

Supporting Information

Monodisperse AuCuSn Trimetallic Nanocube catalysts

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Experimental

Materials. Copper (II) acetylacetonate ($\text{Cu}(\text{acac})_2 \geq 99.99\%$), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), tin (II) chloride (SnCl_2 98%), oleylamine (tech., 70%), 1,2 ethane dithiol were purchased from Sigma-Aldrich. Sodium(II) sulfide flakes ($\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$) were purchased from Merck chemicals. All the chemicals were used without further purification.

Synthesis of AuCuSn (Sn~20%) nanocube. For the synthesis of the nanocubes, we have adopted our optimized synthetic methods.

In a typical synthesis 0.25 mmol (65 mg) copper(II) acetylacetonate, 0.13 mmol (22 mg) tin(II) chloride, were taken into a three neck round bottom flask containing 5 ml of oleylamine. The precursor's mixture was degassed for 12 min at 60 °C. Then temperature of the reaction mixture was elevated to 280 °C. In a separate vial, 0.1 mmol (36 mg) gold(III) chloride with 0.005 mmol (0.3 mg) sodium(II) sulfide flakes were dissolved by gentle stirring in 2 ml of oleylamine and the resulting mixture was first degassed by purging with N_2 gas for 10 min and injected into the three neck round bottom flask at 280 °C. The temperature of the reaction mixture was then lowered to 260 °C and kept there for 1 hr. After 1 hr. the reaction was stopped and the product was purified using ethanol as non-solvent and then dispersed it into chloroform for further use.

Synthesis of Quasi-spherical AuCuSn (Sn~5%) NPs. The synthetic procedure was same like nanocube formation except the use of sodium(II) sulfide flakes. In a typical synthesis 0.25 mmol (65 mg) copper(II) acetylacetonate, 0.13 mmol (22 mg) tin(II) chloride were taken in a three neck round bottom flask containing 5 ml of oleylamine. The precursor mixture was degassed for 12 min at 60 °C and subsequently the temperature of the reaction mixture was increased to 280 °C. In a separate vial, 0.1 mmol (36 mg) gold(III) chloride was dissolved by stirring in 2 ml of oleylamine, degassed by purging with N_2 gas for 10 min and injected into the three neck round bottom flask at 280 °C. The temperature of the reaction mixture was then lowered to 260 °C and kept there for 1 hr. Sample collected after 1 hr. and purified the crude sample using ethanol. Then the purified sample was dispersed in chloroform for further use.

Synthesis of bimetallic AuCu NPs. AuCu bimetallic nanostructures were prepared using a modified literature method.¹ In a typical synthesis 0.25 mmol (65 mg) copper(II) acetylacetonate

were taken into 4 ml of oleyl amine in a three neck flask and degassed the reaction mixture by purging with N₂ gas for 12 min at 60 °C. Temperature of the reaction mixture was taken to 280 °C. In an another vial 0.1mmol (36 mg) of gold(III) chloride was taken in 2 ml oleyl amine, stirred the solution to completely dissolve the gold chloride and degassed the solution by purging with N₂ for 12min and injected the gold chloride solution into the three neck flask at 280 °C. After that temperature lowers to 260 °C and annealed the solution for 1 hr. The reaction was stopped and purified using ethanol as non solvent.

Materials Characterization.

Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, EDS spectra for atomic percentage and elemental mapping were captured on a UHR FEG-TEM, JEOL JEM-2100F electron microscope using a 200kV electron source. The X-ray diffraction (XRD) analysis of the nanocrystals was performed using a Bruker D8 advance powder diffractometer, using Cu K α (λ = 1.54 Å) as the incident radiation. Thermo scientific vacuum oven was used for the preparation of active material for electrochemical measurement.

Electrochemical Measurements.

The electrochemical measurements were carried out with a standard three electrodes cell system in a CHI 760 D electrochemical work station. The electrochemical measurements were carried out with a standard three electrodes cell system in a CHI 760 D electrochemical work station. For the preparation of active material for electrochemical measurement we had exchanged the oleylamine ligands of the purified nanocrystals with 1,2 ethane dithiol. For this, we first dispersed the nanostructures in chloroform and then added 2-3 ml of 1,2 ethane dithiol and shake the mixture for 1 hr. After that thiol ligand exchanged NPs were precipitated using ethanol and then again dispersed in chloroform. Then this sample was drop casted on ITO coated glass substrate and the ITO coated glass samples were placed into thermo scientific vacuum oven for 1 hr and then temperature of the oven was increased to 250 °C, kept there for another 1 hr to make completely ligand free nanoparticles. Samples on ITO coated glass substrates was used as working electrode for electrochemical measurement along with Pt wire as counter electrode and

Ag/AgCl as reference electrode. A nitrogen saturated 0.1 M KOH solution was used as supporting electrolyte for all electrochemical analysis. The concentration of hydrazine stock solution used in the present study is 0.5 M. Cyclic voltammetry was executed over a potential window of -0.3 to 0.5 V at a scan rate of 20 mV/s with 10 mM hydrazine solution in supporting electrolyte. Electrochemical impedance spectroscopic measurements were carried out with the same electrode configuration and same electrolyte over a frequency domain of 1 Hz to 1MHz accompanied with a sinusoidal AC perturbation of 5 mV.

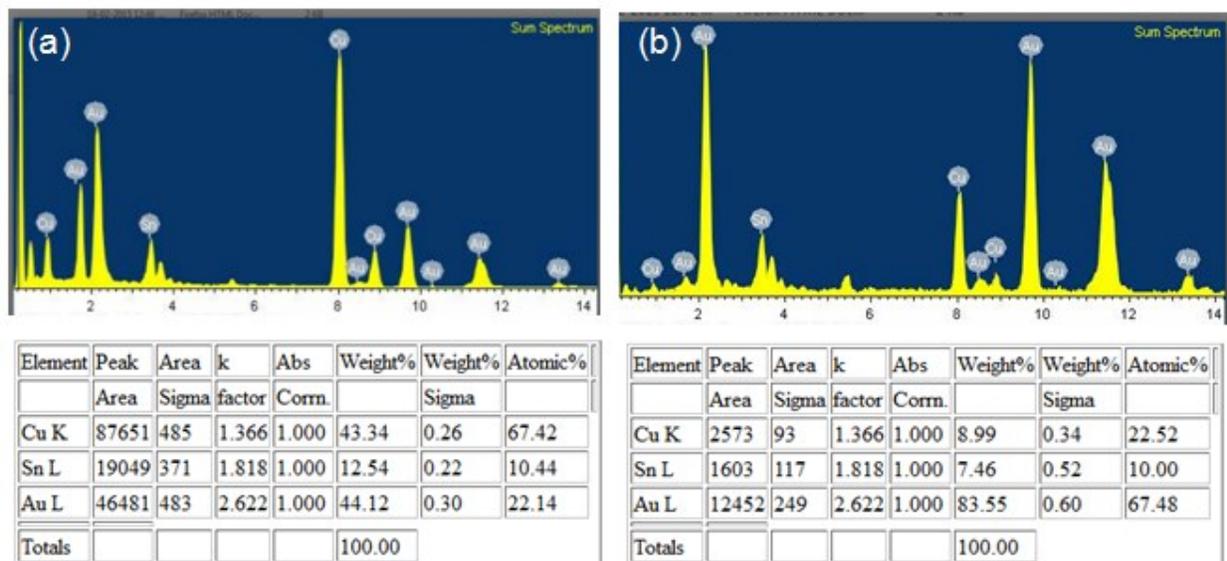


Figure S1. (a) EDS spectra of the AuCuSn nanocubes taken in Cu microscopic grid. (b) EDS spectra of the same sample taken in Au microscopic grid. Bottom tables show the comparable percentage of three elements. The data shows Sn and Au ratio in (a) is $\sim 1:2$ and in (b) Sn and Cu ratio is $\sim 1:2$. Hence the overall Au, Cu and Sn ratio remains 2:2:1.

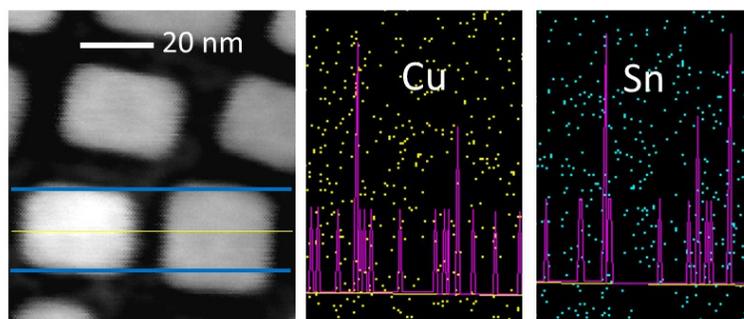


Figure S2. HAADF-STEM image of the trimetallic nanocube and the line scan mapping for Cu and Sn elements. The measurement has done in Au microscopic grid.

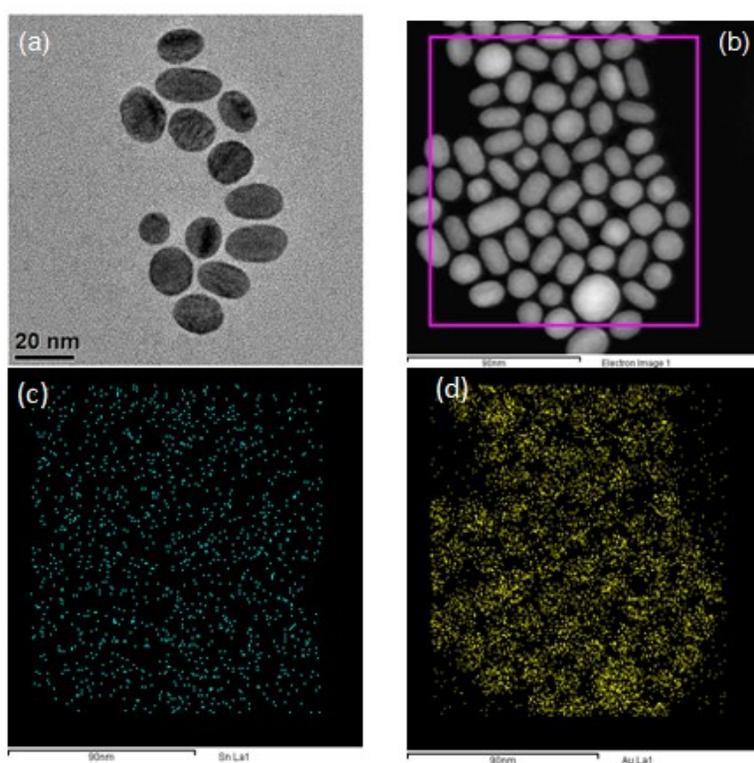
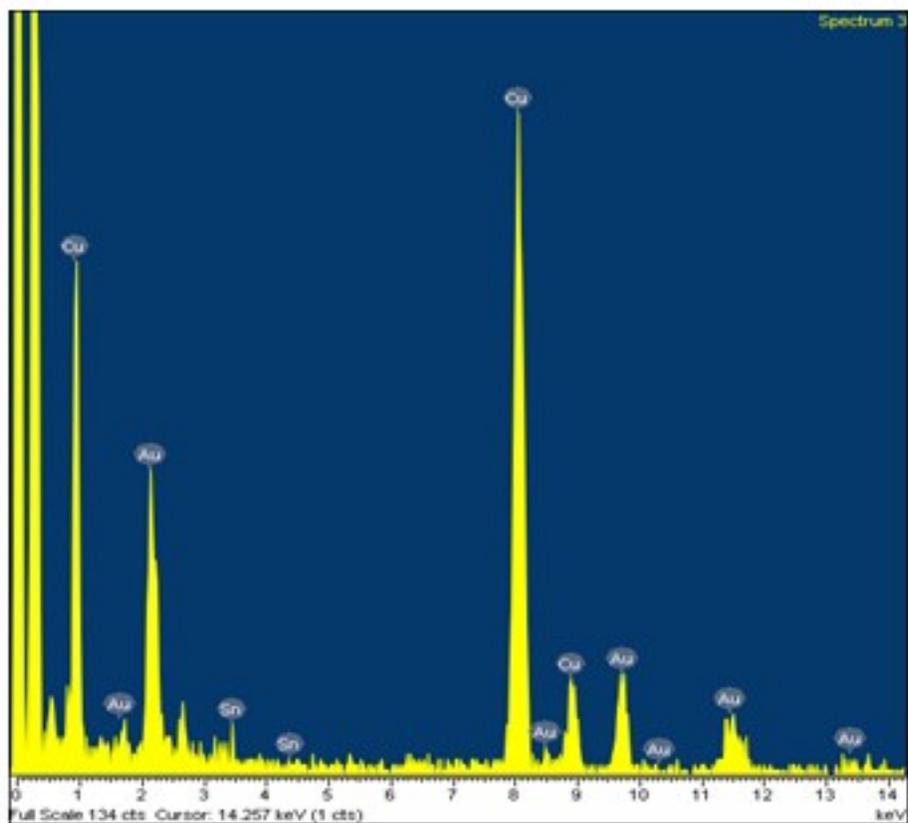


Figure S3. (a) HRTEM images of AuCuSn (5% Sn) (b) HAADF-STEM images of AuCuSn (5% Sn). (c-d) Elemental mapping for Sn & Au on the selected area in (b) indicates very small percentage of Sn into the lattice. All the images are taken on Cu microscopic grid.



Element	Peak Area	Area Sigma	k factor	Abs <u>Corrn.</u>	Weight%	Weight% Sigma	Atomic%
Sn L	22	42	1.818	1.000	0.93	1.74	0.67
Au L	618	74	2.622	1.000	37.41	3.00	16.26

Figure S4. EDS spectra of AuCuSn (5% Sn) measured on Cu microscopic grid.

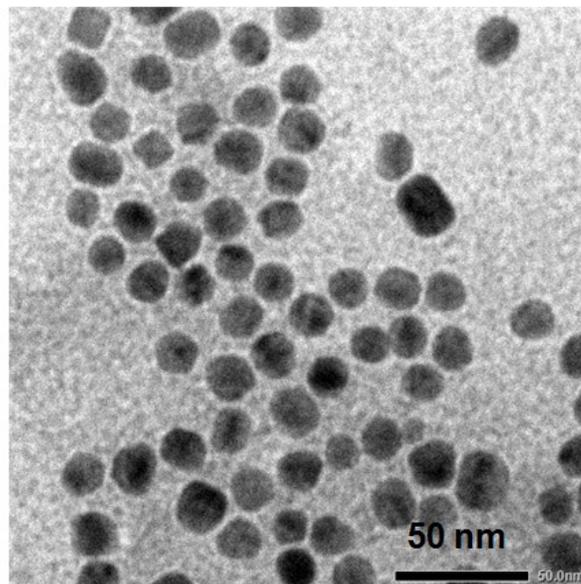


Figure S5. TEM image of AuCu bimetallic nanocrystals. This has been synthesized following a modified literature methods.¹

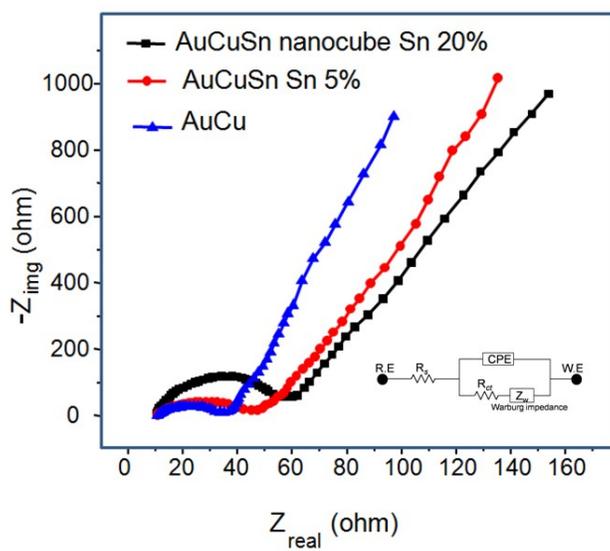


Figure S6. The Nyquist plots of different catalysts. Inset shows the equivalent circuit diagram.

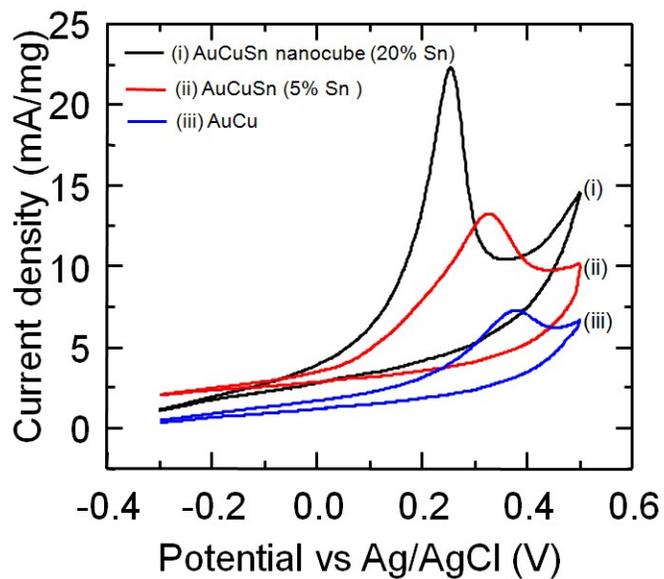


Figure S7. CVs of different catalysts from which mass activity was estimated.

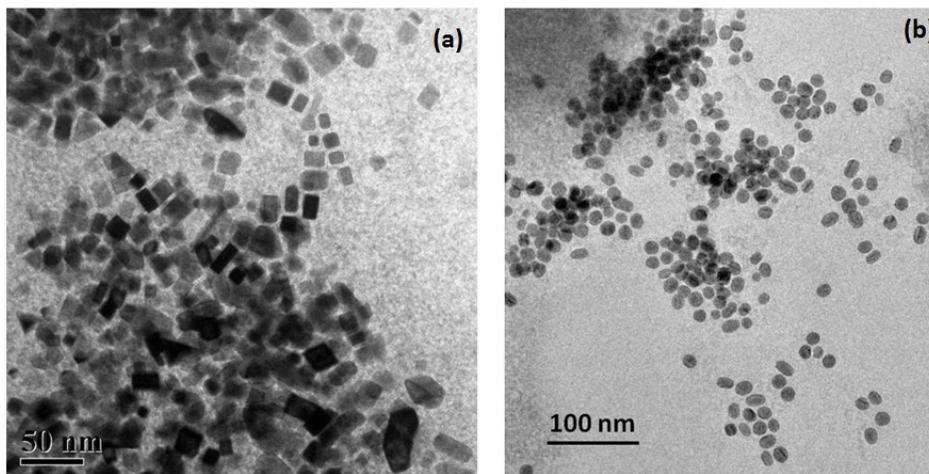


Figure S8. TEM images after 300 CV cycles are presented for AuCuSn nanocube (Sn 20%) in (a), and for AuCuSn (Sn 5%) in (b). Morphologies of the samples after electrochemical measurements remain same.

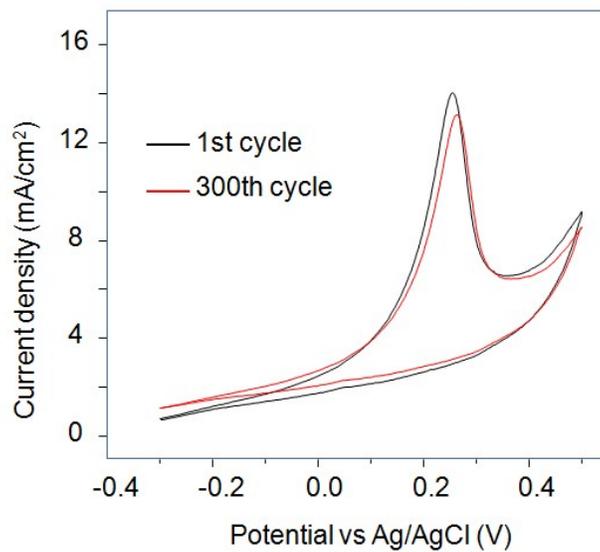


Figure S9. CV plots (1st and 300th cycle) for hydrazine oxidation using AuCuSn nanocube (20% Sn) indicating the stability of electro catalyst.

1 Liu, Y.; Walker, A. R. H. *Angew. Chem., Int. Ed.*, 2010, **49**, 6781.