Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Unexpectedly high stability and surface reconstruction of PdAuAg nanoparticles for formate oxidation electrocatalysis

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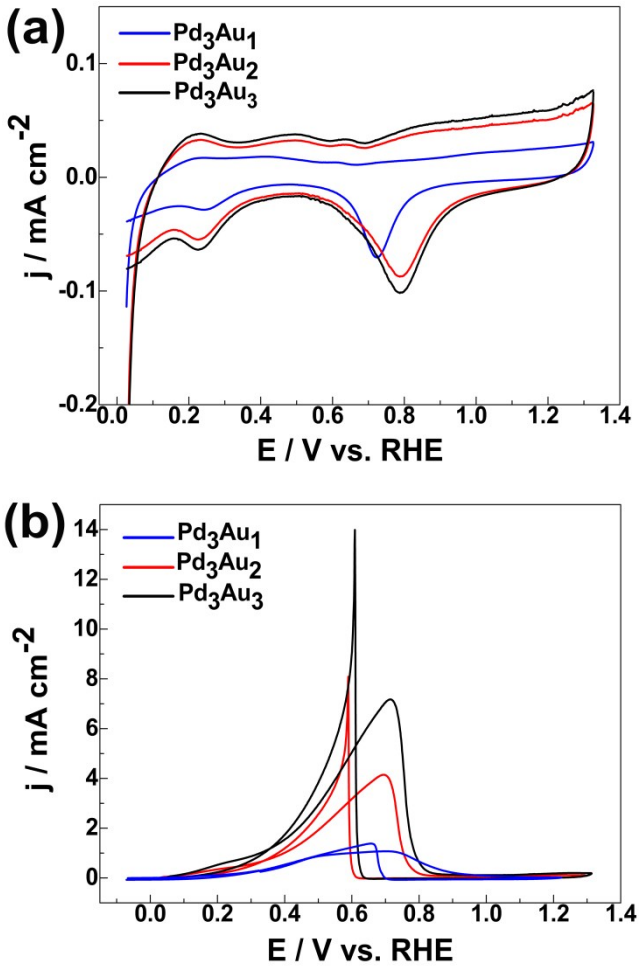

Figure S1. Catalytic properties of various PdAu NPs on carbon nanotubes. (a) CV curves in N_2-saturated 1 M KOH. (b) CV curves for formate oxidation reaction in 1 M KOH + 1 M HCOOK.

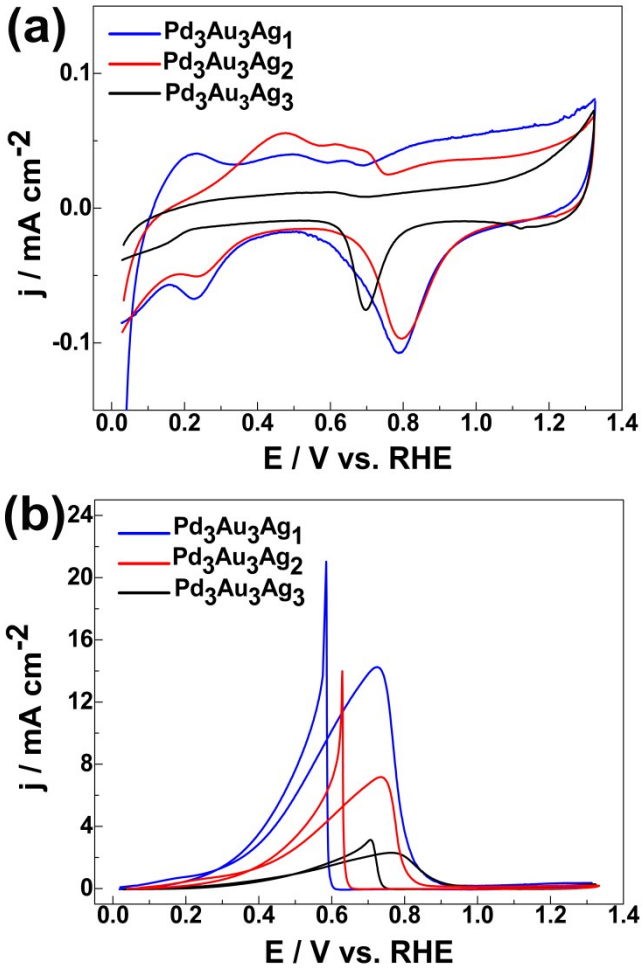

Figure S2. Catalytic properties of various PdAuAg NPs on carbon nanotubes. (a) CV curves in N_2-saturated 1 M KOH. (b) CV curves for formate oxidation reaction in 1 M KOH + 1 M HCOOK.

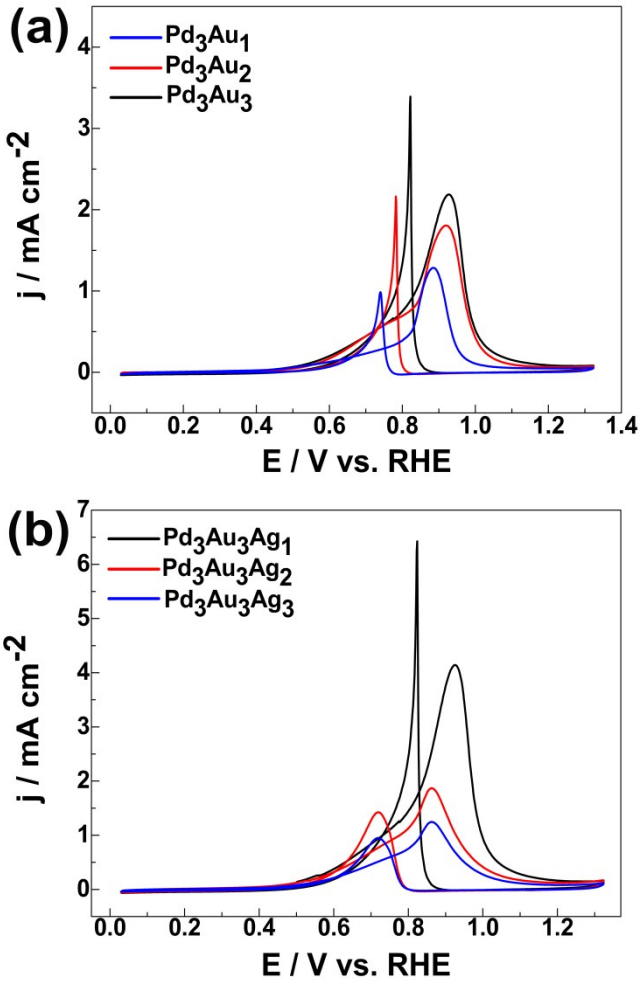

Figure S3. (a) CV curves of various PdAu NPs on carbon nanotubes for methanol oxidation reaction in 1 M KOH + 1 M CH_3OH. (b) CV curves of various PdAuAg NPs on carbon nanotubes for methanol oxidation reaction in 1 M KOH + 1 M CH_3OH

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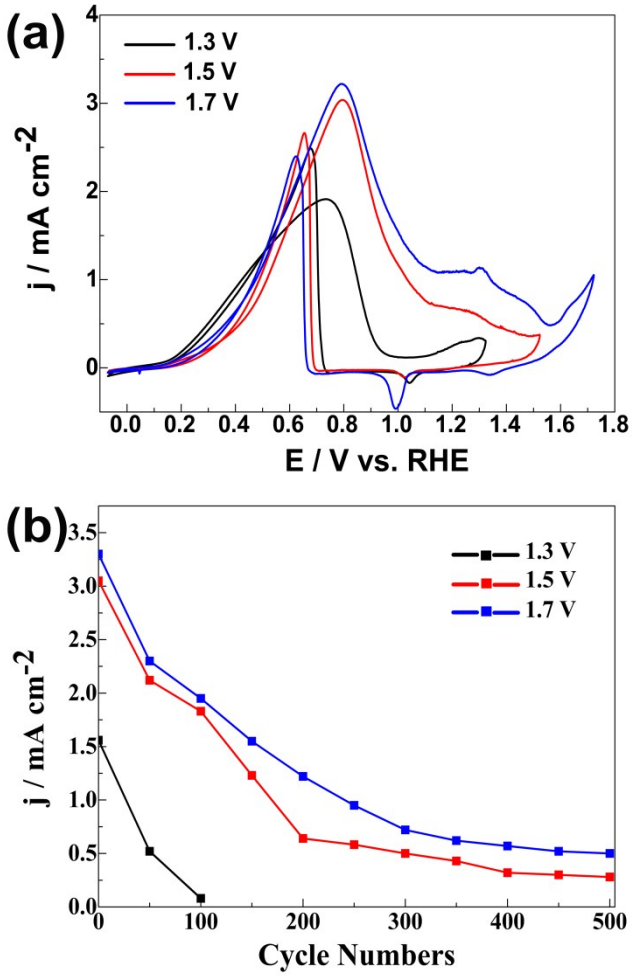

Figure S4. (a) CV curves of $Pd_3Au_3Ag_3$ NPs on carbon nanotubes for formate oxidation reaction in 1 M KOH + 1 M HCOOK with various potential ranging from -0.1 to 1.3 V, 1.5 V and 1.7 V vs. RHE. (b) Cycling stability curves of $Pd_3Au_3Ag_3$ NPs on carbon nanotubes after pretreatment in potential range from -0.1 to 1.3 V, 1.5 V and 1.7 V vs. RHE.

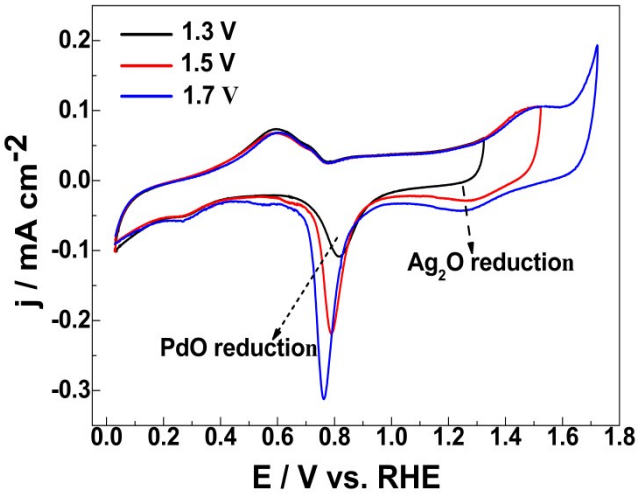

Figure S5. CV curves of $Pd_3Au_3Ag_1$ NPs on carbon nanotubes in 1 M KOH with various potential ranging from -0.1 to 1.3 V, 1.5 V and 1.7 V vs. RHE.

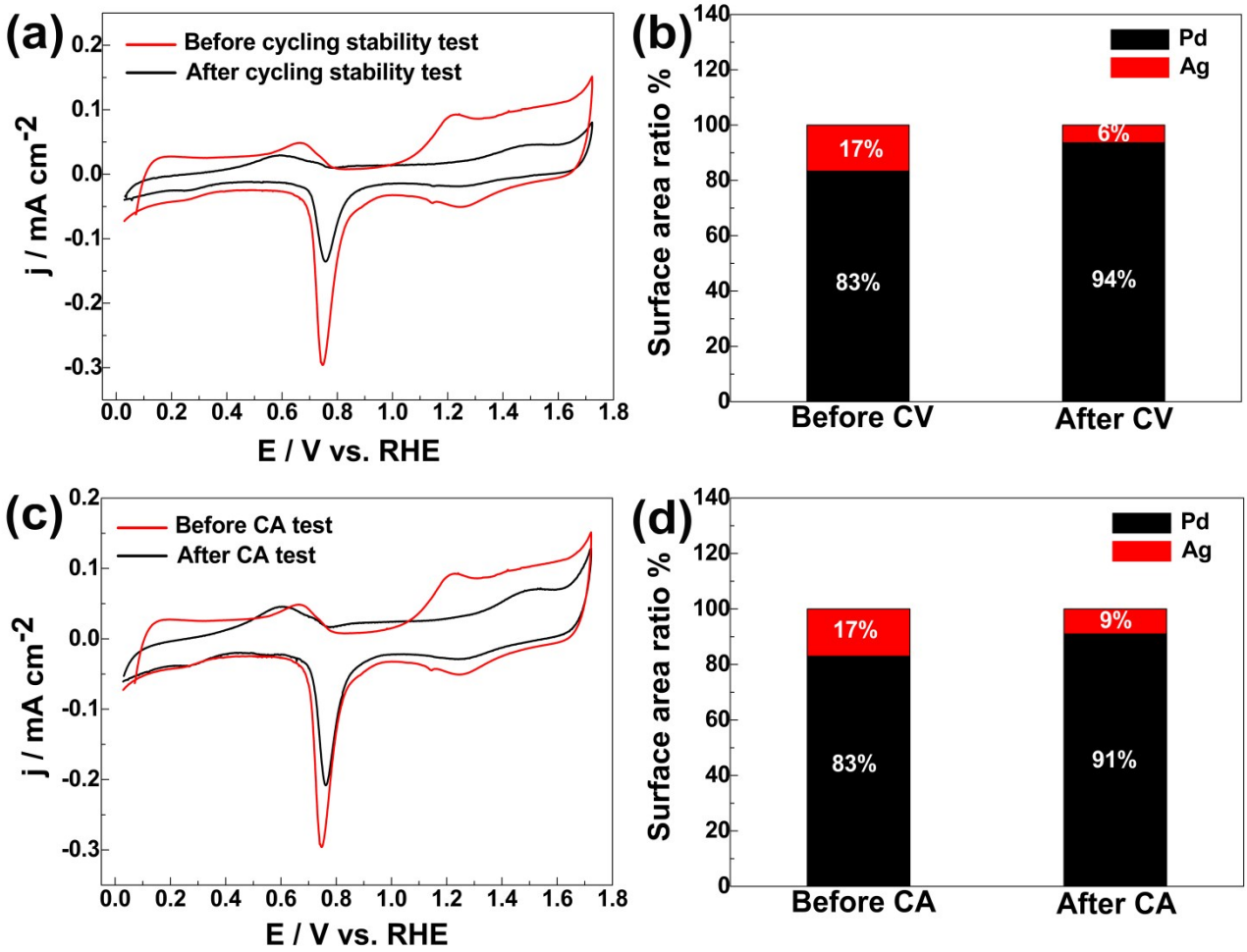

Figure S6. (a) CV curves of $Pd_3Au_3Ag_1$ NPs on carbon nanotubes before and after FOR cycling stability test in 1 M KOH. (b) Surface area ratio of Pd and Ag before and after FOR cycling stability test. (c) CV curves of $Pd_3Au_3Ag_1$ NPs on carbon nanotubes before and after CA stability test in 1 M KOH. (d) Surface area ratio of Pd and Ag before and after CA stability test.

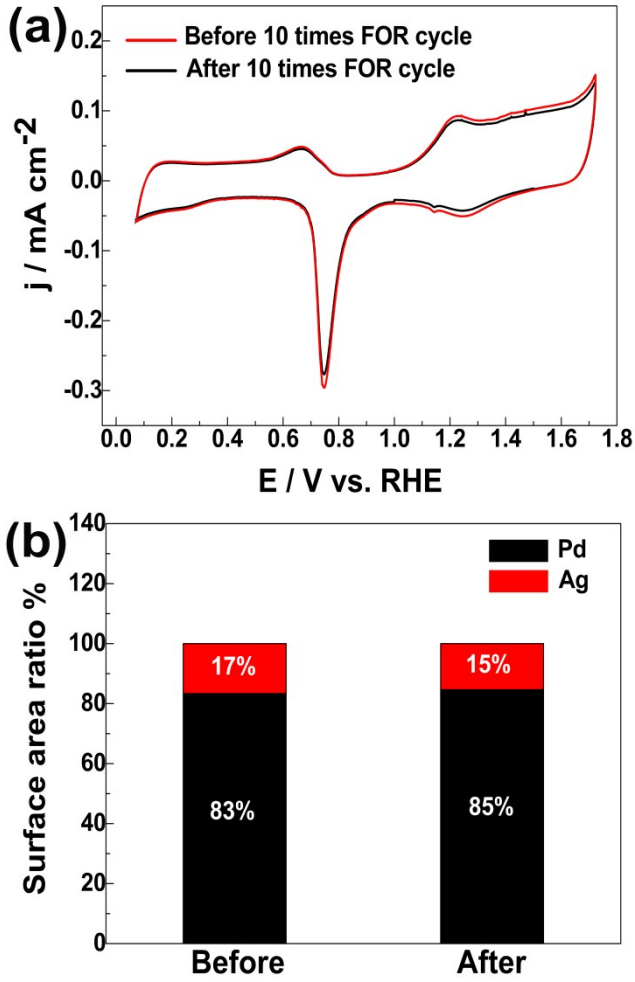

Figure S7. (a) CV curves of $Pd_3Au_3Ag_1$ NPs on carbon nanotubes before and after 10 times FOR cycles in 1 M KOH. (b) Surface area ratio of Pd and Ag before and after 10 times FOR cycles.

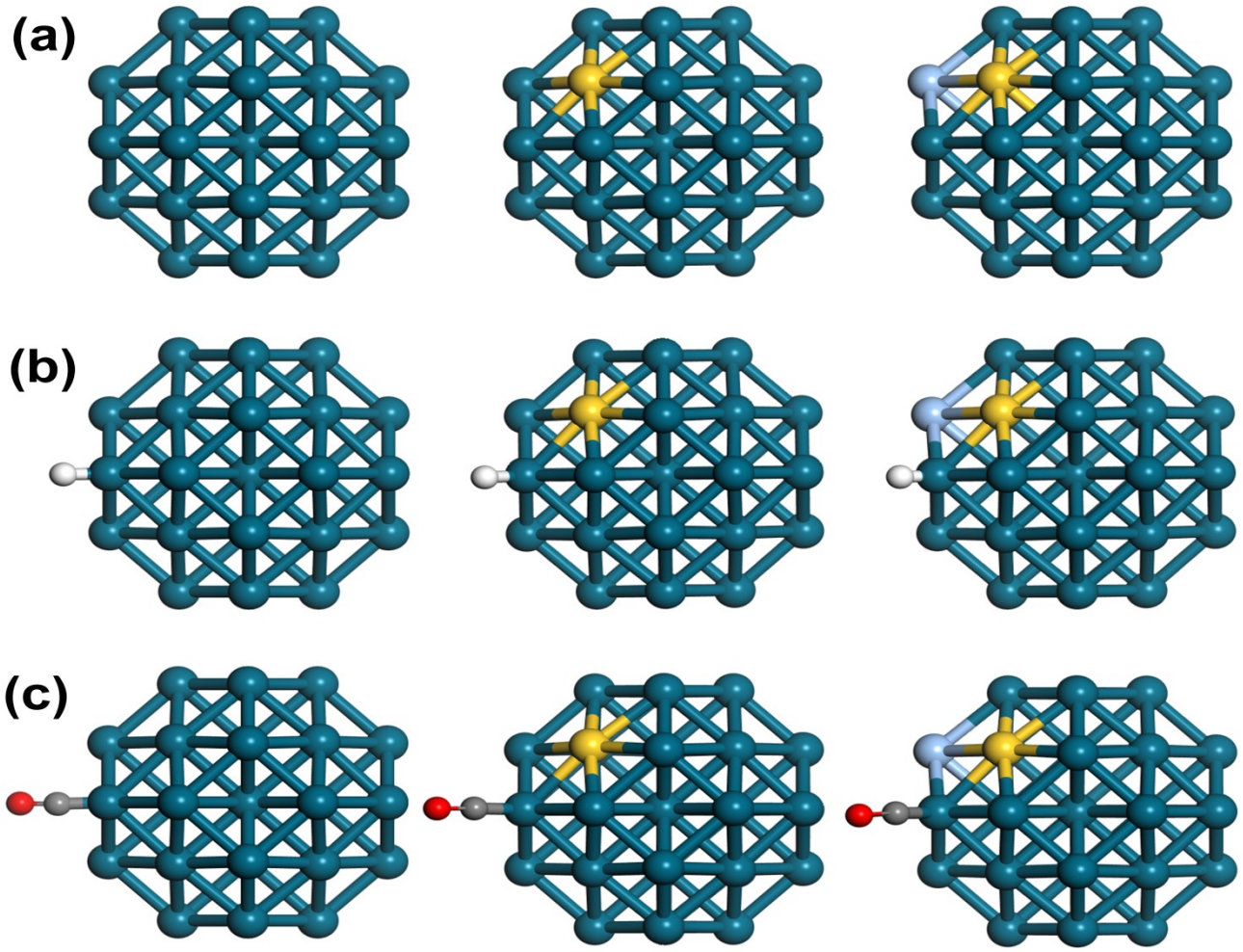

Figure S8. Structure models of (a) Pure Pd_{38}, $Pd_{37}Au$ and $Pd_{36}AuAg$. (b) Pure Pd_{38}, $Pd_{37}Au$ and $Pd_{36}AuAg$ with H adsorption. (c) Pure Pd_{38}, $Pd_{37}Au$ and $Pd_{36}AuAg$ with CO adsorption. (Green, yellow, blue, white, gray and red spheres indicate Pd, Au, Ag, H, C and O)

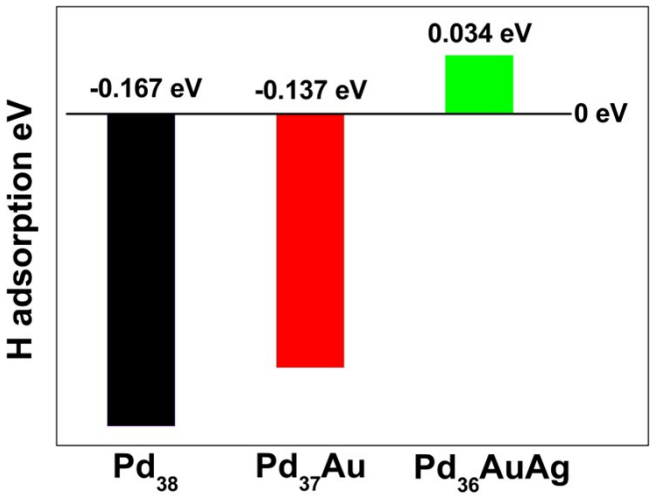

Figure S9. Hydrogen adsorption energy (eV) on pure Pd_{38}, $Pd_{37}Au$ and $Pd_{36}AuAg$ nanoalloy.

Table S1. Molar rations of metal precursors during the synthetic process and EDS composition for different PdAu/CNT and PdAuAg/CNT catalysts.

Catalyst Name	$Pd(NO_3)_2$ (10 mM)	$HAuCl_4$ (10 mM)	$AgNO_3$ (10 mM)	EDS composition (wt %) Pd	Au	Ag	C
Pd_3Au_1/CNT	9 mL	3 mL	-	21.3	13.3	-	65.4
Pd_3Au_3/CNT	6 mL	6 mL	-	13.4	25.4	-	61.2
$Pd_3Au_3Ag_1$/CNT	5.1 mL	5.1 mL	1.7 mL	11.2	20.3	3.9	64.6
$Pd_3Au_3Ag_3$/CNT	4 mL	4 mL	4 mL	8.2	14.5	8.8	68.5

Table S2. Calculated adsorption energies (eV) of H and CO on the surface of Pd_{38}, $Pd_{37}Au$ and $Pd_{36}AuAg$

	adsorption energy of H^*	adsorption energy of CO^*
Pd_{38}	-0.167	-1.381
$Pd_{37}Au$	-0.137	-1.376
$Pd_{36}AuAg$	0.034	-1.372

Table S3. A literature survey of the activity of Pd-based FOR catalysts in alkaline media

Catalyst	Electrolyte	Scan rate ($mV \cdot s^{-1}$)	Specific Activity ($mA \cdot cm^{-2}$)	Mass activity ($A \cdot mg_{Pd}^{-1}$)	Reference
$Pd_3Au_3Ag_1$/CNT	1 M KOH + 1 M HCOOK	50	14.47	4.51	**This work**
PdH/C	1 M KOH + 0.1 M HCOOK	20	0.1	-	1
Pd_4Ag_1/C	1 M NaOH + 0.1 M HCOONa	50	-	0.04	2
PdCu/C	1 M KOH + 1 M HCOOK	30	3.5	-	3
PdAu/Ni foma	0.5 M NaOH + 0.1 M HCOONa	50	0.8	-	4
CuPdAu/C	0.5 M KOH + 0.5 M HCOOK	50	-	1.2	5
PdAgCu aergels	1 M KOH + 1 M HCOOK	50	10.1	2.7	6
PdAgPt aergels	0.5 M KOH + 0.5 M HCOOK	50	3.5	2.9	7
$Pd_{2.3}Co$/C	1 M KOH + 1 M HCOOK	50	-	2.5	8
PdNi/C	1 M KOH + 1 M HCOOK	50	12	4.5	9
PdRh/C	1 M KOH + 1 M HCOOK	50	8.1	4.5	10
$Pd_{72}Ce_{28}$/C	1 M KOH + 1 M HCOOK	50	19.4	1.1	11
AgPd/rGO	1 M KOH + 1 M HCOOK	50		4.21	12

Table S4. Durability of Pd-based FOR catalysts after CA measurements for 3600 s

Catalyst	Electrolyte	The retained mass activity after CA measurements for 3600 s ($A \cdot mg_{Pd}^{-1}$)	Reference
$Pd_3Au_3Ag_1$/CNT	1 M KOH + 1 M HCOOK	1.32	**This work**
Pd_4Ag_1/C	1 M NaOH + 0.1 M HCOONa	0.01	2
CuPdAu/C	0.5 M KOH + 0.5 M HCOOK	0.03	5
PdAgCu aergels	1 M KOH + 1 M HCOOK	0.01	6
$Pd_{2.3}Co$/C	1 M KOH + 1 M HCOOK	0.2	8
PdRh/C	1 M KOH + 1 M HCOOK	0.5	10
$Pd_{72}Ce_{28}$/C	1 M KOH + 1 M HCOOK	0.01	11
AgPd/rGO	1 M KOH + 1 M HCOOK	0.12	12

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