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Supporting Information

Pd-Zn Nanocrystals for High-Efficient Formic Acid Oxidation

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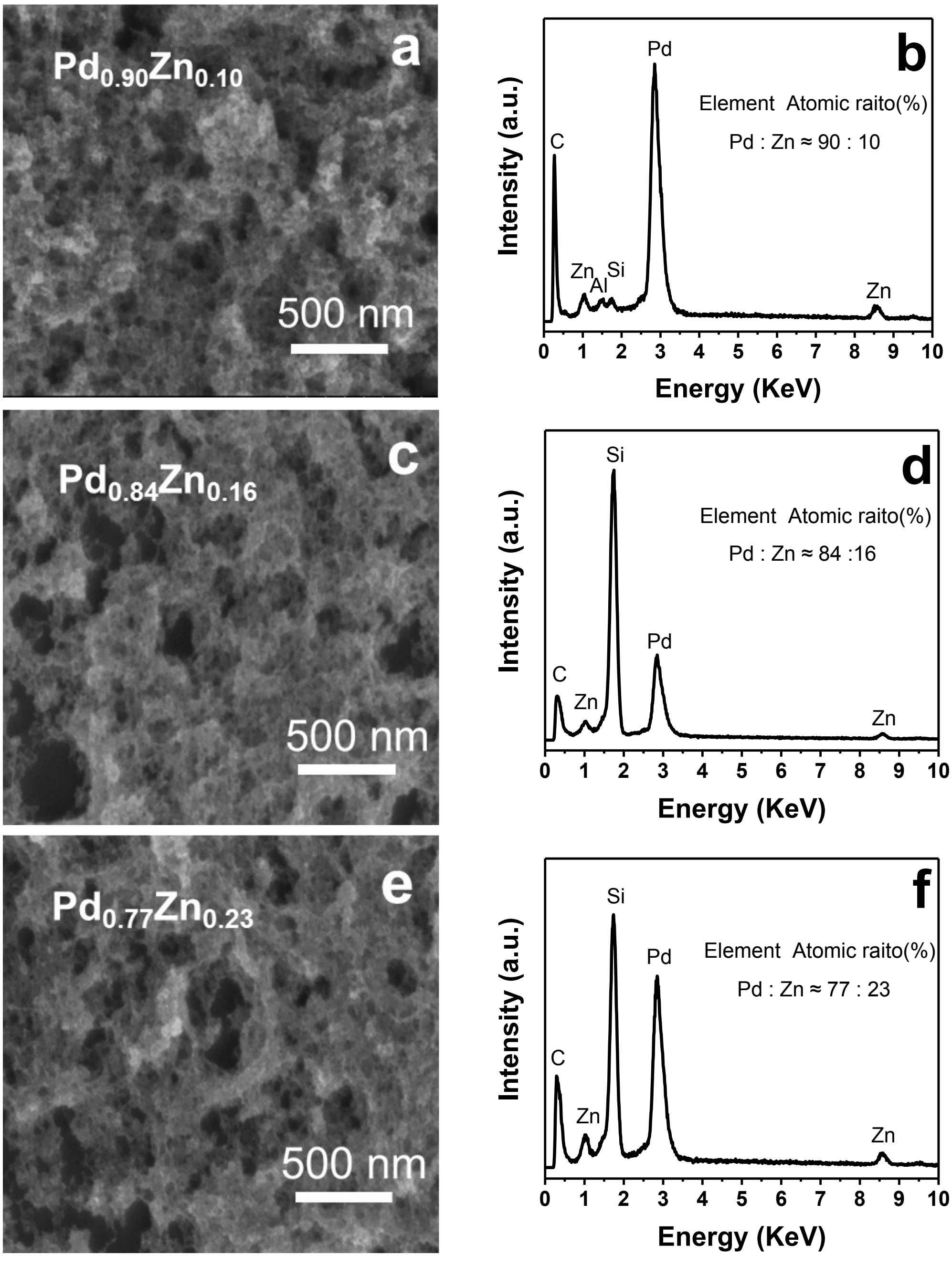

Fig. S1 SEM images and EDS spectral of the series of Pd_xZn_{1-x} NCs, (a) and (b) $Pd_{0.90}Zn_{0.10}$, (c) and (d) $Pd_{0.84}Zn_{0.16}$, (e) and (f) $Pd_{0.77}Zn_{0.23}$.

Table S1 Pd/Zn Atomic Ratios (%) for the series of Pd_xZn_{1-x} NCs determined by ICP-MS and EDS.

samples	**$Pd_{0.90}Zn_{0.10}$**	**$Pd_{0.84}Zn_{0.16}$**	**$Pd_{0.77}Zn_{0.23}$**
ICP-MS	89.7/10.3	83.7/16.3	76.8/23.2
EDS	90.1/9.9	82.81/17.9	77.5/22.5

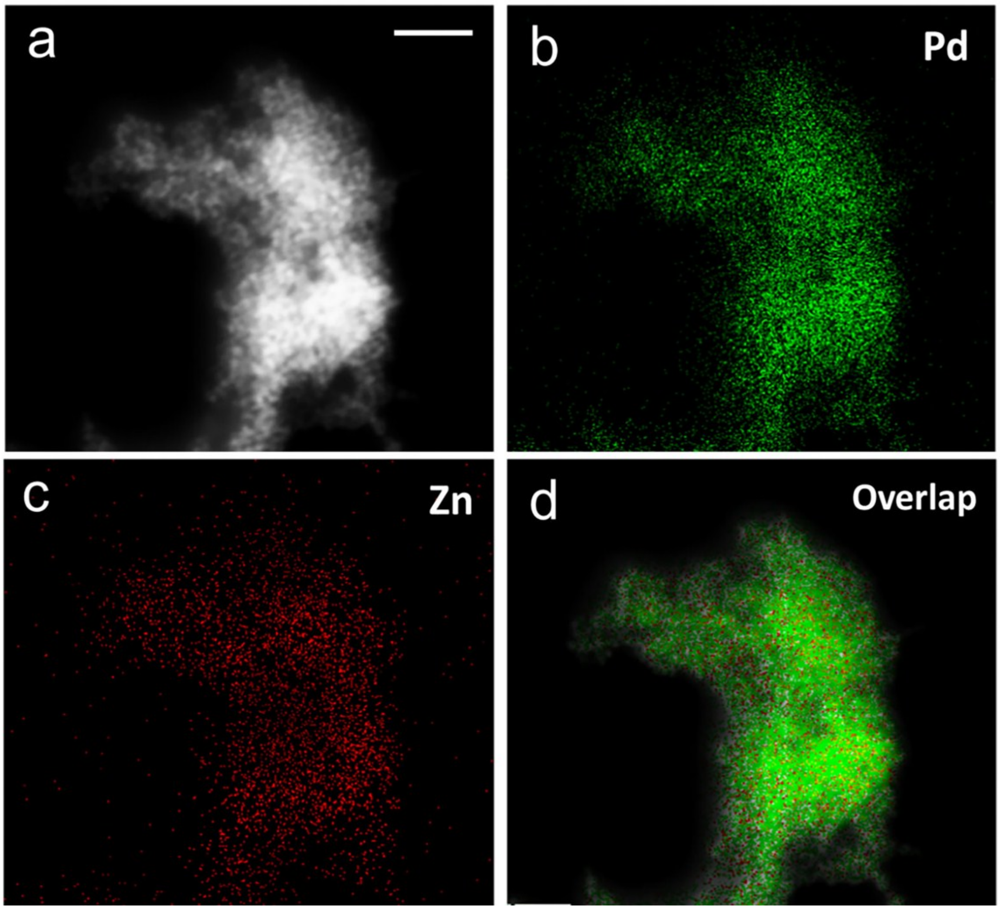

Fig. S2 (a) HAADF-STEM image of $Pd_{0.90}Zn_{0.10}$, (b) Pd mapping in green, (c) Zn mapping in red, and (d) Overlapped mapping of Pd and Zn. Scale bar: 200 nm.

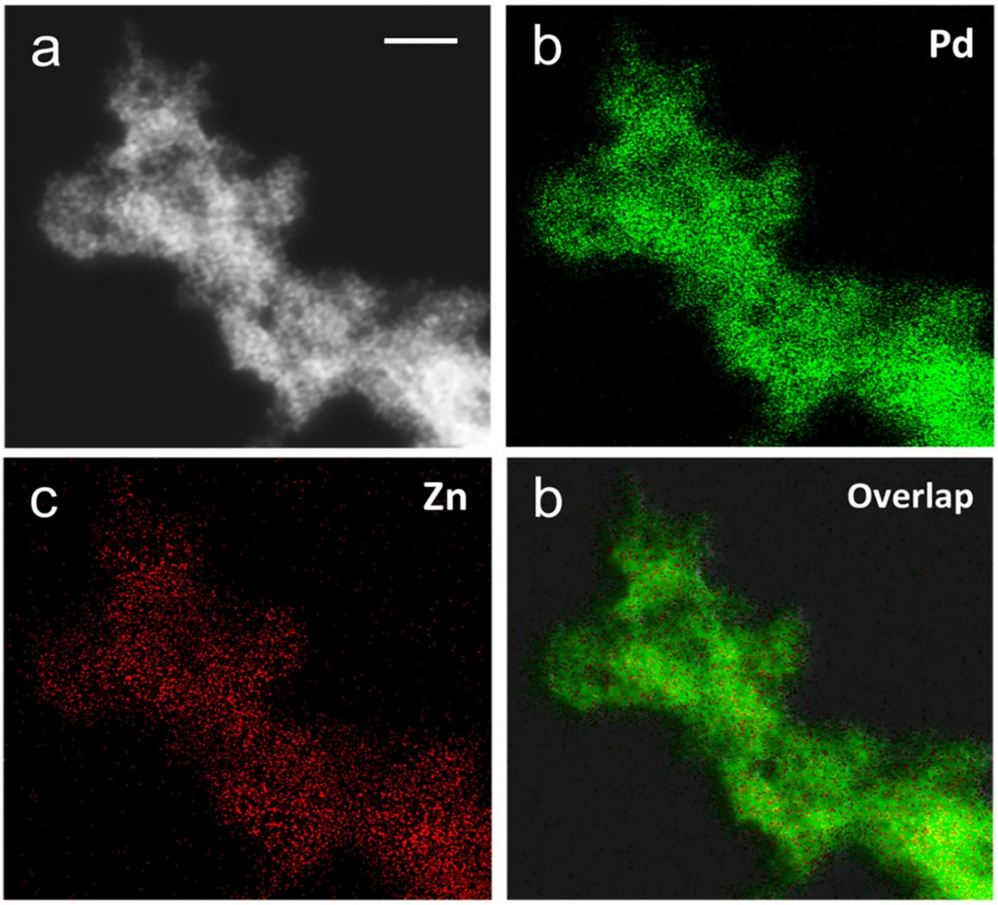

Fig. S3 (a) HAADF-STEM image of $Pd_{0.84}Zn_{0.16}$, (b) Pd mapping in green, (c) Zn mapping in red, and (d) overlapped mapping of Pd and Zn. Scale bar: 200 nm.

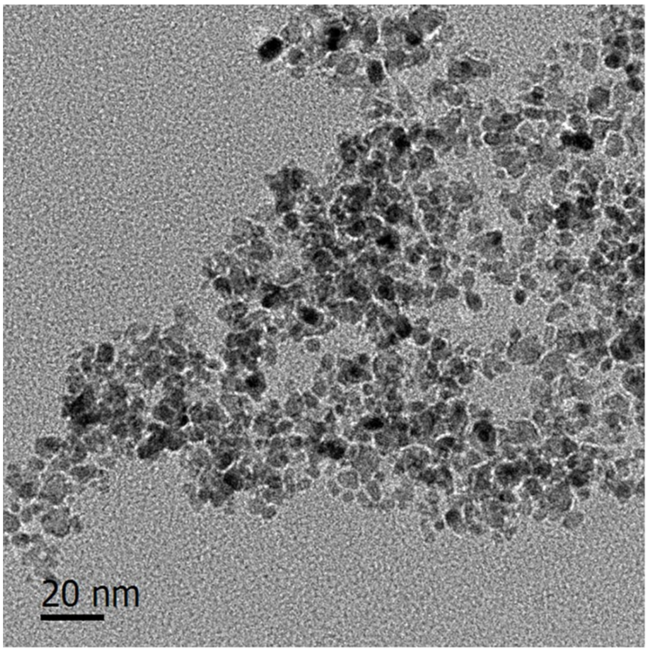

Fig. S4 TEM image of the irregularity Pd NCs which were synthesized in the absence of Zn precursor.

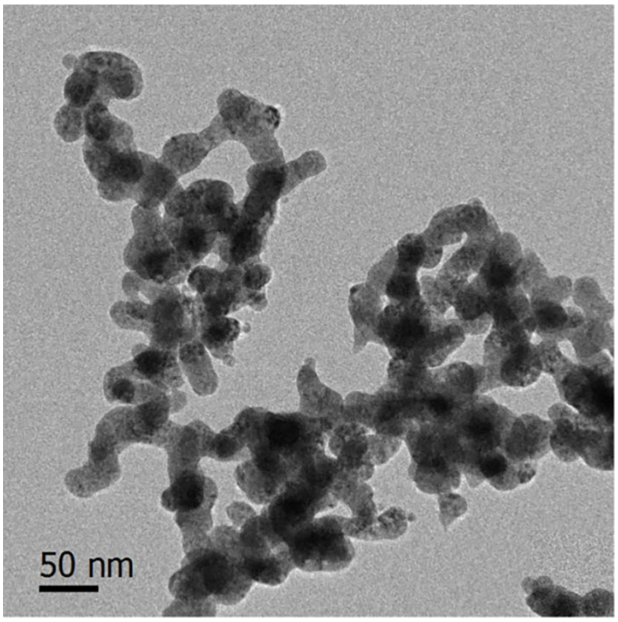

Fig. S5 TEM image of $Pd_{0.77}Zn_{0.23}$ NCs alloy which was synthesized in the absence of DMF.

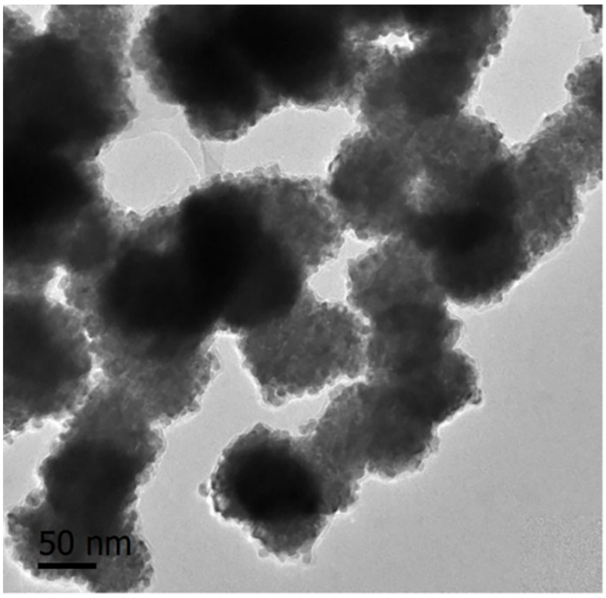

Fig. S6 TEM image of $Pd_{0.77}Zn_{0.23}$ NCs alloy which was synthesized in the absence of PVP.

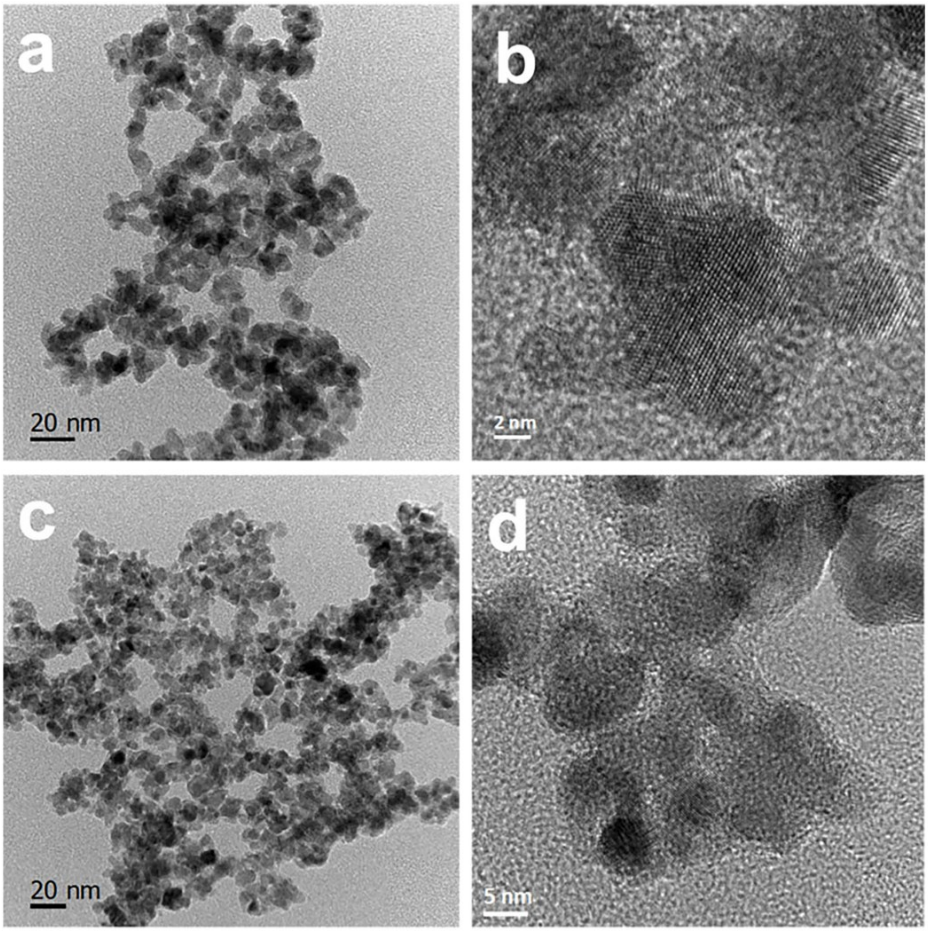

Fig. S7 The representative TEM images of $Pd_{0.77}Zn_{0.23}$ NCs obtained with different precursor species. Replacing $ZnCl_2$ with (a-b) $Zn(NO_3)_2$ and (c-d) $Zn(acac)_2$.

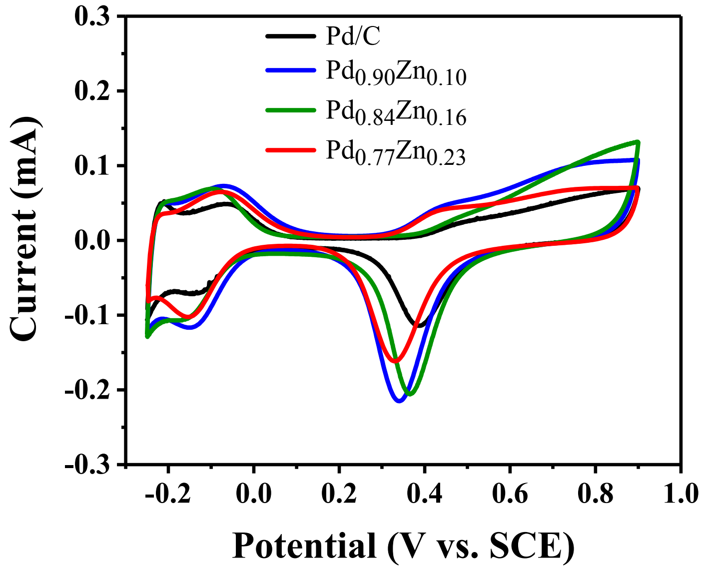

Fig. S8 CV of the Pd_xZn_{1-x} NCs and Pd/C catalyst in Ar-saturated in 0.1 M $HClO_4$ at a scan rate of 50 mV s^{-1}.

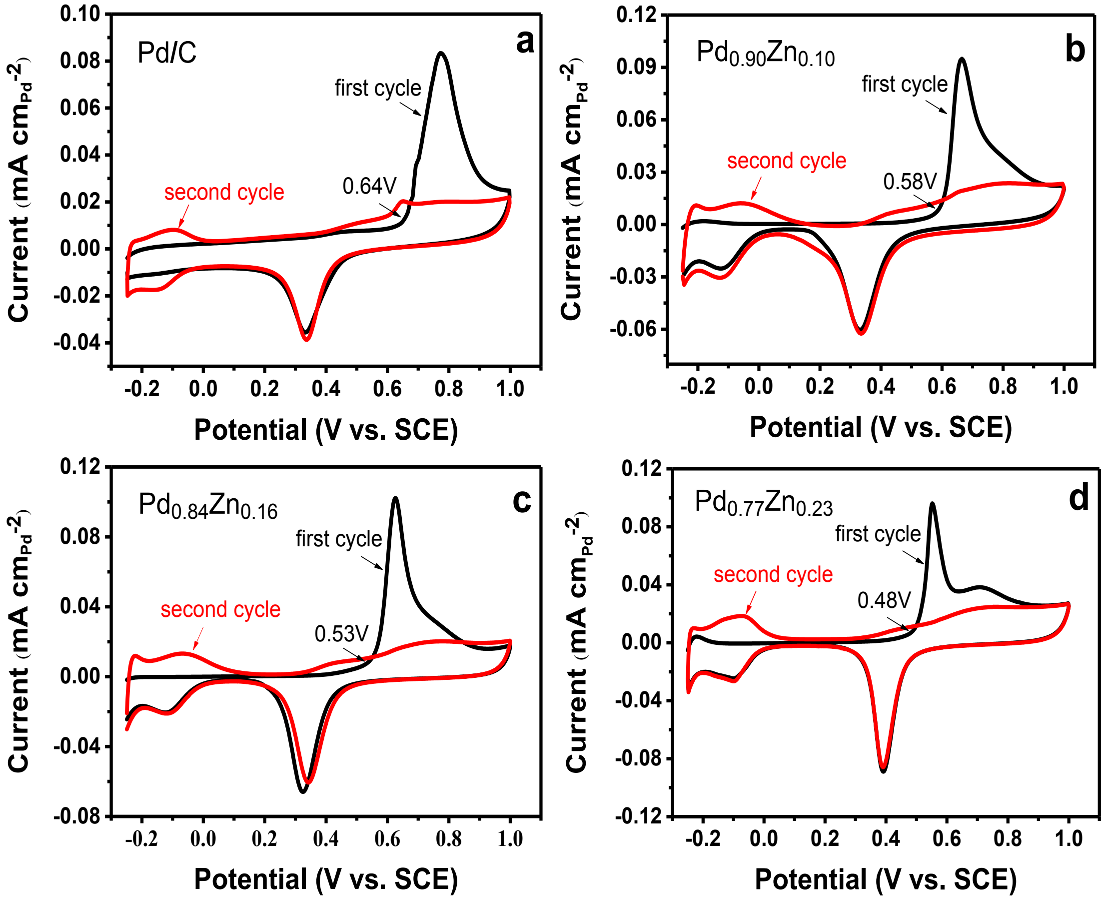

Fig. S9 CO stripping voltammograms of (a) Pd/C, (b) $Pd_{0.90}Zn_{0.10}$, (c) $Pd_{0.84}Zn_{0.16}$ and (d) $Pd_{0.77}Zn_{0.23}$ NCs in 0.1 M $HClO_4$ at a scan rate of 20 mV s^{-1}.

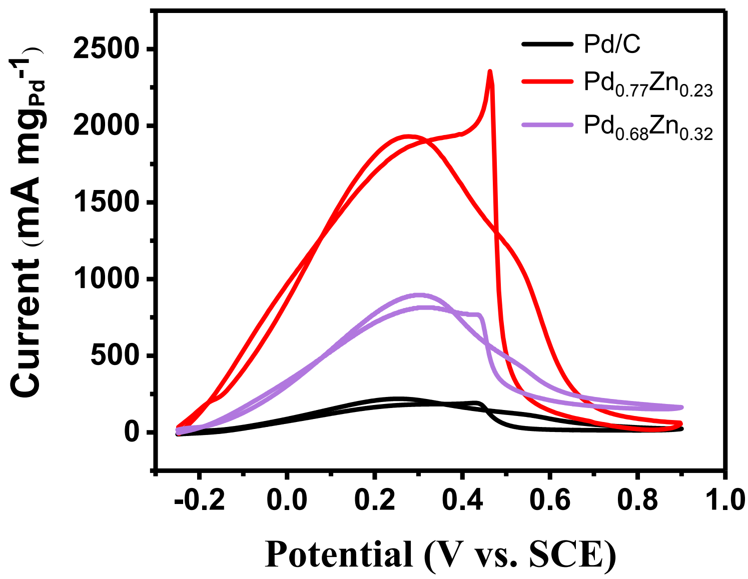

Fig. S10 CV curves of $Pd_{0.68}Zn_{0.32}$ and Pd/C catalyst in 0.1 M $HClO_4$ and 0.5 M HCOOH at a scan rate of 50 mV s^{-1}.

Table S2 Formic acid oxidation behavior on various Pd or Pd-based electrocatalysts is to compare it to Pd-Zn NCs catalysts.

Catalysts	Test condition	specific activity (mA cm_{Pd}^{-2})	Mass activity (mA mg_{Pd}^{-2})	CO-stripping onset potential (V)	Ref
$Pd_{0.77}Zn_{0.23}$	**0.1 M $HClO_4$ and 0.5 M HCOOH**	**13.5**	**1945.0**	**0.48**	**this**
Pd bipyramids	0.5 M $HClO_4$ and 0.5 M HCOOH	20.8	/	/	1
Pd_3Pt Half-Shells	0.5 M $HClO_4$ and 0.5 M HCOOH	/	318.0	0.63	2
np-$Pd_{50}Cu_{50}$	0.1 M $HClO_4$ and 0.1 M HCOOH	6.40	640.5	0.68	3
Cu–Pd multipods	0.1 M $HClO_4$ and 1 M HCOOH	2.14	/	0.89	4
Pd nanochains	0.5 M H_2SO_4 and 0.5 M HCOOH	40.2	283.8	0.80	5
CuPd@Pd tetrahedra	0.5 M H_2SO_4 and 0.5 M HCOOH	4.93	501.8	0.52	6
PdNiCu/C	0.5 M H_2SO_4 and 0.5 M HCOOH	3.30	792.0	0.70	7
ordered Pd_3Fe/C	0.5 M H_2SO_4 and 0.5 M HCOOH	/	696.4	/	8
Pd–Cu Tripods	0.5 M $HClO_4$ and 0.5 M HCOOH	5.81	1580.0	/	9
Pd-Cu network	0.5 M H_2SO_4 and 0.5 M HCOOH	1.50	517.0	/	10
PdNi nanowire	0.5 M H_2SO_4 and 0.5 M HCOOH	/	604.3	/	11

Pd–Ni–P	0.5 M H_2SO_4 and 0.5 M HCOOH	/	1457.0	/	12
Pd-Fe/RGO	0.1 M H_2SO_4 and 0.5 M HCOOH	2.71	1000.0	/	13
Pd_4Ni/rGO	0.5 M H_2SO_4 and 0.5 M HCOOH	/	1435.0	/	14
Pd–Mo_2N/rGO	0.5 M H_2SO_4 and 0.5 M HCOOH	1.03	532.7	0.82	15
PdO/Pd-CeO_2 hollow sphere	0.5 M H_2SO_4 and 0.5 M HCOOH	/	1620.0	0.69	16
PdAu/rGO	0.5 M H_2SO_4 and 0.5 M HCOOH	3.67	2040.0	0.68	17

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