Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

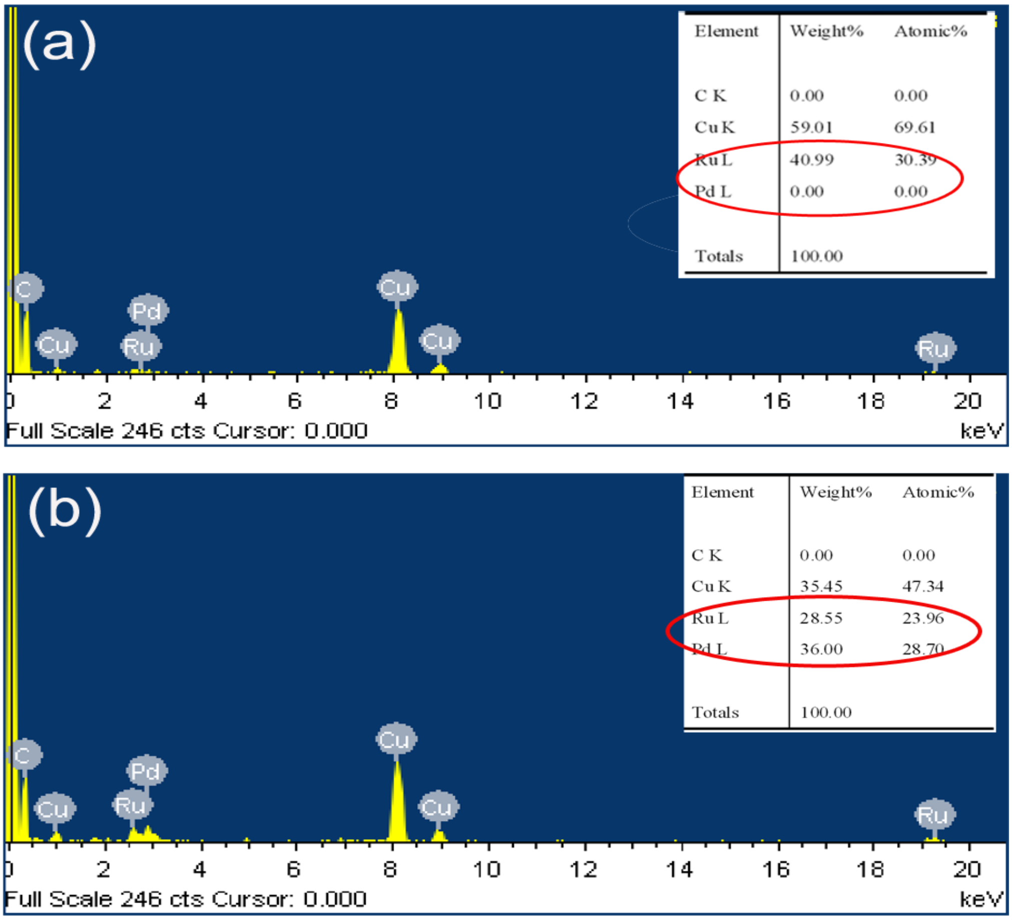
Electronic Supplementary Information for

Mixed-phase PdRu bimetallic structure with high activity and stability for formic acid electrooxidation

Dongshuang Wu, Zhaoliang Zheng, Shuiying Gao, Minna Cao and Rong Cao*

State Key Laboratory of Structural Chemistry, Fujian Insistitute of Research on the Structure of Matter Chinese Academy of Science, 155 Yangqiao West Road Fuzhou Fujian, China

*****Corresponding author. E-mail: rcao@fjirsm.ac.cn



(a)

Element	Weight%	Atomic%
C K	0.00	0.00
Cu K	59.01	69.61
Ru L	40.99	30.39
Pd L	0.00	0.00
Totals	100.00	

(b)

Element	Weight%	Atomic%
C K	0.00	0.00
Cu K	35.45	47.34
Ru L	28.55	23.96
Pd L	36.00	28.70
Totals	100.00	

Fig. S1 EDS analysis of a single nanodendrites NPs in Fig. 2c. Up-right inset are the corresponding element composition tables. (a) The white cycles in Fig. 2c, the corresponding table shows that the Pd content is 0, indicating the element in white cycles is Ru. (b) A nanodendrites NPs (both the black cycle and white cycles in Fig. 2c), indicating the black cycle is Pd.

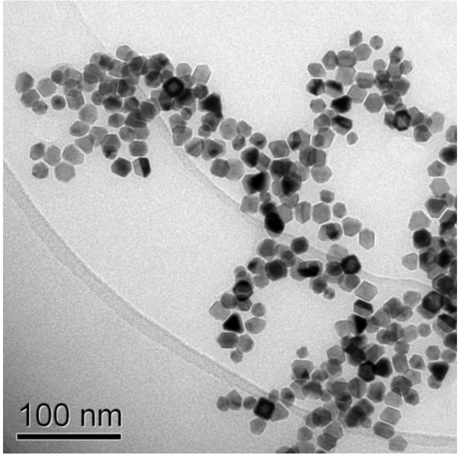
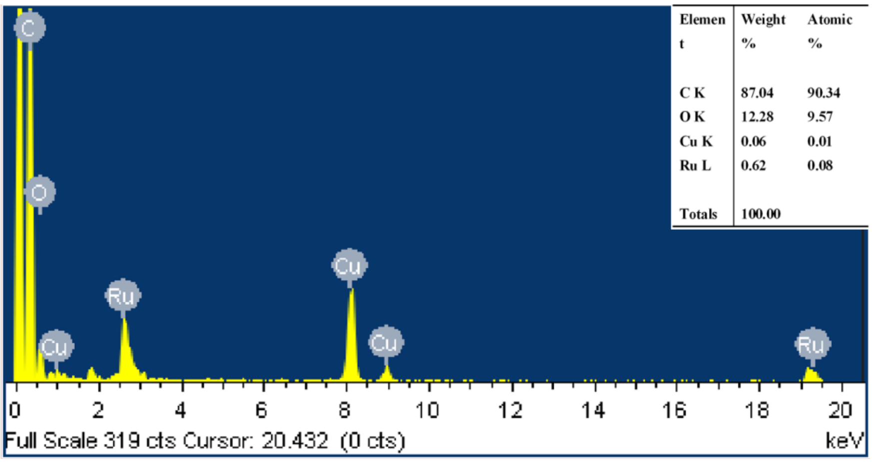
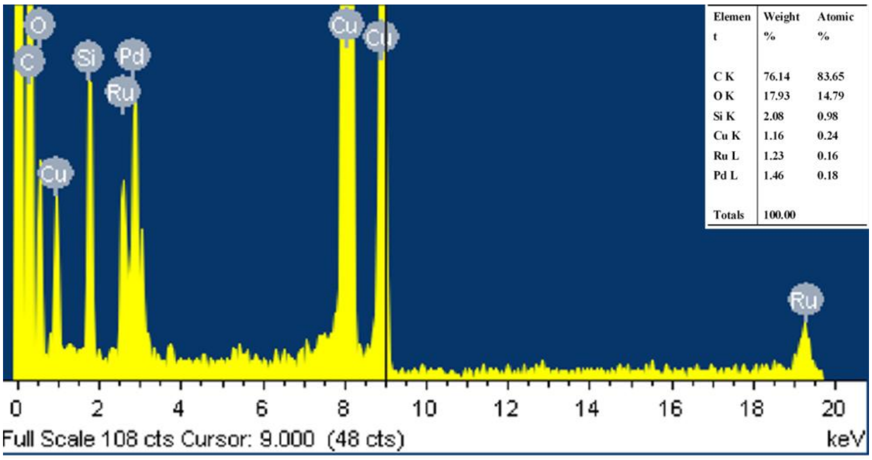


Fig. S2 TEM images of polyhedron $Pd_{99}Ru_1$ NPs. Reaction condition: 383 K, $K_2PdCl_4/RuCl_3$=1:1 (molar ratio), 3-h reaction.



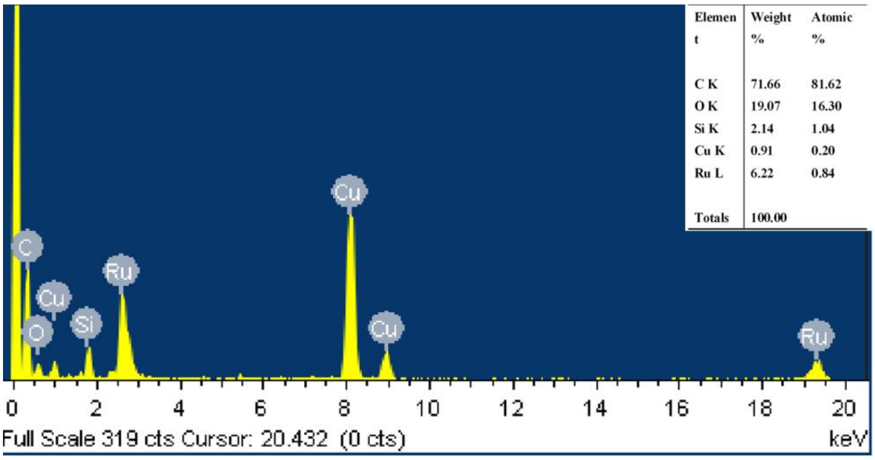
Element	Weight %	Atomic %
C K	87.04	90.34
O K	12.28	9.57
Cu K	0.06	0.01
Ru L	0.62	0.08
Totals	100.00	

Fig. S3 EDS of the chain-like NPs in Fig. 3(circled in white oval), indicates that the chain-like NPs are monometallic Ru NPs. Up-right inset is the corresponding element composition table. Due to the monometallic Ru NPs are highly dispersed in the nanodendrites NPs, to avoid the nanodendrites, only a small area of NPs on the Cu grid could be selected to accept the EDS analysis. So the atomic ratio is very small in the EDS elemental composition table.



Element	Weight %	Atomic %
C K	76.14	83.65
O K	17.93	14.79
Si K	2.08	0.98
Cu K	1.16	0.24
Ru L	1.23	0.16
Pd L	1.46	0.18
Totals	100.00	

Fig. S4 EDS of the nanodendrites in one random chosen area in Fig. 3, indicates that the nanodendrites are consisted with Pd and Ru. The corresponding element composition (up-right inset) shows that Ru and Pd in the as-chosen area is nearly equal molar. This result is in line with that $Pd_{50}Ru_{50}$ detected by ICP, implying a homogenous distribution of PR-2.



Element	Weight %	Atomic %
C K	71.66	81.62
O K	19.07	16.30
Si K	2.14	1.04
Cu K	0.91	0.20
Ru L	6.22	0.84
Totals	100.00	

Fig. S5 EDS of the worm-like NPs in Fig. 4c. Up-right inset is the corresponding element composition table.

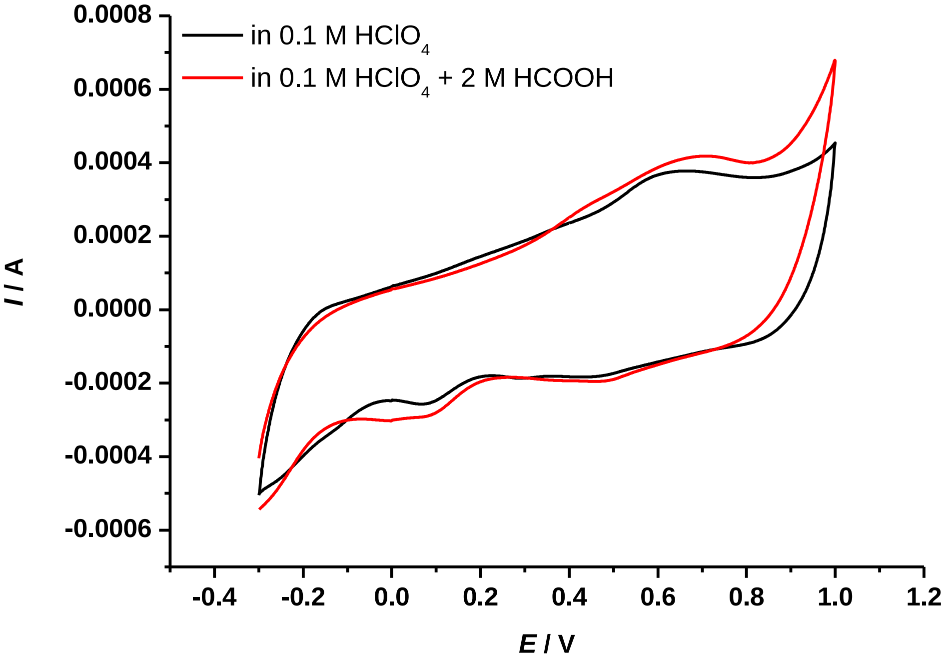


Fig. S6 **The original CVs of monometallic Ru in N_2-purged 0.1 M $HClO_4$ with (black line) HCOOH and without (red line) HCOOH. The similar behavior of the two CVs indicates that the monometallic Ru NPs don't have the electrocatalytic ability toward formic acid itself.**

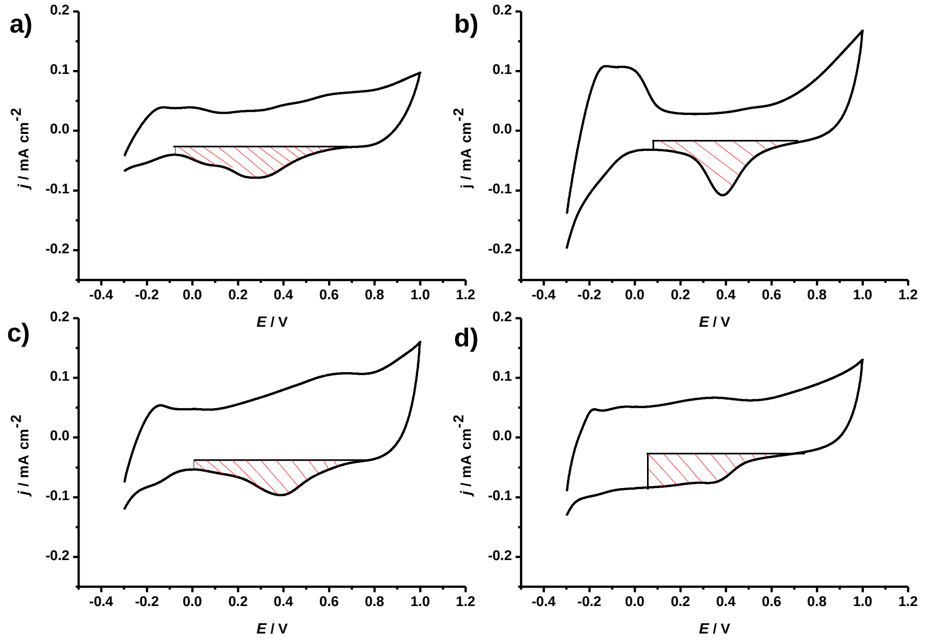


Fig. S7 Cyclic voltammograms (CVs) of a) PR-1, b) PR-2, C) PR-3, d) commercial Pd/C recorded in 0.1 M $HClO_4$ at a scan rate of 50 mV s^{-1}. The charges intergraded from the region hatched with red lines in each curve correspond to the electrochemical surface area (ECSA) of that catalyst. And 424 μC cm^{-2} is used as the conversion factor.

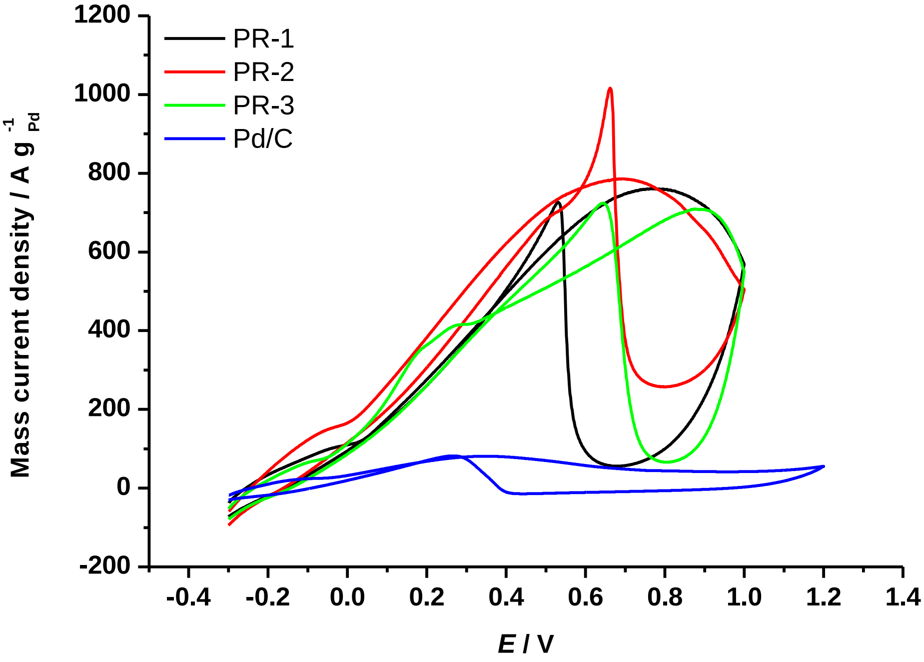


Fig. S8 CVs for determining the mass activity of PR-1, PR-2, PR-3 and commercial Pd/C in 0.1 M $HClO_4$ + 2 M HCOOH at a scan rate of 50 mV s^{-1}.

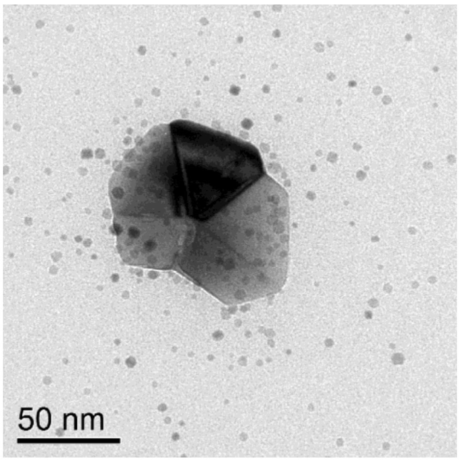


Fig. S9 A large-area TEM images of Pd NPs. Reaction condition: 383 K, 0.008 g K_2PdCl_4, 3-h reaction.

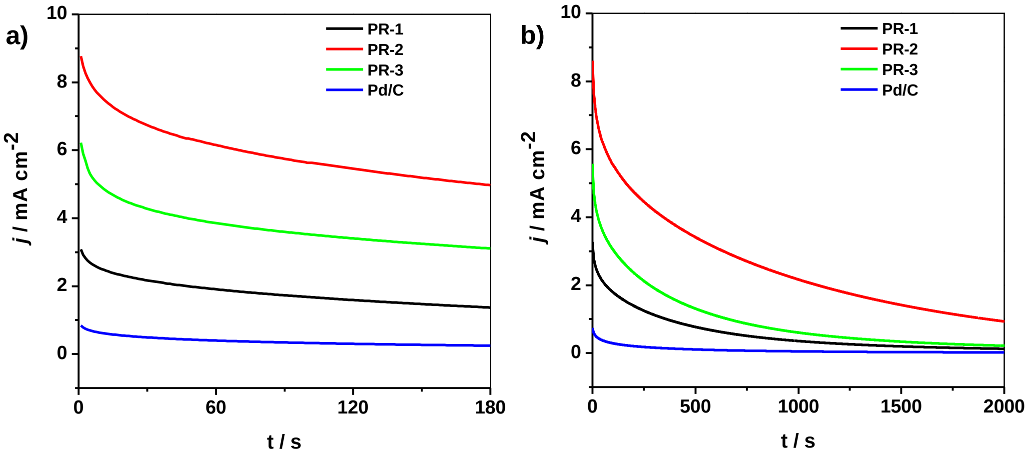


Fig. S10 Current density–time dependence curves measured by chronoamperometry (CA) at 600 mV (a) and DC potential amperometry (DCPA) at 400 mV (b) in 0.1 M $HClO_4$ + 2 M HCOOH for the electrodes.

Table S1. Anodic peak potential and the corresponding peak current density for PdRu NPs and commercial Pd/C.

	Peak potential (V)	Area peak current density (mA/cm^2)	Mass peak current density (A/g)
PR-1	0.745	1.78	759.29
PR-2	0.662	5.69	782.05
PR-3	0.873	3.38	708.14
Pd/C	0.350	0.30	81.10