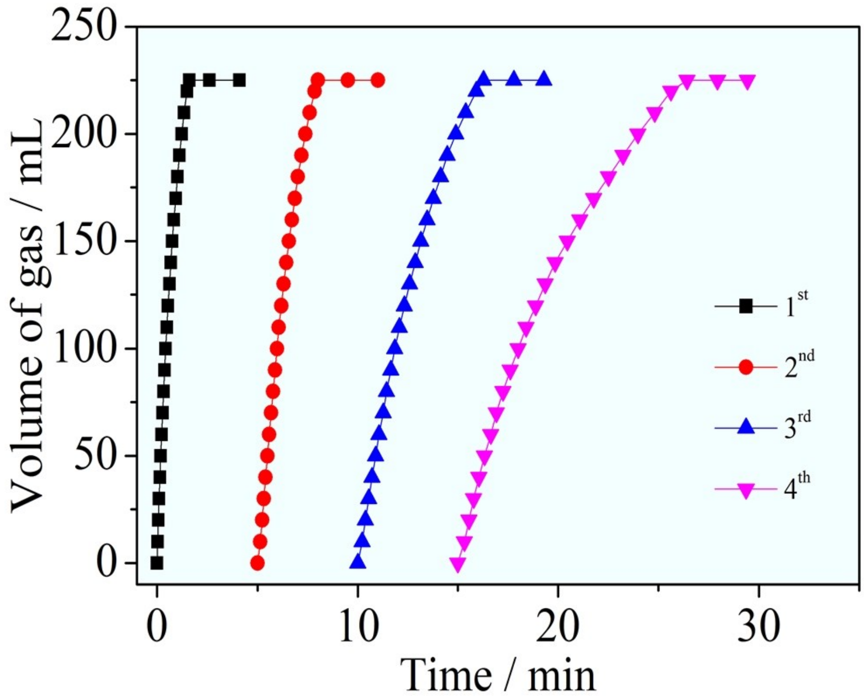

Fig. S12 Durability test of $Au_{0.3}Pd_{0.7}$/A-M-β-CD towards the dehydrogenation of FA.

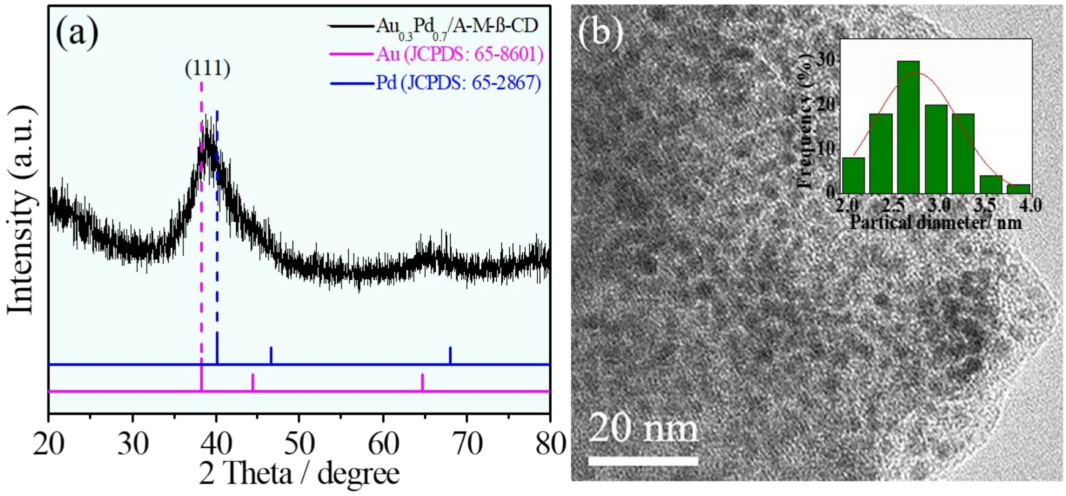

Fig. S13 (a) XRD spectrum; (b) TEM image and the corresponding particle size distribution (inset) of $Au_{0.3}Pd_{0.7}$/A-M-β-CD after the 4th run.