Supporting Information

Facile, Rapid and Surfactant-free Synthesis of Bimetallic Pt-Cu Nanoparticles via Ultrasound-Assisted Redox Replacement

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Estimation of the number densities of Cu and Pt-Cu NPs: Assuming a sphere model and uniformity in particle size, the number of Cu NPs per gram of NCNTs (N_{Cu})at a given loading (A) can be calculated by $A/(\rho_{Cu}V_{Cu})$. ρ_{Cu} and V_{Cu} are the density of Cu and the volume of a single Cu particle ($4\pi r_{Cu}^3/3$), respectively. Given a molar ratio of Cu-to-Pt at B in the alloy NPs, the remaining mass of Cu (m_{Cu}) after the displacement is $AB/(B+1)$; the mass of Pt (m_{Pt}) is $AM_{Pt}/(M_{Cu}(B+1))$, where M_{Pt} and M_{Cu} are the molecular weight of Pt and Cu, respectively. The number of Pt-Cu NPs per gram of NCNTs ($N_{Pt\text{-}Cu}$) can thus be estimated by $(m_{Cu}+m_{Pt})/(\rho_{Pt\text{-}Cu}V_{Pt\text{-}Cu})$, that is $(AB/((B+1)\rho_{Pt\text{-}Cu}V_{Pt\text{-}Cu})) + (AM_{Pt}/(M_{Cu}(B+1)\rho_{Pt\text{-}Cu}V_{Pt\text{-}Cu}))$. In cases of $B = 1$, M_{Cu} = 64 g mol^{-1}, M_{Pt} = 195 g mol^{-1}, the equation can be simplified as $2.02A/(\rho_{Pt\text{-}Cu}V_{Pt\text{-}Cu})$. Moreover, based on the approximation of $\rho_{Pt\text{-}Cu} \approx 2\ \rho_{Cu}$ when $B = 1$, $N_{Pt\text{-}Cu}$ can be approximated as $A/(\rho_{Cu}V_{Pt\text{-}Cu})$. In such a scenario, $N_{Pt\text{-}Cu}/N_{Cu} = (r_{Pt\text{-}Cu}/r_{Cu})^3$, which is determined to be about 35 given that the diameters of Cu and Pt-Cu NPs are 9.4 and 2.89 nm, respectively.

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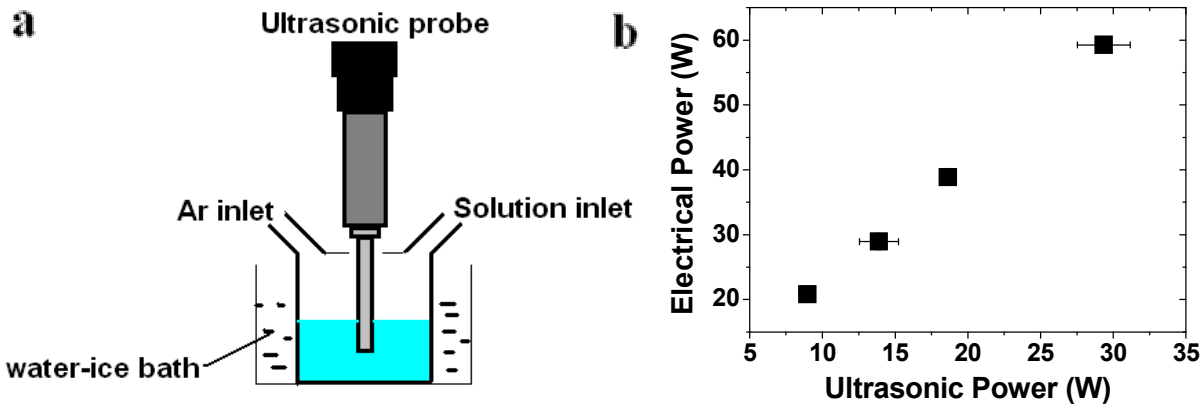

Figure S1. (a) Sonochemical system used in this work to prepare the metal nanoparticles. (b) Electrical power versus ultrasonic power for the system used in this work.

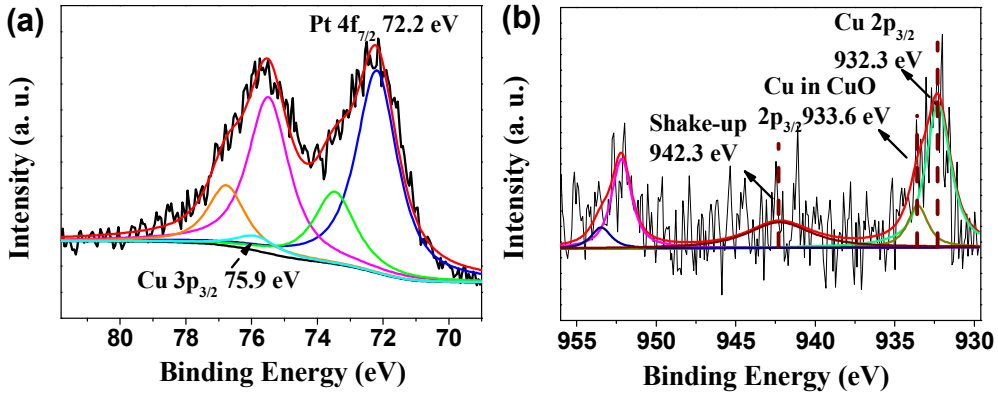

Figure S2. (a) Pt 4f and (b) Cu 2p core level XPS spectra of Pt-Cu/NCNT. The molar ratio of Pt:Cu in the sample is 1:1.

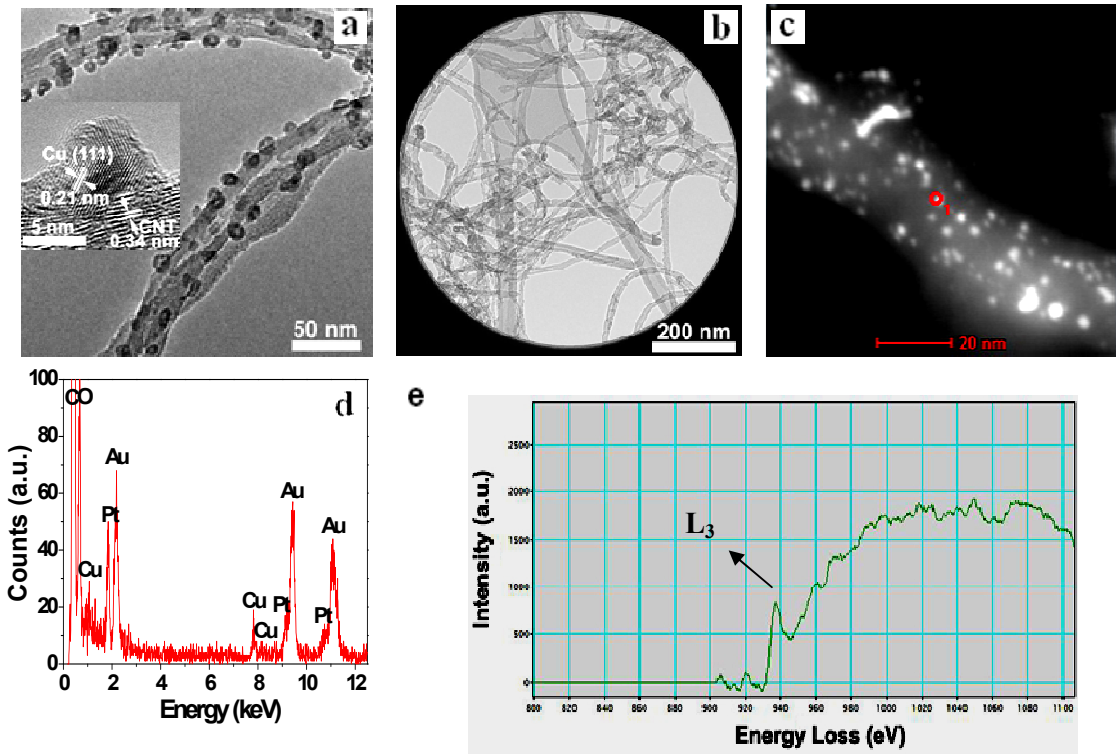

Figure S3. TEM images of (a) Cu/NCNTs at 7.3 wt.% of Cu loading, the inset shows HRTEM observation of the sample, (b) Pt-Cu/NCNTs, SAED pattern of the circled sample is displayed in Fig. 4e. (c) STEM image of an individual Pt-Cu/NCNT. (d) EDX pattern of the circled individual NP shown in c. The Au peaks are from the TEM grid. (e) EELS Cu spectrum.

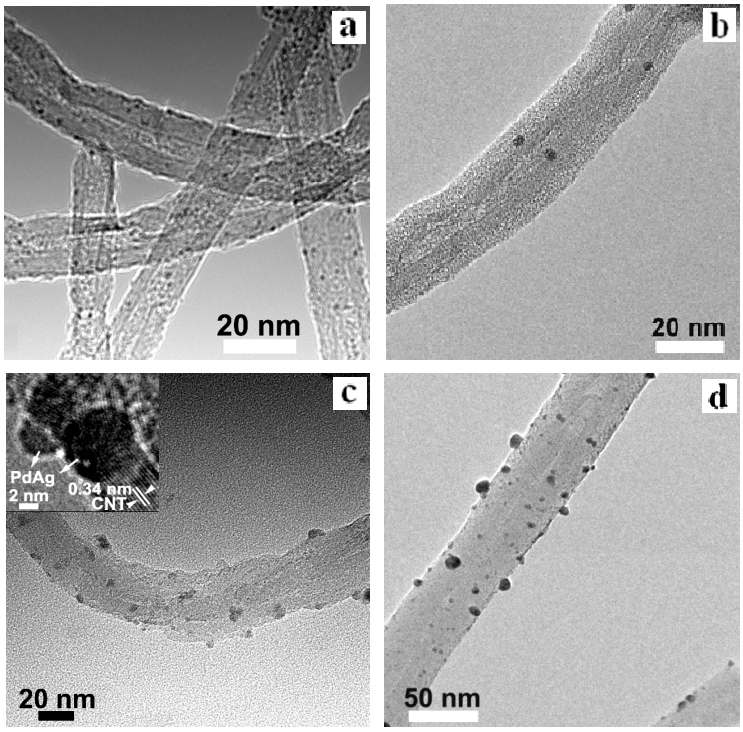

Figure S4. TEM images of (a) Pt-Cu/NCNTs prepared via tip sonication for 10 s, (b) Pd-Cu/NCNT, (c) Pd-Ag/NCNT and (d) Au-Pd/NCNT. The inset in c is a HRTEM image of the sample.

Table S1. Quantitative SEM-EDX analysis results for the Pt-Cu/NCNT shown in Figure 3

Element	Wt. %	At. %	K-Ratio	Z	A	F
C K	52.40	72.76	0.0978	1.0471	0.1782	1.0001
O K	2.13	2.22	0.0037	1.0295	0.1689	1.0006
Al K	38.86	24.02	0.3089	0.9589	0.8289	1.0000
Cu K	2.47	0.65	0.0214	0.8406	1.0091	1.0189
Pt L	4.14	0.35	0.0277	0.6436	1.0407	1.0000
Total	100.00	100.00				

Table S2. Tafel slopes of Pt-Cu/NCNTs with varying Pt:Cu molar ratios and Pt-ETEK (20% Pt on Vulcan carbon)

Catalyst	Tafel slopes	
Pt:Cu	mV / dec	mV / dec
25: 75	57.5 ± 4.5	80.5 ± 7.2
50: 50	88.8 ± 5.2	130.3 ± 13.4
75: 25	86.0 ± 13	132.2 ± 24.8
Pt-ETEK	74.1 ± 11.4	134.9 ± 21.6