Supporting Information

Sn-Doped PdCu Alloy Nanosheets Assemblies as an Efficient Electrocatalyst for Formic Acid Oxidation

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I Supplementary Experimental Section

Preparation of PdCuSn Ns a and PdCuSn Ns b

On the basis of PdCu, different proportions of PdCuSn Ns catalysts were synthesized by adjusting the content of Sn. The specific synthesis method is as follows: the newly prepared PdCu Ns catalyst was ultrasonically dispersed in 5 ml ethylene glycol for later use. Take 7 mg of Tin (IV) acetate, 25 mg of ascorbic acid and 25 mg of PVP, add them to a round-bottom flask containing 5 ml of ethylene glycol, sonicate for half an hour to completely mix the mixture solution, and then add the above prepared PdCu Ns ethylene glycol solution. Continue to mix homogeneously ultrasonically, heat to 160 °C in an oil bath for another 1 h, centrifuge at 6000 rpm with a mixture of ethanol and water. Finally, the products PdCuSn Ns a was obtained. Meanwhile, the amount of Tin (IV) acetate was changed to 13 mg, and PdCuSn Ns b was obtained by the same method.

II Supplementary Structural Section

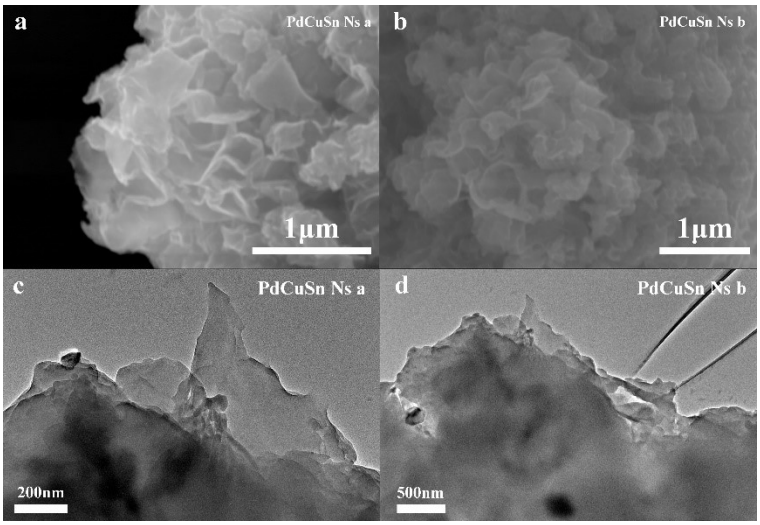

Fig.S1 The morphology images of (PdCuSn Ns a) and (PdCuSn Ns b) (a,b) SEM, (c,d) TEM.

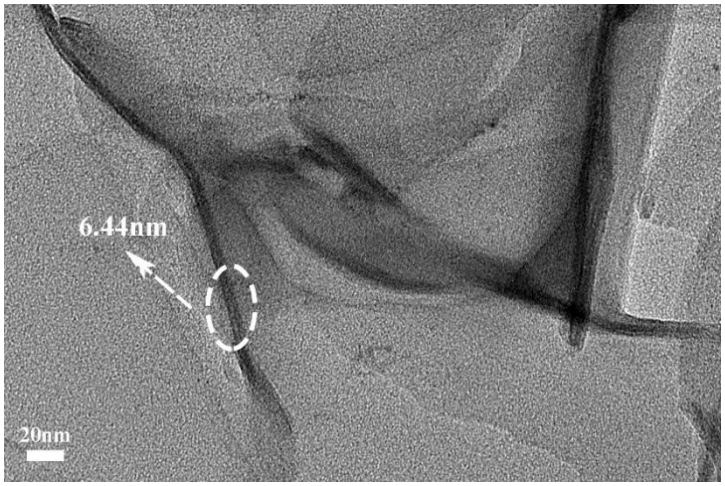

Fig.S2 The TEM of the PdCuSn Ns to measure the thickness of nanosheet.

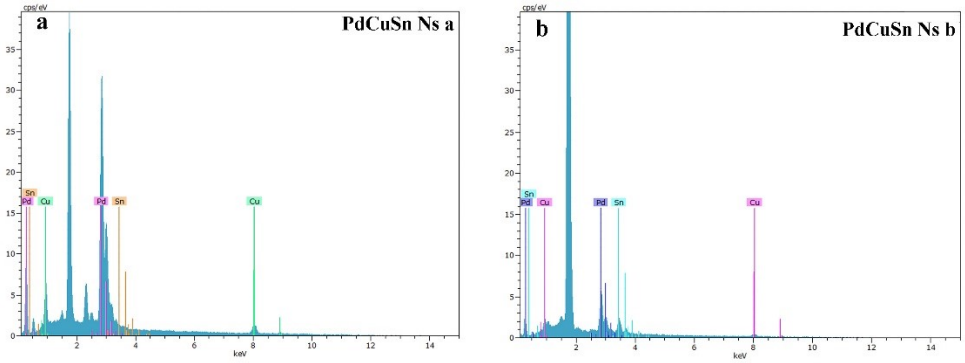

Fig.S3 The EDAX of (PdCuSn Ns a) and (PdCuSn Ns b) .

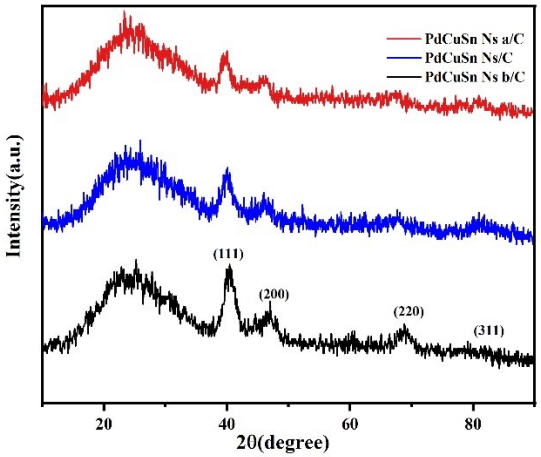

Fig.S4 XRD patterns of Pd-based catalysts.

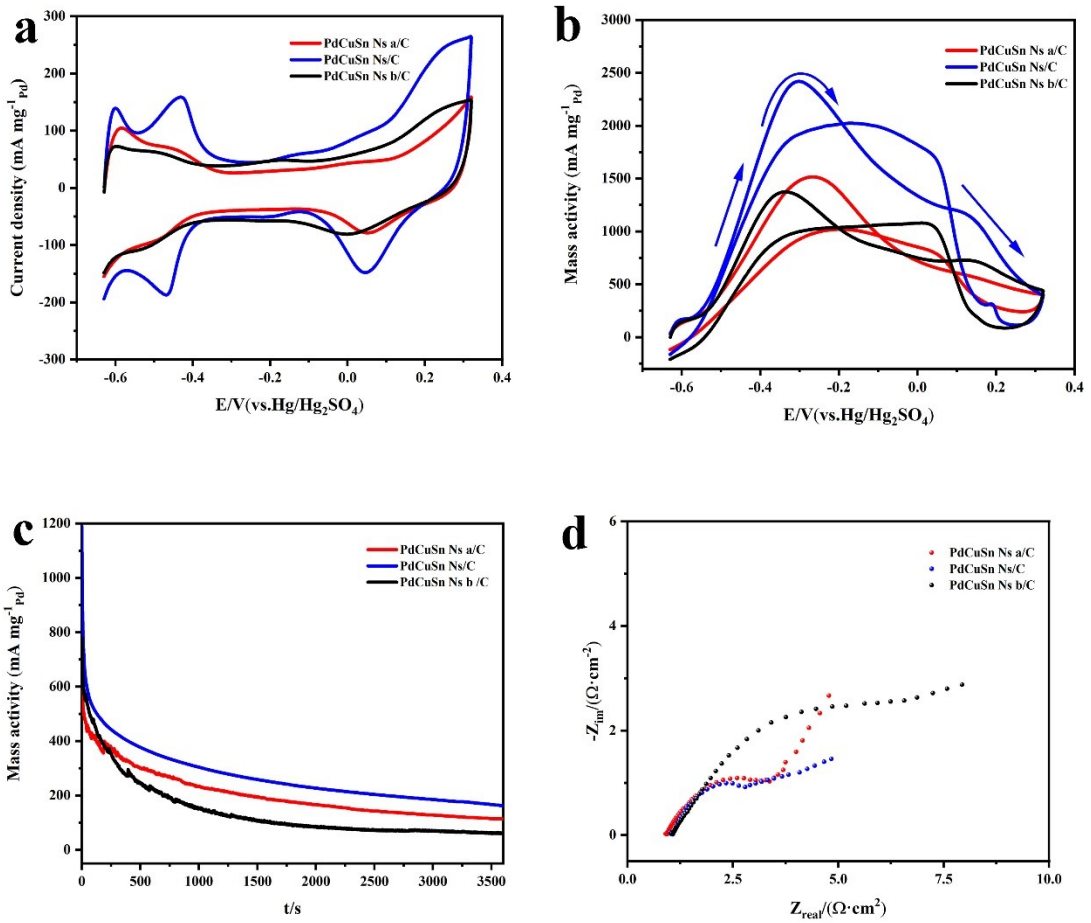

Fig.S5 The Electrochemical characterization of Pd-based catalysts (a) CV curves in N_2-saturated 0.5 mol L^{-1} H_2SO_4 solution, (b) CV curves of in N_2-saturated 0.5 mol L^{-1} H_2SO_4 +0.5 mol L^{-1} HCOOH solutions, (c) Amperometric i-t curves of Pd-based catalysts at -0.4 V in N_2-saturated 0.5 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} HCOOH solution, (d) EIS experiments.

We also performed electrochemical tests on different proportions of PdCuSn Ns to explore the optimal proportions. The stable cyclic voltammetry (CV) curves of the palladium-based catalyst are shown in N_2-saturated 0.5 mol L^{-1} H_2SO_4 solution. According to the formula, the ECSA of PdCuSn Ns a/C and PdCuSn Ns b/C are 58.3 m^2 g^{-1}_{Pd} and 44.4 m^2 g^{-1}_{Pd}, respectively, which are both smaller than PdCuSn Ns/C. The scan rate of 50 mV s^{-1} was obtained in 0.5 mol L^{-1} H_2SO_4 and 0.5 mol L^{-1} HCOOH solution saturated with N_2. The current densities of PdCuSn Ns a/C and PdCuSn Ns b/C are 1516.7 mA mg^{-1}_{Pd} and 1373.8 mA mg^{-1}_{Pd}, respectively, are smaller than PdCuSn Ns /C. It can be found from the amperometric i-t curves that the current density of PdCuSn Ns /C at 3600s is higher than that of the other two catalysts, indicating that the PdCuSn Ns /C has the best stability. The EIS test shows that the formic acid oxidation kinetics of PdCuSn Ns /C is the fastest. In conclusion, PdCuSn Ns /C catalyst has the best electrocatalytic activity and stability for formic acid oxidation, and its ratio is the best ratio in this experiment.

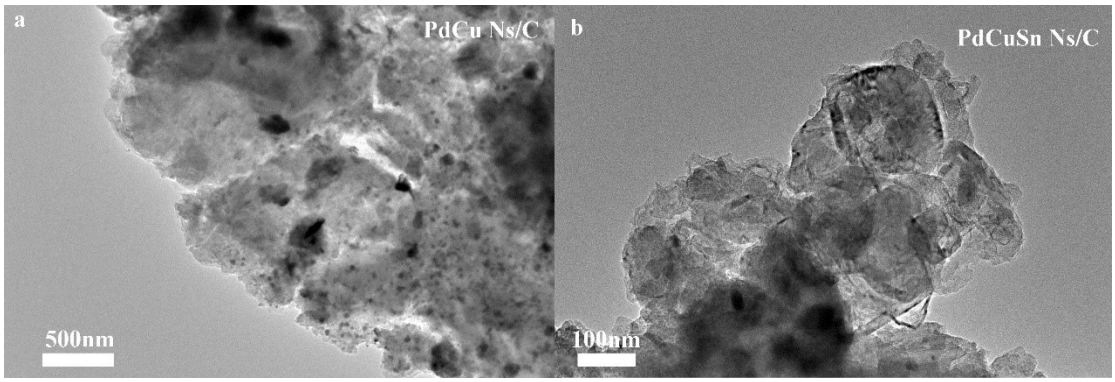

Fig.S6 The TEM image of palladium-based catalyst after stability test.

It can be seen from the TEM images of PdCu Ns/C and PdCuSn Ns/C after the stability test that the catalyst can still maintain the morphology of nanosheet, indicating that the nanosheet structure has good stability, and the morphology of PdCuSn Ns/C nanosheet is more clear and complete. It further verifies the result that PdCuSn Ns/C stability is the best in previous electrochemical tests.

Table S1 Performance comparison of Pd-based catalysts in the literature

Catalyst	**Morphology**	**ECSA (m^2 /g)**	**Mass Activity (mA/mg)**	**Condition**	**Reference**
Pd	Nanosheet	35.6 (Pd)	634.3 (Pd)	0.1 M $HClO_4$ + 0.2 M HCOOH	[1]
PdCu	Nanomultipod	65.7 (Pd)	774.7 (Pd)	0.1 M $HClO_4$ + 2 M HCOOH	[2]
PdCuIr	Nanosheet	51.67 (Pd)	1520 (Pd)	0.5 M H_2SO_4 + 0.5 M HCOOH	[3]
PdCuSn	Nanosheet	130.55 (Pd)	2420.1 (Pd)	0.5 M H_2SO_4 + 0.5 M HCOOH	This work

The electrochemical performance of PdCuSn Ns prepared in this paper was compared with that of Pd-based catalysts mentioned in the literature. It can be seen from Table S1 that PdCuSn Ns in this paper has higher ECSA and mass activity, thus showing excellent electrocatalytic performance for formic acid oxidation.

Reference

1. Y. Zhang, M. Wang, E. Zhu, Y. Zheng, Y. Huang and X. Huang, *Nano Lett*, 2015, **15**, 7519-7525.
2. D. Chen, P. C. Sun, H. Liu and J. Yang , *J Mater Chem A*, 2015, 2017, **5**,4421.
3. H. M. An, Z. L. Zhao, L. Y. Zhang, Y. Chen, Y. Y. Chang and C. M. Li, *ACS Appl Mater Interfaces*, 2018, **10**, 41293-41298.