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Promoting Formic Acid Oxidation Performance of Pd Nanoparticles Via Pt and Ru Atoms Mediated Surface Engineering

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1. **Electrochemical analysis results after CA analysis in formic acid oxidation reaction**.

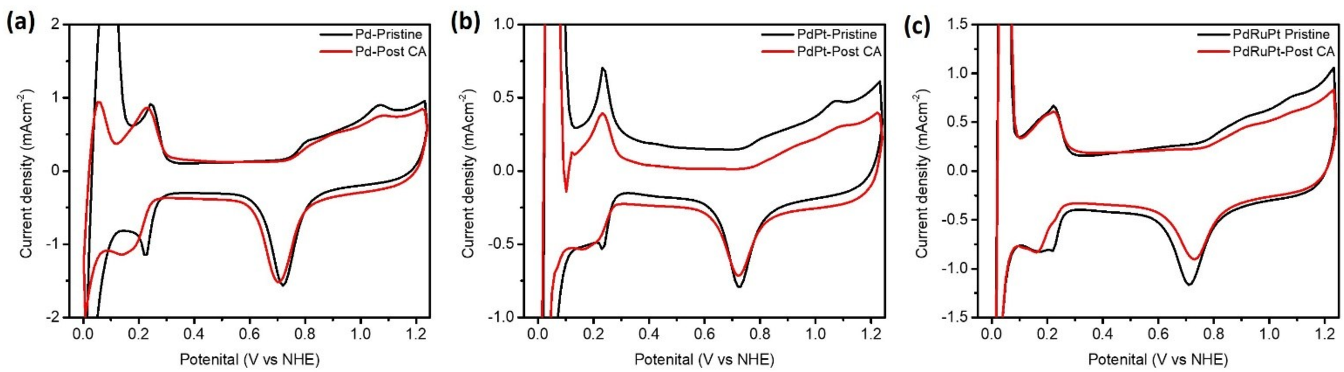

Figure S1. The CV sweeping curves of experimental samples after CA analysis for (a) Pd, (b) PdPt, and (c) PdRuPt recorded in 0.5 M H_2SO_4 saturated with N_2.

2. **Mass activity on experimental NCs at 0.3 V and 0.5 V in forward scan.**

The mass activities (MA) at 0.3 V and 0.5 V vs NHE in forward scan have been calculated by obtaining the FAOR current densities from LSV curves (**Figure 5b**) at corresponding potentials. The mass activity obtained when FAOR current density was normalized to the Pt + Pd loading.

For each catalyst, the current density:

$$Current\ density\ (\frac{mA}{cm^2}) = \frac{mA}{0.19625}$$

Where 0.19625 cm^2 is the geometric surface area of the electrode.

Table S1. Mass activity on experimental NCs at 0.3 V and 0.5 V in forward scan.

Samples	MA_f -0.3 V (Pt&Pd) (A/mg)	MA_f-0.5 V (Pt&Pd) (A/mg)
Pd	0.47	0.48
PdPt	0.96	0.40
PdRuPt	0.95	0.58

3. Benchmark of Pd-based NCs in formic acid oxidation reaction.

The recent advancements in the design of Pd-based nanocatalysts towards formic acid oxidation reaction are summarized in **Table S2**. Accordingly, most bi- and multi-metallic Pd or PdPt NCs reported in previous studies demonstrate mass activities around 0.1-0.6 A/mg. Besides, the PdPt bimetallic NC in the present study possess an optimum mass activity of 1.0 A/mg with ultra-low content of Pt. In addition, we also demonstrate that incorporation of Ru-atoms enhances the CO-tolerance of PdPt NC during CA stability test.

In the following comparison table MA-0.3 V and MA-0.5 V are corresponding to current densities at 0.3 V and 0.5 V, respectively. Whereas MA-maximum is corresponding to the maximum current density in forward scan.

Table S2. Comparison of the formic acid oxidation reaction performance of Pd-based NCs.

Catalysts	MA_f -0.3 V (Pt&Pd) (A/mg)	MA_f 0.5 V (Pt&Pd) (A/mg)	MA_f Maximum (Pt&Pd) (A/mg)	Electrolyte	Reference
Pd	0.47 [a]	0.48	0.6	0.5 M H_2SO_4+0.5 M HCOOH	This work
PdPt	0.96 [a]	0.40	1.0		
PdRuPt	0.95 [a]	0.58	0.9		
Pd_3Pt half-shells	N/A	N/A	0.318		Small 2018, 14, 1703940
Pd_3Pt nanocages			0.220		
Pd black			0.168		
PdPt NP/ILP–CNT			0.358		Ionics 2015, 21, 729-736
PdPt NP/CNT			0.197		Electrochimica Acta 2006, 51, 3477-3483
E-TEK PdPt/C			0.100		
PtAgCu@PtCu			0.314		Nano Energy 2015, 12, 824– 832
PtCu nanoflowers			0.241		
Pd nanochain			0.309		Advanced Functional Materials 2017, 27
Porous PtAg@Pt			0.282		ACS applied materials & interfaces 2016, 8, 31076-31082
Pt_3Zn/C-300	0.0382 [b]	0.265	N/A		J. Mater. Chem. A, 2015, 3, 22129
PtZn/C-300	0.0362 [b]	0.249			
Pt_3Zn/C-700	0.0276 [b]	0.211			
PtZn/C-700	0.222 [b]	0.231			
Pt_3Zn10/C-700	0.0394 [b]	0.332			
Pd	0.35 [b]	N/A		0.1M $HClO_4$+0.5M HCOOH	Nano Lett. 2017, 17, 2727–2731
Pd nanosheets	0.3 [b]			0.5 M H_2SO_4 and 0.25 M HCOOH	Chem. Mater. 2018, 30, 3308
Pd@Au	0.52 [b]			0.1M $HClO_4$+3M HCOOH	Electrochem. Commun. 2007, 9, 1725–1729
PdNi	0.22 [b]			0.5 M H_2SO_4 and 0.5 M HCOOH	Appl. Catal. B 2016, 180, 758–765
PdCu	0.38 [b]				
$Pd_{0.57}Ni_{0.13}Cu_{0.30}$	0.48 [b]				

$Pd_{57}Ni_{43}$ nanowires	0.62 [b]			ACS Appl. Mater. Interfaces 2011, 3, 105–109
$Pd@Ni_{1.6}B_{0.02}$	0.21 [b]			Int. J. Hydrogen Energy 2018, 43, 3216–3222
8 nm $Pd_{0.5}Co_{0.5}$	0.18 [b]		0.1 M $HClO_4$ and 2 M HCOOH	Nano Lett. 2012, 12, 1102–1106
PdCu alloy multipod	0.15 [b]		0.1 M $HClO_4$ and 1M HCOOH	n. J. Mater. Chem. A 2017, 5, 4421–4429
AuPd NPs		0.42	0.1M $HClO_4$+0.5M HCOOH	Angew. Chem. Int. Ed., 2011, 50, 8876 – 8880
Pd/CeO_2 NTs		0.485		Electrocatalysis. 2015, 6, 255-262
NiPd NWs/RGO		0.604		J. Mater. Chem. A. 2015, 3, 14001–14006
AgPd NPs	N/A	0.287		Sci. Rep. 2015, 5, 3703
CuPd/CNTs		0.56	0.5 M H_2SO4+0.5 M HCOOH	Electrochem. Commun. 2016, 69, 55–58
Pd_6Co nanocrystals on 3D graphene		0.43		Nanoscale. 2016, 8, 1905– 1909
Core/shell Au/Pd NPs		0.48		RSC Adv. 2016, 6, 24645– 24650

[a] Mass activities (MA) at 0.3 V and 0.5 V versus the normal hydrogen electrode (NHE).

[b] Mass activities (MA) at 0.3 V versus the reversible hydrogen electrode (RHE)