

Supplementary Information

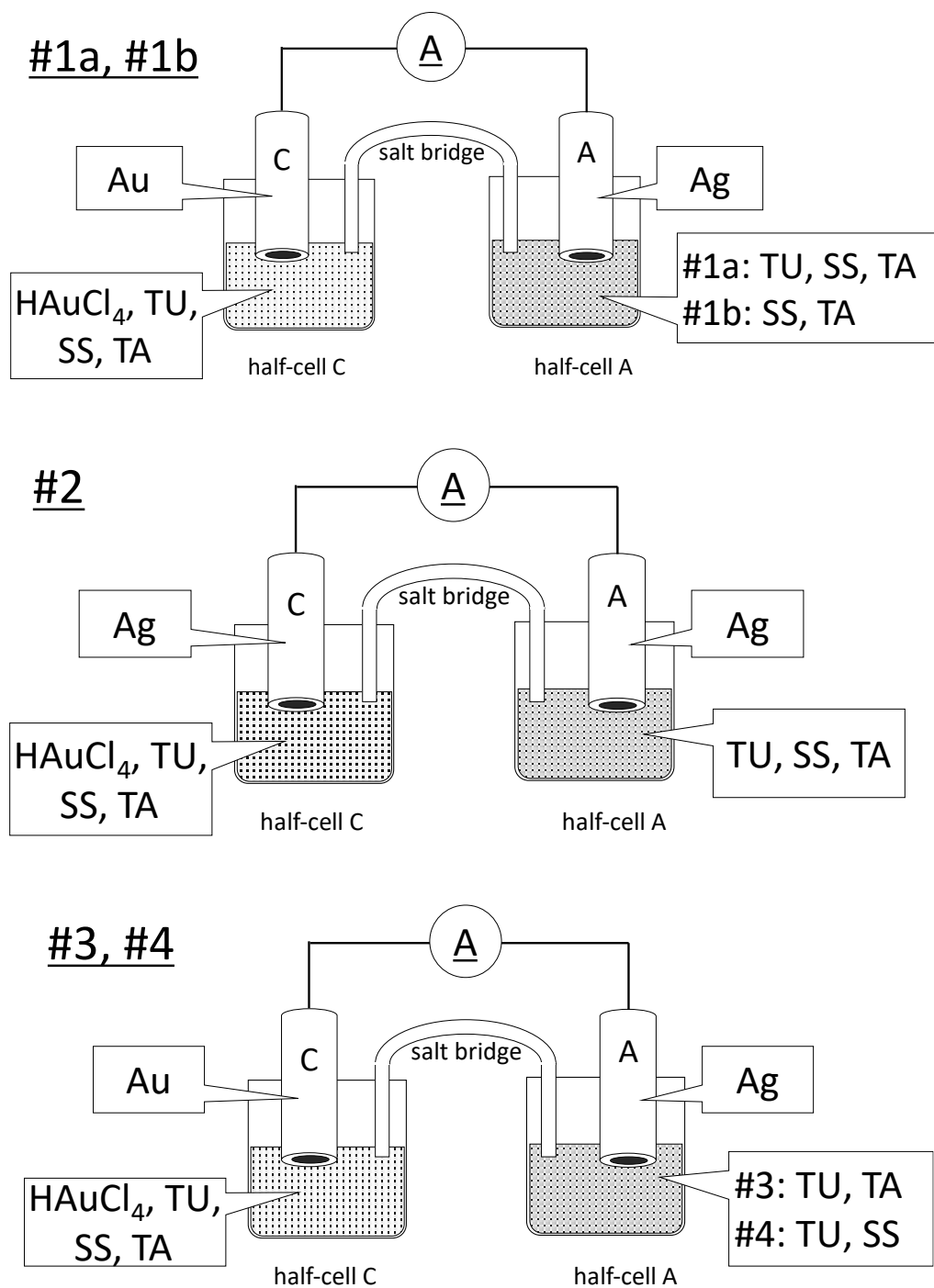
Formation Process of Gold-Silver Hollow Nanostructure via Silver Halide Photographic Techniques: An Electrochemical Model Cell Study

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Graphical expression of the model cell experiments



TU: thiourea, TA: tartaric acid, SS: sodium sulfate (Na_2SO_4)

Fig. S1 Graphical expression of the model cell experiments. Numbers given in each panel correspond to the experimental numbers in Table 2, respectively.

Change in the potential of Ag electrode in GP-2

Fig. S2 shows the change in the potential of the Ag electrode immersed in the GP-2 solution while the solution being stirred. The potential exhibited only a slight change during the reaction, but it lay within the range observed in the model cell experiments. The gradual shift of the potential towards the positive direction corresponds to the decrease in the “bare” silver region where the anodic dissolution takes place, requiring more positive potentials. However, this shift is also unfavorable for the cathodic deposition of gold. The small change in potentials is therefore caused by the balance of these two factors.

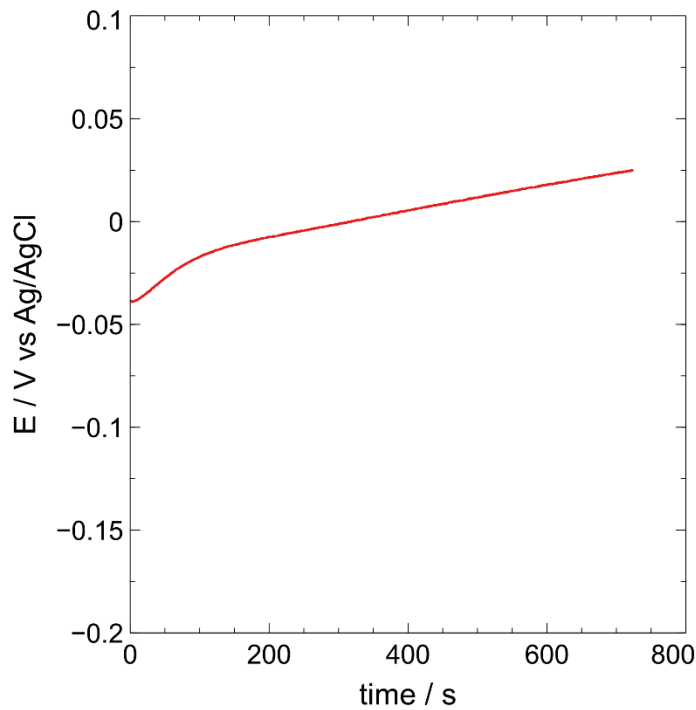


Fig. S2 Change in the potential of Ag electrode in GP-2.

Estimation of surface Ag ratio in pAgNF

The Ag crystal is fcc, and the crystallographic data are as follows:

lattice constant $a = 0.41$ nm, density $\rho = 10.5$ g cm⁻³, molar volume $v_m = \rho/M = 10.3$ cm³ mol⁻¹ (the molar mass of Ag $M = 108$ g mol⁻¹)

The planar densities (surface atomic number densities) of fcc metal crystals are $2/a^2$ for (100), $4\sqrt{3}/(3a^2) \simeq 2.31/a^2$ for (111), and $\sqrt{2}/a^2 \simeq 1.41/a^2$ for (110). As pAgNF is polycrystalline and the predominant face is unclear, we use $2/a^2 = 1.19 \times 10^{17}$ atoms m⁻² as the representative value for the following estimation.

Assuming the shape of pAgNF as a cylinder with the radius r and the length l . As the volume V of the cylinder is $V = \pi r^2 l$, the molar amount of Ag in the cylinder is $\pi r^2 l / v_m$ and the total number of

Ag atoms in the cylinder is $N_A \times \pi r^2 l / v_m$, where N_A is the Avogadro constant. When $l \gg r$, the bottom areas of the cylinder is small enough relative to the lateral area, and the entire surface area S is approximated as $S = 2\pi r l$. The number of Ag atoms on the surface is thus estimated as $4\pi r l / a^2$. In conclusion, the ratio of the surface atoms to the total atoms in the cylinder is given as $(4\pi r l / a^2) \div (N_A \times \pi r^2 l / v_m) = 4v_m / (a^2 N_A r)$.

Assuming $r = 25$ nm, the ratio is calculated as 0.016. If $r = 15$ nm, the ratio is 0.027. The diameter of pAgNF is typically 20 – 50 nm, and the average ratio can be estimated as roughly several %.