

Direct Synthesis of Au-Ag Nanoframes by Galvanic Replacement via a Continuous Concaving Process

*Fang Cheng^a, Wenjie Gu^a, Han Zhang^a, Chunyuan Song^a, Yunfeng Zhu^a, Feiyue Ge^b,
Kuiming Qu^a, Hai Xu^{c,d}, Xuejun Wu^{b*}, Lianhui Wang^{a*}*

^aState Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts and Telecommunications, Nanjing 210023, P. R. China.

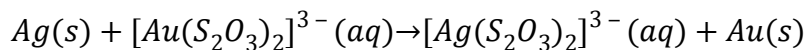
^bState Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, P. R. China.

^cChangchun Institute of Optics Fine Mechanics and Physics Chinese Academy of Science, Changchun 130033, P. R. China.

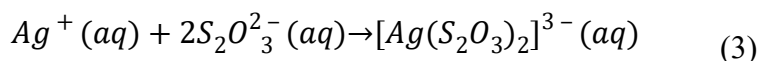
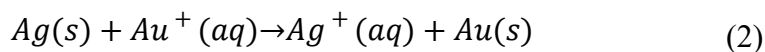
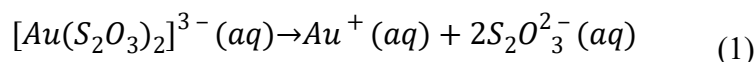
^dCenter of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100040, P. R. China.

Calculation of the standard potential, E° , for the galvanic replacement.

The reaction equation of the galvanic replacement is given in the main text, which is also listed as follows.



To calculate the standard potential of the above reaction, we can split the total reaction into following three steps.



For equation 1, the standard equilibrium constant, $K^\circ(1)$, is the inverse value of the cumulative formation constant (or overall stability constant) of the $Au(S_2O_3)_3^{3-}$.

According to the reference [1], the stability constant of the $Au(S_2O_3)_3^{3-}$ is as high as 10^{27} .

The corresponding standard equilibrium constant for equation 3, $K^\circ(3)$, is the stability constant of the $Ag(S_2O_3)_3^{3-}$, with the value of $10^{13.46}$ referred to the Lange's handbook of chemistry.[2] The standard potential for the equation 2 is $E^\circ(2) = 1.0309$ V (vs. RHE)

based on the following standard electrode potentials, that is, $E^\circ(Au^+/Au) = 1.83$ V and

$$E^\circ(Ag^+/Ag) = 0.7991$$
 V.

According to the chemical thermodynamics, the standard Gibbs free energy change,

ΔG° , of the reaction at room temperature can be expressed as $\Delta G^\circ = -2.303 RT \lg K^\circ$ or

$\Delta G^\circ = -nFE^\circ$, where R , T , n , F represent the universal gas constant, temperature,

electron transfer number, Faraday constant, respectively. Therefore, the standard

potential, E° , for the total galvanic replacement can be calculated by the following

equation.

$$E^{\circ} = E^{\circ}(2) + [2.303RT \lg(K^{\circ}(1) \cdot K^{\circ}(3))/nFE] = 1.0309 + 0.0592 \cdot \lg(10^{13.46}/10^{27}) = 0.229$$

V

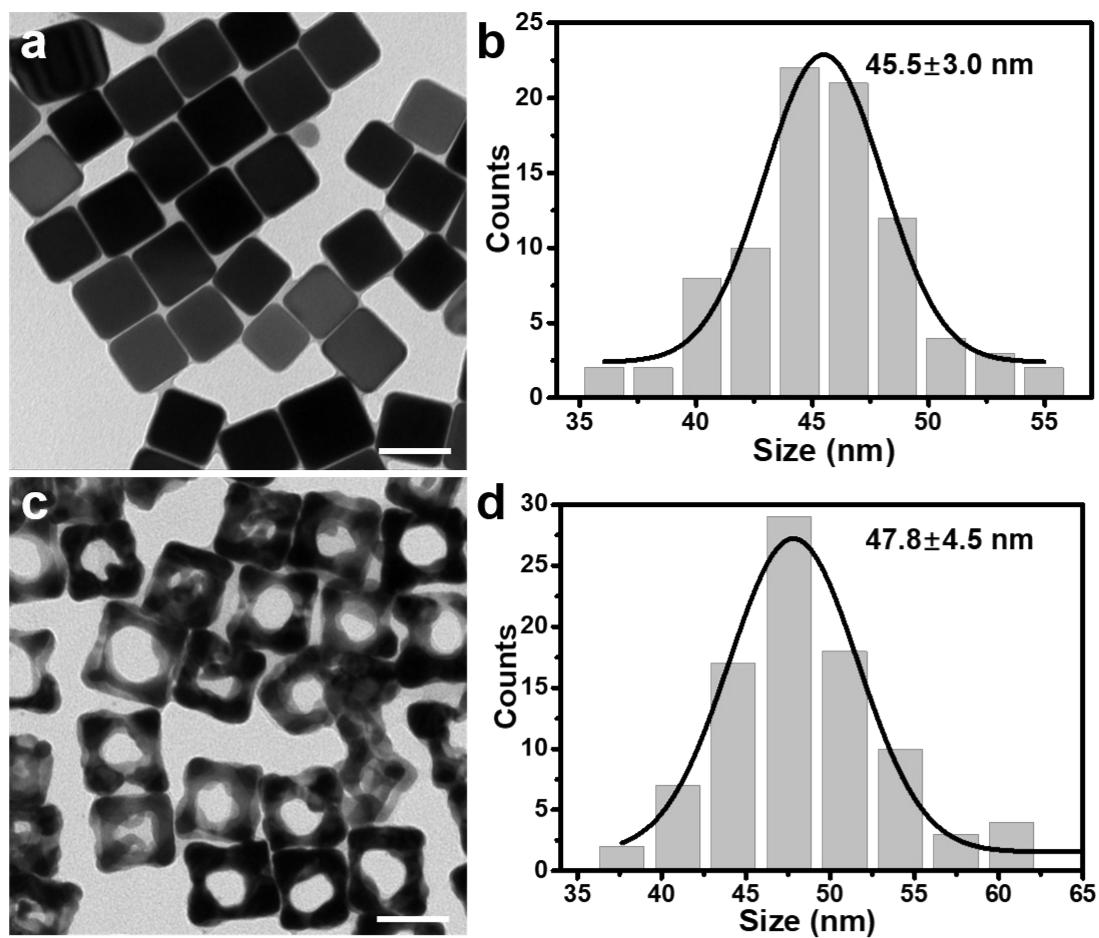


Fig. S1 TEM images and corresponding size distributions of (a, b) Ag NCs and (c, d) Au-Ag nanoframes. Scale bars are 50 nm in (a) and (c).

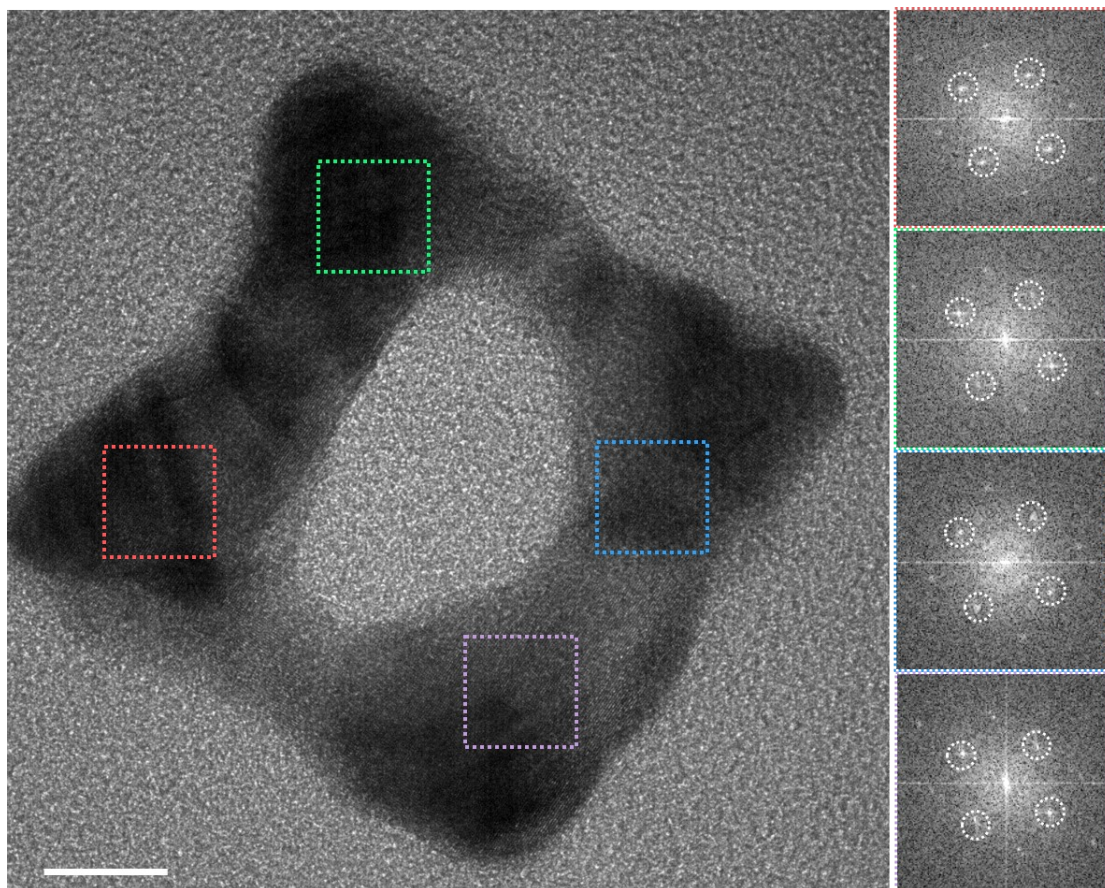


Fig. S2 High-resolution TEM image (left panel) and the fast-Fourier transform (FFT) patterns of the selected areas (right panel) of a single Au-Ag nanoframe. The selected areas are marked by dashed squares with different colors, and the diffraction points are labelled by white dashed circles. Scale bar is 10 nm in left panel.

Noted that the high-resolution TEM image in left panel is the same as the that in Fig 1d. The right panels show the FFT patterns acquired from the selected areas of a single Au-Ag nanoframe, all of which exhibit the square arrangement of the diffraction points. The most adjacent diffraction points (marked by the white dashed circles) can be ascribed to the $\{200\}$ planes. The diffraction points derived from different areas of the Au-Ag nanoframe show slight rotation with each other, which can be attributed to the

stress introduced from the selected deposition of Au and the distortion generated from the ultrathin edges.

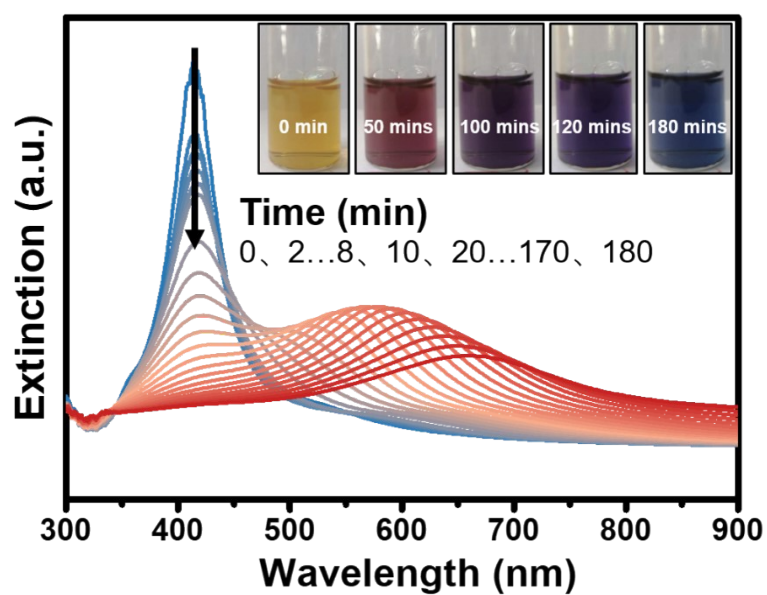


Fig. S3 In-situ UV-vis-NIR extinction spectra acquired to monitor the reaction process.

The spectra were recorded every 2 mins within the first 10 mins, and then every 10 mins from 10 to 180 mins.

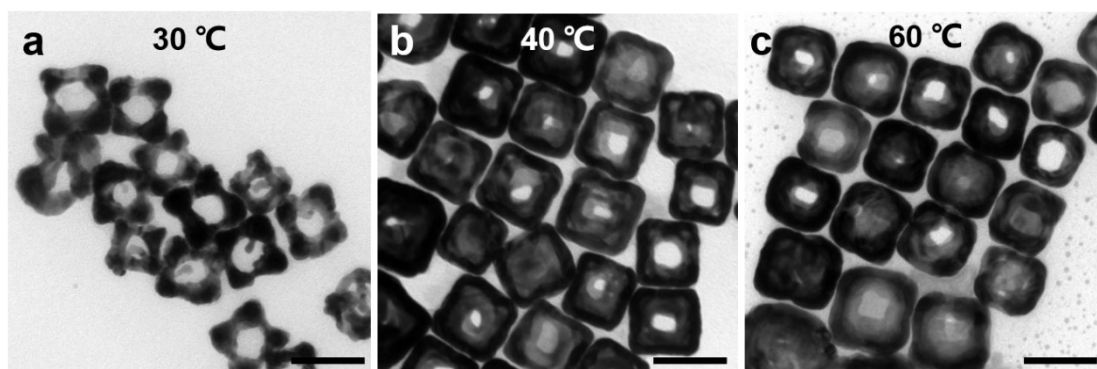


Fig. S4 The influence of temperature on the galvanic replacement reaction. The products were obtained from the reactions occur at (a) 30 °C, (b) 40 °C and (c) 60 °C.

Scale bars are 50 nm.

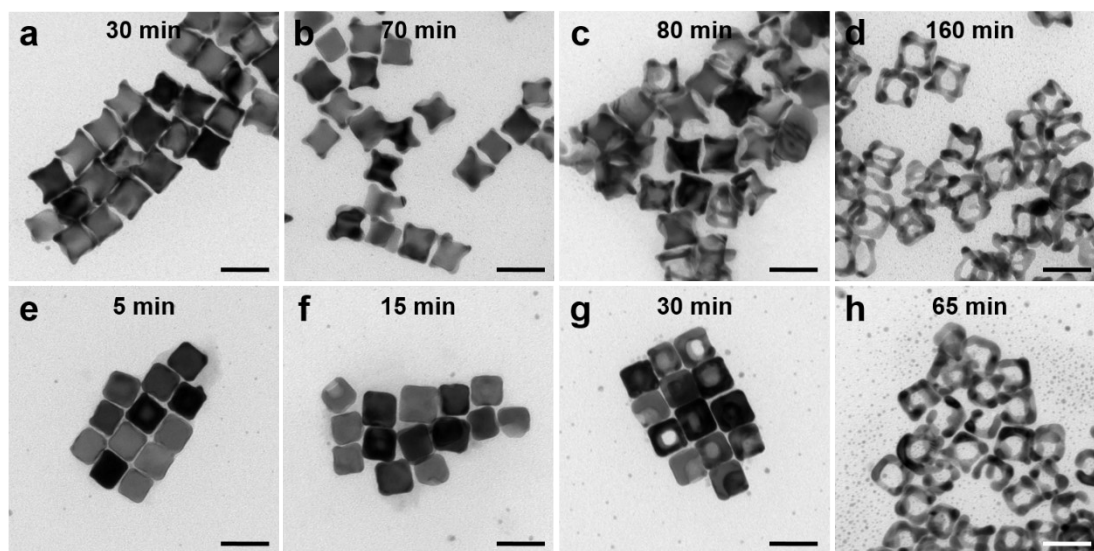


Fig. S5 The impact of capping agent on the reaction. The TEM images were used to track the structural evolution during the reactions using different capping agents. (a-d) CTAC and (e-h) DTAB are used as the capping agent, respectively. Scale bars are 50 nm.

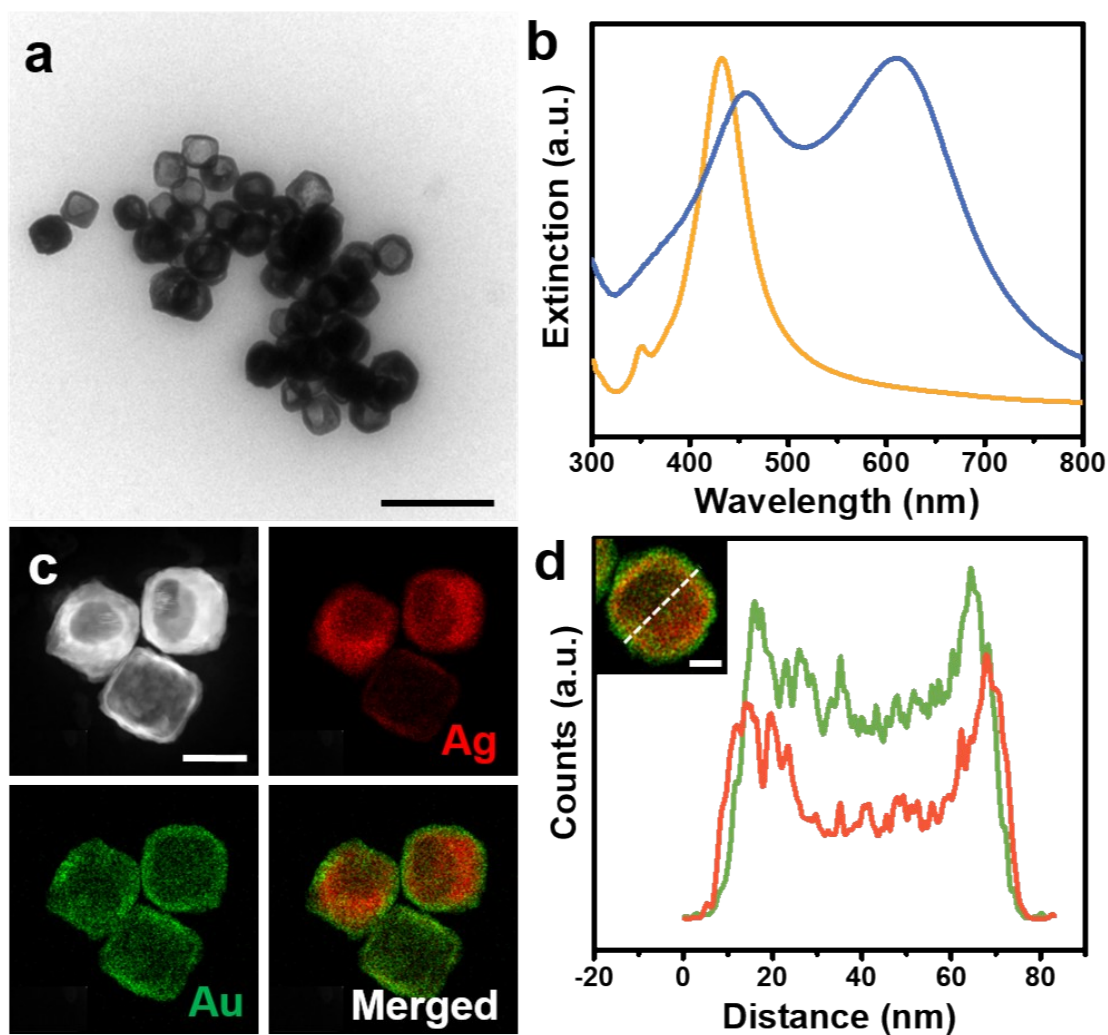


Fig. S6 Structural, compositional and plasmonic characterization of ultrathin Au-Ag nanoboxes. (a) TEM image of the as-prepared Au-Ag nanoboxes. (b) UV-vis-NIR extinction spectra recorded from suspensions of Ag NCs (orange line) and Au-Ag nanoboxes (blue line). (c) HAADF-STEM image and the corresponding EDS elemental mappings of the Au-Ag nanobox. (d) EDS line-scans of Ag (red) and Au (green) recorded along the white dashed line shown in the inset. Scale bars are 200 nm (a), 50 nm (c), and 20 nm (d).

The large-scale TEM image (Fig S6a) and HAADF-STEM image (Fig S6c) of the typical sample reveal that the products are quite inhomogeneous; some of nanoparticles are completely hollow structures with ultrathin shells, while the other nanoparticles still have bulk Ag inside. The EDS elemental mappings and line scans (Fig S6d) indicate that gold is preferably distributed at the outer-layer of the Au-Ag nanoboxes.

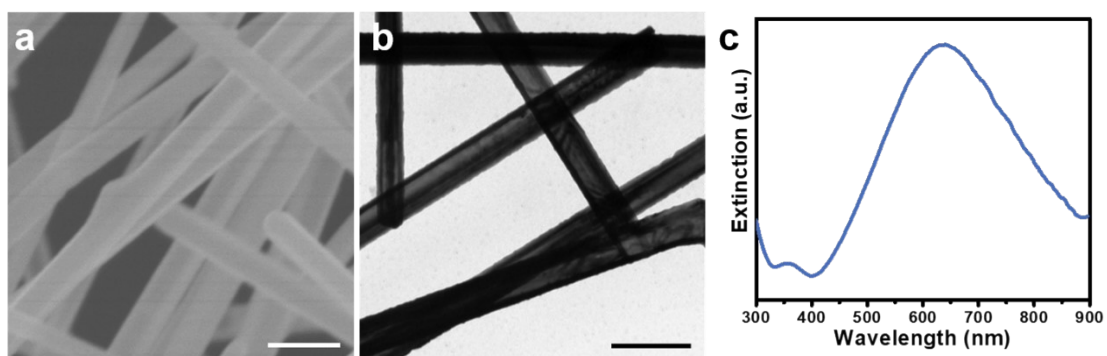


Fig. S7 Characterization of the synthesized Au-Ag nanotube. (a) SEM, (b) TEM and (c) UV-vis-NIR extinction spectra of the Au-Ag nanotube. Scale bars are 200 nm in (a) and (b).

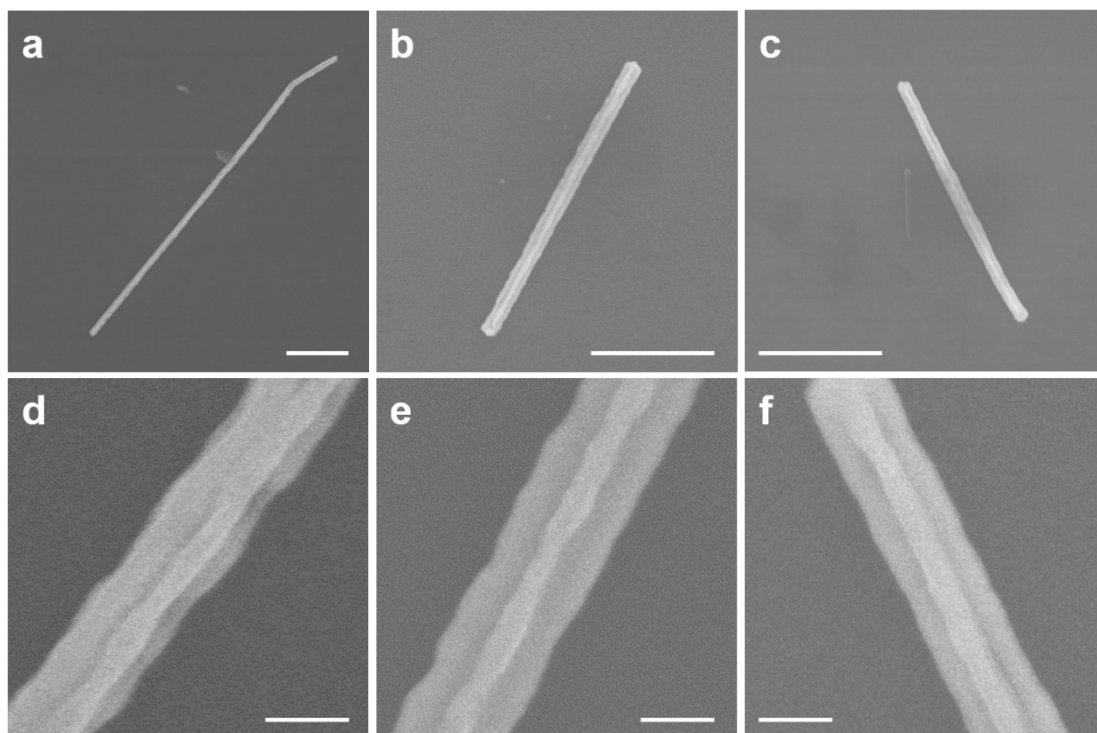


Fig. S8 SEM images of the single-particle wire-like Au-Ag nanoframes. (a-c) Low-magnification and (d-e) high-magnification SEM images of the wire-like Au-Ag nanoframes labelled as number 1, 3, and 4 in Fig 5a, respectively. Scale bars are 1 μm (a-c) and 100 nm (d-f).

REFERENCES:

- [1] T. A. Green and S. Roy, *J Electrochem Soc*, 2006, **153**, C157-C163.
- [2] J. A. Dean, *Lange's Handbook of Chemistry (Fifteenth Edition)*; McGraw-Hill, Inc.,
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