metals

Supporting Information

Facile Synthesis of PdCuRu Porous Nanoplates as Highly Efficient Electrocatalysts for Hydrogen Evolution Reaction in Alkaline Medium

Changhong Chen [1], Ningkang Qian [1], Junjie Li [1], Xiao Li [1], Deren Yang, [1] and Hui Zhang [1,2,*]

[1] State Key Laboratory of Silicon Materials and School of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, China; 21826054@zju.edu.cn (C.C.); 3140102831@zju.edu.cn (N.Q.); 3140104160@zju.edu.cn (J.L.); 11726026@zju.edu.cn (X.L.); mseyang@zju.edu.cn (D.Y.)

[2] Institute of Advanced Semiconductors, Hangzhou Innovation Center, Zhejiang University, Hangzhou 310027, China

* Correspondence: msezhanghui@zju.edu.cn; Tel.: +86-571-87951667

Abstract: Ru is a key component of electrocatalysts for hydrogen evolution reaction (HER), especially in alkaline media. However, the catalytic activity and durability of Ru-based HER electrocatalysts are still far from satisfactory. Here we report a solvothermal approach for the synthesis of PdCuRu porous nanoplates with different Ru compositions by using Pd nanoplates as the seeds. The PdCuRu porous nanoplates were formed through underpotential deposition (UPD) of Cu on Pd, followed by alloying Cu with Pd through interdiffusion and galvanic replacement between Cu atoms and Ru precursor simultaneously. When evaluated as HER electrocatalysts, the PdCuRu porous nanoplates exhibited excellent catalytic activity and durability. Of them, the $Pd_{24}Cu_{29}Ru_{47}$/C achieved the lowest overpotential (40.7 mV) and smallest Tafel slope (37.5 mV dec^{-1}) in an alkaline solution (much better than commercial Pt/C). In addition, the $Pd_{24}Cu_{29}Ru_{47}$/C only lost 17% of its current density during a stability test for 10 h, while commercial Pt/C had a 59.5% drop under the same conditions. We believe that the electron coupling between three metals, unique porous structure, and strong capability of Ru for water dissociation are responsible for such an enhancement in HER performance.

Keywords: Ru-based catalysts; hydrogen evolution reaction; porous structures; nanoplates; multimetallic alloys

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Table S1. ICP-AES data of the PdCuRu multimetallic nanoplates with different atomic ratios and the molar ratio of the Pd, Cu and Ru precursors fed in the synthesis.

Samples	molar ratios of the metal precursors	atomic ratios of Pd/Cu/Ru
$Pd_{32}Cu_{33}Ru_{35}$	29 : 43 : 28	32 : 33 : 35
$Pd_{24}Cu_{29}Ru_{47}$	23 : 33 : 44	24 : 29 : 47
$Pd_{19}Cu_{25}Ru_{56}$	19 : 27 : 54	19 : 25 : 56

Table S2. The variation in the atomic percentage of Pd, Cu, and Ru for the $Pd_{24}Cu_{29}Ru_{47}$ nanoplates with the reaction time measured by ICP-AES technique.

Reaction time	Pd (Atomic %)	Cu (Atomic %)	Ru (Atomic %)
5 min	46.8	40.1	13.1
10min	28.6	36.0	35.4
1h	24.5	31.8	43.7
3h	24.9	30.5	44.6
6h	25.0	29.4	45.6
12h	25.0	29.1	45.9

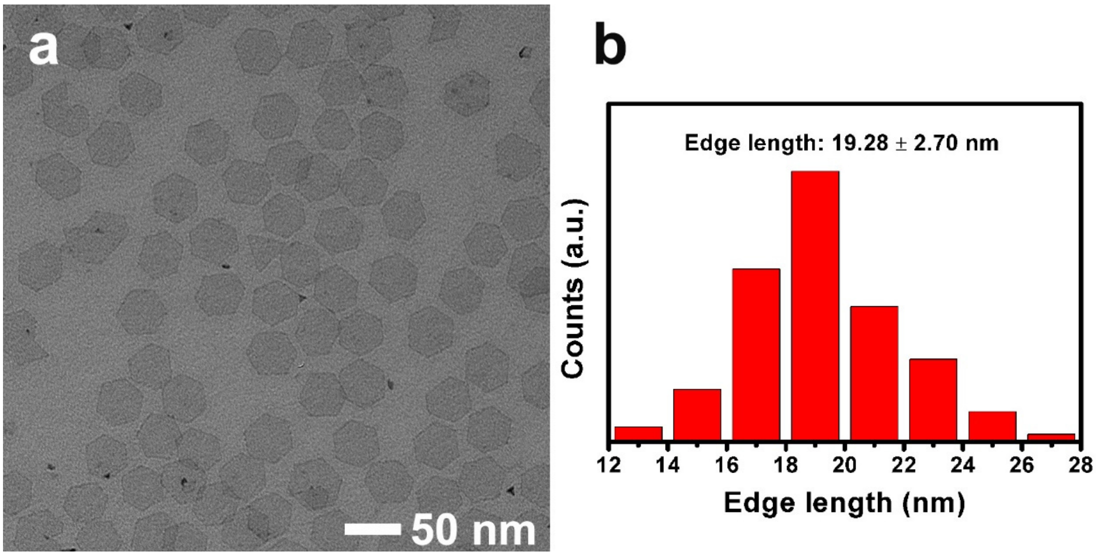

Figure S1. (**a**) TEM image of the Pd plate-like seeds that lay flat on the TEM grid and (**b**) the corresponding edge length.

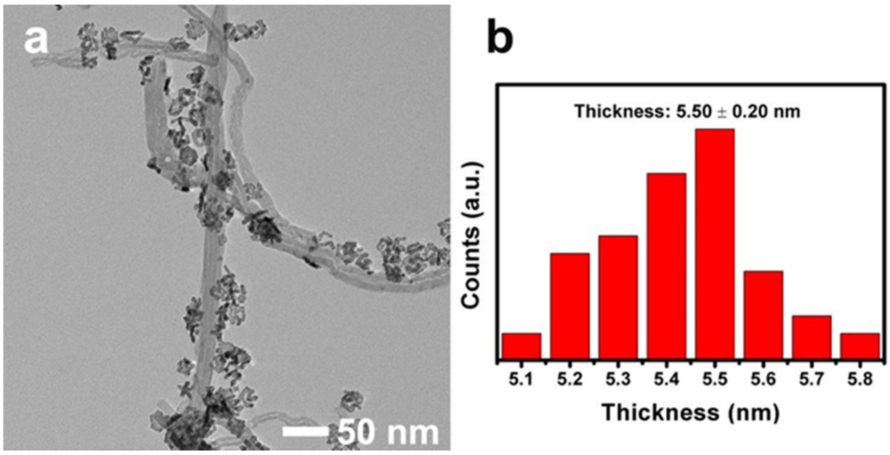

Figure S2. (**a**) TEM image of vertically upstanding of $Pd_{24}Cu_{29}Ru_{47}$ nanoplates and (**b**) the corresponding thickness. The nanoplates were firstly mixed with carbon nanotubes in an aqueous solution. After centrifugation, the product was collected and measured by TEM analysis. The width of the projection for the vertically upstanding nanoplates is the corresponding thickness.

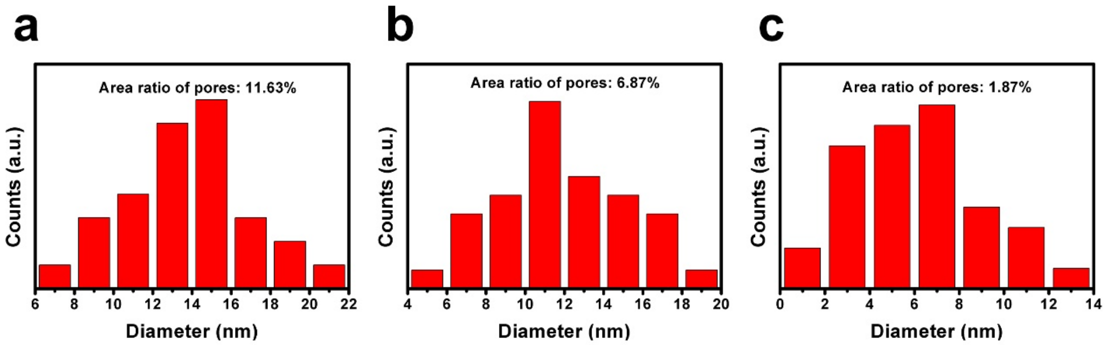

Figure S3. The size and average area percentage of the pores in three nanoplates with different amount of Ru: (**a**) $Pd_{32}Cu_{33}Ru_{35}$ nanoplates, (**b**) $Pd_{24}Cu_{29}Ru_{47}$ nanoplates, and (**c**) $Pd_{19}Cu_{25}Ru_{56}$ nanoplates.

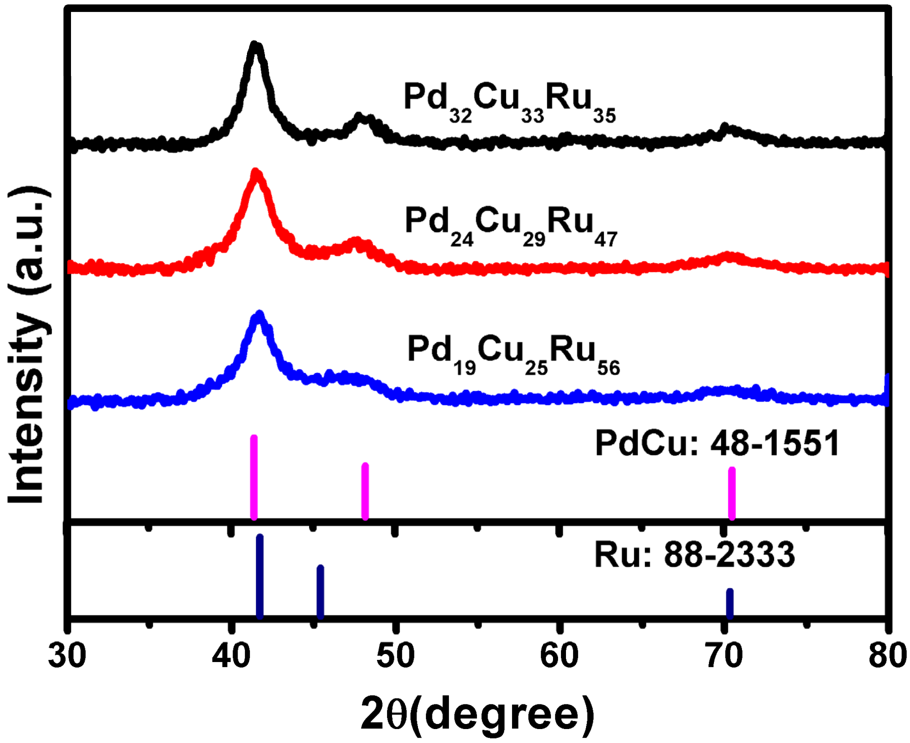

Figure S4. XRD patterns of the $Pd_{32}Cu_{33}Ru_{35}$, $Pd_{24}Cu_{29}Ru_{47}$ and $Pd_{19}Cu_{25}Ru_{56}$ nanoplates.

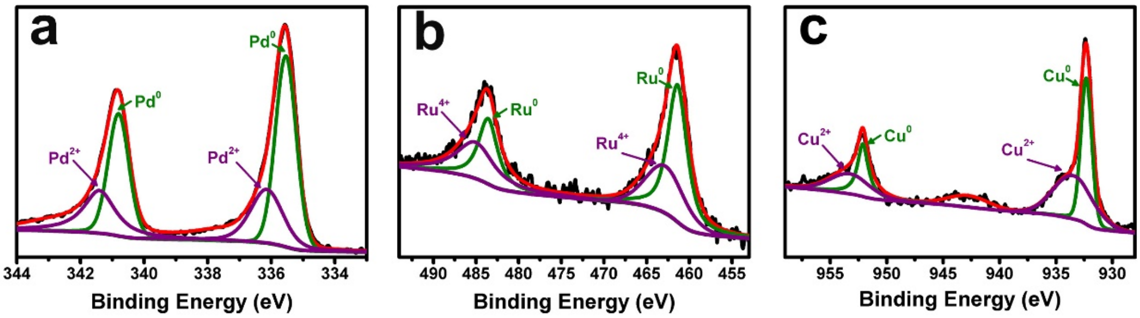

Figure S5. High-resolution (**a**) Pd 3d, (**b**) Ru 3p, and (**c**) Cu 2p XPS spectra of the $Pd_{32}Cu_{33}Ru_{35}$ nanoplates.

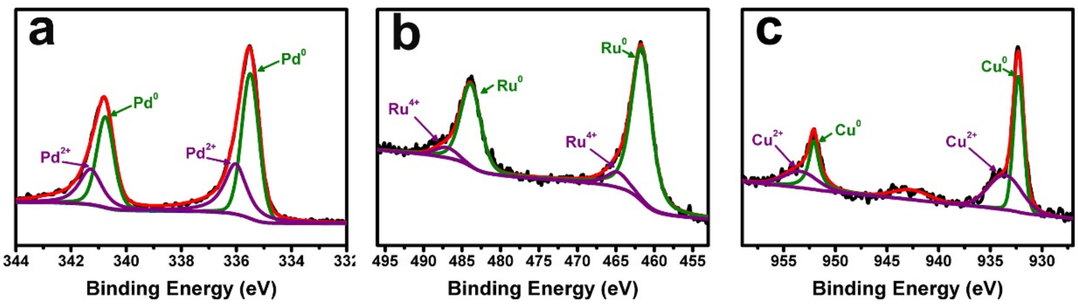

Figure S6. High-resolution (**a**) Pd 3d, (**b**) Ru 3p, and (**c**) Cu 2p XPS spectra of the $Pd_{19}Cu_{25}Ru_{56}$ nanoplates.

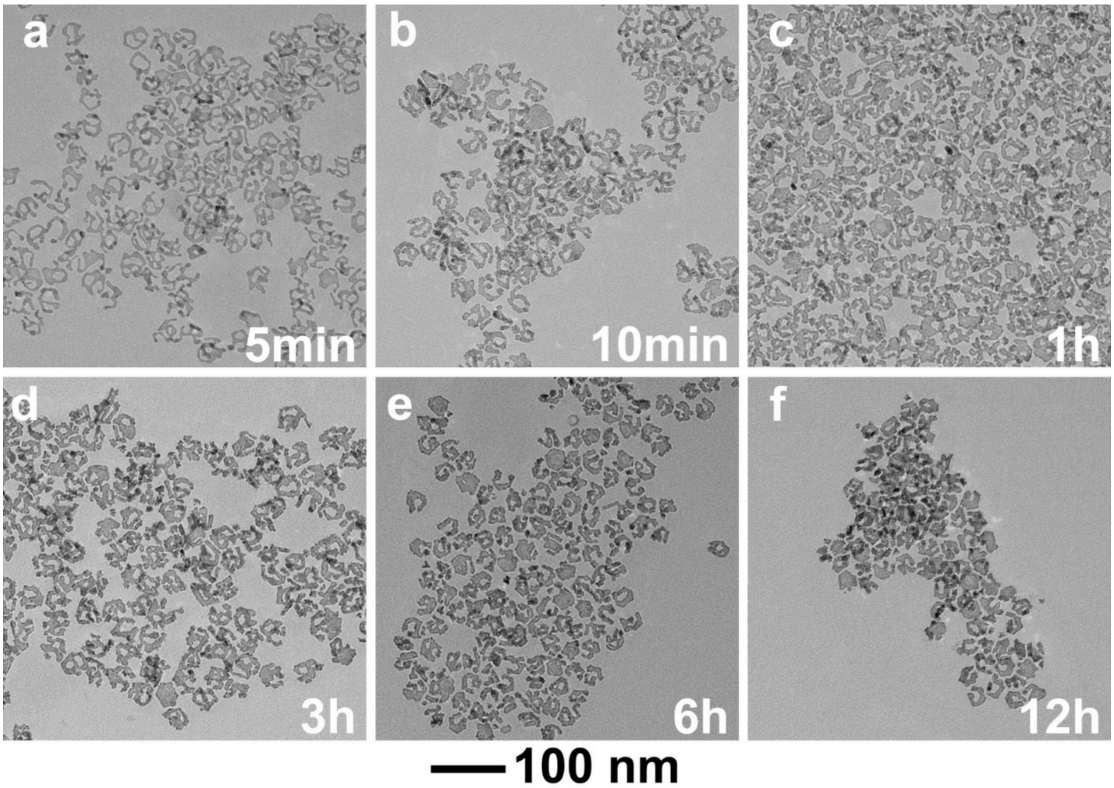

Figure S7. TEM images of the product prepared using the standard procedure except for different reaction times: (**a**) 5 min, (**b**) 10 min, (**c**) 1 h, (**d**) 3 h, (**e**) 6 h, and (**f**) 12 h.

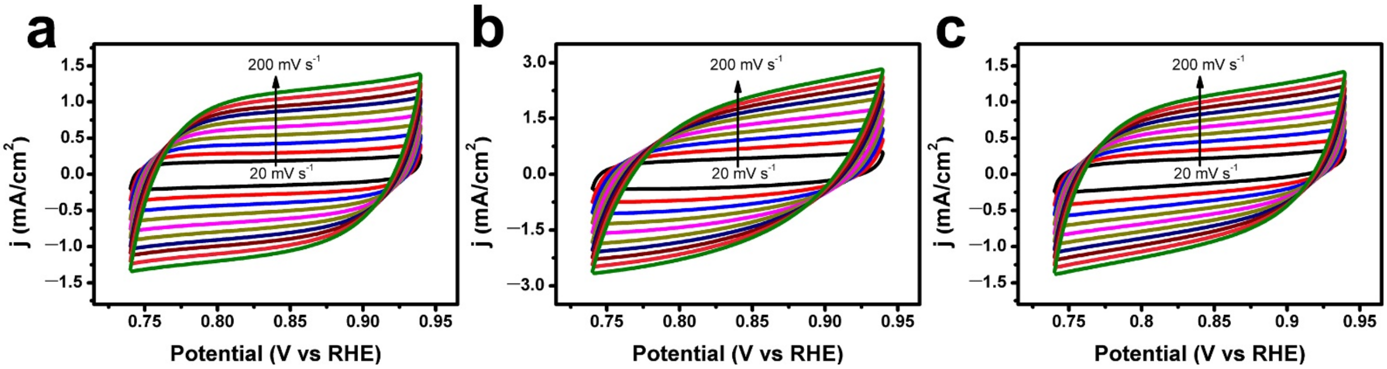

Figure S8. Cyclic voltammograms (CV) with scan rates from 20 to 200 mV s^{-1} of (**a**) $Pd_{32}Cu_{33}Ru_{35}$/C, (**b**) $Pd_{24}Cu_{29}Ru_{47}$/C and (**c**) $Pd_{19}Cu_{25}Ru_{56}$/C that were performed in a potential window without faradaic processes.

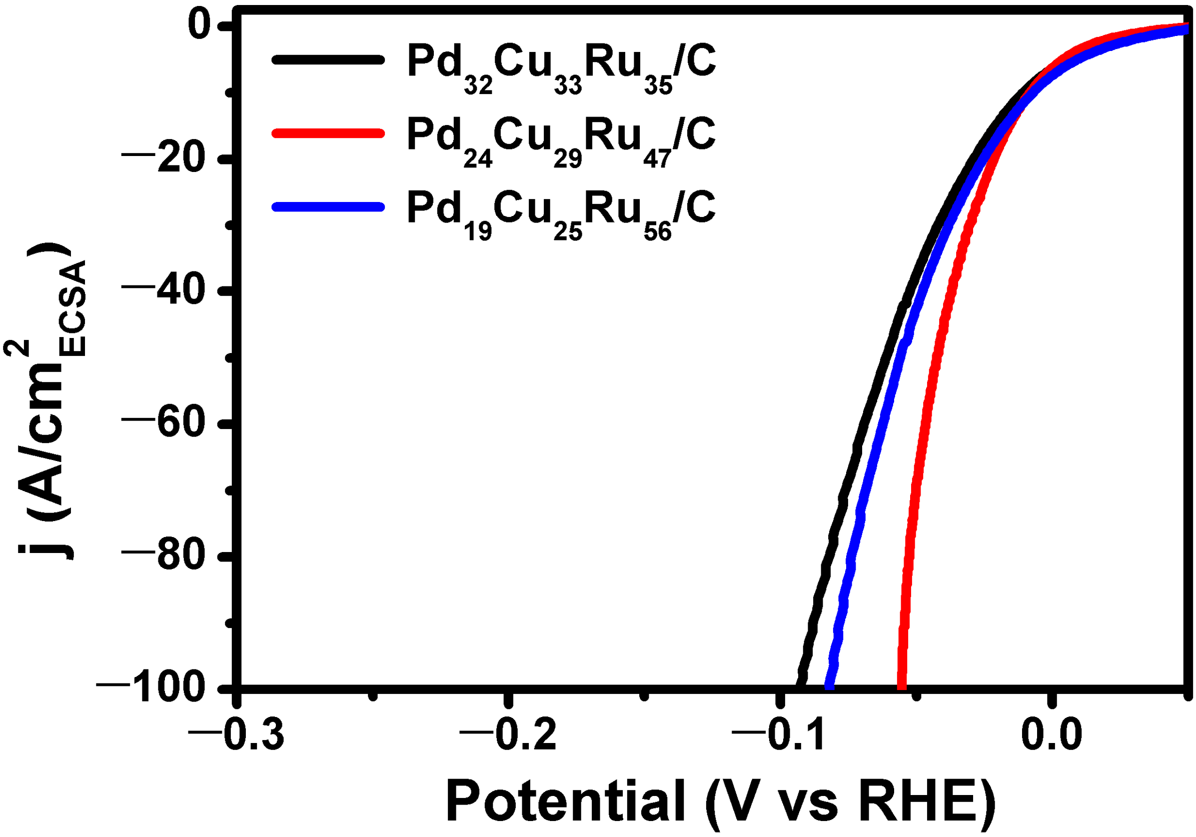

Figure s9. HER polarization curves normalized by the ECSA for the $Pd_{32}Cu_{33}Ru_{35}$/C, $Pd_{24}Cu_{29}Ru_{47}$/C and $Pd_{19}Cu_{25}Ru_{56}$/C in 0.1 M KOH solution.

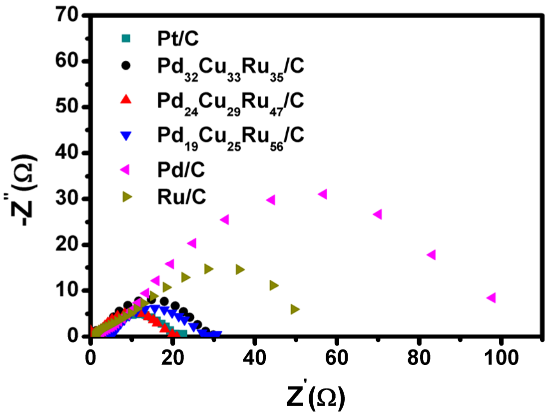

Figure S10. Electrochemical impedance spectroscopy (EIS) curves of various electrocatalysts.

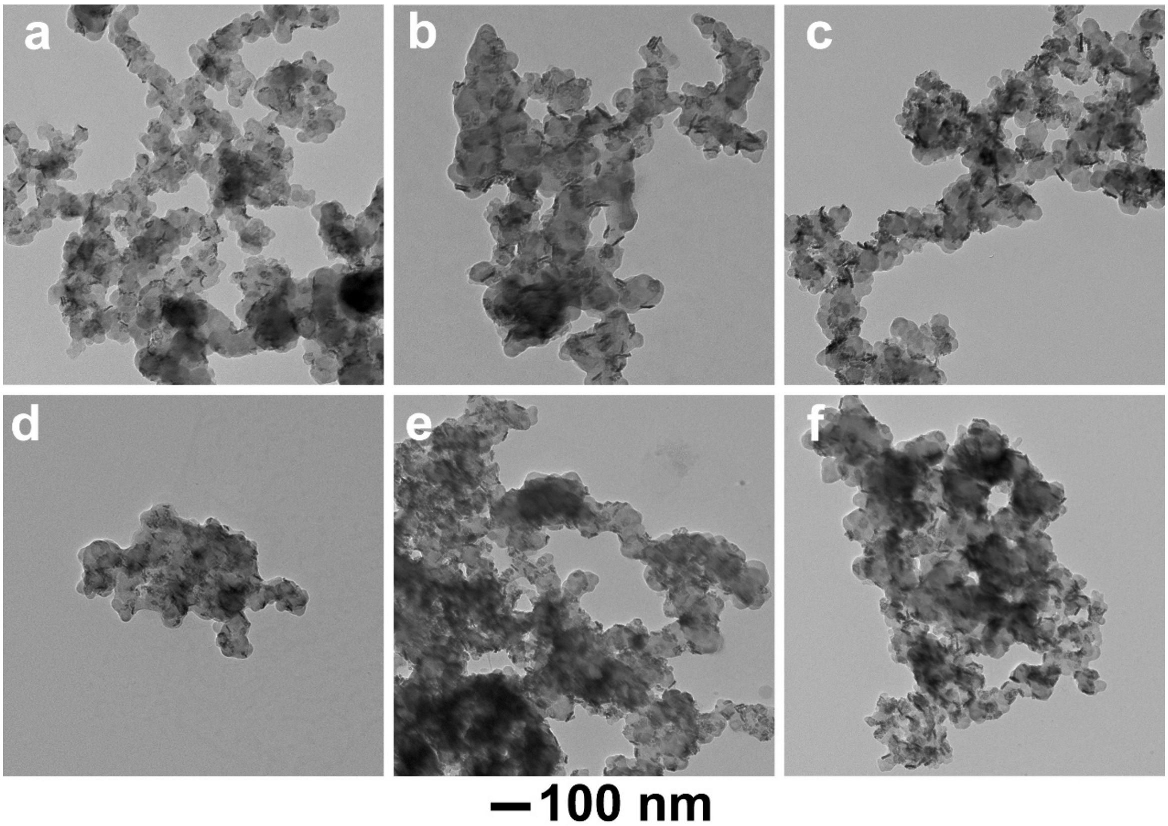

Figure S11. TEM images of (**a**,**d**) $Pd_{32}Cu_{33}Ru_{35}/C$, (**b**,**e**) $Pd_{24}Cu_{29}Ru_{47}/C$ and (**c**,**f**) $Pd_{19}Cu_{25}Ru_{56}/C$ catalysts before and after the chronoamperometric measurement, correspondingly.

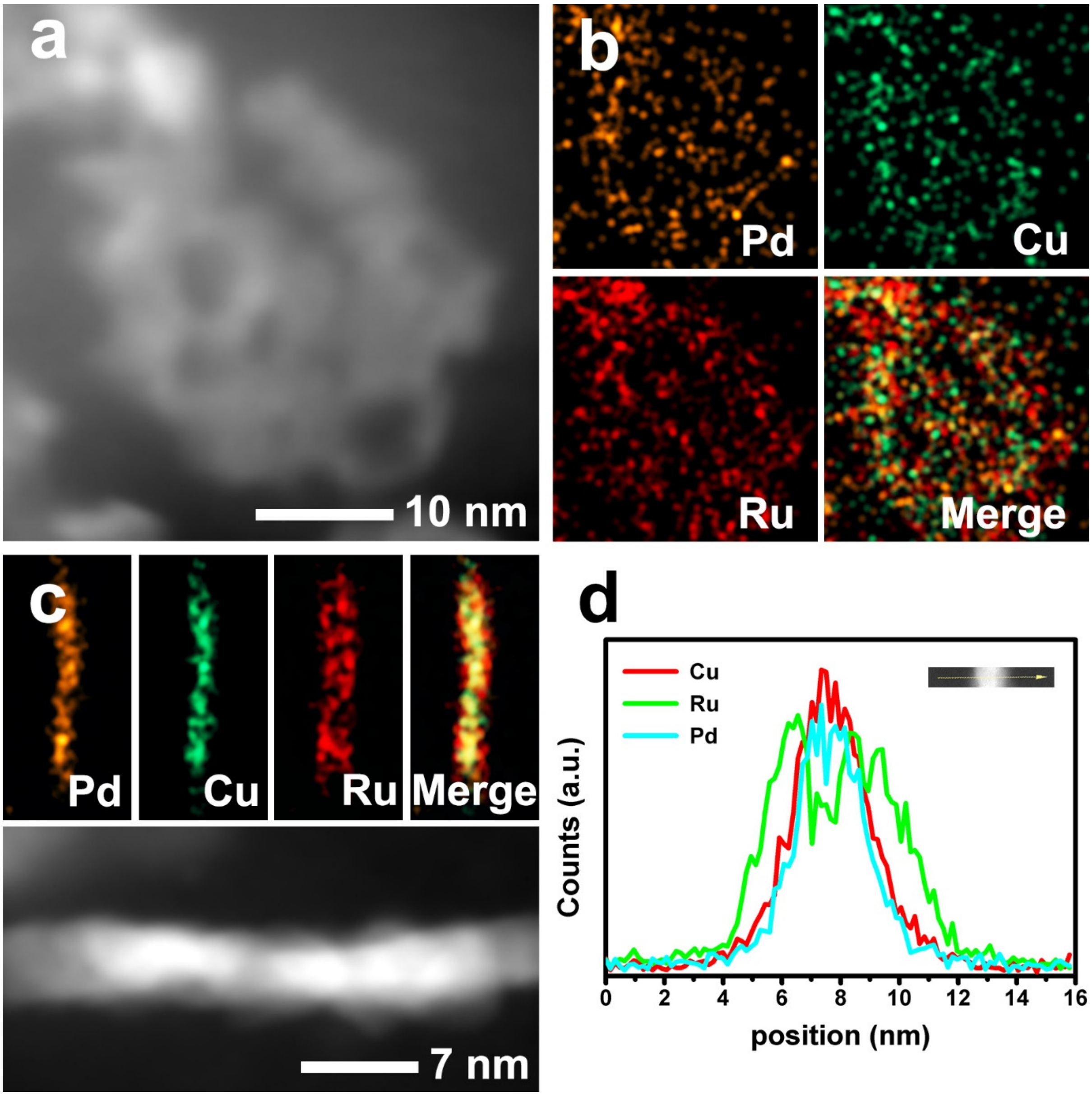

Figure S12. (**a**) HAADF-STEM, (**b**) EDX mapping images of a planar $Pd_{24}Cu_{29}Ru_{47}$ nanoplate after I-t testing. (**c**) HAADF-STEM and EDX images of a vertically upstanding $Pd_{24}Cu_{29}Ru_{47}$ nanoplate after I-t testing. Pd (orange), Ru (red), Cu (green). (**d**) Line-scan profiles along the side of a $Pd_{24}Cu_{29}Ru_{47}$ nanoplate after I-t testing.