Supporting Information

Seed-mediated synthesis of Au@PtCu nanostars with rich twin defects as efficient and stable electrocatalysts for methanol oxidation reaction

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Table S1. ICP-AES data of the Au@PtCu decahedra, Au@Pt NPs and PtCu nanobranches.

Sample No.	Precursors [mmol]			Au/Pt/Cu atomic ratio	Surface chemical formula
	[$HAuCl_4$]	[H_2PtCl_6]	[$Cu(NO_3)_2$]		
1	0.006	0.02	0.006	1 : 2.29 : 0.72	$Pt_{3.2}Cu$
2	0.006	0.02	0.012	1 : 3.53 : 1.55	$Pt_{2.3}Cu$
3	0.006	0.02	0.020	1 : 2.72 : 2.43	$Pt_{1.1}Cu$
4	0.006	0.02	0.040	1 : 3.76 : 3.23	$Pt_{1.2}Cu$
5	0.006	0.02	0.060	1 : 3.27 : 2.79	$Pt_{1.2}Cu$
6	0.006	0.02	0.080	1 : 3.31 : 2.86	$Pt_{1.2}Cu$
7	0.006	0.02	0.100	1 : 2.71 : 2.25	$Pt_{1.2}Cu$
8	0.000	0.02	0.060	0 : 1.00 : 0.84	$Pt_{1.2}Cu$
9	0.006	0.02	0.000	1 : 2.96 : 0.00	$Au@Pt_3$

Table S2. ECSAs, specific activity, mass activity and I_f/I_b ratios of Au@PtCu decahedra, Au@Pt NPs, PtCu nanobranches, and commercial Pt/C catalysts.

Sample	ECSA (m^2/g_{Pt})	Specific activity ($mA\ cm^{-2}$)	Mass activity ($A\ mg^{-1}$)	I_f/I_b
$Au@Pt_{1.2}Cu$	16.8	1.06	0.18	2.0
$Au@Pt_{3.2}Cu$	15.3	0.53	0.08	1.8
$Au@Pt_3$	46.5	0.153	0.07	2.1
$Pt_{1.2}Cu$	11.7	0.267	0.03	2.7
Pt/C	63.1	0.18	0.11	1.2

Table S3. Comparison of Au@PtCu nanostars to recently reported catalysts for MOR.

Electrode materials	Specific activity (times vs. commercial Pt/C)	Mass activity (times vs. commercial Pt/C)	Reference
Au@$Pt_{1.2}$Cu nanostars	5.9	1.6	this work
PtCu octahedra	4.74	7.53	1
Pd@Pt hexapods	5.8	2.6	2
star-like PtCu/rGO NCs	\	3*	3
PtCu NCs	6.2	2.37	4
PtCu@TiO_2 NCs	\	1	5
urchin-like PtCu NCs	\	1.5	6
PtCu hexapod concave NCs	2.5	\	7
porous PtCu NCs	9.8	10.5	8

* compared with Pt/rGO NCs

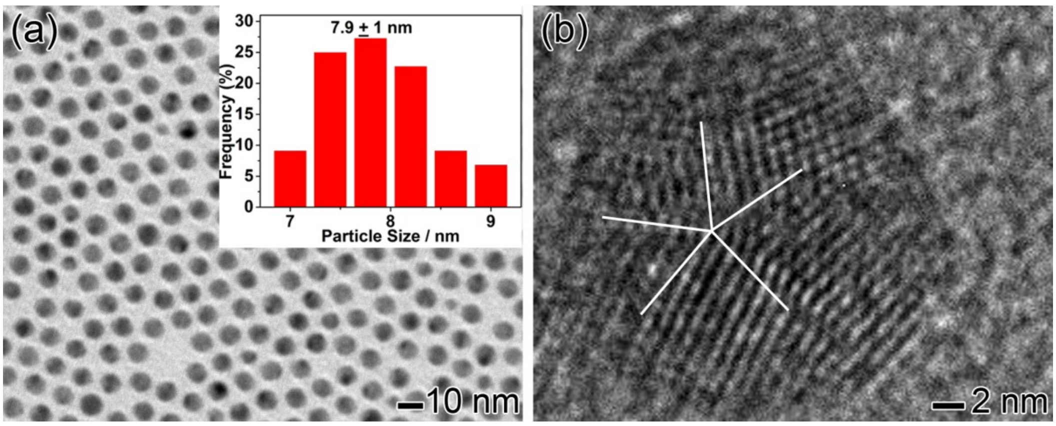

Figure S1. (a) TEM and (b) HRTEM images of the Au seeds. The inset in (a) corresponds to the size distribution.

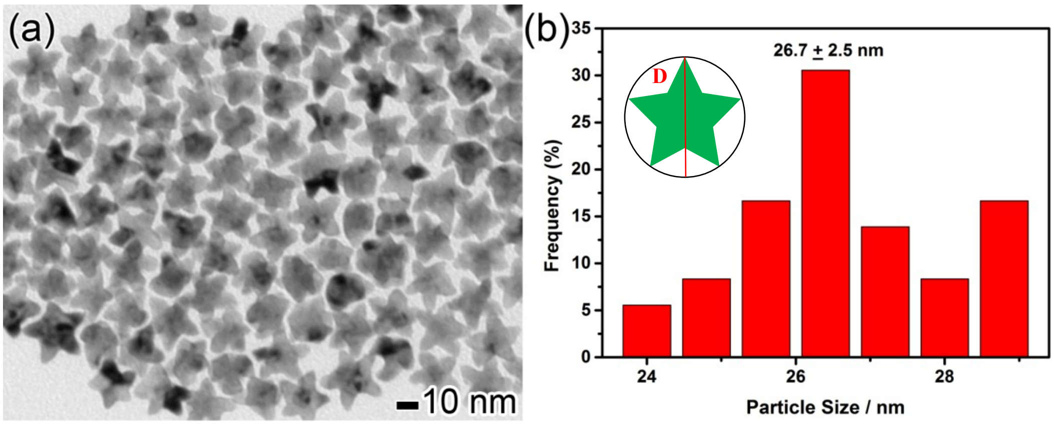

Figure S2. (a) TEM image of the Au@$Pt_{1.2}$Cu nanostars and (b) the corresponding size distribution with a schematic illustration for the size definition of the nanostar.

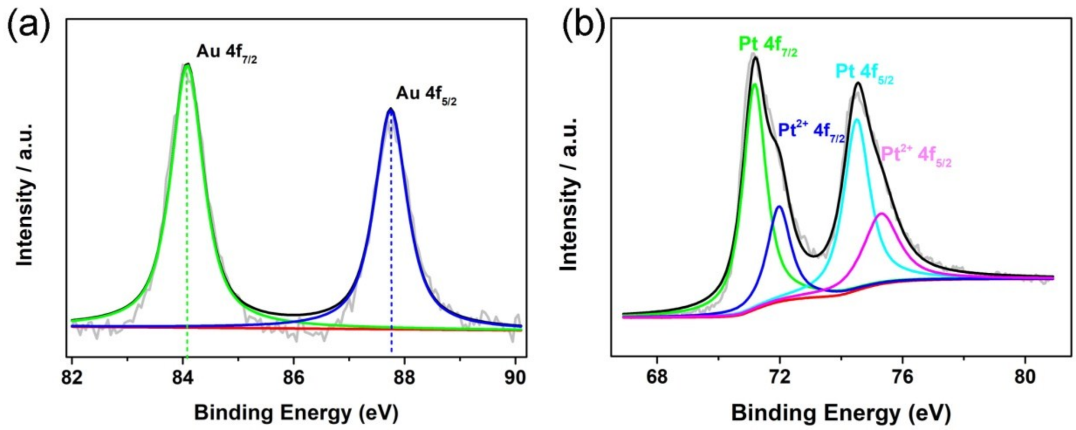

Figure S3. XPS spectra of the Au@Pt_3 NPs for (a) Au 4f and (b) Pt 4f orbitals, respectively.

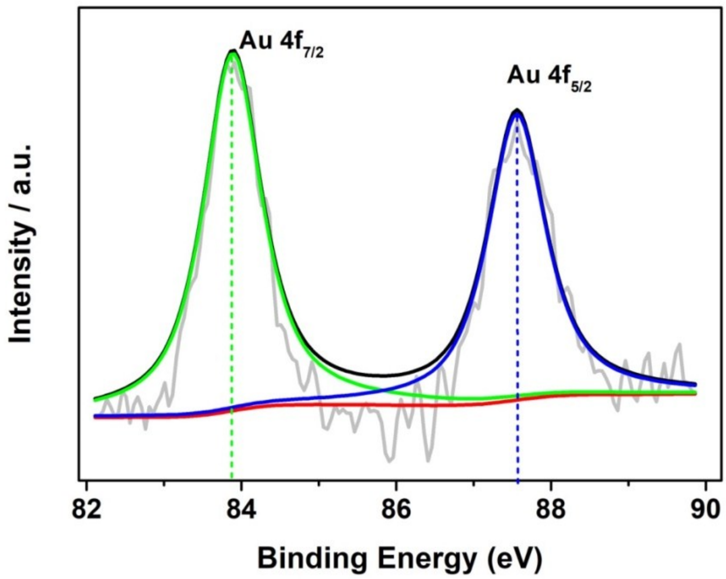

Figure S4. XPS spectra of Au@$Pt_{1.2}$Cu nanostars for Au 4f orbital.

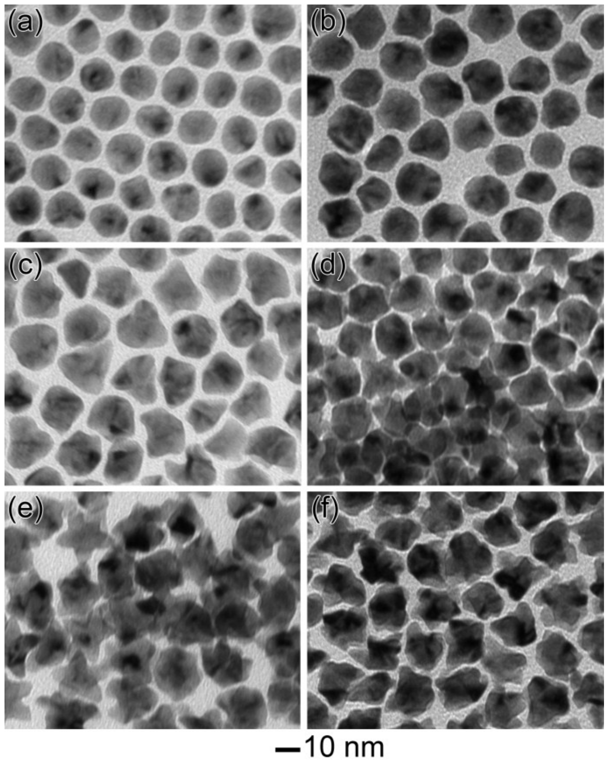

Figure S5. TEM images of Au@PtCu decahedra prepared using the standard procedure by maintaining the amount of Au seeds constant, except for the different Pt/Cu molar ratios fed in the synthesis: (a) 1/0.3, (b) 1/0.6, (c) 1/1, (d) 1/2, (e) 1/4, and (f) 1/5.

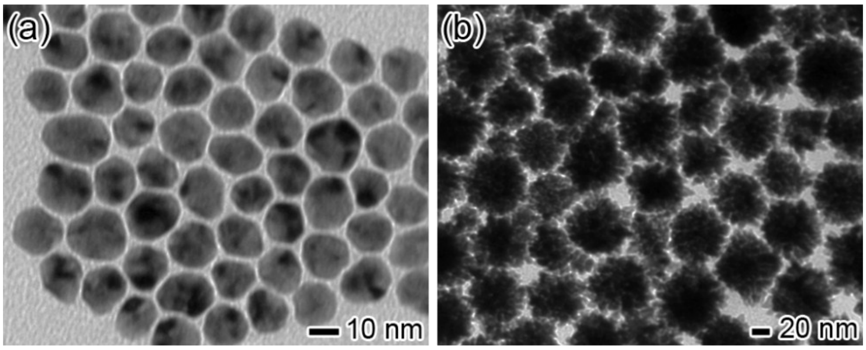

Figure S6. TEM images of (a) $Au@Pt_3$ NCs prepared in the absence of Cu precursors and (b) $Pt_{1.2}Cu$ nanobranches in the absence of Au seeds.

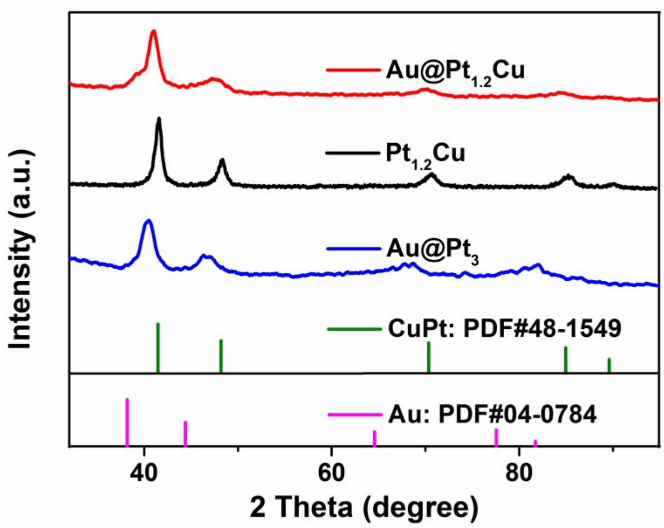

Figure S7. XRD patterns of Au@$Pt_{1.2}Cu$ nanostars, Au@Pt_3 NPs, and $Pt_{1.2}Cu$ nanobranches.

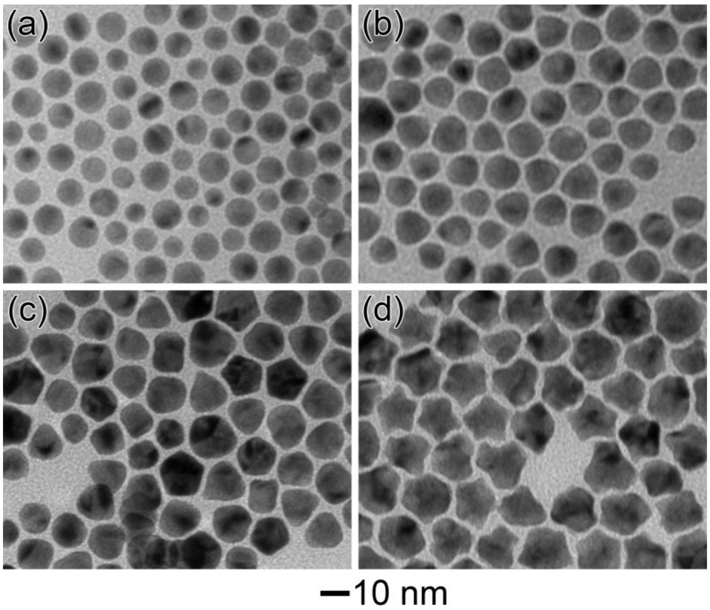

Figure S8. TEM images of Au@PtCu nanocrystals prepared using the standard procedure, except for the reaction temperature: (a) 160, (b) 180, (c) 200, and (d) 220 ℃.

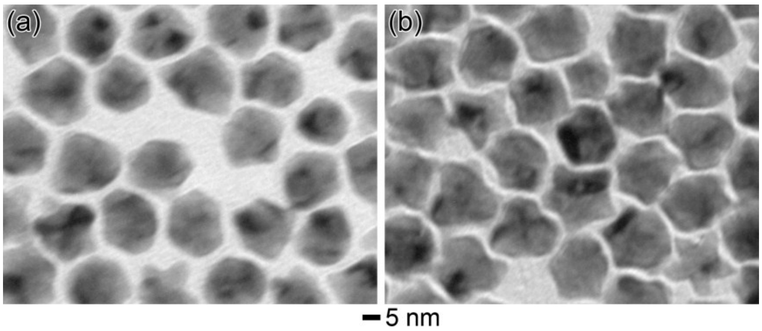

Figure S9. TEM images of Au@PtCu nanostars that were prepared using the standard procedure, except for the difference in the amounts of CTAB: (a) 0 and (b) 100 mg.

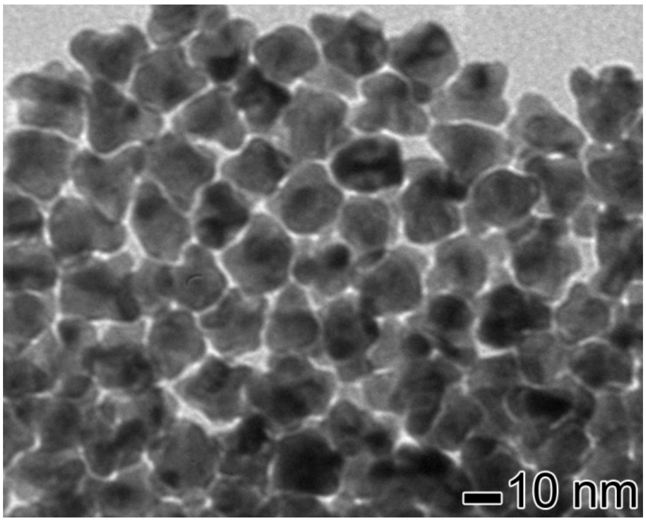

Figure S10. TEM image Au@PtCu nanostars prepared using the standard procedure except for using NH_4Br as the capping agent instead of CTAB.

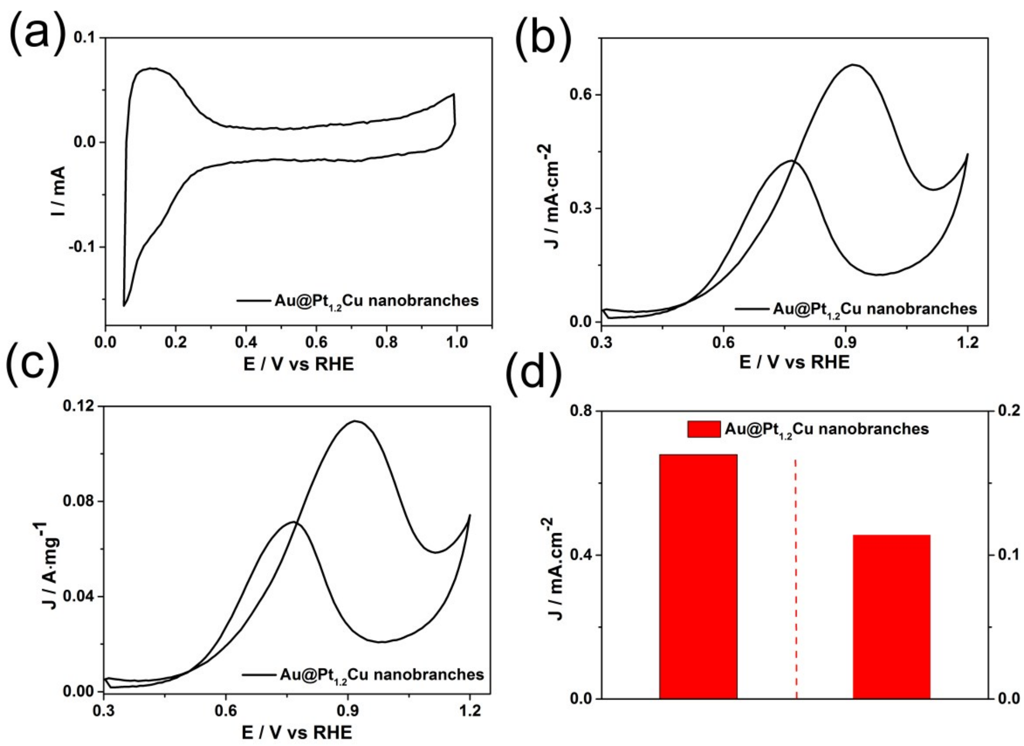

Figure S11. (a) Cyclic voltammograms (CVs) recorded at room temperature with a sweep rate of 50 mV s^{-1} in N_2-saturated 0.1 M $HClO_4$ for Au@$Pt_{1.2}$Cu nanobranches. (b, c) CVs in a 0.1 M $HClO_4$ + 1 M CH_3OH solution at a scan rate of 50 mV/s for MOR normalized by surface area (i_s, mA/cm^2_{Pt}) and Pt mass (i_m, mA/μg_{Pt}), respectively. (d) Specific and mass activities at the peak position of forward curve.

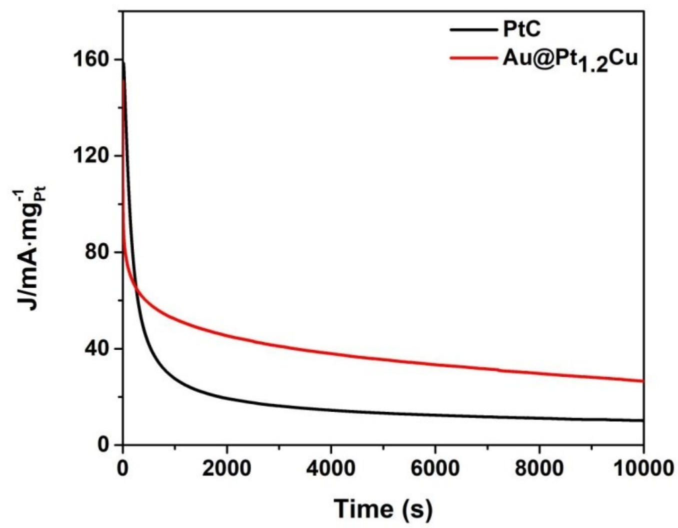

Figure S12. Chronoamperometric curves of Au@$Pt_{1.2}$Cu nanostars and Pt/C obtained at 0.6 V for 10000 s.

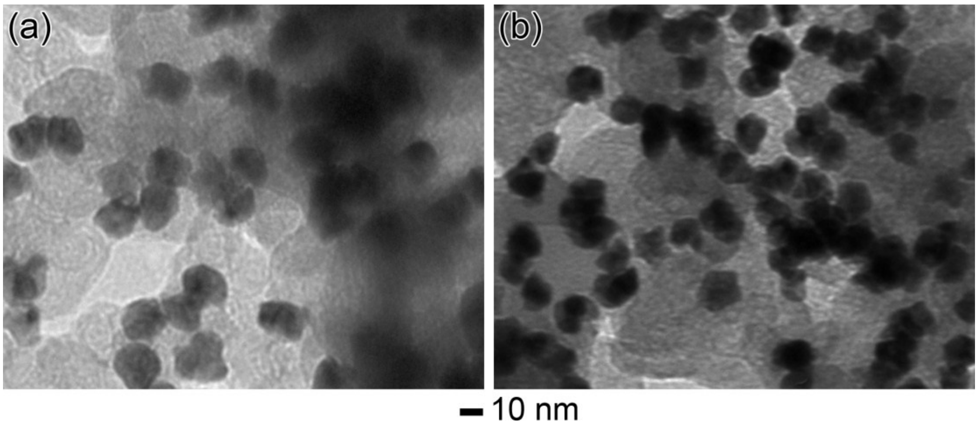

Figure S13. TEM images of the carbon-supported star-shaped Au@$Pt_{1.2}$Cu catalysts (a) before and (b) after 1500 cycles CV tests.

Reference

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