Asymmetric Hollow Nanorod Formation through a Partial Galvanic Replacement Reaction

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Introduction

- Hollow nanostructures or nanocages → Site-specific drug delivery, optical contrasting agent, biomarker, etc.
- Absorption in the near-IR (NIR) range → Photo thermal therapy.

Synthetic methods

- Metal layer deposition and the subsequent removal of templates.
- Galvanic replacement reactions.

Present work

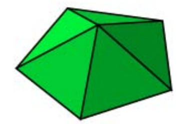
- ❖ Asymmetric hollow formation is demonstrated for the first time in a hetero-metal nanorod system by a partial galvanic replacement reaction.
- ❖ Careful control of the reaction kinetics could yield a single hollow on one end as well as a double hollow on both ends of the silver domain in the Ag-Au-Ag nanorod structure.

Experimental

Seeds

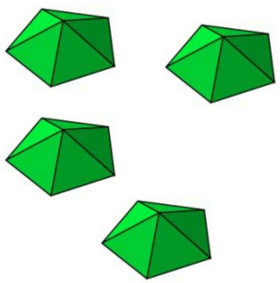
5.0 g of PVP (4.5 10^{-2} mol) in 25 mL DEG + 2.0 mL of $HAuCl_4$ (5.1 10^{-5} mol) in DEG

260 ^{o}C. → 10 min



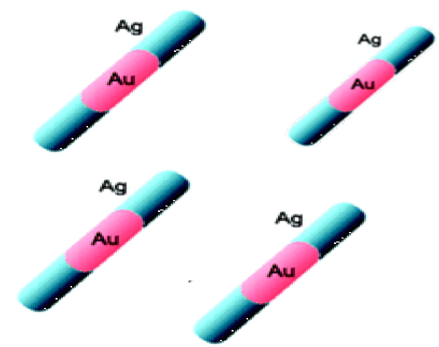
Decahedral seeds

Heterometal nanorods

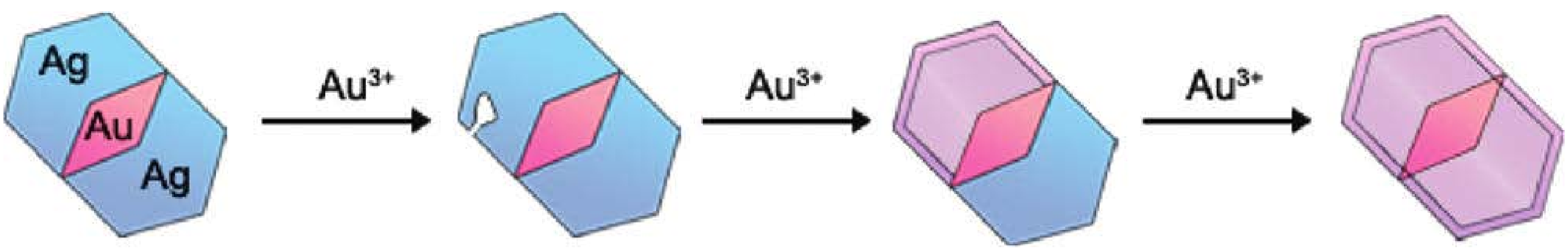


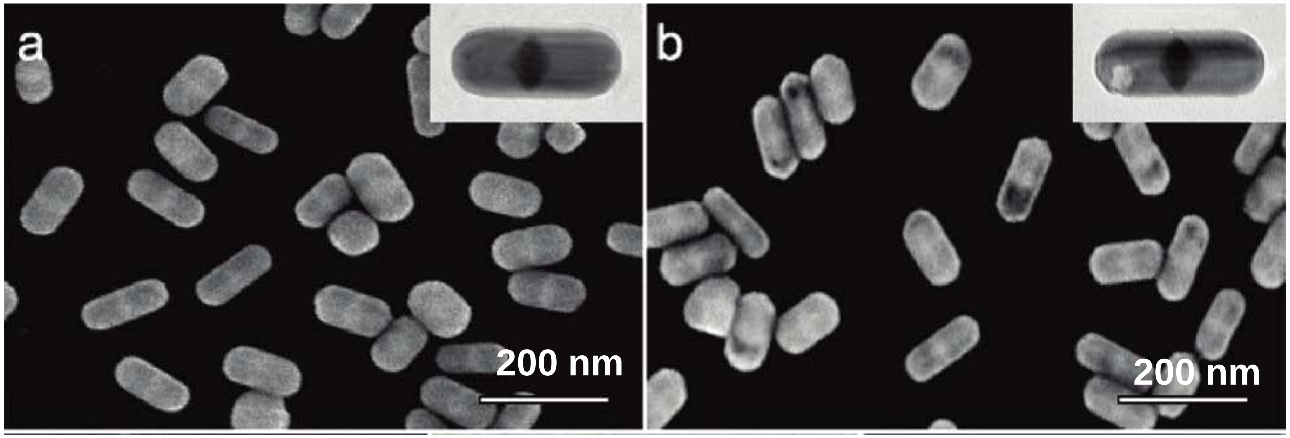
3.0 mL of PVP (61 mM) → 3.0 mL of $AgNO_3$ (20 mM) in DEG

260 ^{0}C, 30 min

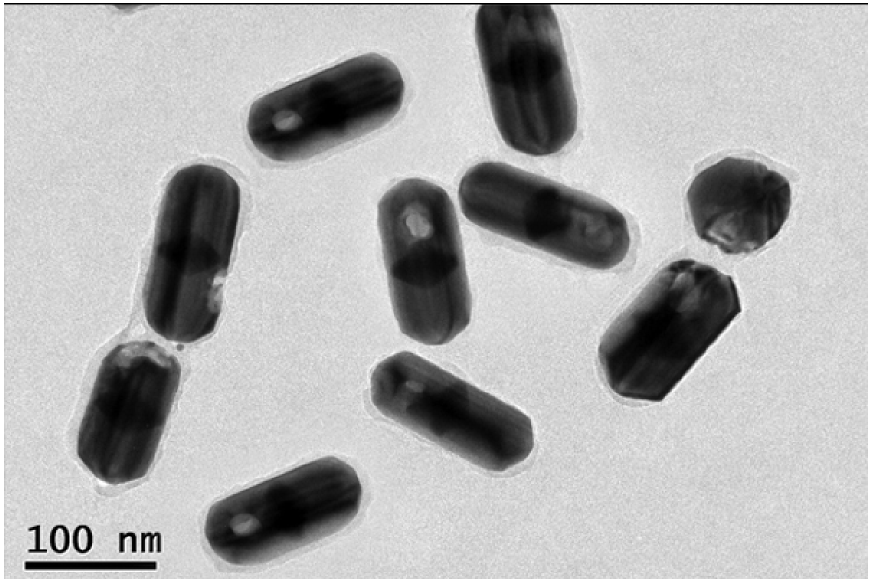


Hollow nanorods

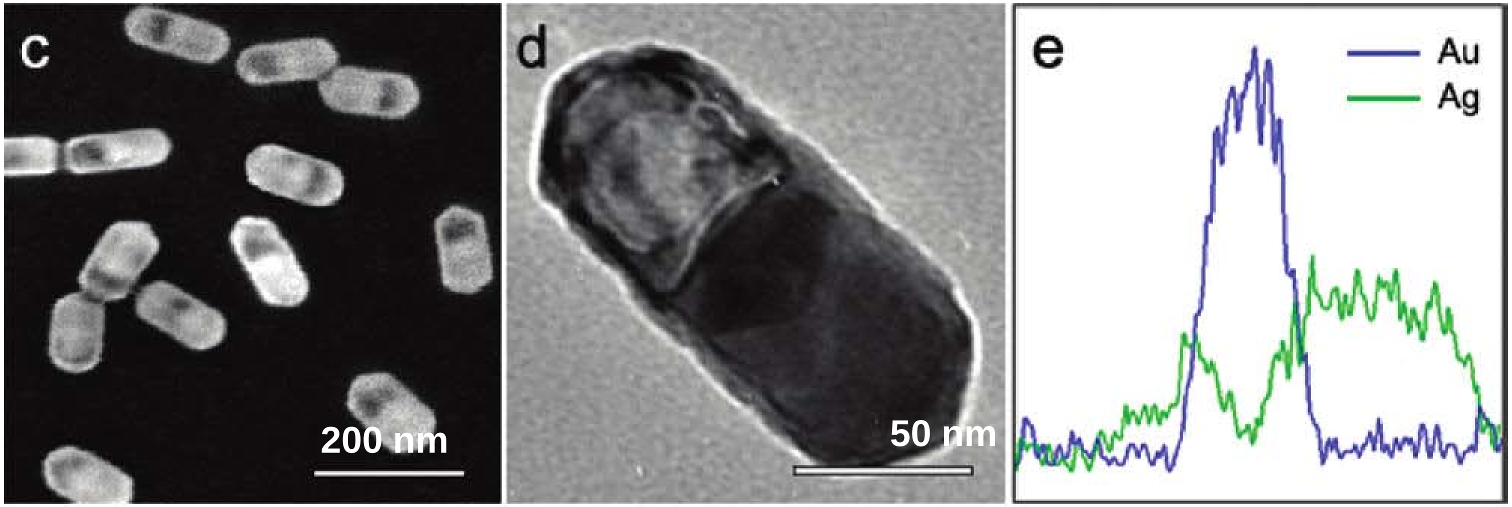




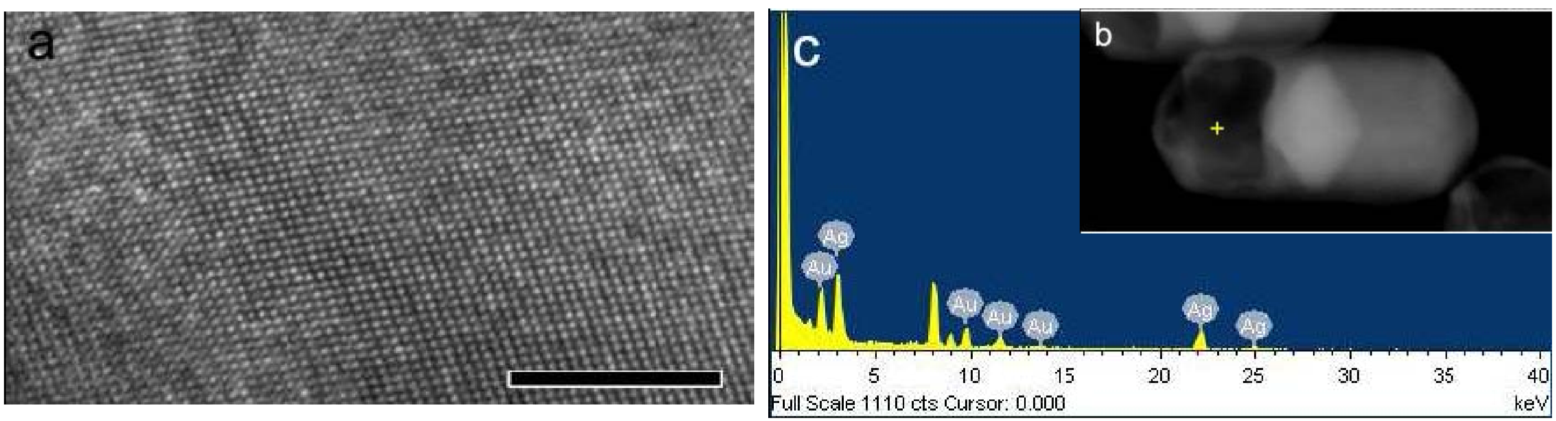
SEM and TEM (insets) images of (a) original heterometal nanorods and (b) hollow structures produced by the addition of 0.02 mL of the Au^{3+} solution.



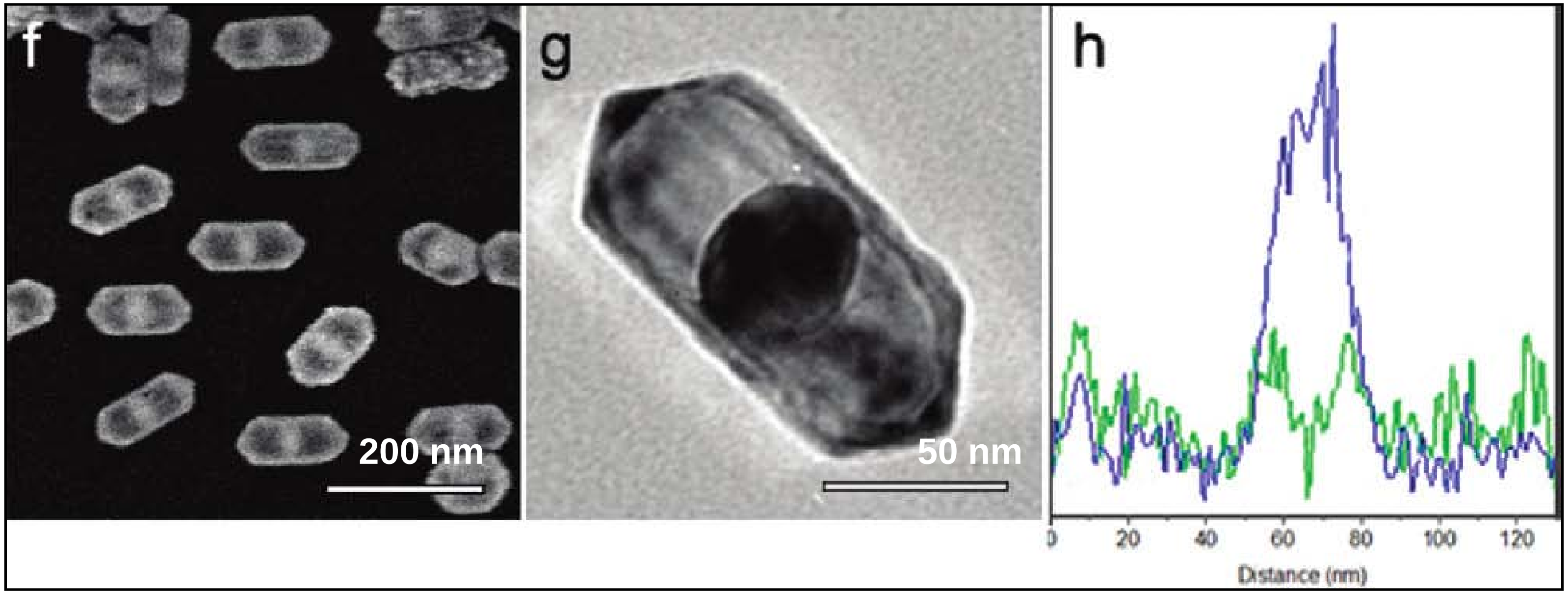
TEM image of the hollow structures by the addition of 0.02 mL of the Au^{3+} solution.



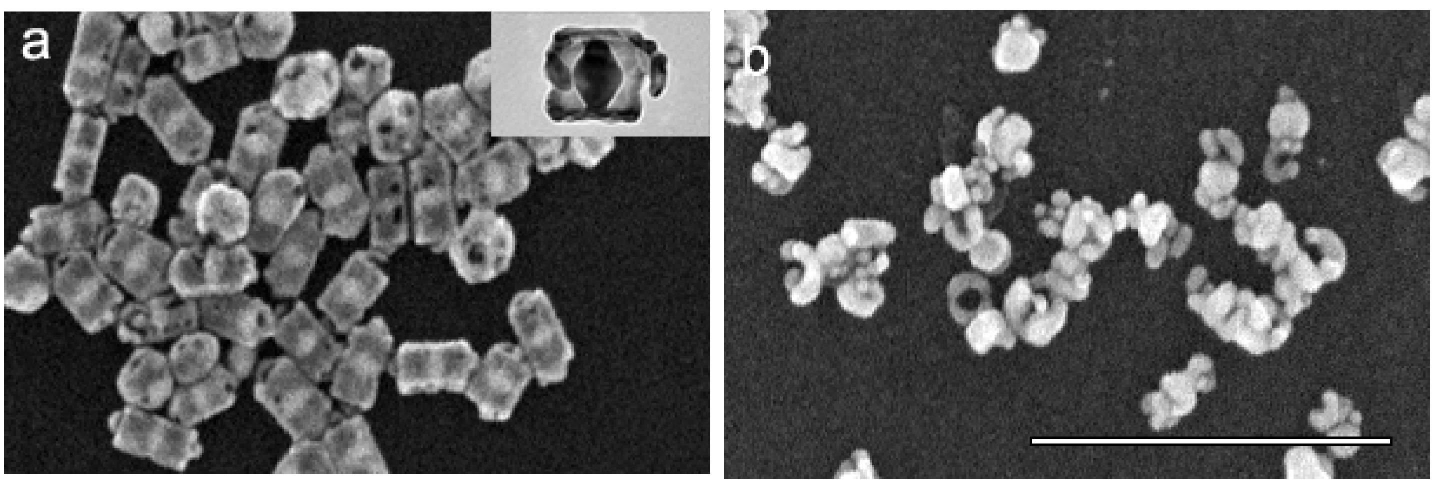
SEM (c) and TEM (d) images, and EDX line profile (e) along the long axes of the hollow structures produced by the addition of 0.04 mL Au^{3+}.



(a) HRTEM and (b) STEM images, and (c) EDX spectrum of an anisotropic single hollow nanorod.

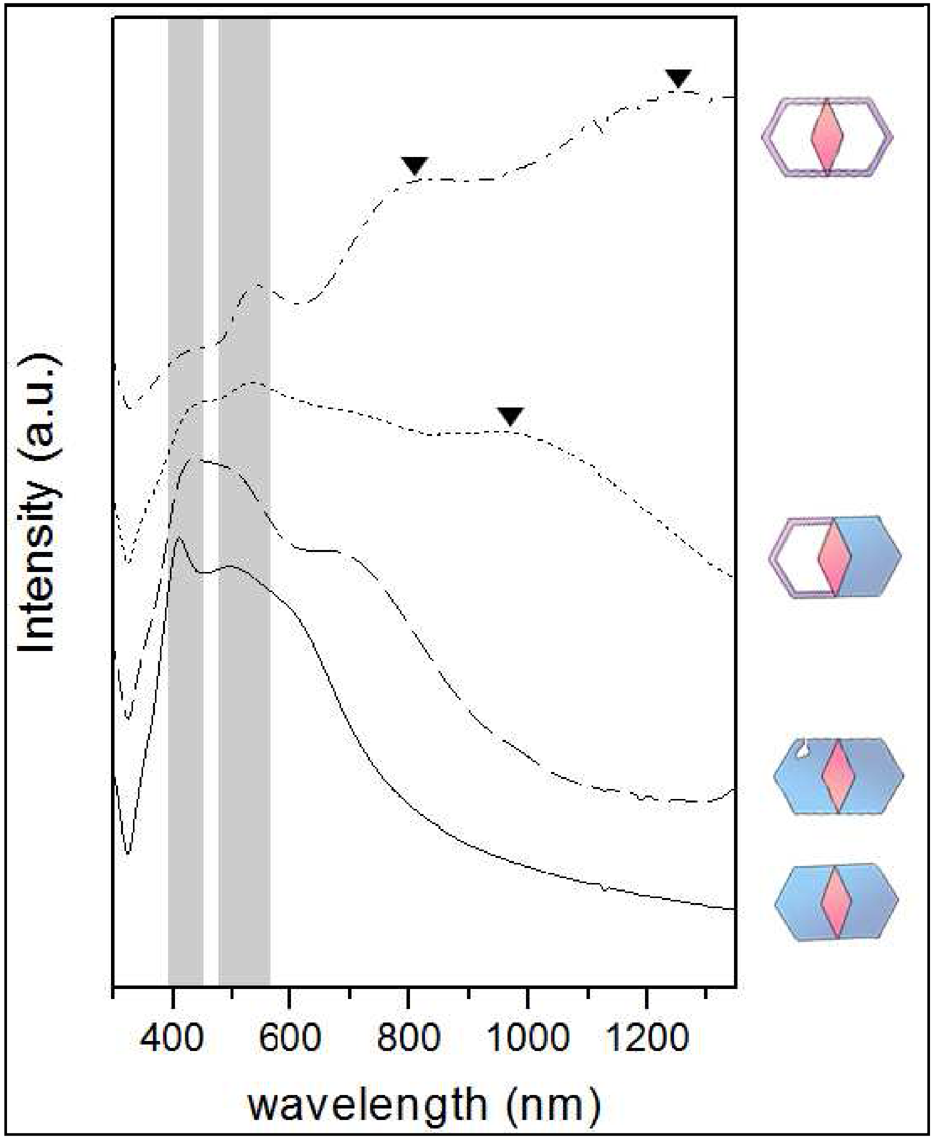


SEM and TEM images, and EDX line profiles along the long axes of the hollow structures produced by the addition of 0.1 mL Au^{3+}.



SEM images of the nanostructures by the addition of (a) 0.15 mL and (b) 0.20 mL of the gold precursor solution. The bar represents 500 nm.

UV-vis-NIR extinction spectra of the original Ag-Au-Ag nanorods and different stages of the hollow nanostructures



410 nm = transverse mode of the Ag domain.

500 nm = transverse mode of the Au domain.

610 nm = longitudinal mode of domain coupling.

The double-hollow rods exhibit two characteristic peaks at 830 and 1250 nm, which are assignable to modes of the anisotropic hollow structure.

Mechanism

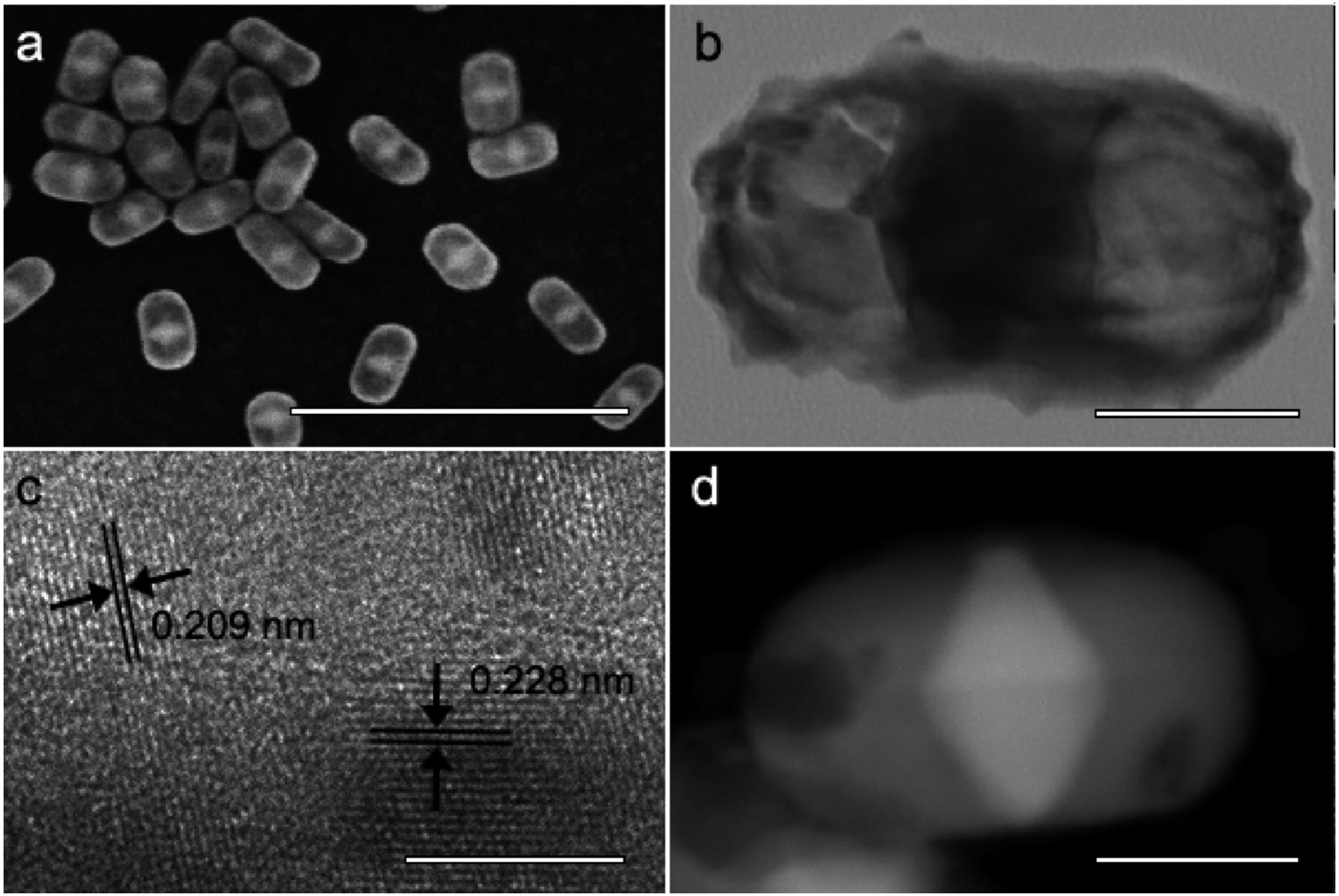
- The key point for asymmetry is the formation of only a single pit at the beginning of galvanic replacement.

- At the early stages of the reaction, gold is evenly deposited on the silver surface in an epitaxial fashion to prevent replacement reactions at multiple positions.

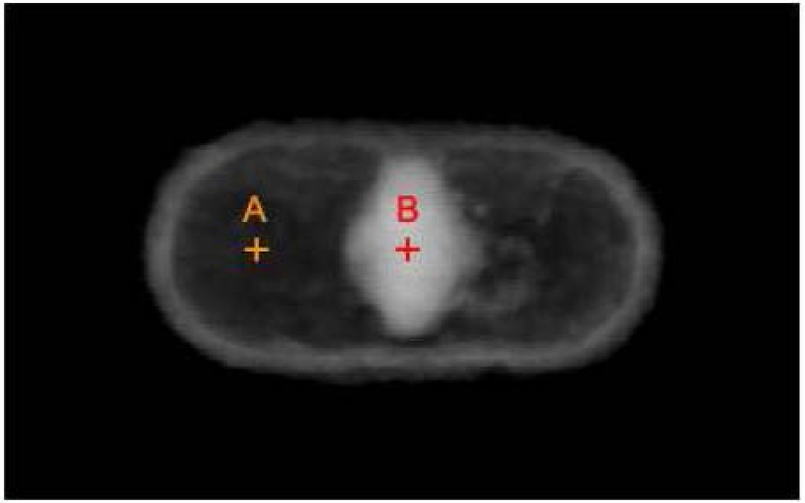
- The pit acts as an active site where exposed Ag(0) is readily oxidized to Ag+.

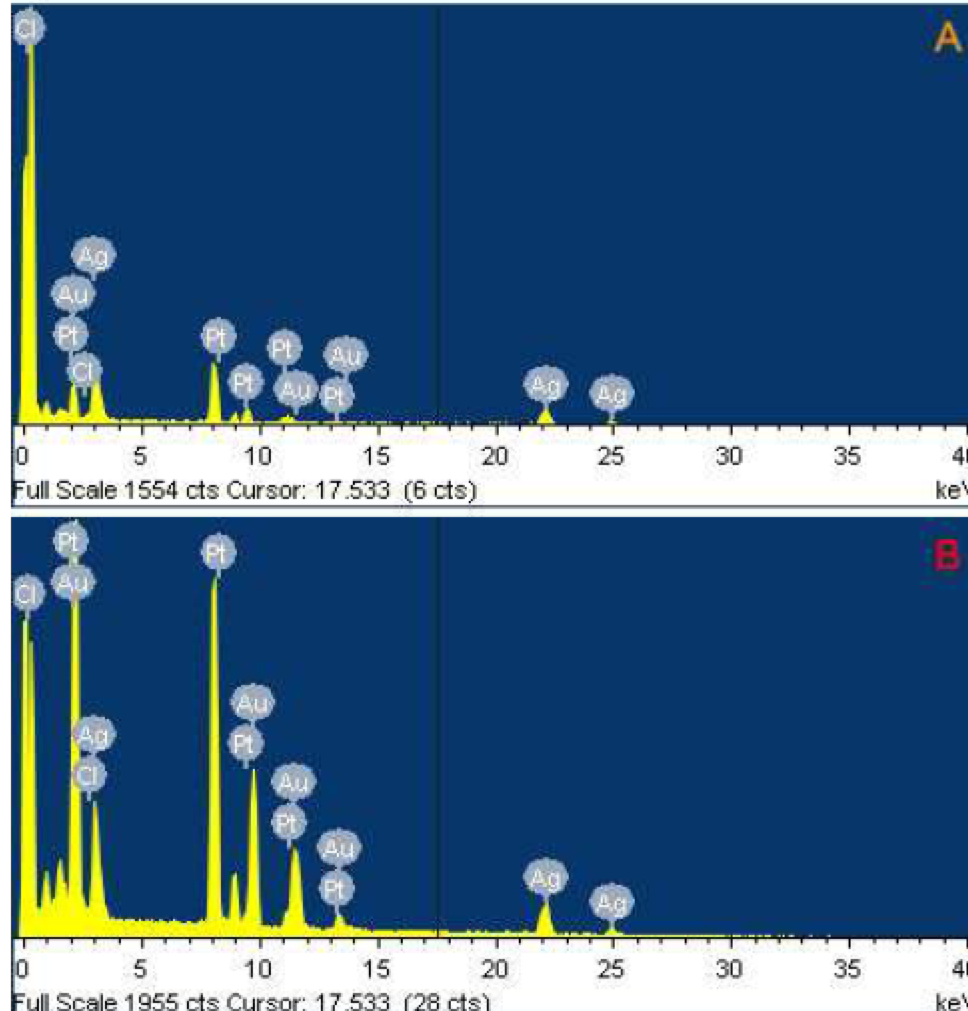
- Another plausible factor is the effective electron transfer from the hole to the rod surface.

- The electrons generated from the oxidation of Ag(0) to Ag+ at the pit are transferred to the rod surface; the Au^{3+} ions in solution are then reduced to Au(0) and evenly deposited on the surface.



(a) SEM, (b) TEM, and (c) HRTEM images of the double hollow nanorods by the addition of 0.10 mL of the platinum precursor solution, and (d) STEM image. The bars represent (a) 500 nm, (b, d) 50 nm, and (c) 5 nm.





Element	A (atomic %)	B (atomic %)
Pt L	24.85	7.71
Au L	0.00	61.51
Ag K	75.15	30.78
Cl K	0.00	0.00

STEM image and EDX data of Pt-exchanged double hollow nanorods.

Conclusion

- Asymmetric single-hollow and symmetric doublehollow nanorods were generated from Ag-Au-Ag heterometal nanorods by partial galvanic replacement reactions.

- The symmetry breaking occurs as a result of the random generation of a single pit on one end of the Ag domain.

- Such control of hollow formation with variable NIR extinctions will be helpful in biorelated applications such as chemical delivery, imaging, and photothermal therapy.