

Supplementary Materials

1. Respective contents of AgBr and AgL

The relative amounts of AgBr and AgL (L represent for sodium citrate) after the addition of CTAB and sodium citrate

1) A theoretical calculation:

The solubility product constant of AgBr is $K_{sp}=5.35\times 10^{-13}$, the stability constant of AgL coordination is $\log\beta=7.1$. With the addition of CTAB and citrate sodium, we suppose that AgBr and AgL are all present in the solution.

$$K_{sp}=[Ag^+][Br^-]=5.35\times 10^{-13} \quad \textcircled{1}$$

$$\beta=[AgL]/([Ag^+][L])=10^{7.1} \quad \textcircled{2}$$

Because in the same solution, the precipitation and the coordination equilibrium of $[Ag^+]$ is the same. By combining $\textcircled{1}$ $\textcircled{2}$ and elimination $[Ag^+]$:

$$K=[AgL] * [Br^-]/[L]=5.35\times 10^{-5.9} \quad \textcircled{3}$$

Suppose $[L] = x$: So the concentration of L that coordination with $Ag^+=$
 $[AgL]= 0.2475\times 10^{-3} -x$. (1)

According to $\textcircled{3}$, $[Br^-]= Kx/(0.2475\times 10^{-3}-x)$, plug $[Br^-]$ into $\textcircled{1}$,

$$\text{So } [Ag^+] = K_{sp}*(0.2475\times 10^{-3}-x)/(Kx) \quad (2)$$

So the concentration of Br^- that precipitate with $Ag^+= [AgBr] =$
 $0.9901\times 10^{-3}- [Br^-]$. (3)

According to the law of material conservation of Ag^+ , so

$$[\text{Ag}^+] + [\text{AgBr}] + [\text{AgL}] = c_{2(\text{Ag}^+)} = 0.2475 \times 10^{-3} \quad \textcircled{4}$$

Plug (1)(2)(3) into $\textcircled{4}$, and

$$K_{sp} * (0.2475 \times 10^{-3} - x) / (Kx) + 0.9901 \times 10^{-3} - Kx / (0.2475 \times 10^{-3} - x) +$$

$$0.2475 \times 10^{-3} - x = 0.2475 \times 10^{-3}$$

$$K_{sp} * (0.2475 \times 10^{-3} - x) / (Kx) + 0.9901 \times 10^{-3} - Kx / (0.2475 \times 10^{-3} - x) - x = 0$$

$$\{ K_{sp} * (0.2475 \times 10^{-3} - x) + 0.9901 \times 10^{-3} \times Kx \} / (Kx) = \{ Kx + x(0.2475 \times 10^{-3} - x) \} /$$

$$(0.2475 \times 10^{-3} - x)$$

K_{sp}

$$\frac{K_{sp}}{K} (0.2475 \times 10^{-3} - x)^2 + 0.9901 \times 10^{-3} \times x(0.2475 \times 10^{-3} - x) = Kx^2 + x^2(0.2475 \times 10^{-3} - x)$$

Substitution of value of K_{sp} and K , so

$$x^3 + 2.450104308 \times 10^{-7} x - 1.244255818 \times 10^{-3} x^2 = -4.865756893 \times 10^{-15}$$

$$\text{Order } f(x) = x^3 + 2.450104308 \times 10^{-7} x - 1.244255818 \times 10^{-3} x^2$$

$$+ 4.865756893 \times 10^{-15}$$

$$f(-1) = -1.001244501$$

$$f(0) = 4.865756893 \times 10^{-15}$$

$$f(0.000245281) = 1.78061 \times 10^{-16}$$

$$f(0.000245282) = -6.82564 \times 10^{-18}$$

$$f(0.0002475) = -4.12576 \times 10^{-13}$$

$$f(1) = 0.998755989$$

$$\text{So } f(-1) * f(0) < 0, f(0.000245281) * f(0.000245282) < 0$$

$$f(0.0002475) * f(1) < 0$$

Therefore, $f(x)$ has three zero point at $(-1,0)$, $(0.000245281, 0.000245282)$, $(0.0002475,1)$, and $(0.000245281, 0.000245282)$ has practical meaning.

If $[L] = x = 0.000245281$, so $0.000245281/0.0002475 = 0.991034343$, the possibility that citrate acting as ligand is less than 1/100. So we can draw a conclusion that the main part in the seed crystal is AgBr but not AgL. Further calculation shows that the concentration of AgL in the solution is 2.218 μmol to 2.219 μmol .

2) An experiment verification:

To verify our calculation results, an experiment was carried out as shown in Fig. S1. It had been reported that AgBr colloidal particles solution had an absorption peak at about 212 nm [1]. The solution (2), (3) or (6) where without AgNO_3 had no absorption peak at 212 nm, while the solution (1) or (5) where without CTAB had an absorption peak at 212 nm. What is more, the solution (4), (7), (8) or (9) where had both AgNO_3 and CTAB had an absorption peak at 212 nm whose absorption intensity was nearly twice higher than those of solution (1) and (5). Based on the above results, we preliminarily confirmed that AgBr colloidal particles were first produced during the preparation process of silver seed in our improved method.

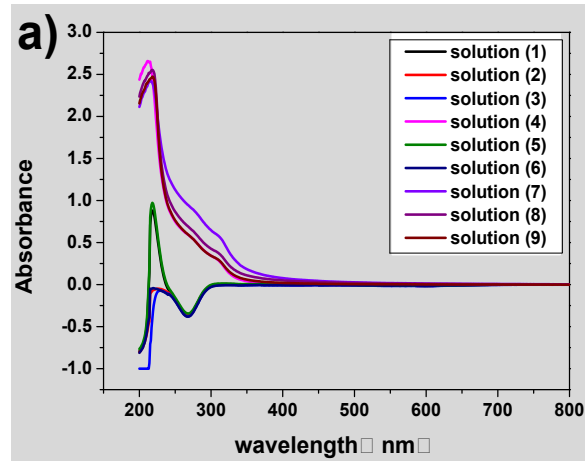


Fig. S1 UV spectra of the solution composed by different agents respectively and the total volume of each solution was 20.8 mL. **(1)**. 0.24 mM AgNO₃; **(2)**. 0.96 mM CTAB; **(3)**. 0.24 mM sodium citrate; **(4)**. 0.2 mM AgNO₃ + 0.96 mM CTAB; **(5)**. 0.24 mM AgNO₃ + 0.24 mM sodium citrate; **(6)**. 0.96 mM CTAB + 0.24 mM sodium citrate; **(7)**. 0.24 mM AgNO₃ + 0.96 mM CTAB + 0.24 mM sodium citrate; **(8)**. 0.24 mM AgNO₃ + 0.24 mM sodium citrate + 0.96 mM NaBr; **(9)**. 0.24 mM AgNO₃ + 0.96 mM NaBr.

2.Photo of seed colloidal solution

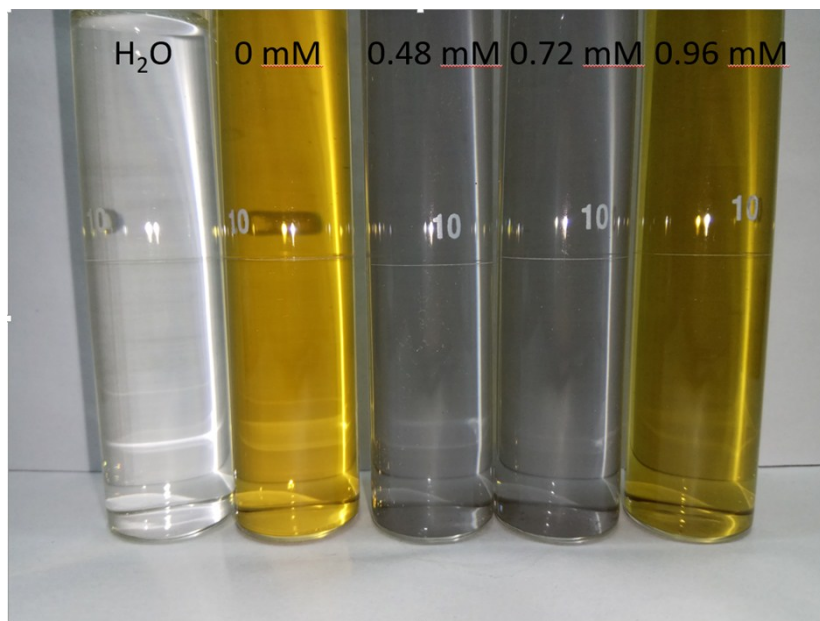


Fig. S2 Photo of seed colloidal solution of different concentrations of CTAB and aged for 20 min.

When the concentrations of CTAB were 0.48 and 0.72 mM, these two seeds were almost colorless but with a little dark in color, we thought that they were unstable and aggregated into large particles that without plasmon resonance absorption.

References

1. Chakraborty, M., et al., *Surfactant-Assisted Synthesis and Characterization of Stable Silver Bromide Nanoparticles in Aqueous Media*. Langmuir, 2012. **28**(25): p. 7282-7290.