Electronic Supplementary Information

Bimetallic Cu-Pd alloy multipods and their highly electrocatalytic performance for the formic acid oxidation and oxygen reduction

Dong Chen,[a,b] Pengcheng Sun,[a] Hui Liu[a,c] and Jun Yang[a,b,c]*

[a] State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China 100190. Tel: 86-10-8254 4915; Fax: 86-10-8254 4915; *E-mail: jyang@ipe.ac.cn

[b] University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing, 100049, China

[c] Center for Mesoscience, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

Financial supports from the National Natural Science Foundation of China (Grant No.: 21376247, 21506225, 21573240), and Center for Mesoscience, Institute of Process Engineering, Chinese Academy of Sciences (COM2015A001) are gratefully acknowledged.

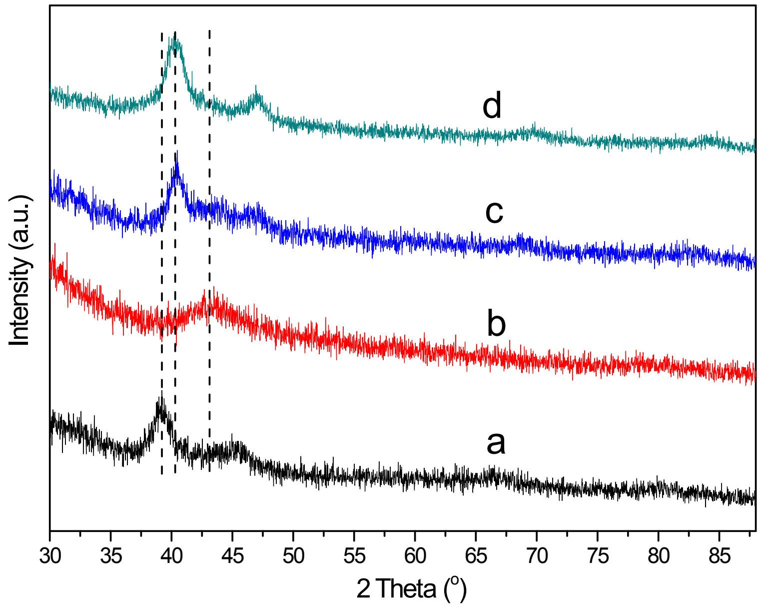

Fig. S1 X-ray diffraction (XRD) patterns of commercial Pd/C catalyst (a), Cu nanoparticles synthesized in oleylamine (b), Cu-Pd alloy multipods (c) and Cu-Pd alloy nanoparticls (d).

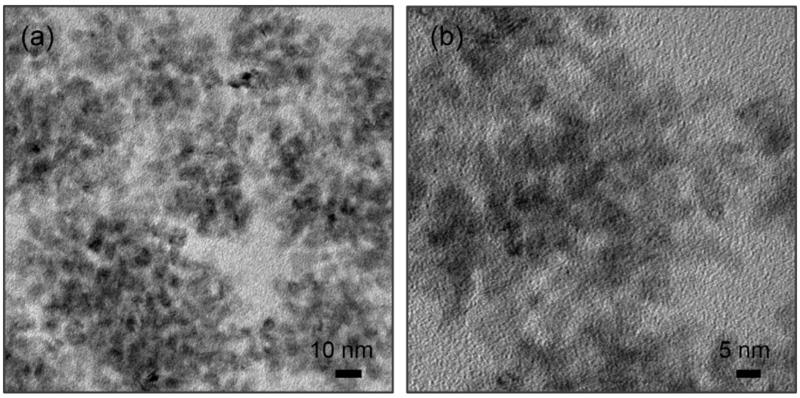

Fig. S2 TEM images (a) and HRTEM images (b) of the as-synthesized Cu nanoparticles in oleylamine.

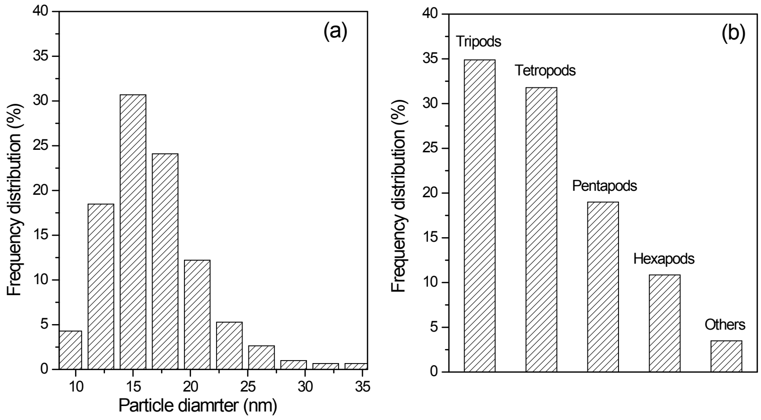

Fig. S3 Histograms to show the distributions of the size (a) and shape (b) of as-prepared Cu-Pd alloy multipods.

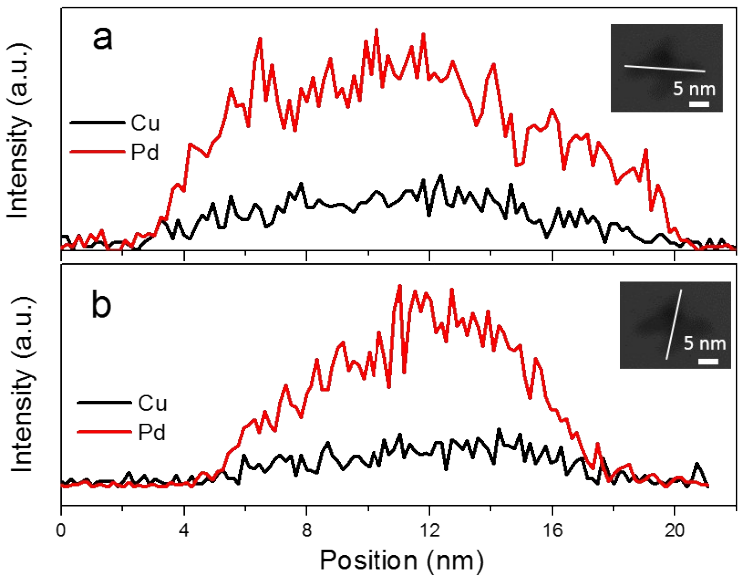

Fig. S4 The line profile of an arbitrary single particle across transversal (a) and longitudinal (b) direction in STEM mode. The inset is the analyzed tetrapod.

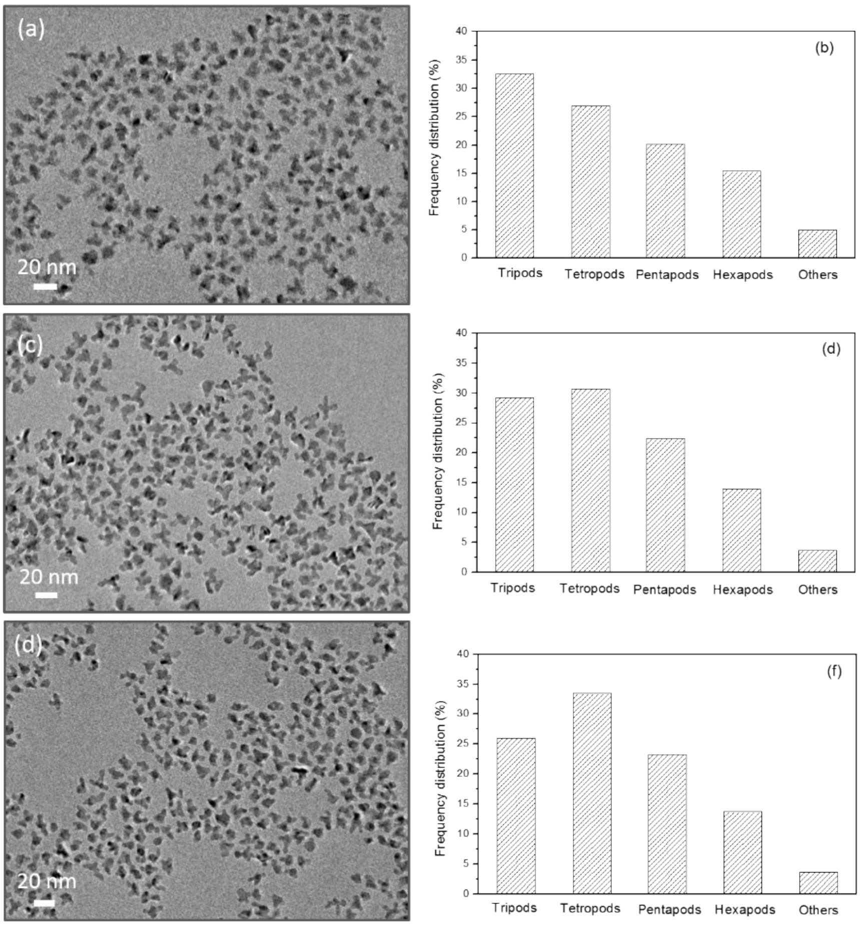

Fig. S5 TEM images (a,c,e) and of Cu-Pd alloy multipods gained in three different batches and corresponding histograms to show the distributions of the multipods.

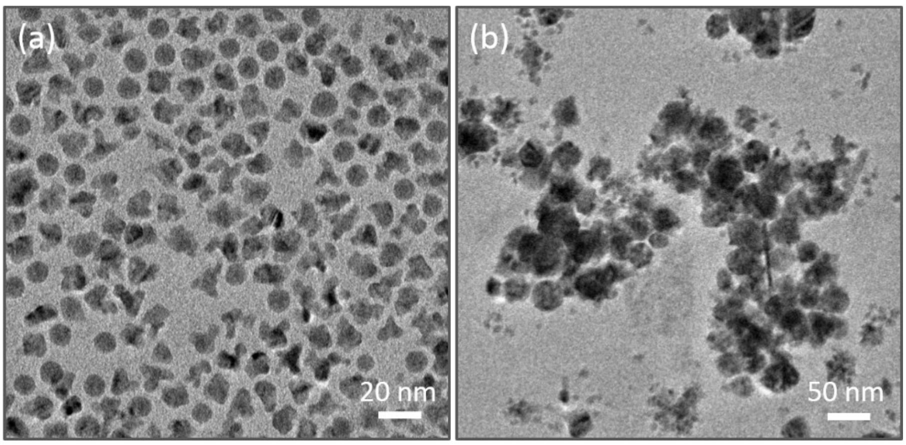

Fig. S6 The TEM images of the bimetallic Cu-Pd products gained with the same synthetic procedure for Cu-Pd alloy multipods but using Cu/Pd ratios at 6:8 and 6:11, respectively.

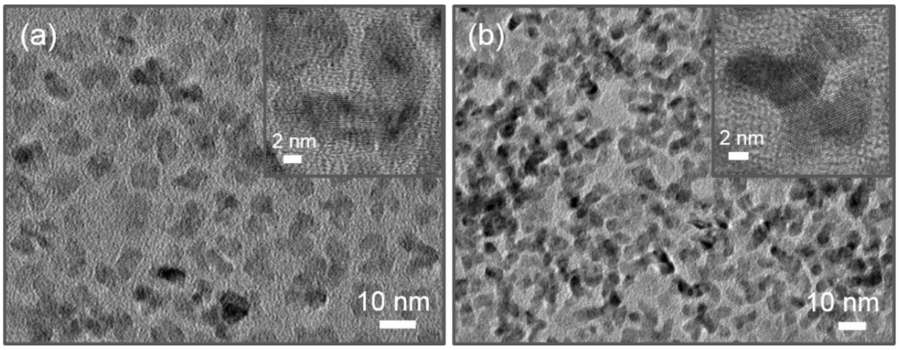

Fig. S7 TEM images and HRTEM images (insets) of the bimetallic Co-Pd (a) and Ni-Pd (d) nanostructures by the same synthetic protocol for bimetallic Cu-Pd alloy multipods.

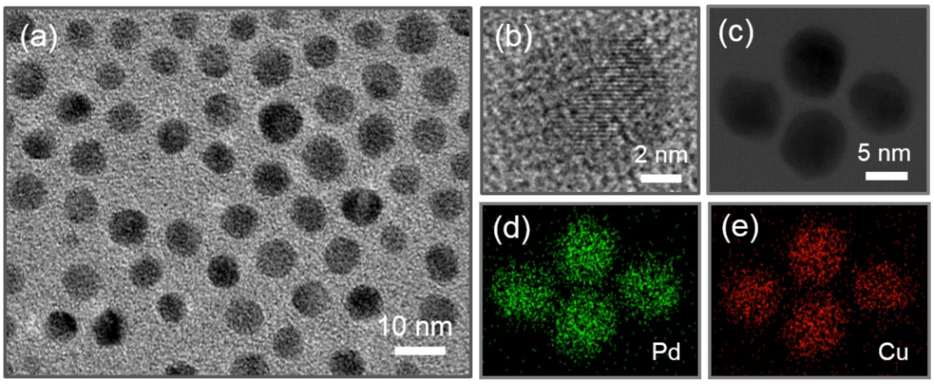

Fig. S8 TEM image (a), HRTEM image (b), STEM image (c) and elemental mapping (d,e) of bimetallic Cu-Pd alloy nanospheres synthesized by co-reducing $Pd(acac)_2$ and $Cu(acac)_2$ in oleylamine at 195^{o}C for 2 h.

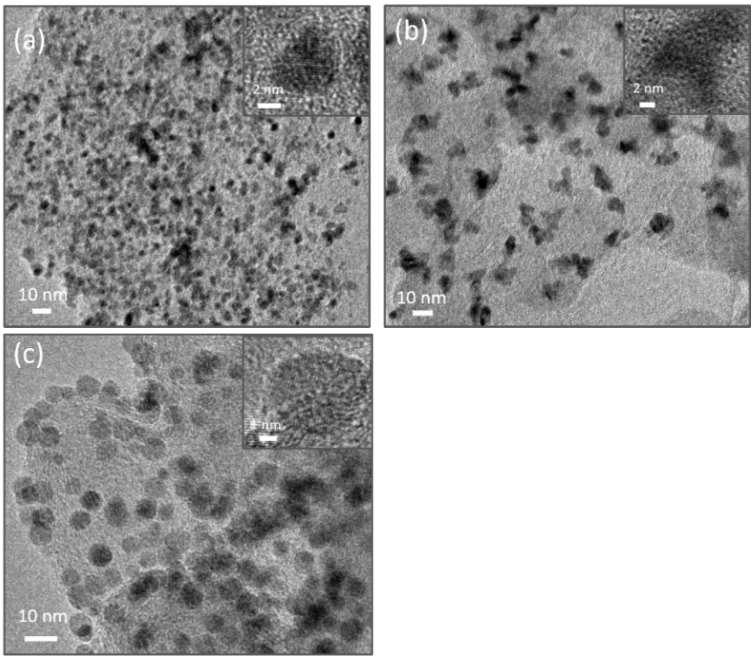

Fig. S9 TEM images and HRTEM images (insets) of commercial Pd/C catalyst (a), Cu-Pd alloy multipods (b), Cu-Pd alloy nanospheres (c) loaded on Vulcan carbon supports.

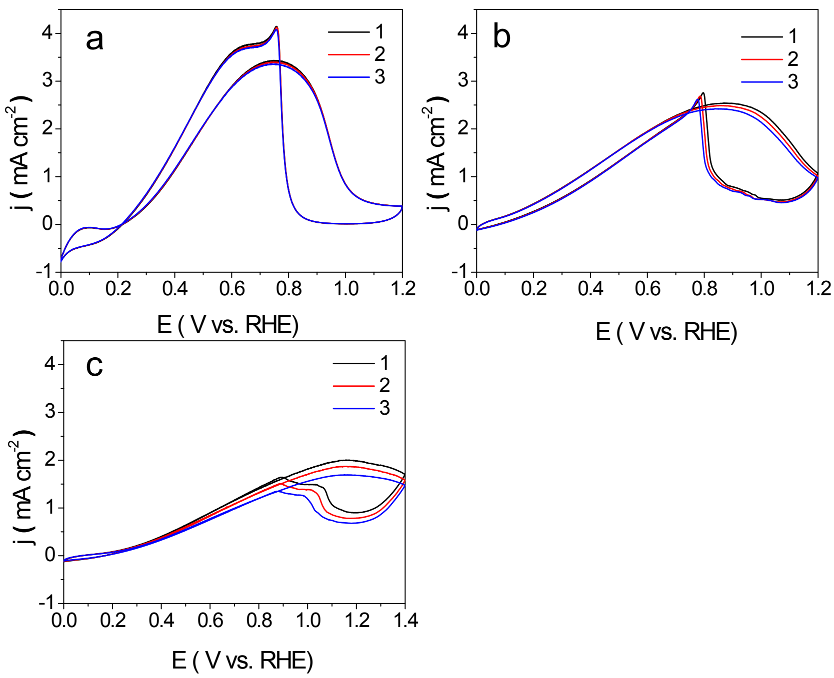

Fig. S10 Cyclic voltammograms of three successive RDE measurements over Cu-Pd alloy multipods (a), Cu-Pd alloy nanospheres (b), and commercial Pd/C catalyst (c) in 0.1 M $HClO_4$ and 1 M formic acid at a scan rate of 50 mV s^{-1} and a rotating speed of 1600 rpm, after the maximum formic acid oxidation current densities are reached.

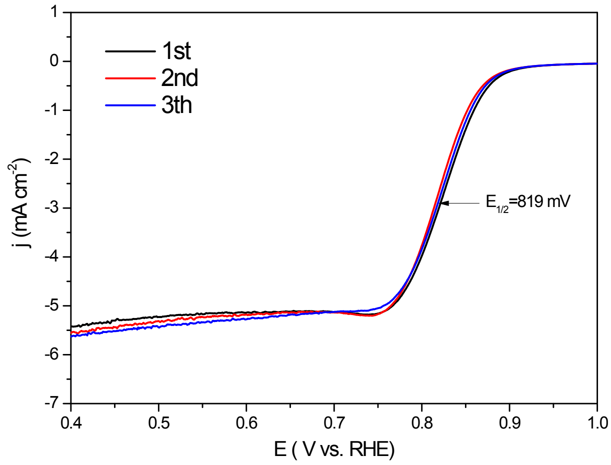

Fig. S11 Negative-going linear sweep voltammograms of Cu-Pd alloy multipods produced in three different batches in O_2 saturated 0.1 M $HClO_4$ electrolyte at a scan rate of 10 mV s^{-1} and a rotating speed of 1600 rpm.

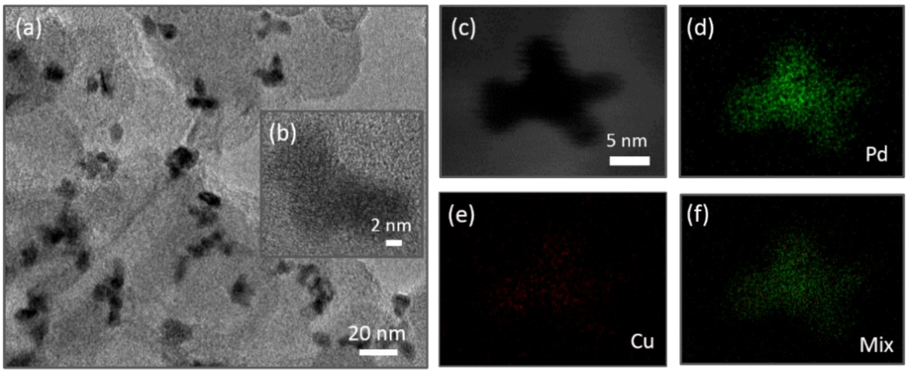

Fig. S12 TEM image (a), HRTEM image (b) and element mappings (c–f) of Cu-Pd alloy multipods after the durability test.

Table S1 Electrochemical measurements of formic acid oxidation on Cu-Pd alloy multipods, Cu-Pd alloy nanoparticles and commercial Pd/C catalyst.

Catalyst	FPP (V)	EPCD (mA cm^{-2})	BPP (V)	BPCD (mA cm^{-2})
multipods	0.75	1.67	0.78	2.14
nanospheres	0.83	1.36	0.82	1.55
Pd/C	0.99	1.18	0.78	0.97

FPP: Forward peak potential; FPCD: Forward peak current density; BPP: Backward peak potential; BPCD: Backward peak current density. The data were obtained from Fig. 5a.

Table S2 Comparison of catalytic performance of different ORR catalysts

Catalysts	Half-wave potential (V vs. RHE)	Electrolyte solution	Ref.
Cu-Pd alloy multipods	**0.819**	**0.1 M $HClO_4$**	**This study**
Cu-Pd alloy nanospheres	**0.807**	**0.1 M $HClO_4$**	**This study**
Pd-Cu nanodendrites	ca. 0.8	0.1 M $HClO_4$	*Elecchimi. Acta,* 2013, **89,** 24.
Pd-Cu alloy	About 0.78	0.1 M $HClO_4$	*J. Electroanal. Chem.,* 2009, **636,** 1.
Pd-Fe	About 0.77	0.5 M H_2SO_4	*Energy Environ. Sci.,*2011, **4,**558.
Pd-Co alloy	About 0.78	0.1 M $HClO_4$	*Electrochimi. Acta,* 2008, **53,** 6662.
Pd-Co alloy	About 0.71	0.1 M $HClO_4$	*J. Power Sources,* 2007, **167,** 243.
Pd-Co/C	About 0.75	0.1 M $HClO_4$	*Int. J. Hydrogen Energ.,*2010, **35,** 1864.
Cubic Pd nanoparticles	About 0.8	0.5 M H_2SO_4	*Electrochem. Commun.,*2011, **13,** 734.
Core-shell Au-Pd nanoparticles	0.771	0.5 M H_2SO_4	*Chem. Mater.,* 2011, **23,** 4694.
Core-shell Au-Pd nanoparticles	0.780	0.1 M $HClO_4$	*J. Mater. Chem. A,* 2016, **4,** 3813.
Pt/C	0.786	0.1 M $HClO_4$	*J. Phys. Chem. C,* 2015, **119,** 19947.