Ag-Au-Ag Heterometallic Nanorods Formed through Directed Anisotropic Growth

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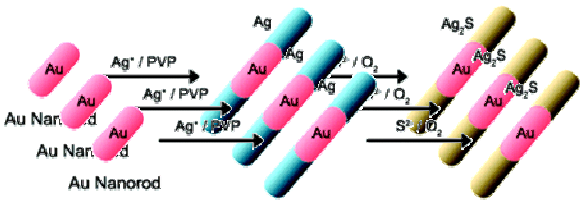

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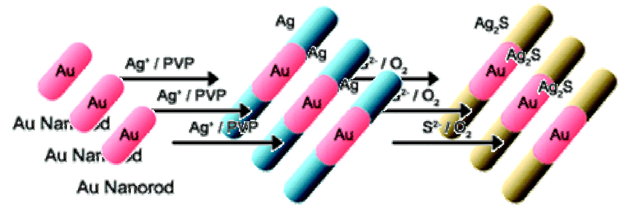

2008, *130*, 2940-2941

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08-03-2008

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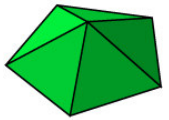
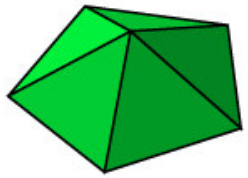
Introduction

- **Heterostructured nanocrystals → Multifunctional properties due to the effective coupling of different domains.**
- **Semiconducting heterostructured nanocrystals → Gas-phase deposition.**
- **Metallic heterostructures → AAO templated electrochemical deposition.**
- **Present work → Synthesis of Ag-Au-Ag heterometallic nanorods through directed overgrowth from gold decahedrons and rods by adding silver ions and poly(vinyl pyrrolidone).**

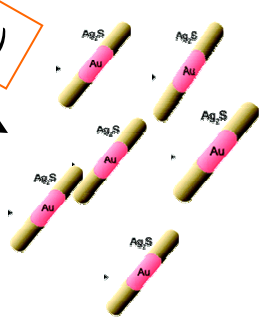
Experimental

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 °C., 10 min →  **Decahedra**



3.0 mL of PVP (0.13 M)
3.0 mL of HAuCl4 (1.0×10^{-4} M) in PD
260 °C & 60 min

3.0 mL of PVP (0.13 M)
3.0 mL of $AgNO_3$ (3.4×10^{-2} M) in DEG
260 °C&1 h

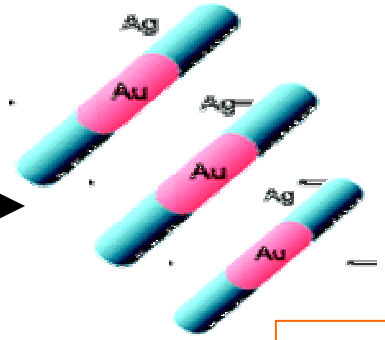


Small nanorods

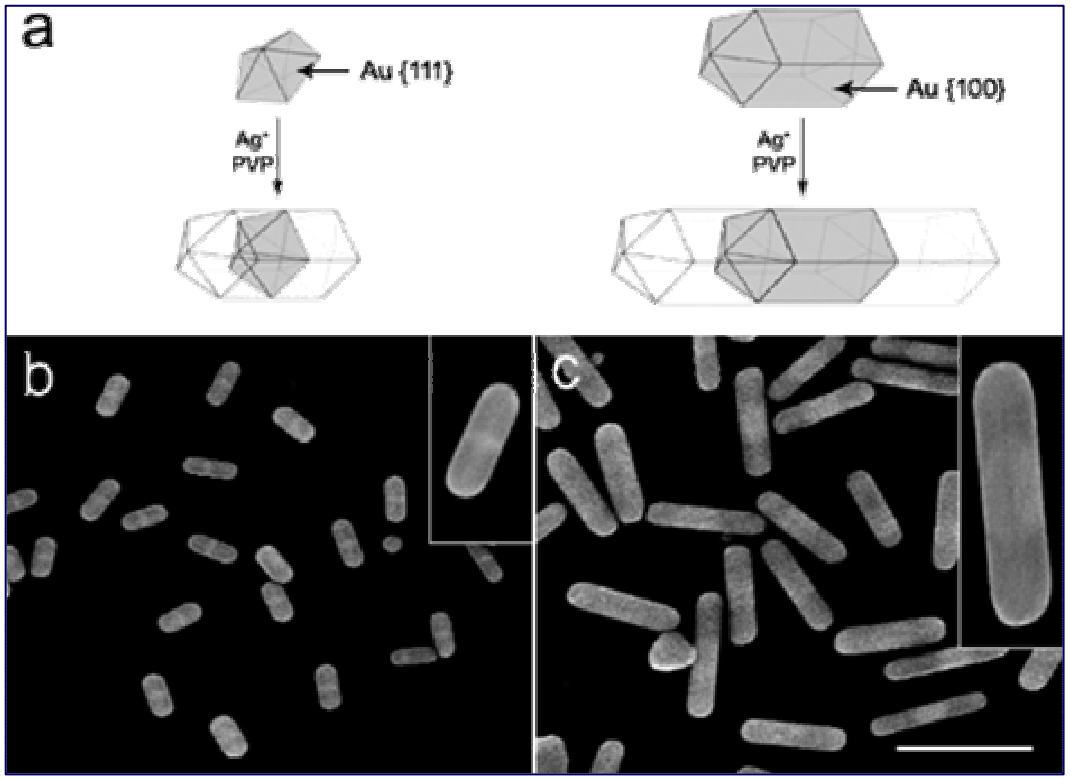
5 mL

3.0 mL of PVP (7.6×10^{-2} M)

3.0 mL of $AgNO_3$ (1.7×10^{-2} M) in PD



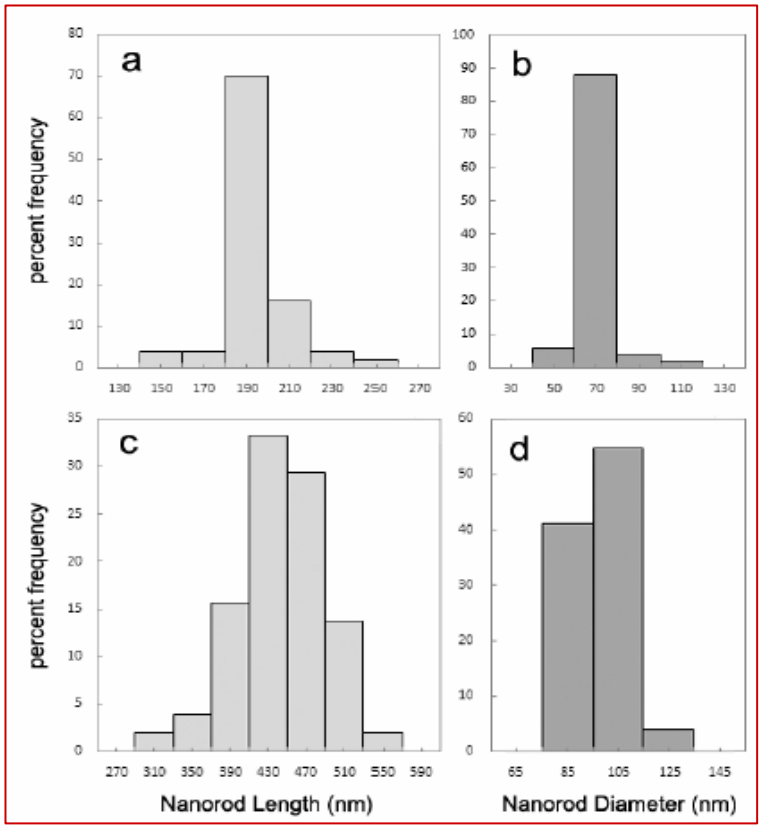
Long nanorods



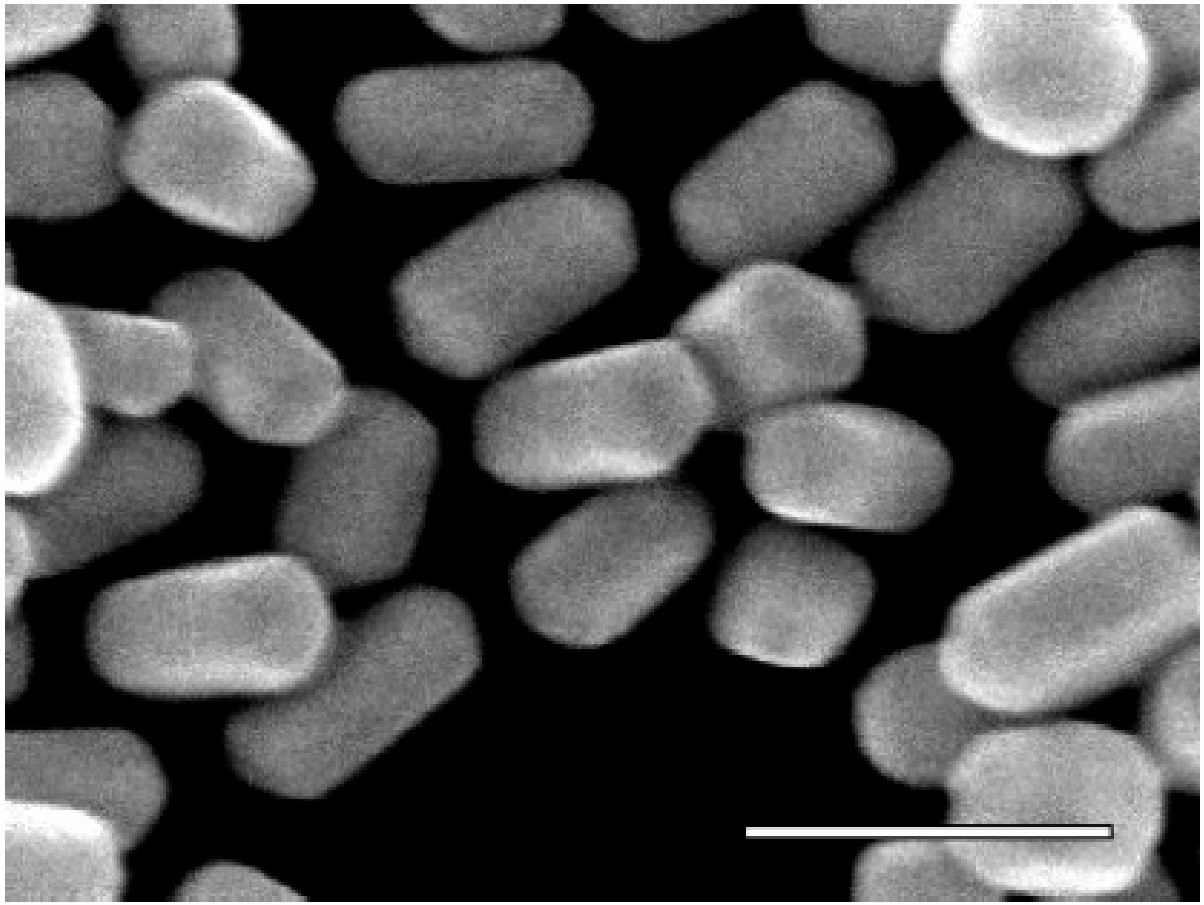
Aspect ratio=2.5

Aspect ratio=4.5

(a) Synthesis of Ag-Au-Ag heterometallic nanorods from gold decahedrons and rods. SEM images of Ag-Au-Ag heterometallic nanorods grown from (b) gold decahedrons and (c) rods. The bar represents 500 nm.



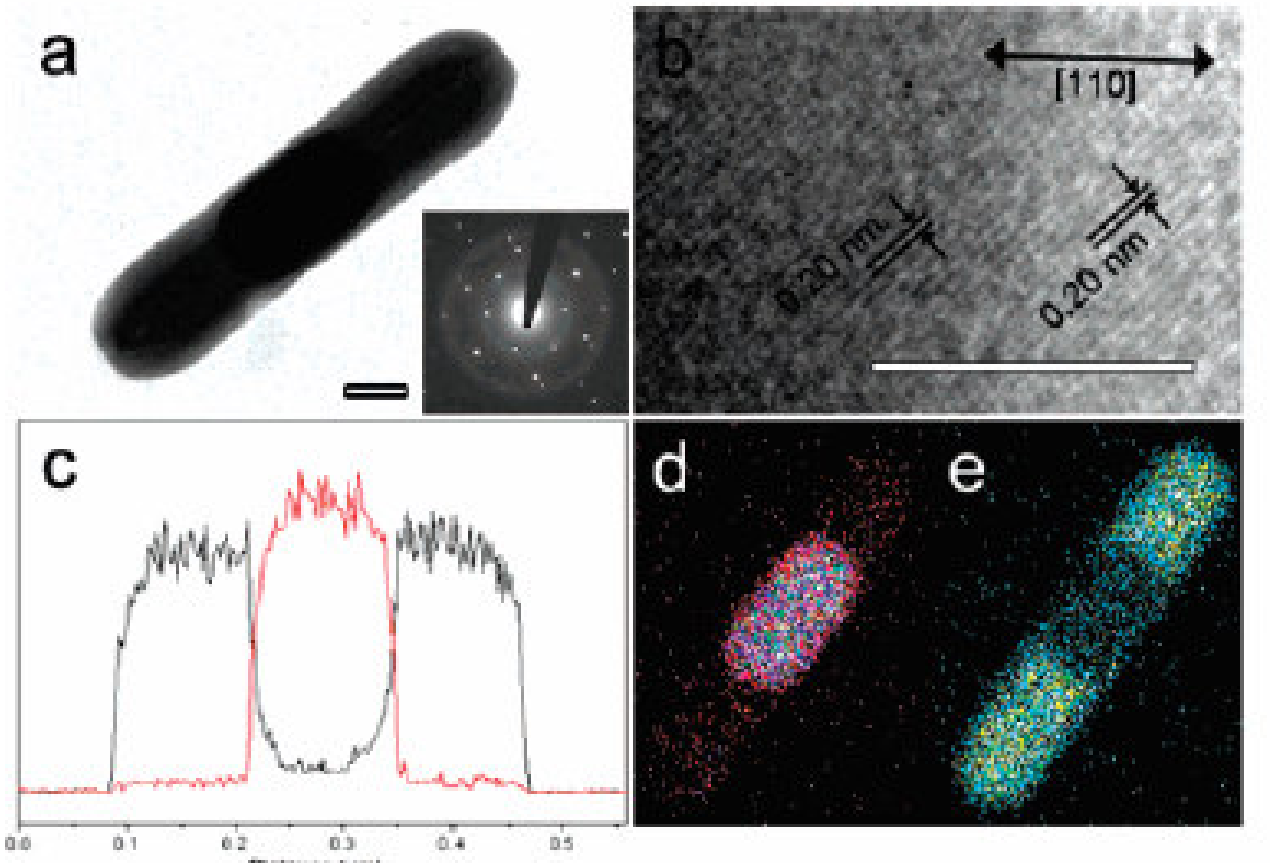
The distribution histograms of lengths and diameters of the Ag-Au-Ag heterometallic nanorods; (a,b) for the short Ag-Au-Ag nanorods with a decahedral gold segment, and (c,d) the long Ag-Au-Ag nanorods with a rod-type gold segment.



SEM image of gold segments after HNO_3 treatment of the Ag-Au-Ag heterometallic nanorods. The bar represents 200 nm.

- No Ag-Au alloy formation in the interface

- The gold segments are nearly unchanged from those of the original seeds after the silver overgrowth.

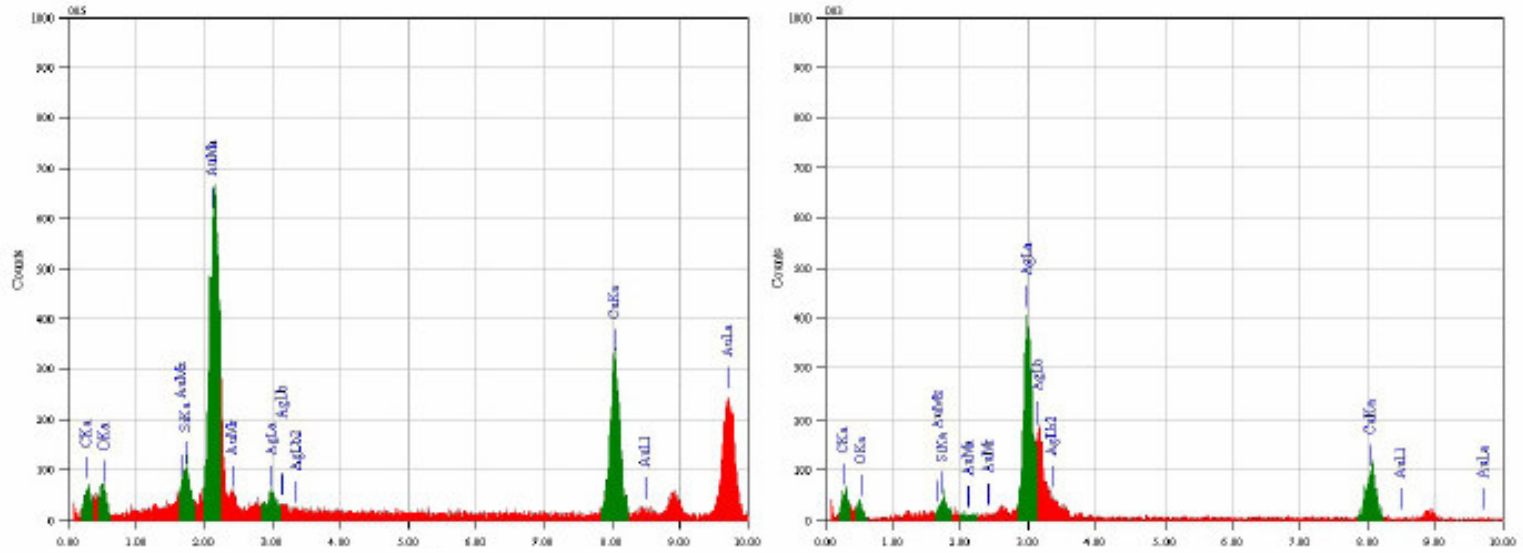


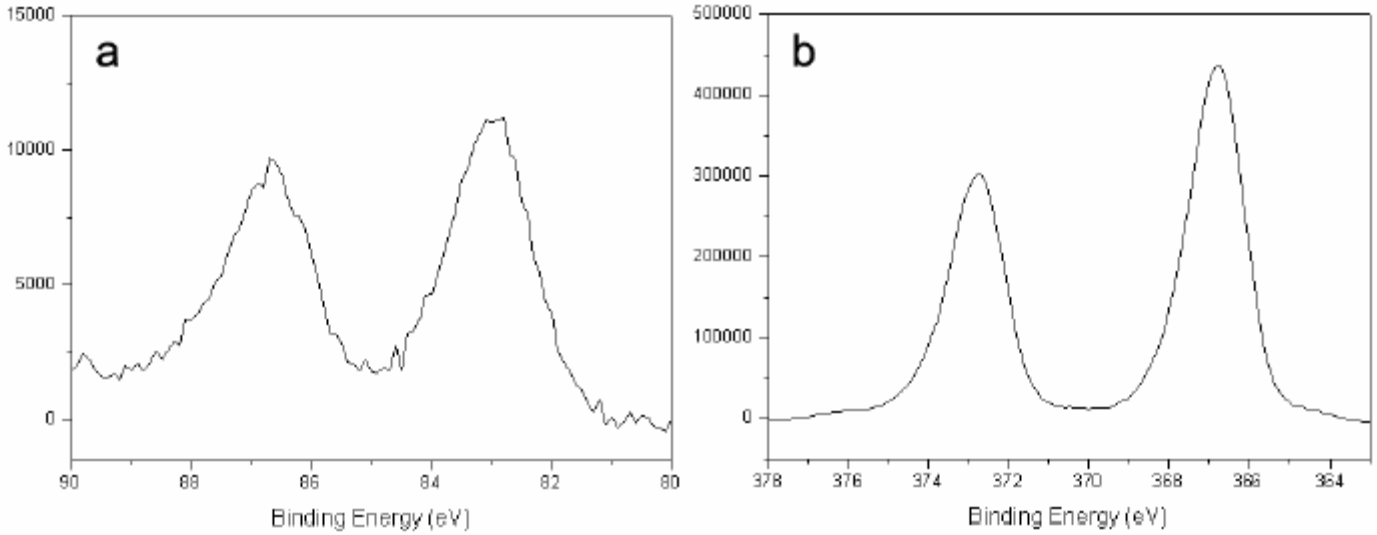
The silver segments are grown epitaxially on the gold nanorod surface.

Ag, Au, and Ag segments intensity ratio = 1:1:1.

(a) TEM image and SAED pattern of a single Ag-Au-Ag nanorod; (b) HRTEM image of a nanorod at the boundary of gold and silver; (c) line profile analysis of silver (black) and gold (red) along the long axis of a nanorod; elemental mapping of gold (d) and silver (e). The bars represent 50 nm (a) and 2 nm (b).

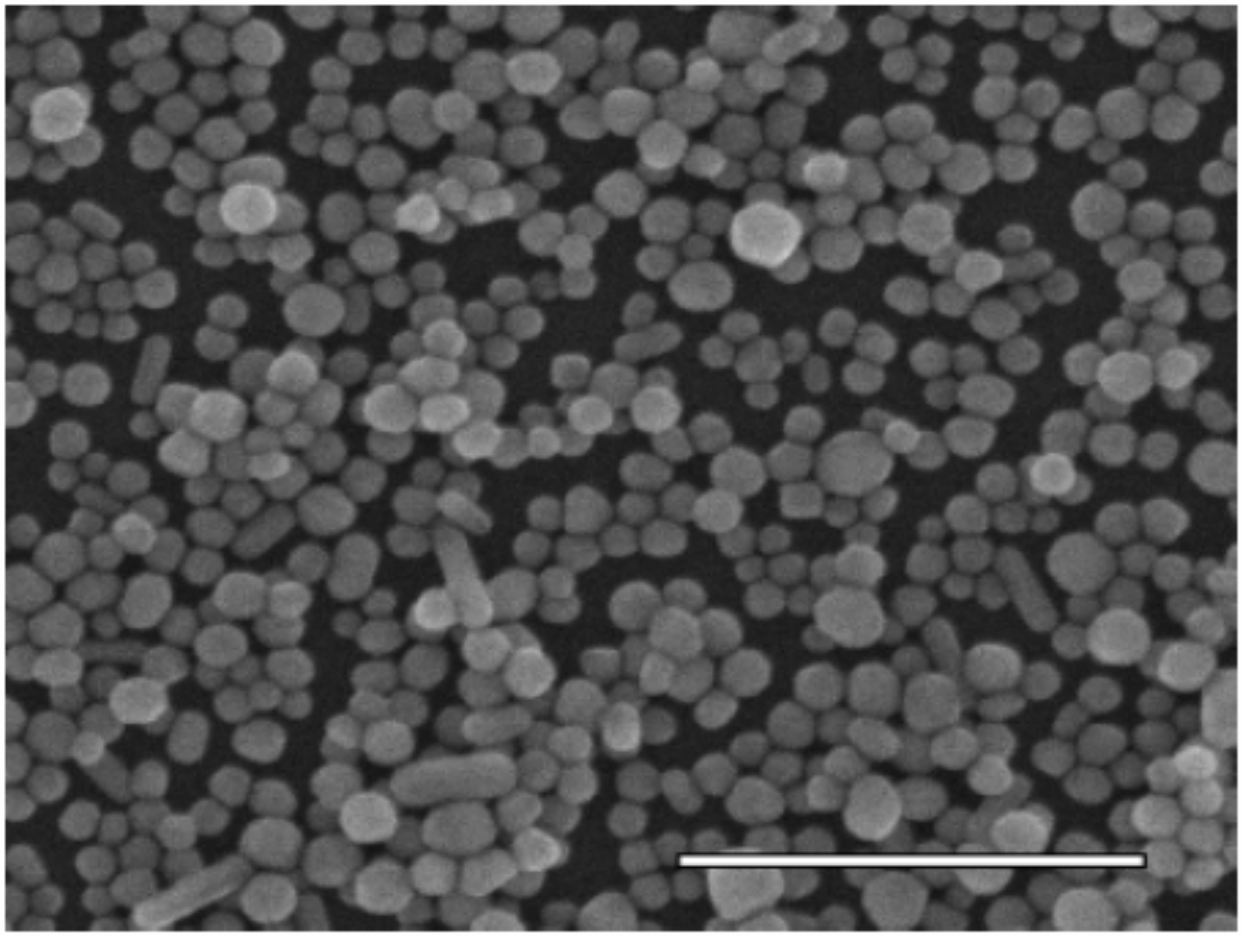
EDS analysis of the Ag-Au-Ag nanorod at gold and silver domains.





Ag 3d and Au 4f bands, indicating that both segments are exposed on the surface.

XPS spectra of the Au-Ag-Au nanorods with a decahedral gold segment from the (a) Au(4f) and (b) Ag(3d) energy regions.

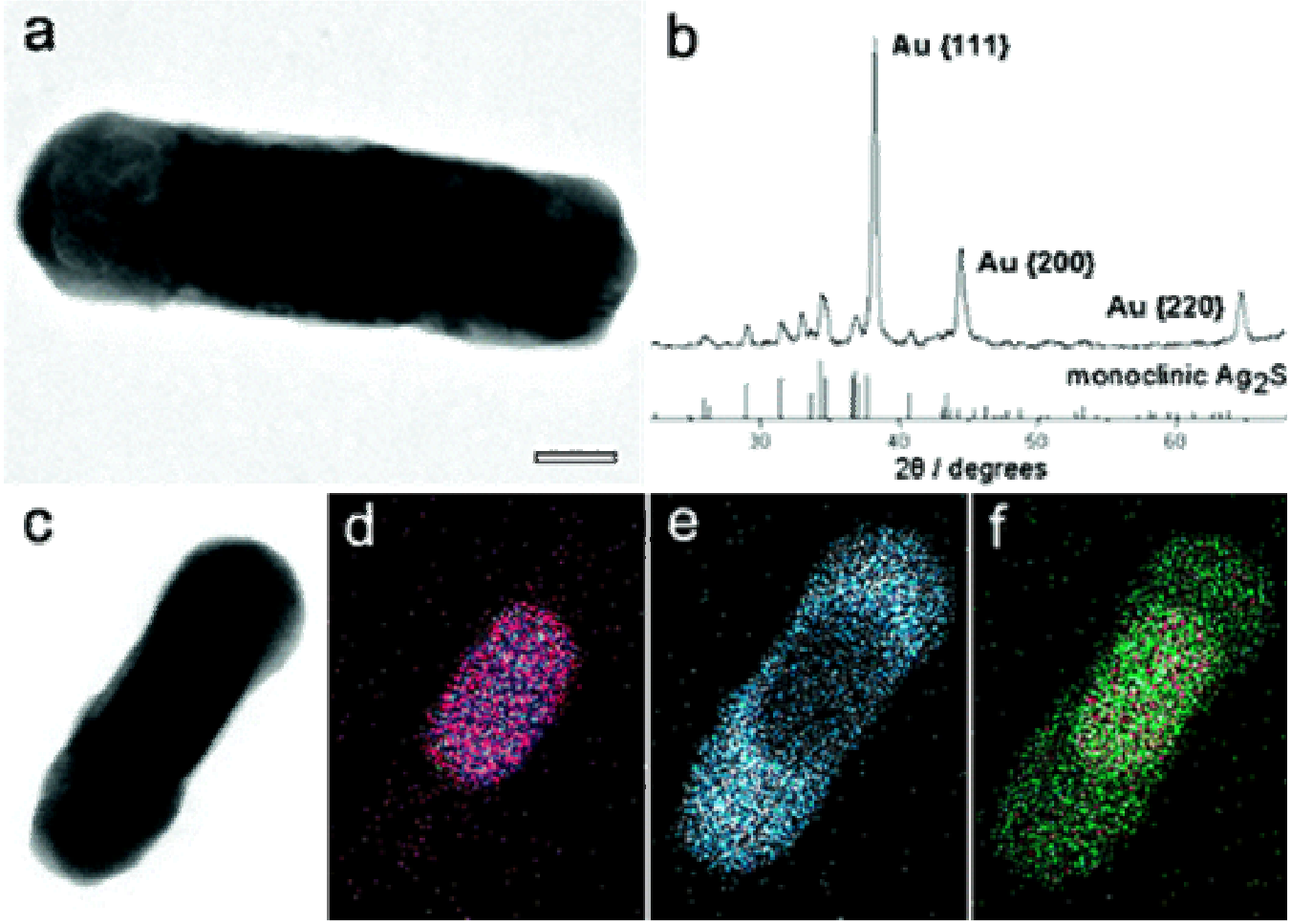


SEM image of Ag nanoparticles formed under the identical condition to the rod synthesis without gold decahedral seeds. The bar represents 500 nm.

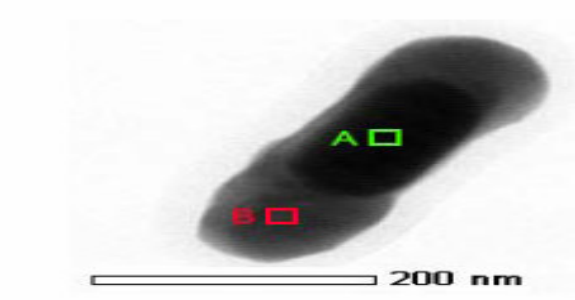
Mechanism

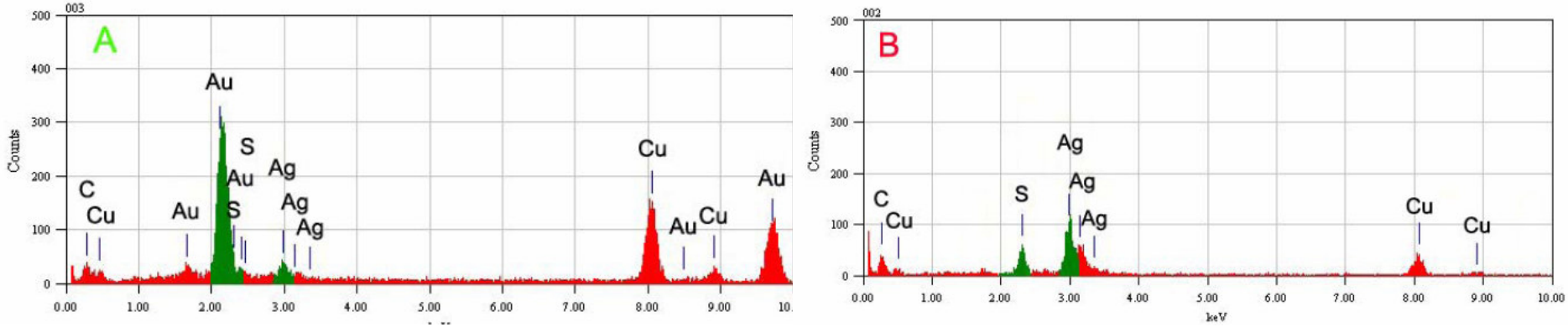
The silver deposition on the decahedral seeds led to the formation of high-energy surfaces such as {100} and {110}, where PVP binds more efficiently than on the {111} surface. The silver segments were grown fast along the longitudinal direction of the nanorods, but slow along the lateral direction

Chemical property of each segments of Ag-Au-Ag nanocrystal

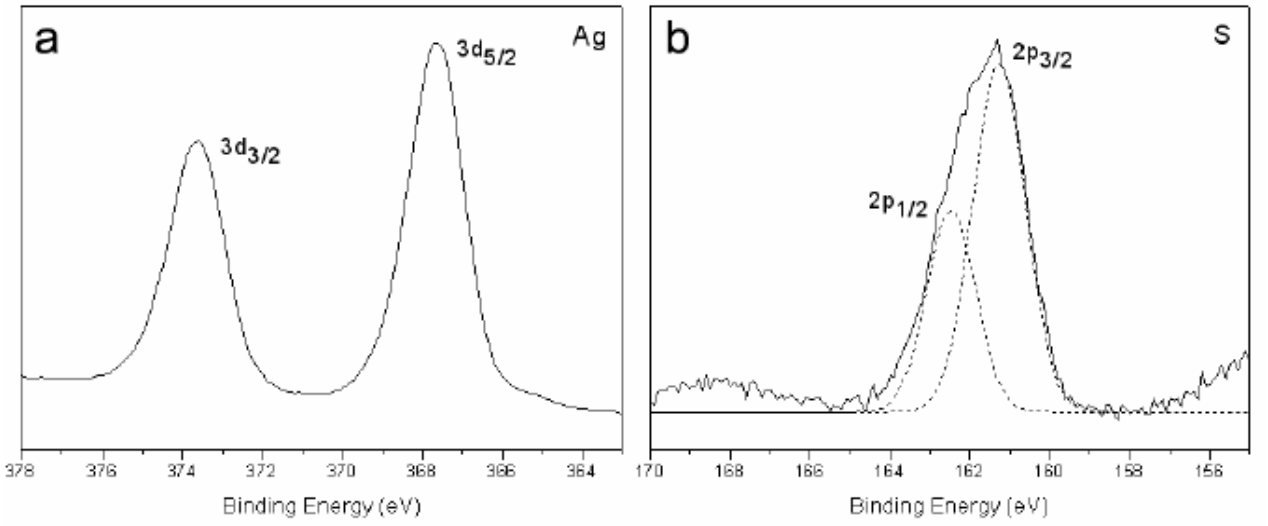


(a) TEM image and (b) XRD pattern of Ag_2S-Au-Ag_2S nanorods; (c) scanning TEM image and elemental mapping of gold at 2.120 keV (d), silver at 2.984 keV (e), and both gold and sulfur at 2.307 keV (f).
The bar represents 50 nm.

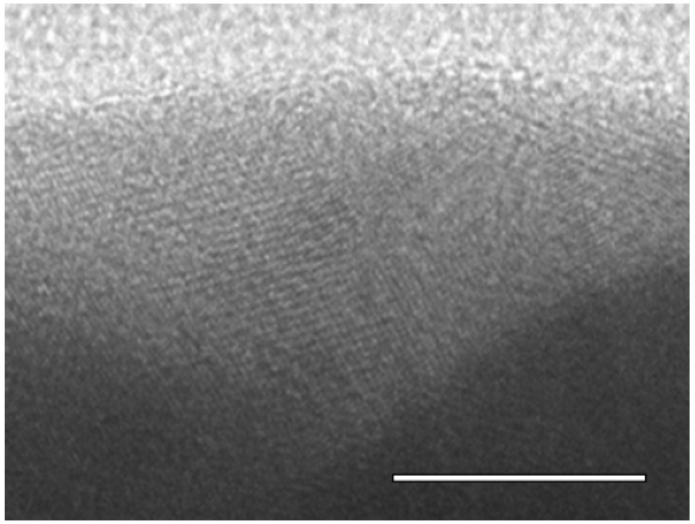




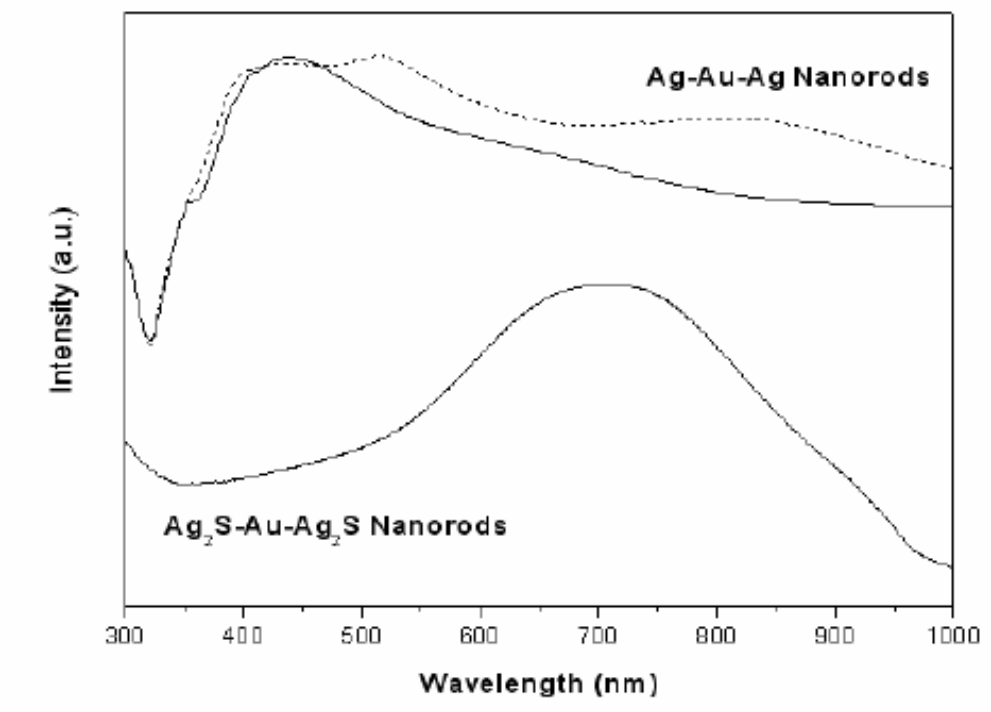
EDS analysis of the Ag_2S-Au-Ag_2S nanorod at (a) gold and (b) silver sulfide domains.



XPS spectra of the Ag_2S-Au-Ag_2S nanorods from the (a) Ag(3d) and (b) S(2p) energy regions.



HRTEM image of a Ag_2S domain in the Ag_2S-Au-Ag_2S nanorod. The bar represents 10 nm.



UV-vis extinction spectra of the Ag-Au-Ag nanorods with the mean lengths of 194 nm (above, solid line) and 440 nm (above, dotted line), and Ag_2S-Au-Ag_2S nanorods (bottom, solid line) dispersed in ethanol.

Conclusion

- Ag-Au-Ag heterometallic nanorods were synthesized by directed anisotropic growth from multiply twinned gold decahedrons and rods.
- Ag_2S-Au-Ag_2S heterojunctions were generated in the nanorods by reaction with sulfide ions.
- This template-free synthesis may be generalized to other metal and metal oxide systems for electronic, sensing, and catalytic applications.