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Composition-Tunable Synthesis of Pt-Cu Octahedral Alloy Nanocrystals from PtCu to $PtCu_3$ via Underpotential-deposition-like Process and Their Electrocatalytic Properties

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Table S1. The calculated lattice parameters and the Cu contents of the as-prepared Pt-Cu alloy NCs based on XRD.

Sample No.	*n*-butylalcohol [mmol]	Cell constant a [Å]	Cu atom fraction [%] XRD	Chemical formula
1	0	3.7953(1)	50.17	PtCu
2	0.2	3.7828(1)	52.02	$Pt_{48}Cu_{52}$
3	1.0	3.7774(2)	54.94	$Pt_{45}Cu_{55}$
4	2.0	3.7630(7)	58.77	$Pt_{41}Cu_{59}$
5	8.0	3.7466(3)	62.13	$Pt_{38}Cu_{62}$
6	20.0	3.7157(3)	71.35	$Pt_{29}Cu_{71}$
7	40.0	3.7015(1)	75.05	$Pt_{25}Cu_{75}$
8	50.0	3.7017(1)	75.07	$PtCu_3$

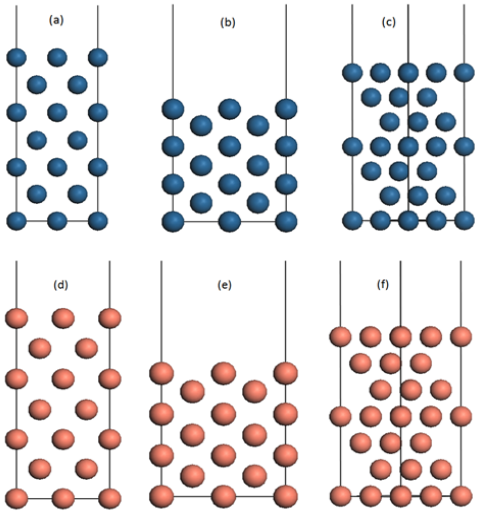

Figure S1. The structures of supercell for (a) (100), (b) (110) and (c) (111) surfaces of Pt, (d) (100), (e) (110) and (f) (111) surfaces of Cu.

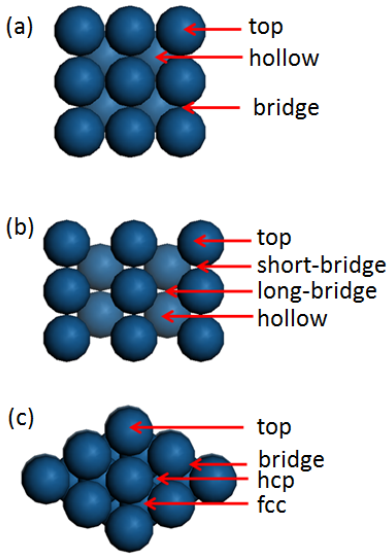

Figure S2. All three surfaces and their high-symmetry active sites: (a) (100), (b) (110) and (c) (111). (Short-bridge and long-bridge is named as bridge 1 and bridge 2, respectively.)

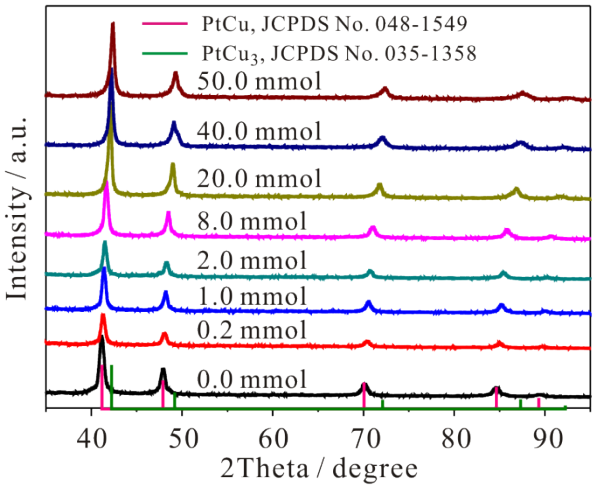

Figure S3. XRD patterns of the as-prepared Pt-Cu alloy NCs obtained from different amounts of *n*-butylalcohol.

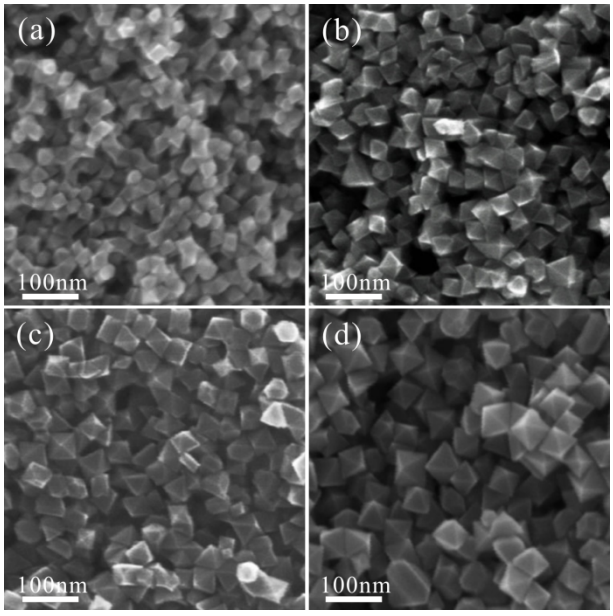

Figure S4. SEM images of the four samples obtained from different amounts of *n*-butylalcohol. (a) 0.0 mmol; (b) 0.2 mmol; (c) 8.0 mmol; (d) 40.0 mmol.

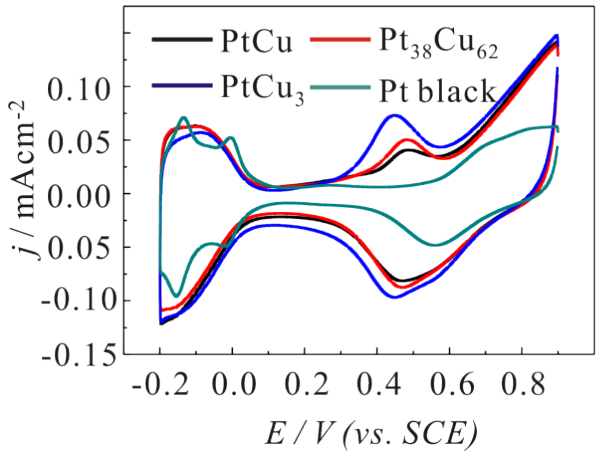

Figure S5. The CV curves measured for three Pt-Cu alloy NCs with different composition and commercial Pt black in a N_2-purged solution of 0.25 M H_2SO_4. Scan rate: 50 mV s^{-1}. It should be noticed that there is an extra oxidation peak at about 0.48 V for three Pt-Cu alloy catalysts compared with Pt black, indicating Cu can be electrochemically dissolved. The peak of current density increases with the increase of Cu content, suggesting Cu dissolved more apparently. Thus, each electrode loading catalysts loops 15 cycles in 0.25 M H_2SO_4 solution in advance, then it was used to test the activity of methanol electro-oxidation.