Electronic Supplementary Material

Highly Excavated Octahedral PtCu-O Alloy Nanostructures Built with Nanodendrites for Superior Alcohol Electroxidation

Fengxia Wu,[a,b] Ling Zhang,[c] Jianping Lai,[a] Wenxin Niu,*[,a,b] Rafael Luque,*[d,e] Guobao Xu*[, a,b]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[b] University of Science and Technology of China, Hefei, China
[c] School of Science, Harbin Institute of Technology (HIT), Shenzhen, HIT Campus of University Town of Shenzhen, Shenzhen 518055, China
[d] Departamento de Química Orgánica, Universidad de Córdoba Campus de Rabanales, Edificio Marie Curie (C-3), Km 396, Córdoba, Spain
[e] Peoples Friendship University of Russia (RUDN University), 6 Miklukho Maklaya Str., 117198, Moscow, Russia
*Email - q62alsor@uco.es

Calculation of ECSA

The loading amounts of Pt for the PtCu-O EOND nanostructures and commercial Pt/C were all kept at 1.5μg, as calculated by ICP-AES measurement. For the CV at room temperature in 0.5 M KOH solution, the equation for the calculation of electrochemically active surface area (ECSA) is shown as follows:

$$ECSA(m^2/g)=\frac{Q_H(C)}{210\mu C/cm^2 * m_{Pt}(mg) * V(v/s)} * 10^5$$

where Q_H (C) is the hydrogen desorption charge calculated from the CV. 210 μC/cm^2 is used as the conversion factor. m_{Pt} is the working electrode Pt loading. V is the scan rate (0.05 V/s). The calculated ECSA of Pt/C is 33.4 m^2/g, which is similar to that in alkaline media in reported literatures.[1,2] ECSA of PtCu-O EOND nanostructures (29.3 m^2/g) is smaller than that of Pt/C, which is attributed to the prevention of hydrogen adsorption/desorption by oxidative Cu of PtCu-O EOND nanostructures.

Thus we further conduct CO-stripping experiment to calculate ECSA of the catalysts. The equation for the calculation of ECSA is shown as follows:

$$ECSA(m^2/g)=\frac{Q_{CO}(C)}{420\mu C/cm^2 * m_{Pt}(mg) * V(v/s)} * 10^5$$

Where Qco (C) is CO adsorption charge calculated from the CV. 420 μC/cm^2 is used as the conversion factor. m_{Pt} is Pt loading of the working electrode. V is the scan rate (0.05 V/s). The calculated ECSA of Pt/C is 43.6 m^2/g. The ECSA of PtCu-O EOND nanostructures is 75.5 m^2/g. The large difference of calculated ECSAs of EOND nanostructures between Q_H and Qco could be result from oxidative Cu surface of EOND nanostructures. To consistent with previously reported literature, we adopt the ECSA calculated from hydrogen desorption charge to calculate specific activity.

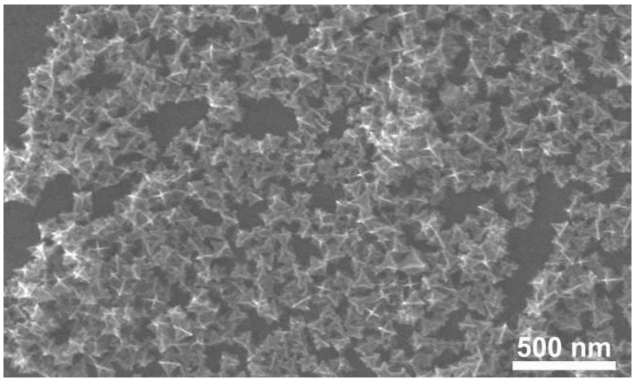

Figure S1. Low-magnification SEM image of PtCu-O EOND nanostructures.

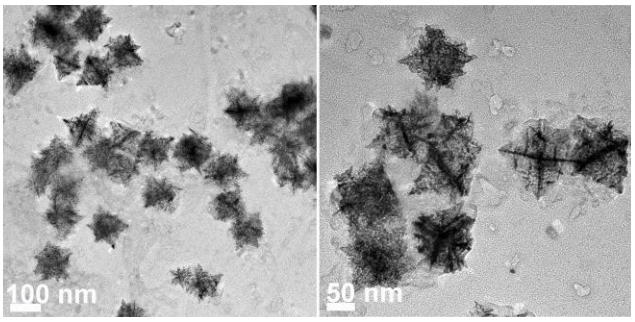

Figure S2. Low-magnification TEM image of PtCu-O EOND nanostructures.

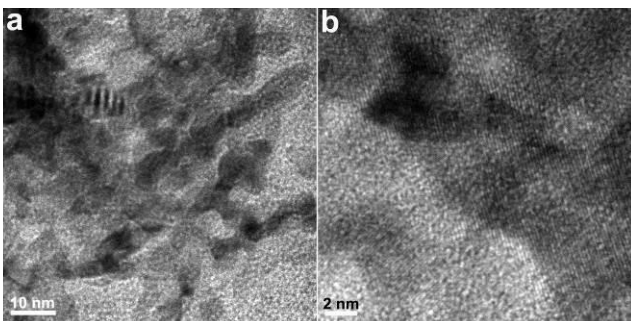

Figure S3. HRTEM images of the nanodendrites of PtCu-O EOND nanostructures.

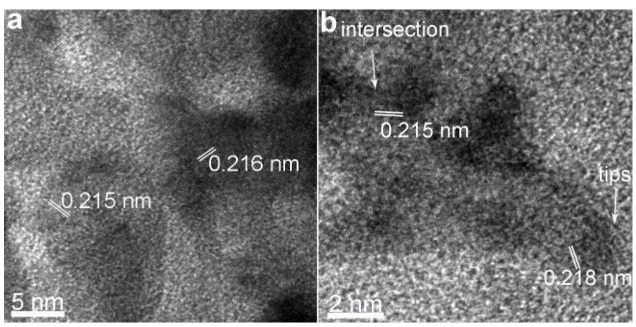

Figure S4. HRTEM images of the PtCu-O EOND nanostructures**.**

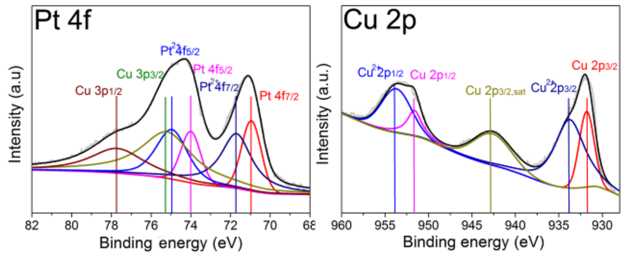

Figure S5. XPS spectra of the PtCu-O EOND nanostructures.

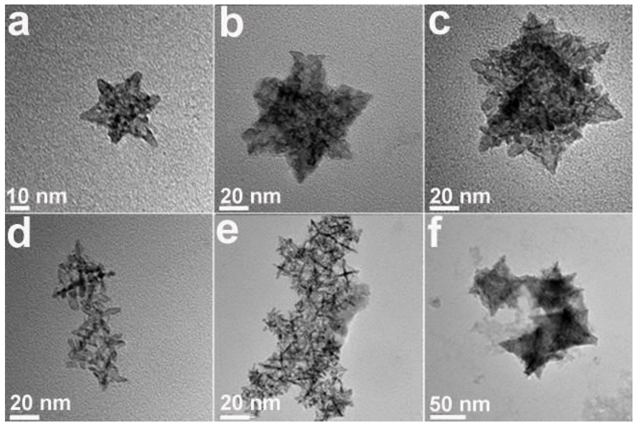

Figure S6. TEM images of the PtCu-O nanostructures formed after different reaction times. a, d) 2 h, b, e) 2.5 h, and c, f) 3 h.

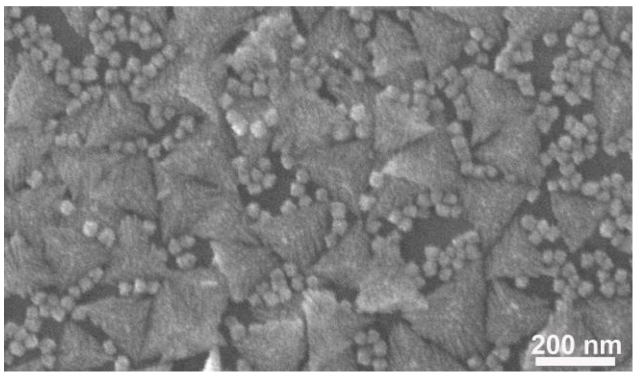

Figure S7. SEM image of PtCu-O nanostructures obtained without the addition of ethanolamine in the synthesis while keeping the other parameters constant.

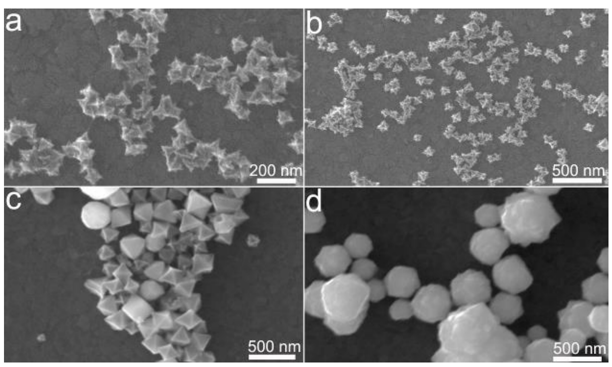

Figure S8. SEM image of PtCu-O nanostructures obtained with different amount of ethanolamine in the synthesis while keeping the other parameters constant. a)0.3 ml b)0.5 ml c)0.7 ml d)0.9 ml.

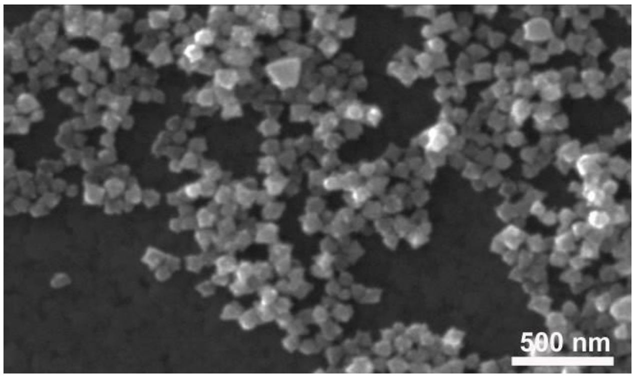

Figure S9. SEM image of PtCu-O nanostructures obtained without the addition of acetamide in the synthesis while keeping the other parameters constant.

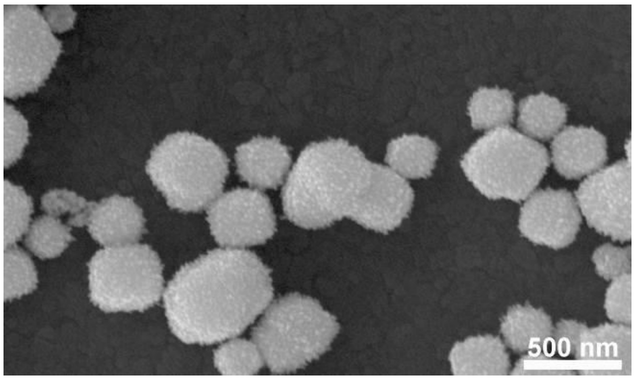

Figure S10. SEM image of Pt nanoparticles obtained without the addition of $CuCl_2$ in the synthesis while keeping the other parameters constant.

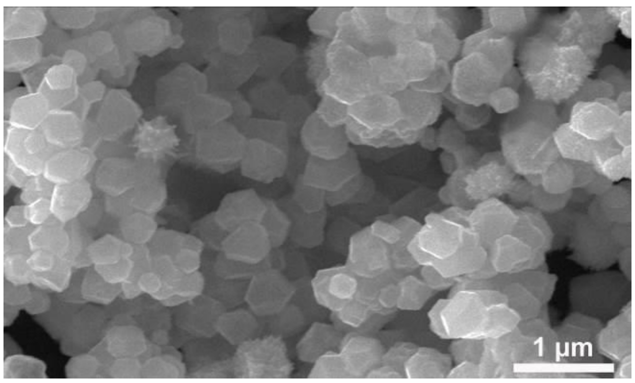

Figure S11. SEM image of PtCu-O nanostructures obtained without the addition of KI in the synthesis while keeping the other parameters constant.

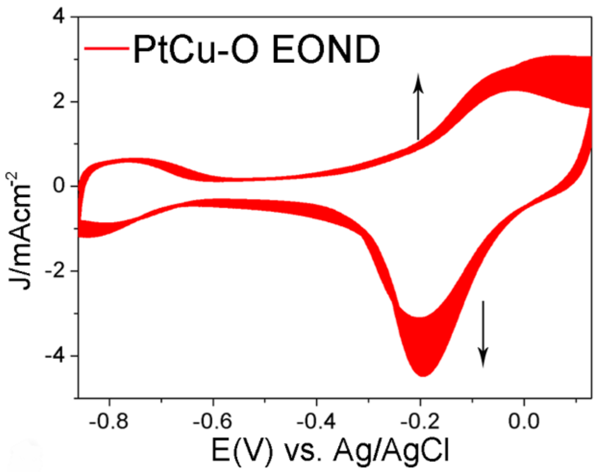

Figure S12. Activated CV curves of PtCu-O EOUD nanostructures in 0.5 M KOH solution for 100 cycles.

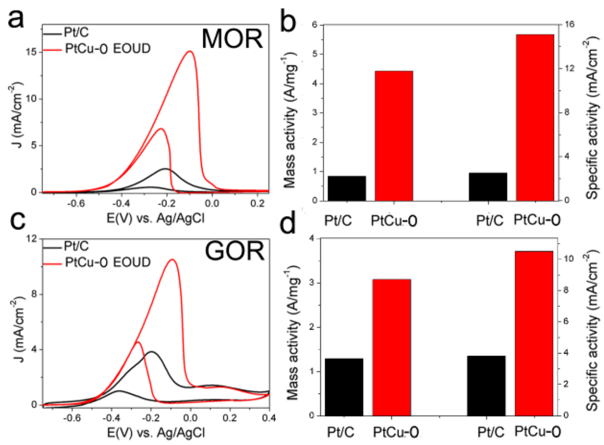

Figure S13. Specific activity and mass activity of commercial Pt/C and PtCu-O EOUDs for methanol (a, b) and glycerol (c, d) at a scan rate of 50 mV s^{-1}.

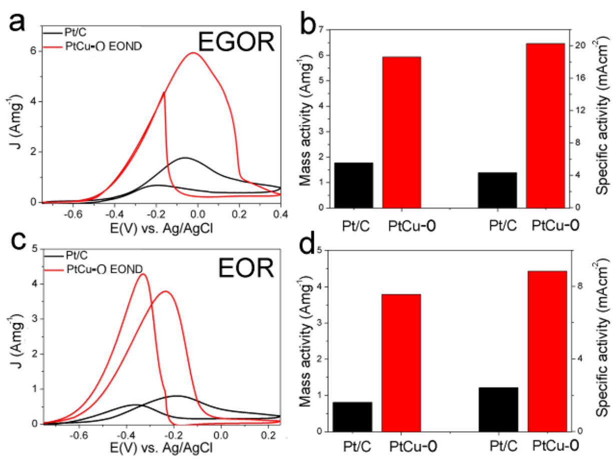

Figure S14. Specific activity and mass activity of commercial Pt/C and PtCu-O EOUDs for ethylene glycol (EGOR) (a, b) and ethanol (EOR) (c, d) at a scan rate of 50 mV s^{-1}.

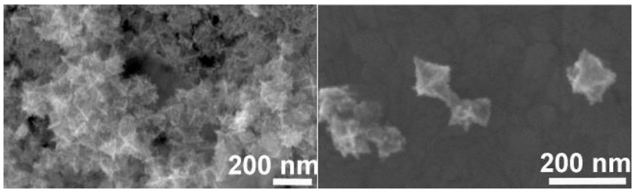

Figure S15. SEM images of PtCu-O nanostructures after catalytic operation.

Table S1. MOR activities of the recently reported catalysts

Catalysts	Jm	Electrolyte	References
PtCu-O EOND	4.43A/mg	0.5 M KOH + 1 M methanol	**This work**
Pt/Ni(OH)2/rGO ternary hybrids	1.07 A/mg	1 M KOH + 1 M methanol	Nat. Commun. **2015**, 6, 10035
PtNi/C	1.2A/mg	1 M NaOH + 1 M methanol	Catal. Commun. **2010**, 12, 67
Popcorn-like PtAu	0.6A/mg	1 M KOH + 1 M methanol	J. Mater. Chem. A **2014**, 2, 8386
PtAu/RGO/GC	1.6 A/mg_{Pt+Au}	1 M KOH + 1 M methanol	J. Mater. Chem. A **2013**, 1, 7255
Pt_mAg	3A/mg	0.5 M KOH + 1 M methanol	J. Catal. **2012**, 290, 18
Pt_1Ni_1/C	1.75A/mg	1 M KOH + 1 M methanol	Nano Res. **2018**, 11, 2058
Pt3.5Pb nerve nanowires	2.84A/mg	0.5 M KOH + 1 M methanol	Nanoscale **2017**, 9, 201
PtAg popcorns	1.65A/mg	1 M KOH + 1 M methanol	ACS Nano **2012**, 6, 7397
PtCu nanoframes	2.26A/mg	0.5 M KOH + 1 M methanol	Adv. Mater. **2016**, 28, 8712
PdAgRhPt nanoframes	2.33A/mg	1 M KOH + 1 M methanol	Small **2016**, 12, 5261
PtZn/MWNT	0.55A/mg	0.1 M KOH + 0.5 M methanol	J. Am. Chem. Soc. **2017**, 139, 4762

Table S2. GOR activities of the recently reported catalysts

Catalysts	Jm	Electrolyte	References
PtCu-O EOND	3.08A/mg	1 M KOH + 0.1 M glycerol	**This work**
$Pd_{55}Pt_{30}$ nanowire networks	1.8 A/mg	1 M KOH + 0.1 M glycerol	Energy Environ. Sci. **2015**, 8,2910
Pd_4Bi catalysts	0.75A/mg	1 M KOH + 0.1 M glycerol	J. Am. Chem. Soc. **2014**, 136, 3937
Pd nanosheet	1.5A/mg	0.5 M NaOH + 0.5 M glycerol	ACS Appl. Mater. Interfaces **2016**, 8, 20642
$Pd_{62}Au_{21}Ni_{17}$ nanosponges	3.3 A/mg_{Pt+Au}	1 M KOH + 0.1 M glycerol	Energy Environ. Sci. **2017**, 9,3097
Pd-CNx/G	1.1A/mg	0.5 M NaOH + 0.5 M glycerol	ACS Catal. **2015**, 5, 3174
Au_1Cu_1 triangular nanoprisms	2.26A/mg	1 M KOH + 1 M glycerol	J. Mater. Chem. A **2017**, 5, 15932
PdSn3 catalysts	1.1A/mg	1 M KOH + 0.1 M glycerol	Appl. Catal. B: Environ. **2015**, 176, 429
ultrafine Pt_3Fe nanowires	2A/mg	1 M KOH + 1 M glycerol	Nanoscale **2018**, DOI: 10.1039/c8nr04918a
PtAg/C	1.1A/mg	1 M KOH + 1 M glycerol	Green Chem. **2016**, 18,386

References

1. W. Huang, H. Wang, J. Zhou, J. Wang, P. N. Duchesne, D. Muir, P. Zhang, N. Han, F. Zhao, M. Zeng, J. Zhong, C. Jin, Y. Li, S. T. Lee and H. Dai, Nat. Commun. 2015, **6**, 10035.

2. Z. Zhang, Z. Luo, B. Chen, C. Wei, J. Zhao, J. Chen, X. Zhang, Z. Lai, Z. Fan, C. Tan, M. Zhao, Q. Lu, B. Li, Y. Zong, C. Yan, G. Wang, Z. J. Xu and H. Zhang, Adv. Mater. 2016, **28**, 8712.