

# Role of humic acid in the stability of Ag nanoparticles in sub-oxic conditions

## SUPPORTING INFORMATION

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## **DETAILS OF PREPARATION OF CITRATE- AND PVP-STABILIZED AGNP**

### **Preparation of silver nanoparticles.**

#### **Citrate stabilised**

Clean glassware is essential for this method to work.

1. Weigh 0.0200g sodium citrate tribasic dehydrate and dissolved in 250ml H<sub>2</sub>O.
2. Weighed 0.0106g silver nitrate and dissolved in 250ml H<sub>2</sub>O.
3. Weighed 0.0318g sodium borohydride and dissolved in 100ml H<sub>2</sub>O.
4. Stirred together 100ml sodium citrate soln, and 100ml silver nitrate solution.
5. Added 6 ml of sodium borohydride solution and stirred for 10 minutes.
6. Bring to the boil and simmer for 3 hours.
7. Cool and store in a cupboard for 16 hours
8. Reduce volume to 50% by ultrafiltration, top up to original volume with sodium citrate solution at half the concentration in step 1, to clean particles

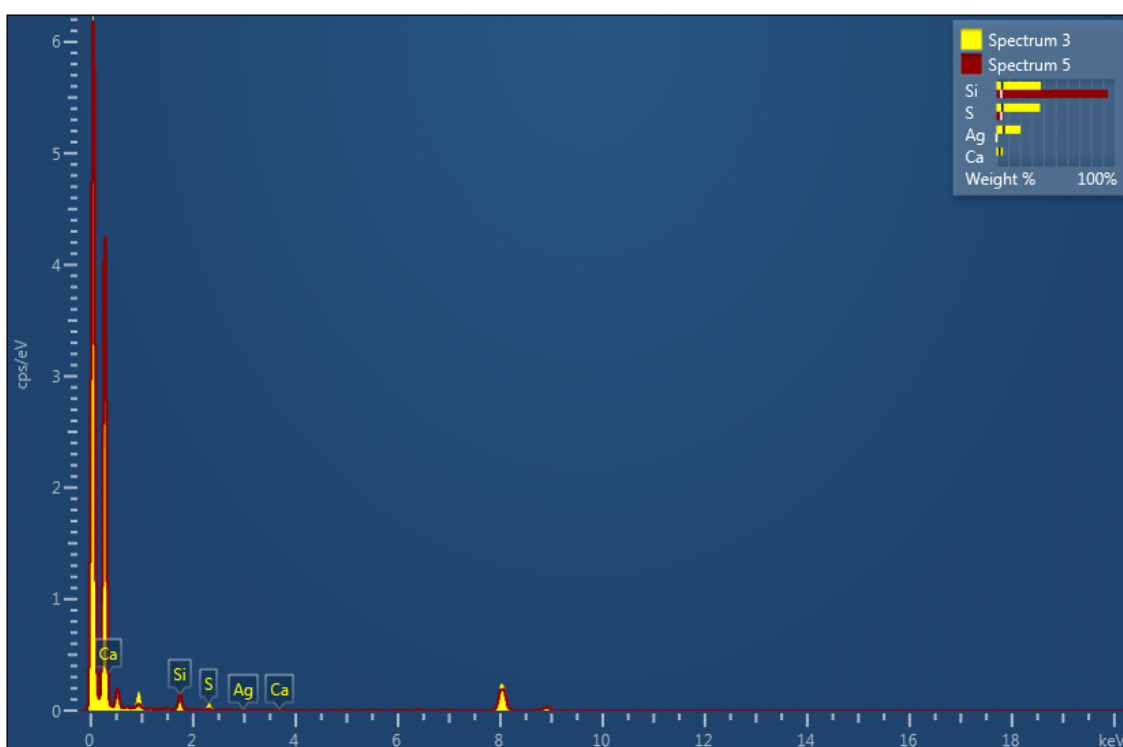
Repeat step 8 twice more.

#### **PVP stabilised**

1. Take 300ml citrate stabilised silver nanoparticle suspension,
2. Add 12 ml 3% PVP solution, with stirring
3. Reduce volume to 150ml by ultrafiltration.
4. Add 3 ml 3%PVP solution and 150 ml H<sub>2</sub>O, with stirring
5. Reduce volume to 150ml.
6. Repeat 4 and 5 again.
7. Store in refrigerator in the dark.

## **ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (EDX) DATA**

Figure S1. Energy-dispersive X-ray spectroscopy (EDX) of TEM samples for experiment C2, cit-AgNP with 0.01 M (320 mg/L) sulfide ions, in CaCl<sub>2</sub> matrix. No HA present. Comparing elemental composition of analysis of imaged nanoparticle with analysis of background and showing clear concentration of the S associated with the Ag. Contributions from Cu, C and O have been eliminated from integrations to remove influence of Cu-based TEM support grid.



Element	Silver nanoparticle Atomic %	Background Atomic %
Si	47.2	91.9
S	40.7	4.70
Cl	0.63	0.84
Ca	4.79	2.57
Ag	6.67	0.00
Total	100.0	100.0