

Supporting Information

An Unconventional Mechanism of Hollow Nanorod Formation: Asymmetric Cu Diffusion in Au-Cu Alloy Nanorods during Galvanic Replacement Reaction

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Experimental Section:

Chemicals:

Gold (III) chloride trihydrate (99%), copper (II) acetyl acetonate (97%), octadecylamine (90%), oleylamine (70%), *p*-nitrophenol (99%), sodium borohydride (NaBH_4 , 98%) and methoxypoly (ethylene glycol) amine (PEG-NH₂) (MW=5000) were purchased from Sigma Aldrich and used without any further purification. Tetradecylamine (95%) was obtained from TCI and used as received.

Synthesis of AuCu₃ Alloy Nanorods:

Monodisperse AuCu₃ alloy nanorods with aspect ratio of 1:3 (34.2 nm in length and 11.1 nm in diameter) were obtained following a protocol developed by Chen et. al¹ with slight modifications. The samples obtained from a single batch synthesis were used as sacrificial templates for a set of galvanic replacement reactions in order to maintain the same experimental conditions.

Galvanic Replacement Reaction:

In a typical galvanic replacement reaction, 1 mL of 0.30 mg/mL AuCu₃ rod sample in toluene was added to a small glass vial. Then 0.20 mL of oleylamine was introduced into the vial while being magnetically stirred followed by the addition of freshly prepared gold precursor solution. The gold precursor was prepared by adding 1.0 mg of H₂AuCl₄ salt to 1.0 mL of chloroform. The reaction was monitored for different reaction times. In order to obtain the intermediate, the reaction was arrested by adding excess ethanol and immediately centrifuging the mixture for 5 minutes at 7000 rpm to remove the unreacted gold precursor. Then precipitate was washed in toluene and chloroform twice by centrifuging at 12000 rpm for 10 minutes to remove excess ligands in the solution and was used for further characterization.

Phase Transfer Reaction:

PEG-NH₂ (10 mg) was dissolved in 15 mL chloroform in a 25 mL round bottomed flask and degased with nitrogen for 10 min. 2.0 mL of Au-Cu hollow rod sample (~2.0-3.0 mg/mL concentration) in toluene was added to the flask drop wise and reaction was allowed to continue for 15 hrs under nitrogen environment in dark. After the reaction, products were separated by precipitating, using 10 mL hexane and centrifuging at 12000 rpm for 20 min, followed by washing with ethanol and water and finally dispersing them in water. The same procedure was applied to AuCu₃ solid rod sample.

Catalytic Reaction:

p-nitrophenol (1.4 mM) and NaBH₄ (0.42 M) stock solutions were prepared in DI water. 3.5 mL DI water was mixed with 0.25 mL *p*-nitrophenol and 0.50 mL NaBH₄. 0.20 mL of phase-transferred Au-Cu nanorods were added to this mixture. The final concentration of *p*-nitrophenol is 7.8×10^{-5} M and NaBH₄ is 4.67×10^{-2} M. The approximate concentration of the catalysts was 3.0×10^{11} rods/mL for solid rods and 9.0×10^{10} rods/mL for hollow rods. 1 mL of this mixture was immediately transferred to a cuvette and was monitored using UV-VIS spectrometer. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to determine gold concentration in both phase transferred solid and hollow rod samples of same concentration (1.0 mg/ mL). It was found hollow rods have ~3.4 times more gold compared to solid rods. The concentration of Au in solid rods was 1.439×10^4 μg/L while it was 4.846×10^4 μg/L for hollow rod sample. Therefore, hollow rod sample was diluted accordingly to make sure both of the catalysts have the same gold concentration.

Instrumentation:

UV-Vis spectrometer (Cary 60, Agilent technologies) was used to measure the extinction spectra of the nanoparticles and the absorbance of *p*-nitrophenol. A Rigaku ultima IV power X-ray diffractometer with Cu K α radiation operated at a tube voltage of 40 KV and current of 44 mA was used to obtain the XRD patterns. TEM images were captured using a Tecnai T-12 operated at 120 KV. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images and Energy dispersive x-ray (EDX) elemental mapping was performed using FEI -Talos microscope at an accelerating voltage of 200 KV.

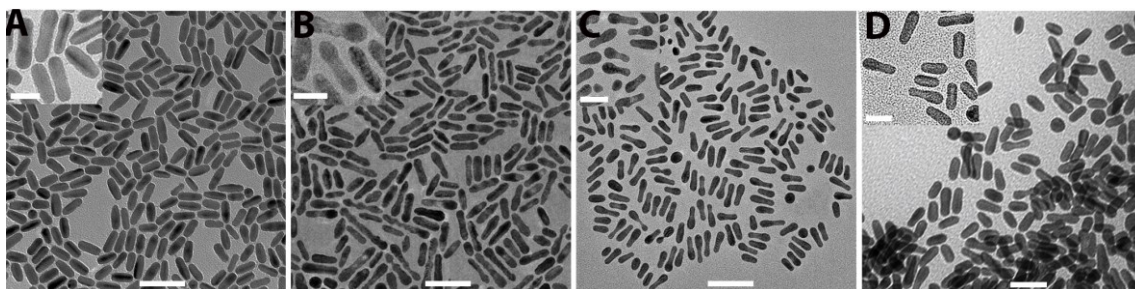


Figure S1. TEM images of the samples (A) AuCu₃ rods, and aliquots acquired at different reaction times after the injection of gold precursor (B) 5 min (C) 15 min (D) 1 hr. Scale bar = 50 nm. The scale bar in the insets = 20 nm.

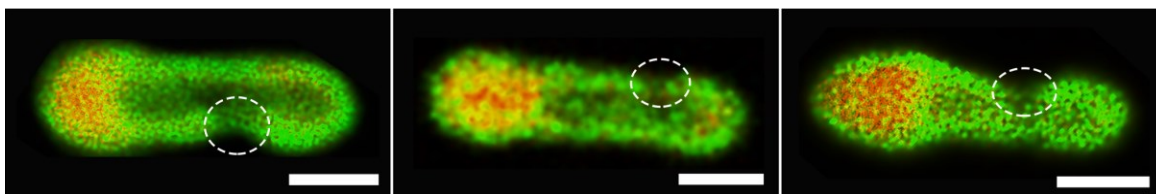


Figure S2. EDX elemental mapping of nanorodss acquired at 15 min of reaction. The white circles denote the holes formed in the rods. The Cu at the end close to the hole has dissolved. The diameter of the other end has increased and showed a Cu rich phase. Scale bar = 10 nm.

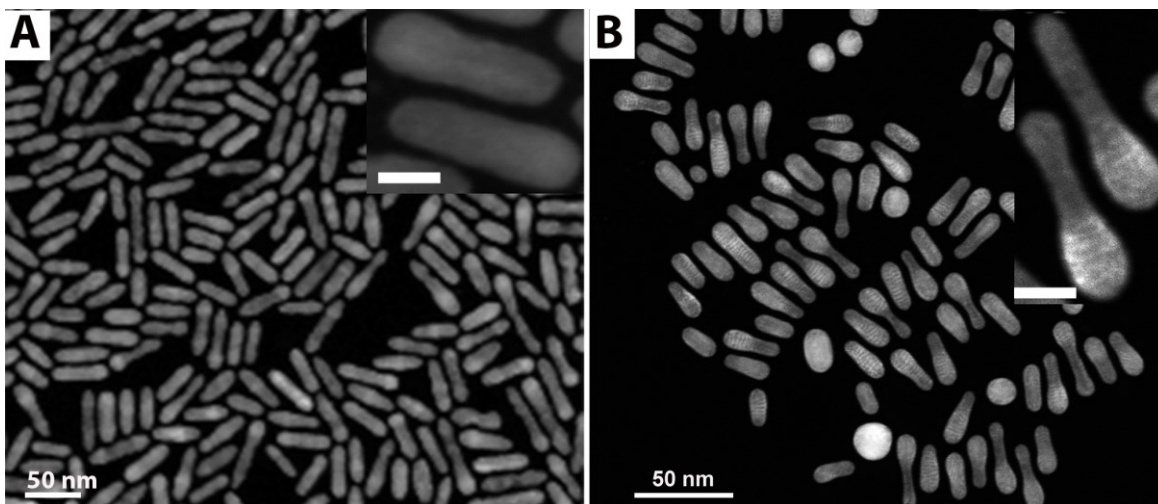


Figure S3. Comparison between the initial nanorod templates (A) and the 15-min sample (B). The insets clearly indicate transformation from regular rod to asymmetric structure with increased diameter of one end. The scale bar in the insets = 10 nm.

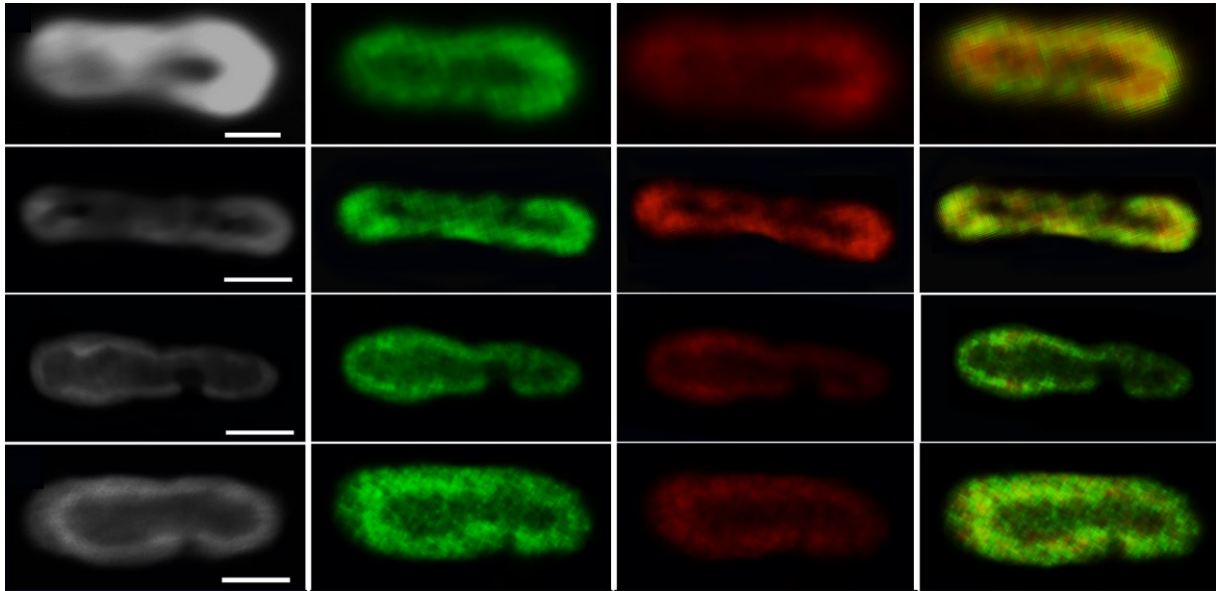


Figure S4. EDX elemental mapping of hollow rods obtained after 1-hr reaction. The mapping images show that the rods are hollow with uniform alloy composition in the walls. Scale bar = 10 nm.

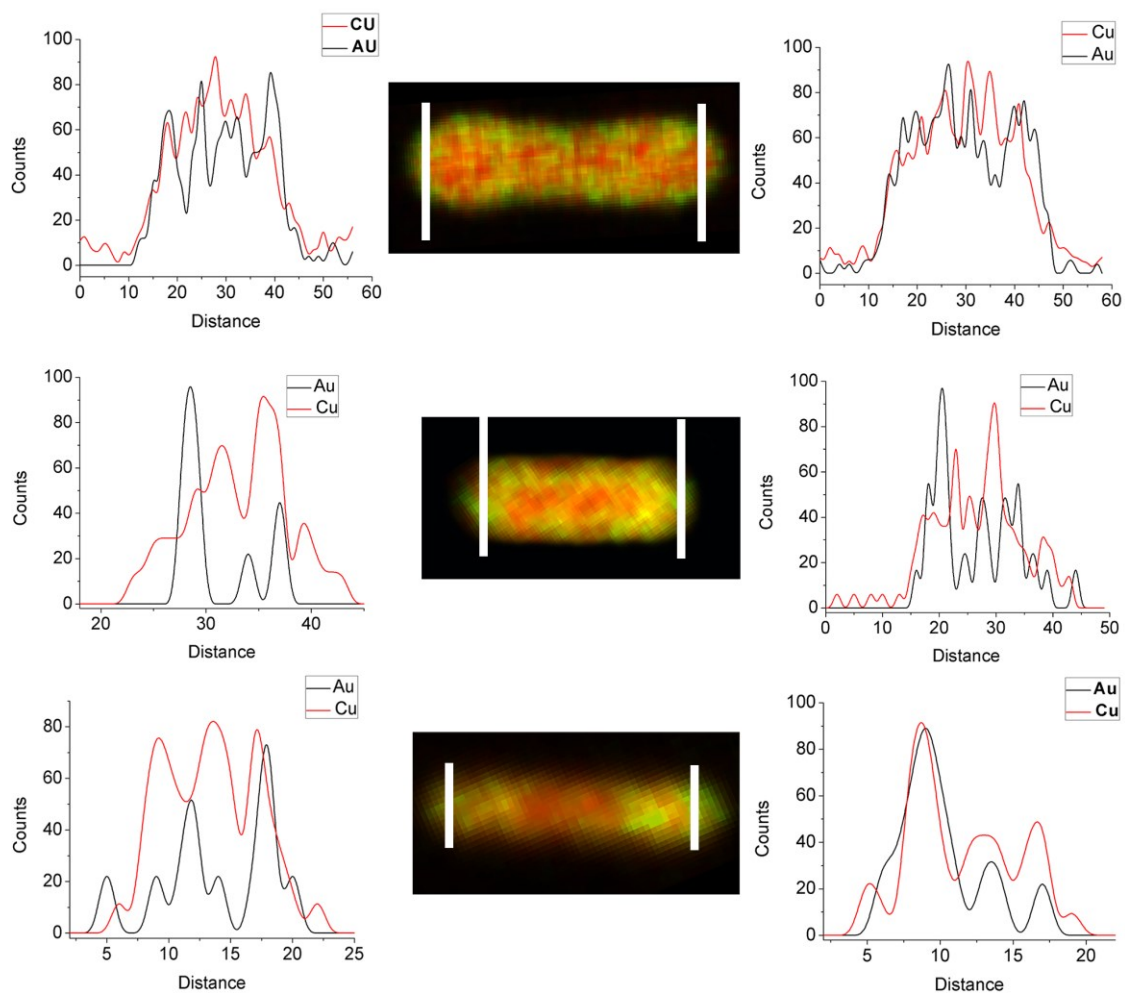


Figure S5. Additional line scans performed on two ends of the initial AuCu_3 alloy rods. The line scans clearly indicate two ends have unequal distribution of copper (red line).

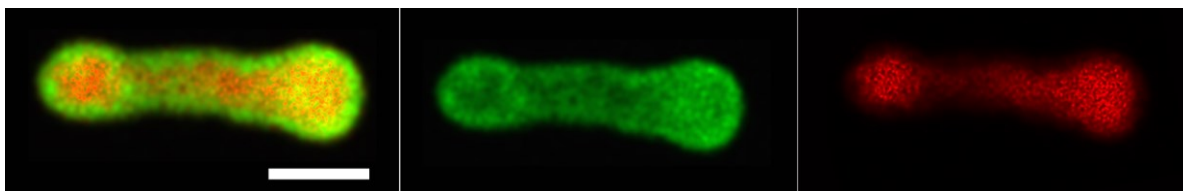


Figure S6. EDX elemental mapping images of an intermediate obtained at 15 mins of reaction, in which copper is migrating to both the ends of the rod. Scale bar = 10 nm.



Figure S7. Photograph of Au-Cu nanorods in oil phase on the left and in water on the right after the phase-transfer.

(1) Chen, S.; Jenkins, S. V.; Tao, J.; Zhu, Y.; Chen, J. *J. Phys. Chem. C* **2013**, *117*, 8924-8932.