Supporting Information

A Green Chemical Approach for Preparation of Pt_xCu_y Nanoparticles with a Concave Surface in Molten Salt for Methanol and Formic Acid Oxidation Reaction

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Preparation of the Pt_xCu_y alloy concave nanoparticles.

The $Pt_{51}Cu_{49}$ alloy concave nanoparticles were prepared as follows: 6.6 g of KNO_3 (Tianjin Hengxing Chemical Reagent, AR, 99.0%), 3.4 g of $LiNO_3$ (Aladdin Reagent, CR, 98.0%) were mixed together in a 50 mL three-neck round-bottom flask and slowly heated to 180 ºC with magnetic stirring, 50 mg KOH (Tianjin Hengxing Chemical Reagent, AR, 85.0%) was adding into the molten salt solution. Then 8.8 mg of tetra-ammine platinum oxalate $\{Pt(NH_3)_4C_2O_4\}$ and 6.1 mg of copper nitrate trihydrate $\{Cu(NO_3)_2 \cdot 3H_2O\}$ (Tianjin Hongyan Chemical Reagent, AR, 99.0%) were added simultaneously into the flask with vigorously stirring. The reaction was kept at 180 ºC for 2 h. The black molten salt solution was cooled down to room temperature by removing the heating bath, and then 50 mL distilled water was injected into the flask to dissolved the mixture with magnetic stirring. The solution was centrifuged at 5000 rpm for 2 min. After centrifuging, the transparent supernatant was collected for recycles and the precipitate was rinsed with distilled water for additional 2 times to remove the remained molten salt.

The other Pt_xCu_y nanocave alloy nanoparticles were using the same preparation method. 4.4 mg of $Pt(NH_3)_4C_2O_4$ and 9.1 mg of $Cu(NO_3)_2{\cdot}3H_2O$ for $Pt_{23}Cu_{77}$, 13.2 mg of $Pt(NH_3)_4C_2O_4$ and 3.0 mg of $Cu(NO_3)_2{\cdot}3H_2O$ for $Pt_{74}Cu_{26}$, 15.1 mg of $Pt(NH_3)_4C_2O_4$ and 1.7 mg of $Cu(NO_3)_2{\cdot}3H_2O$ for $Pt_{83}Cu_{17}$.

FIGURES

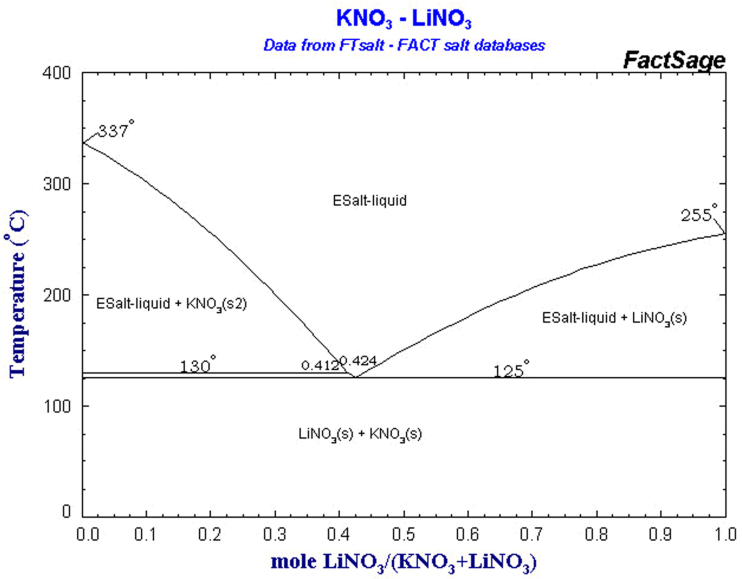

Fig. S1 Diagram phase of the mixture of KNO_3 and $LiNO_3$. Citing from internet: http://www.crct.polymtl.ca/fact/phase_diagram.php?file=KNO3-LiNO3.jpg&dir=FTsalt

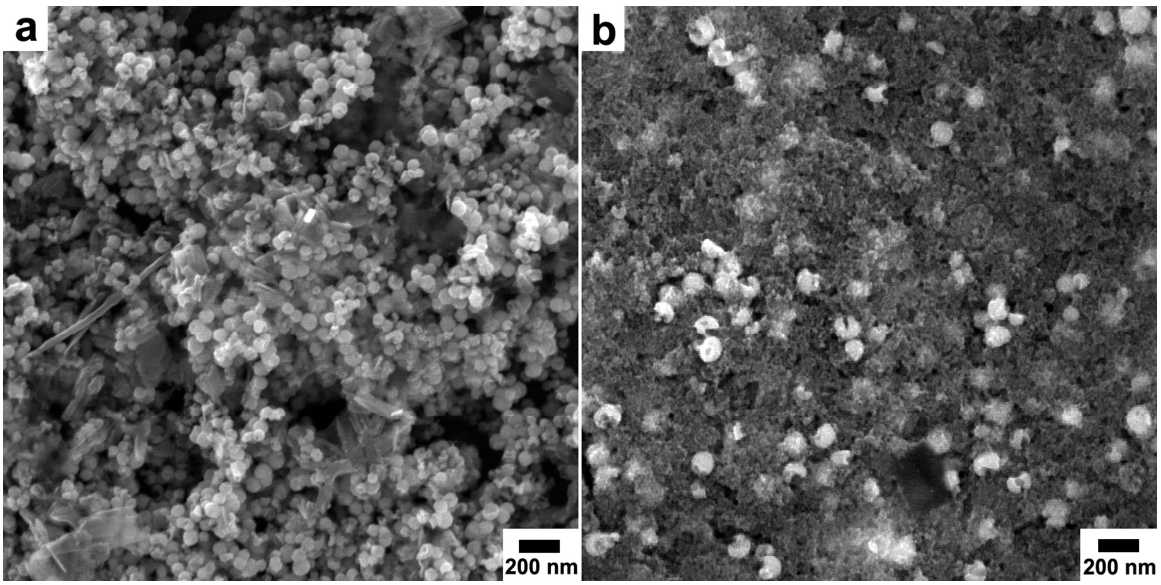

Fig. S2 SEM images of the samples with high Cu molar feeding ratios, and the $Pt(NH_3)_4C_2O_4$ /$Cu(NO_3)_2{\bullet}3H_2O$ feeding molar ratios were 1:3(a) and 1:6 (b), respectively.

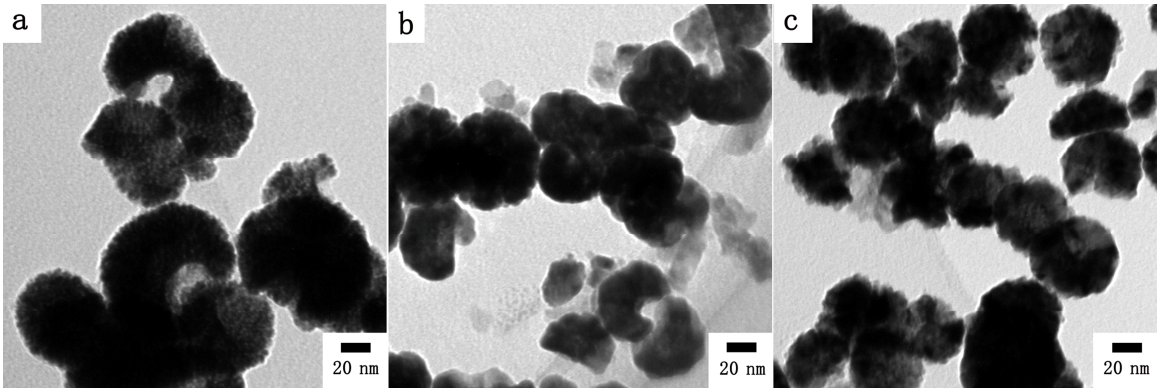

Fig. S3 TEM images of the (a) $Pt_{51}Cu_{49}$, (b) $Pt_{74}Cu_{26}$ and (c) $Pt_{83}Cu_{17}$.

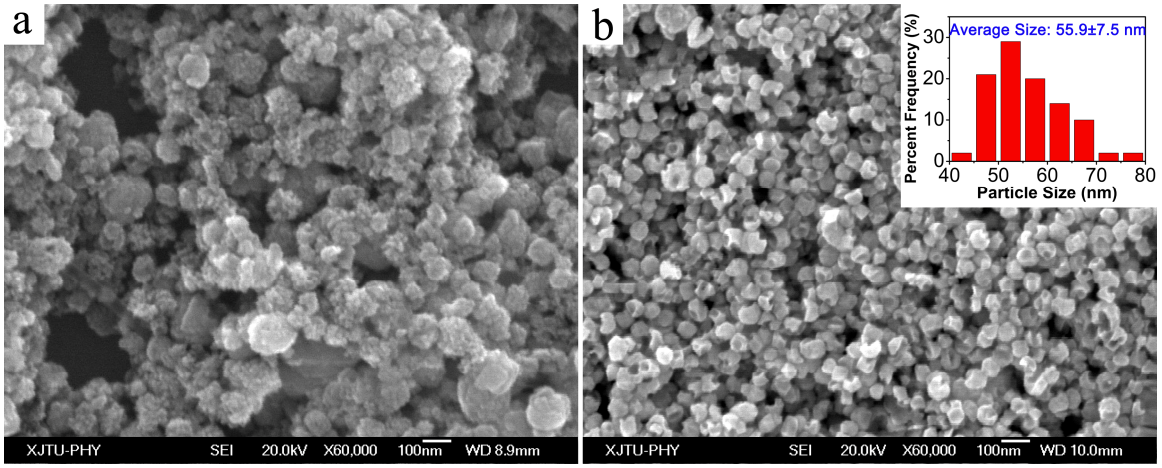

Fig. S4 SEM images of the CuO (a) and Pt (b) synthesized in the KNO_3-$LiNO_3$ molten salt system.

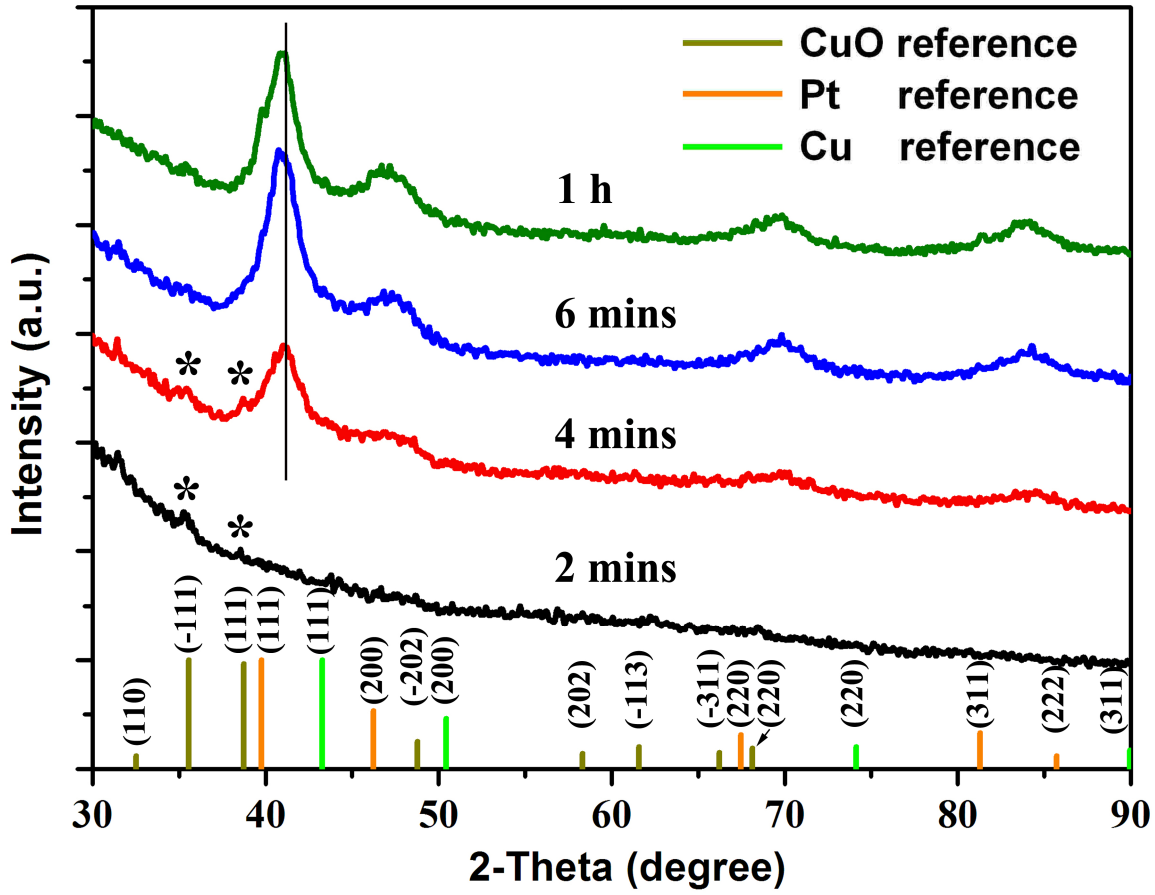

Fig. S5 XRD patterns of the Pt-Cu nanocrystal samples synthesized under different reaction times. The reaction times are 2 mins, 4 mins , 6 mins and 1h, respectively.

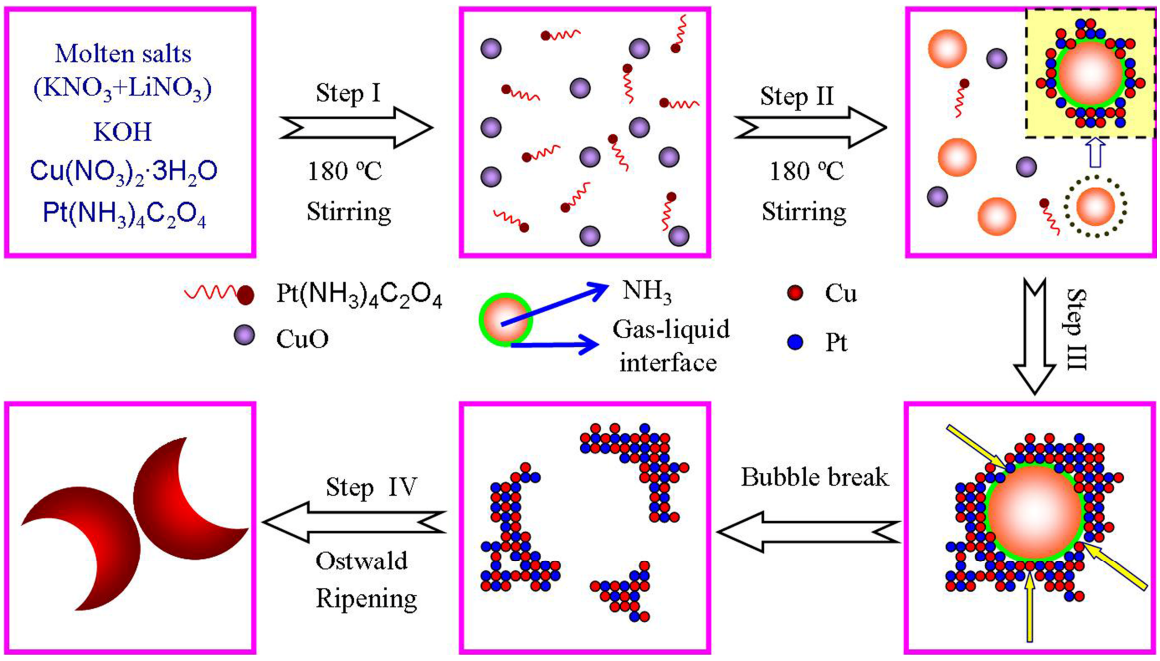

Fig. S6 Schematic illustration of the formation of Pt_xCu_y alloy concave nanoparticles.

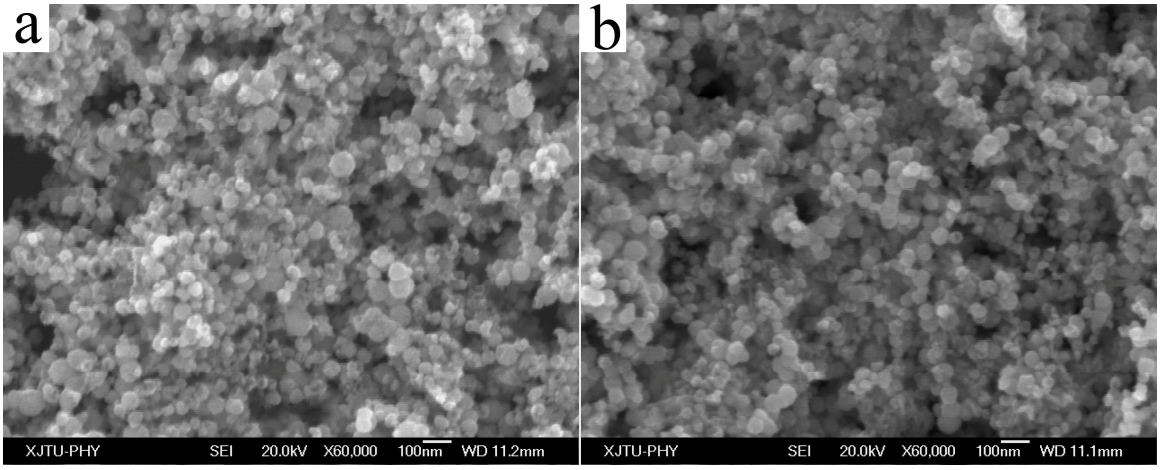

Fig. S7 SEM images of concave Pt-Cu NPs obtained at the temperature of 170 ºC (a) and 190 ºC (b).

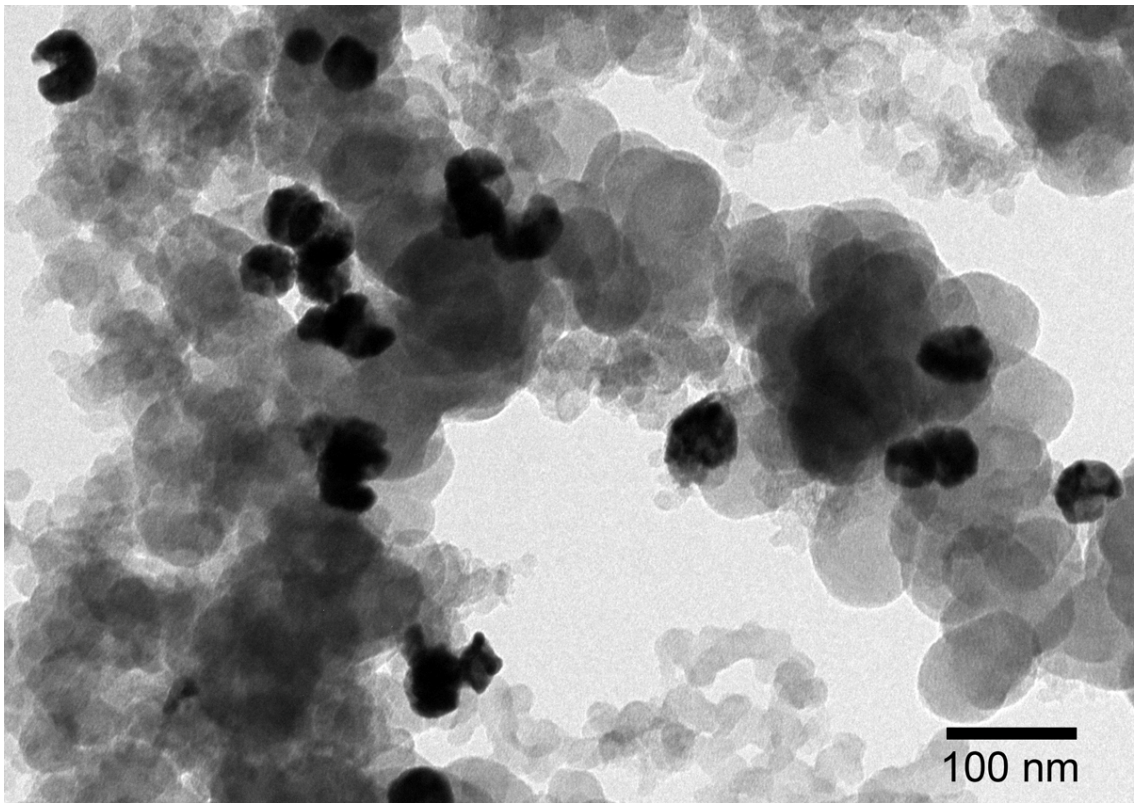

Fig. S8 TEM image of $Pt_{74}Cu_{26}$ nanoparticles loaded on carbon black.

Table S1 The summary of Pt/C (JM), $Pt_{23}Cu_{77}$/C, $Pt_{51}Cu_{49}$/C, $Pt_{74}Cu_{26}$/C, and $Pt_{83}Cu_{17}$/C catalysts for methanol electrooxidation in 0.1 M $HClO_4$ + 1 M MeOH

Samples	Pt/C (JM)	$Pt_{83}Cu_{17}$/C	$Pt_{74}Cu_{26}$/C	$Pt_{51}Cu_{49}$/C	$Pt_{23}Cu_{77}$/C
j（mA/cm^2_{Pt}）	1.74	4.46	8.46	2.67	2.82
Peak potentials (V)*	0.88	0.82	0.84	0.84	0.85
I_f/I_b	0.83	2.0	1.69	1.65	1.59

Table S2 The summary of Pt/C (JM), $Pt_{23}Cu_{77}$/C, $Pt_{51}Cu_{49}$/C, $Pt_{74}Cu_{26}$/C, and $Pt_{83}Cu_{17}$/C catalysts for formic acid electrooxidation in 0.1 M $HClO_4$ + 0.5 M HCOOH

Samples	Pt/C (JM)	$Pt_{83}Cu_{17}$/C	$Pt_{74}Cu_{26}$/C	$Pt_{51}Cu_{49}$/C	$Pt_{23}Cu_{77}$/C
j（mA/cm^2_{Pt}）	0.52	2.15	3.23	1.89	2.61
Peak potentials (V)*	0.51	0.55	0.56	0.62	0.59