Electronic Supplementary Material

Hierarchical Concave Layered Triangular PtCu Alloy Nanostructures: Rational Integration of Dendritic Nanostructures for Efficient Formic Acid Electrooxidation

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Supplementary Figures

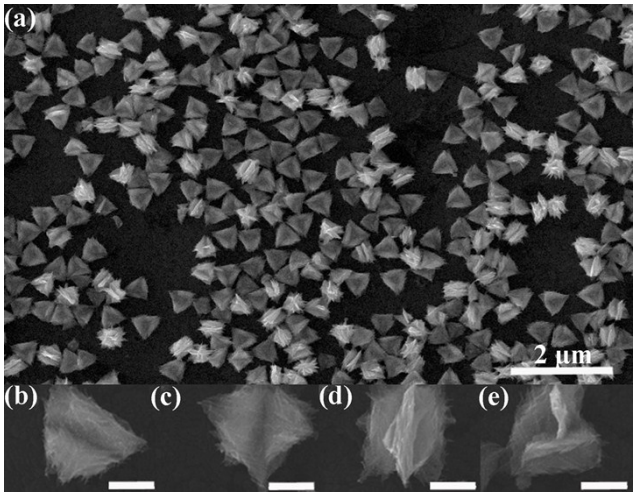

Figure S1. a) Large scale SEM image of PtCu HCLT nanostructures, b-e) SEM images of an individual with curved layers in various orientations. The scale bar is 200 nm.

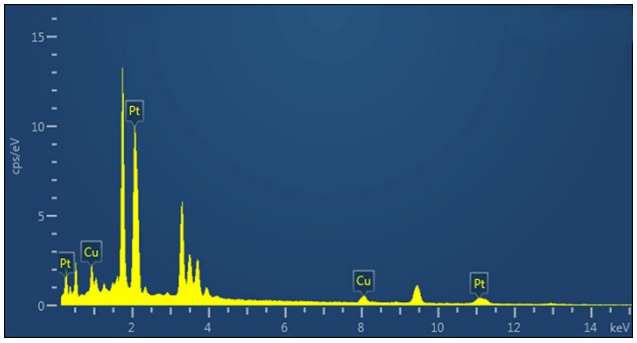

Figure S2. EDS of PtCu HCLT nanostructures. (The other signals arise from indium tin oxide (ITO) glass)

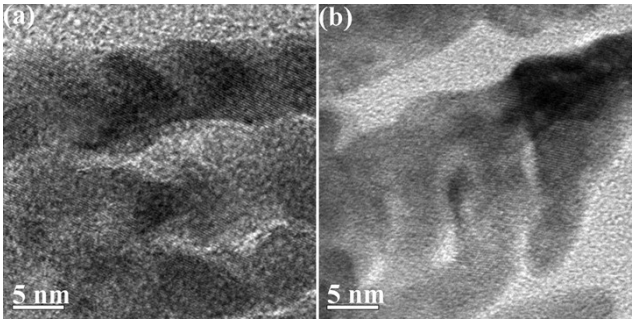

Figure S3. HAADF-HRTEM images of the dendrites of PtCu HCLT nanostructures.

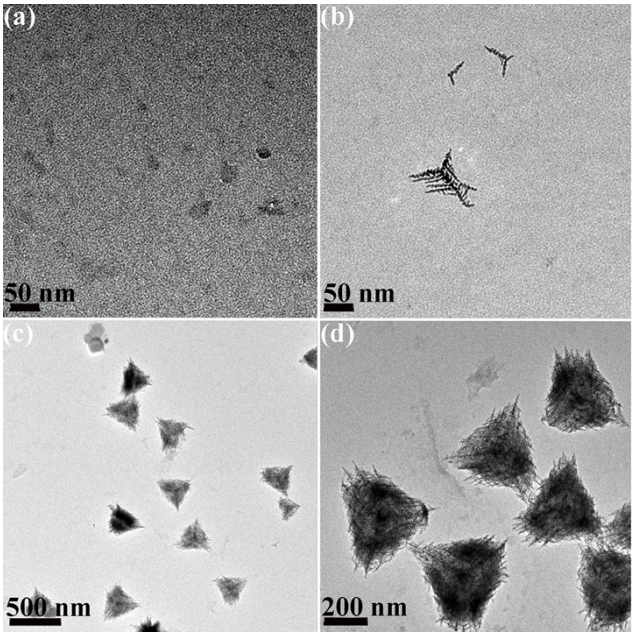

Figure S4. TEM images of the PtCu HCLT nanostructures formed after different reaction times, a) 50 min, b) 55 min, c) 60 min, and d) 70 min.

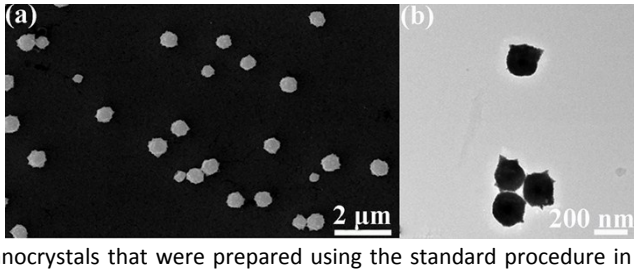

Figure S5. a) SEM images of Pt nanocrystals that were prepared using the standard procedure in absence of $CuCl_2$ for 2 hr. b) TEM images of Pt nanocrystals that were prepared using the standard procedure in absence of $CuCl_2$ for 1h.

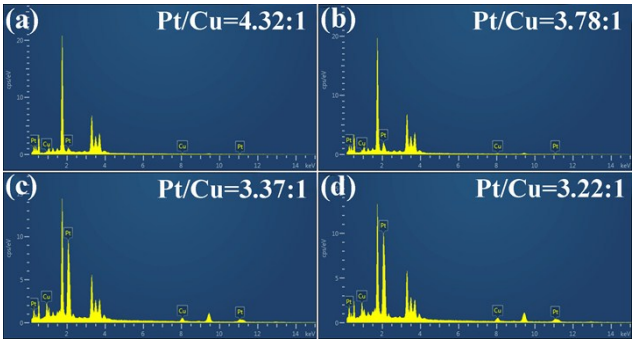

Figure S6. EDS of PtCu HCLT nanostructures formed after different reaction times. a) 50 min, b) 55 min, c) 60 min, and d) 70 min. (The other signals arise from indium tin oxide (ITO) glass)

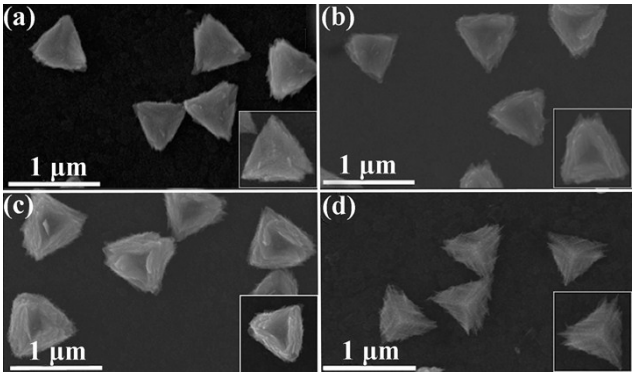

Figure S7. SEM images of PtCu HCLT nanostructures and HTBNF nanostructures obtained solutions containing 200 mg of DL-carnitine, 100 mg KI, 400 mg of PVP, 4 mL of water, and different $H_2PtCl_6/CuCl_2$ molar ratios. a) 4:1(20 mM:5 mM), b) 2:1(20 mM:10 mM), c) 1:2(10 mM:20 mM), and d) 1:4(5 mM:20 mM).

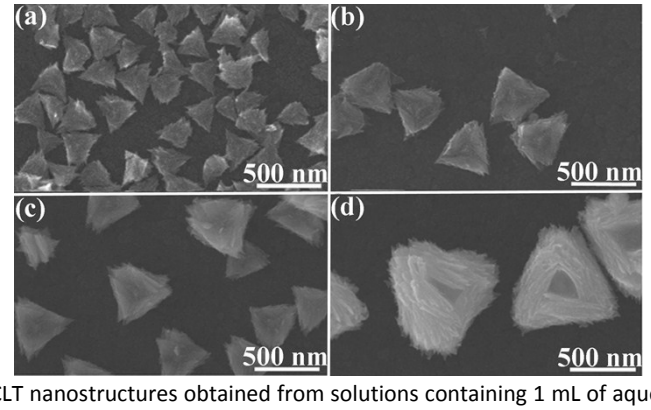

Figure S8. SEM images of PtCu HCLT nanostructures obtained from solutions containing 1 mL of aqueous $CuCl_2{\cdot}2H_2O$ (20 mM), 1 mL of aqueous $H_2PtCl_6{\cdot}6H_2O$ (20 mM), 100 mg of KI, 400 mg of PVP, 4 mL of water, and different amounts of DL-carnitine. a) 30 mg, b) 100 mg, c) 200 mg, and d) 400 mg.

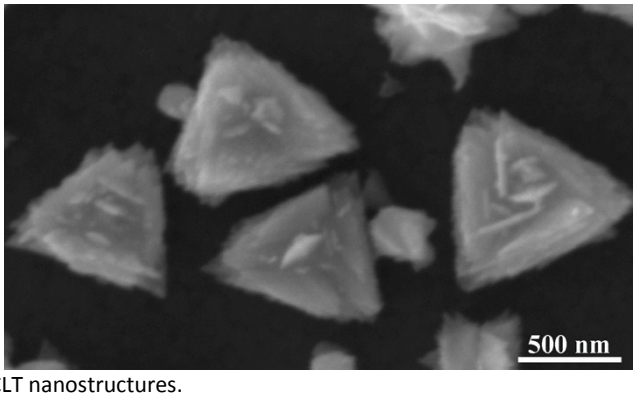

Figure S9. SEM images of $Pt_{1.40}Cu$ HCLT nanostructures.

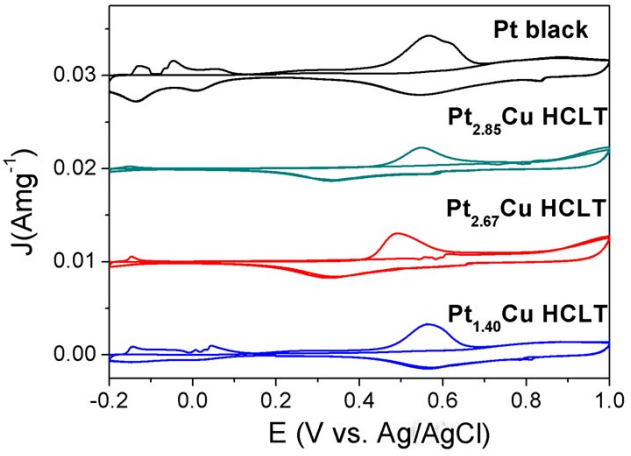

Figure S10. Mass normalized CO stripping curves of Pt black and Pt_xCu HCLT nanostructures in 0.5 M H_2SO_4 solution.

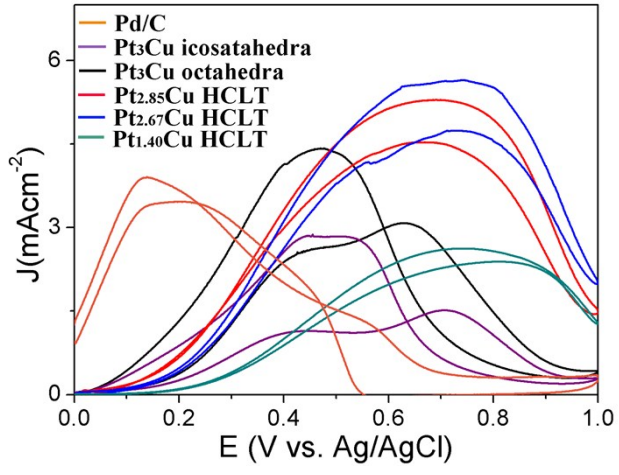

Figure S11. Specific activities of formic acid oxidation recorded in the 0.5 M H_2SO_4 + 0.25 M HCOOH solution at a scan rate of 50 mVs^{-1}.

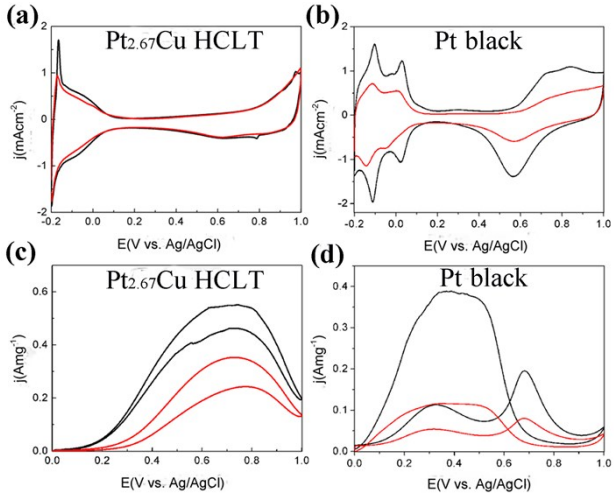

Figure S12. a,b) CV curve and c,d) mass activities of the prepared catalysts recorded in 0.5 M H_2SO_4 solution and 0.5 M H_2SO_4 + 0.25 M HCOOH solution at a scan rate of 50 mVs^{-1} before(black curve) and after (red curve)1000 cycles.

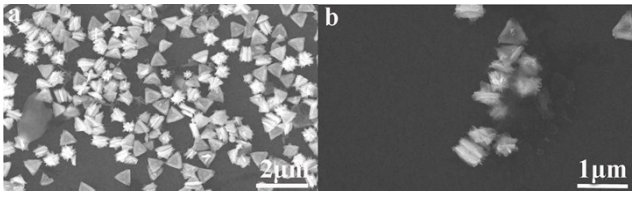

Figure S13.SEM images of $Pt_{2.67}Cu$ HCLT nanostructures before (a) and after (b) durability test.

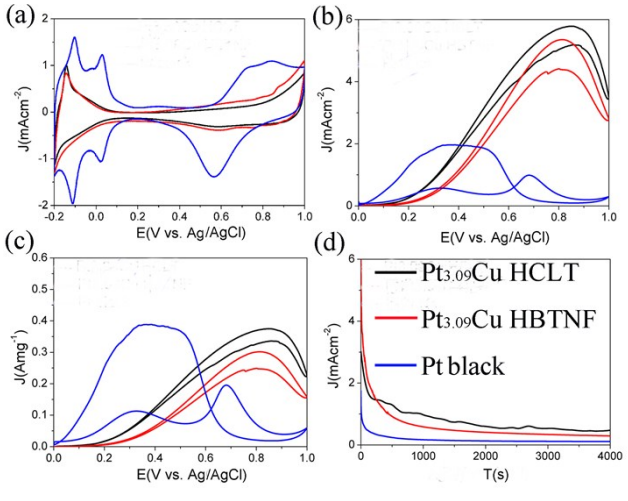

Figure S14. a) CV curves of as-prepared $Pt_{3.09}Cu$ HCLT nanostructures and HTBNF nanostructures in 0.5M H_2SO_4 solution at a scan rate of 50 mVs^{-1}. b) Specific activities, c) mass activities of formic acid oxidation recorded in the 0.5 M H_2SO_4 + 0.25 M HCOOH solution at a scan rate of 50 mVs^{-1}. d) Chronoamperometry curves of formic acid oxidation measured on the catalysts in the 0.5 M H_2SO_4 + 0.25 M HCOOH solution at 0.75 V.

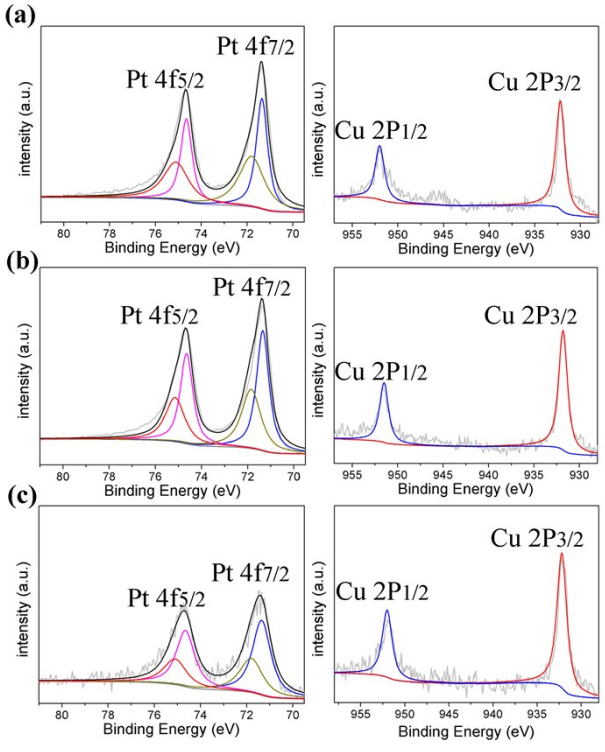

Figure S15. XPS spectra of as-prepared PtCu HCLT: a) $Pt_{2.85}Cu$, b) $Pt_{2.67}Cu$, and c) $Pt_{1.40}Cu$. The ratio of Pt/Cu is determined to be a) 2.98, b) 2.91, and c) 1.49.

Table S1. Synthesis conditions of different composition ratio of PtCu nanostructures

Catalysts	$H_2PtCl_6{\cdot}6H_2O$	$CuCl_2{\cdot}2H_2O$	KI	PVP	DL-carnitine	water	Temperature	Time
$Pt_{1.40}Cu$ HCLT	20 mM	20 mM	180 mg	400 mg	200 mg	4 mL	150 °C	5 h
$Pt_{2.67}Cu$ HCLT	20 mM	20 mM	140 mg	400 mg	200 mg	4 mL	150 °C	5 h
$Pt_{2.81}Cu$ HCLT	20 mM	20 mM	100 mg	400 mg	200 mg	4 mL	150 °C	5 h
$Pt_{2.85}Cu$ HCLT	20 mM	20 mM	60 mg	400 mg	200 mg	4 mL	150 °C	5 h
$Pt_{3.09}Cu$ HCLT	20 mM	20 mM	100 mg	400 mg	100 mg	4 mL	150 °C	5 h
$Pt_{3.09}Cu$ HTBNF	20 mM	20 mM	20 mg	400 mg	200 mg	4 mL	150 °C	5 h

Table S2. Composition variation of the intermediates based on ICP results

Time/min	Pt:Cu
50	3.24:1
55	3.06:1
60	2.92:1
70	2.81:1

Table S3. FAOR activities of the recently reported catalysts

Catalysts	Jm	Testing environment	References
$Pt_{2.67}Cu$ HCLT	0.71A/mg	0.25M HCOOH+0.5M H_2SO_4	**This work**
ERD PtCu3	0.82 A/mg	0.25M HCOOH+0.5M H_2SO_4	*J. Am. Chem.Soc.*, 2014, **136**, 3748-3751.
Trimetallic PtAgCu@PtCu core@shell concave Nanooctahedrons	0.28A/mg	0.5M HCOOH+0.5M H_2SO_4	*Nano Energy*,2015, **12**, 824-832.
PtCu HTBNFs	0.64A/mg	0.25M HCOOH+0.5M H_2SO_4	*Angew. Chem. Int. Ed.*, 2014, **54**, 108- 113.
PorousPtAg@Pt nanooctahedra	0.28 A/mg	0.5M HCOOH+0.5M H_2SO_4	*ACS Appl. Mater. Interfaces*, 2016, **45**, 31076-31082.
Atomically Thick Pt-Cu Nanosheets	0.28A/mg	0.1M HCOOH+0.5M H_2SO_4	*Adv. Mater.*, 2015, **12**, 2013-2018.
PtCu@PdRh Self-assembled nanosandwich structures	0.76A/mg	0.1M HCOOH+0.5M H_2SO_4	*Adv. Mater.*, 2015, **12**, 2013-2018.
Pt_3Sn Nanocube	0.63 A/mg	1.0M HCOOH+0.1M $HClO_4$	*Adv. Mater.*, 2015, **28**, 2540-2546.
Core/Shell Pt3Pb/Pt	1.4 A/mg	0.5M HCOOH+ 0.1MH_2SO_4	*ACS Nano*, 2012, **6**, 2818-2825.