Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Monodispersity and Size Control in the Synthesis of 20-100 nm Quasi-Spherical Silver Nanoparticles by Citrate and Ascorbic Acid Reduction in Glycerol/Water Mixtures

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Experimental section

Materials

AppliChem
- Glycerol
- Ethylene glycol

Carl Roth
- Polyvinylpyrrolidone K30 (PVP)

Sigma-Aldrich
- Silver nitrate
- Sodium citrate
- L-ascorbic acid
- Gold(III) chloride hydrate
- Hydroxylamine hydrochloride
- Sucrose
- Sodium borohydride
- Sodium hydroxide
- Ethanol
- Ammonium hydroxide 30%
- Agarose

Instruments

The TEM images were obtained with a Zeiss EM 902 instrument. The localized surface plasmon resonance (LSPR) spectra were recorded with a Perkin Elmer Lambda 35 UV/Vis absorption spectrometer. Ultrapure water was prepared by a TKA MicroPure UF filtration device.

Nanoparticle synthesis

Mondisperse silver nanoparticles (**30 nm**)
- 50 mL water/glycerol; 40 vol% glycerol (1200 rpm, 2.5 cm stirring bar) in a 100 mL flask at 95°C.
- + 9 mg silver nitrate
- + 1 mL (3%) sodium citrate (one minute later)
- One hour at 95°C
- Store the colloid at 4 °C

*Alternatives (best result with the addition of glycerol):
- 50 vol% ethanol
- 90 vol% ethylene glycol
- 0.2 vol% agarose
- 66 wt% sucrose (sucrose particles were stored at 4 °C in a plastic box)

Monodispere silver nanoparticles (**40-100 nm**)
- 138 mL water, 23 mL glycerol and 0.58 g PVP (1200 rpm, 2.5 cm stirring bar) in a 250 mL breaker at RT

- + 30.0 nm seeds, synthesized by modified method (40 vol% glycerol).

Particle size	Seed volume
44.1 nm	14.4 mL
69.6 nm	11.5 mL
85.5 nm	4.6 mL
98.4 nm	2.6 mL

- + 20 seconds later: diamine silver complex (20 mg silver nitrate in 1 mL water plus 220 µl ammonium hydroxide 30%)

Particle size	Diamine silver complex volume
44.1 nm	290 µL
69.6 nm	1.15 mL
85.5 nm	1.15 mL
98.4 nm	1.15 mL

- + 92 mL ascorbic acid solution (together with diamine silver complex)

Particle size	Ascorbic acid concentration
44.1 nm	9.2 mg
69.6 nm	36.8 mg
85.5 nm	36.8 mg
98.4 nm	36.8 mg

- + 6 g PVP (one hour later)
- Store the colloid at 4 °C

Sodium citrate (Au)
- 50 mL water (1200 rpm, 2.5 cm stirring bar) in a 100 mL flask at 95°C.
- + 9 mg Gold(III) chloride hydrate
- + 1 mL (3%) sodium citrate (one minute later)
- One hour at 95°C.

Sodium citrate (Au) with glycerol
- 50 mL water/glycerol; 40 vol% glycerol (1200 rpm, 2.5 cm stirring bar) in a 100 mL flask at 95°C
- + 9 mg Gold(III) chloride hydrate
- + 1 mL (3%) sodium citrate (one minute later)
- One hour at 95°C.

Lee and Meisel (sodium citrate; Ag)
- 50 mL water (1200 rpm, 2.5 cm stirring bar) in a 100 mL flask at 100°C.
- + 9 mg silver nitrate
- + 1 mL (1%) sodium citrate (one minute later)
- One hour at 100°C

Ascorbic acid (Ag)
- 50 mL water (1200 rpm, 2.5 cm stirring bar) in a 100 mL flask at 95°C.
- + 9 mg silver nitrate
- + 1 mL (3%) ascorbic acid (one minute later)
- One hour at 95°C

Ascorbic acid (Ag) with glycerol
- 50 mL water/glycerol; 40 vol% glycerol (1200 rpm, 2.5 cm stirring bar) in a 100 mL flask at 95°C.
- + 9 mg silver nitrate
- + 1 mL (3%) ascorbic acid (one minute later)
- One hour at 95°C

Hydroxylamine hydrochloride (Ag)
- 90 mL hydroxylamine hydrochloride ($1.67 \cdot 10^{-3}$ M) plus sodium hydroxide ($3.33 \cdot 10^{-3}$ M)
- + 10 mL silver nitrate (10^{-2} M)

Hydroxylamine hydrochloride (Ag) with glycerol

- 54 mL hydroxylamine hydrochloride ($2.78 \cdot 10^{-3}$ M) plus sodium hydroxide ($5.55 \cdot 10^{-3}$ M)
- + 40 mL glycerol
- + 6 mL silver nitrate ($1.66 \cdot 10^{-2}$ M)

Polyvinylpyrrolidone (Ag)
- 2 g PVP in 13 mL ethylene glycol at 120 °C
- + 317.4 mg silver nitrate in 2 mL ethylene glycol
- One hour at 120°C.

Polyvinylpyrrolidone (Ag) with glycerol
- 2 g PVP in 7.8 mL ethylene glycol and 5.2 mL glycerol at 120 °C
- + 317.4 mg silver nitrate in 2 mL ethylene glycol
- One hour at 120°C.

Sodium borohydride (Ag)
- 1 mL (10^{-3} M) silver nitrate
- + 3 mL ($2 \cdot 10^{-3}$ M) sodium borohydride (ice cold)

Sodium borohydride (Ag) with glycerol
- 0.6 mL ($1.6 \cdot 10^{-3}$ M) silver nitrate and 1.6 mL glycerol
- + 1.8 mL ($3.3 \cdot 10^{-3}$ M) sodium borohydride (ice cold)

Au/Ag nanoshells
- 8x 1.5 mL of 60 nm silver nanoparticles were centrifugated and resuspended in 30 mL water/PVP (1 mg/mL)
- Fast stirring at 100 °C
- + 2 mL of $HAuCl_4$ (0.01%) were added (dropwise)

Seed-mediated synthesis (Ag; citrate)
- 161 mL water (1200 rpm, 2.5 cm stirring bar) in a 250 mL breaker at RT
- + optional 40 vol% glycerol; 0.58 g PVP
- + 5 mL 30.0 nm (modified Lee and Meisel method) silver nanospheres
- + 1.15 mL diamine silver complex (20 mg silver nitrate in 1 mL water plus 220 µl ammonium hydroxide 30%)
- + 92 mL ascorbic acid (36.8 mg) solution (together with diamine silver complex)

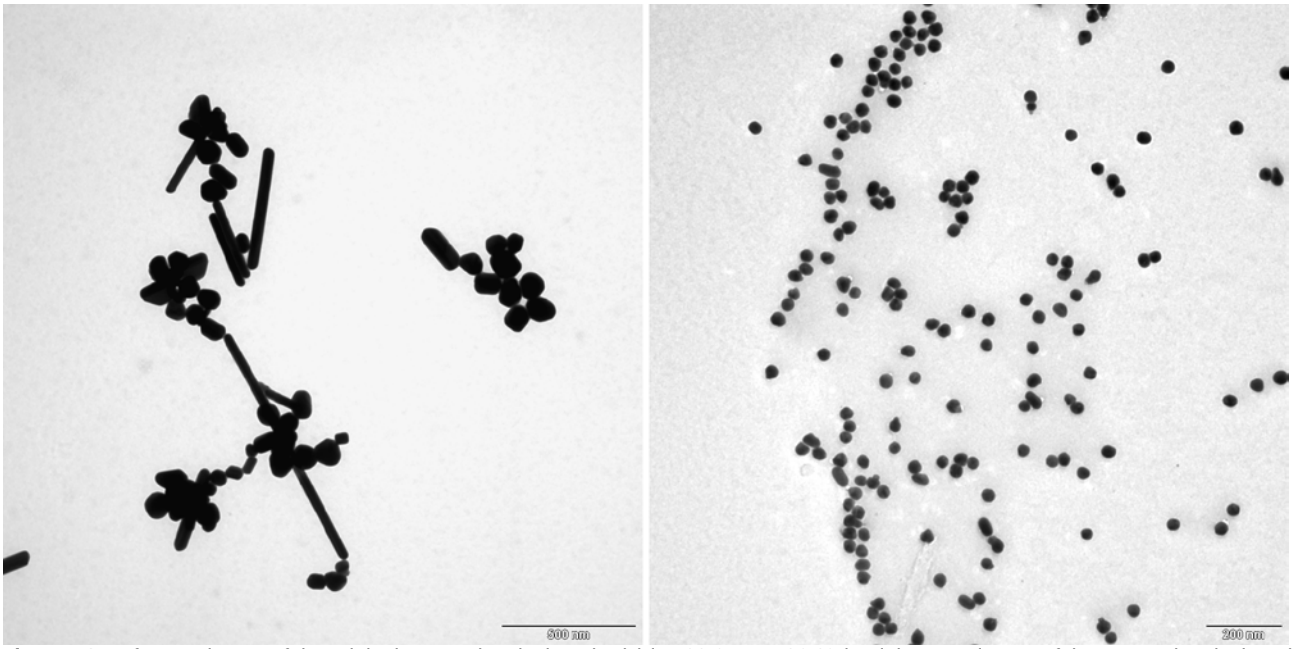

Figure 1S. Left: TEM image of the original Lee and Meisel method (size 83.9 nm ± 26.2%). Right: TEM-image of the Lee and Meisel method with 25 vol% glycerol (size 35.8 nm ± 6.9%).

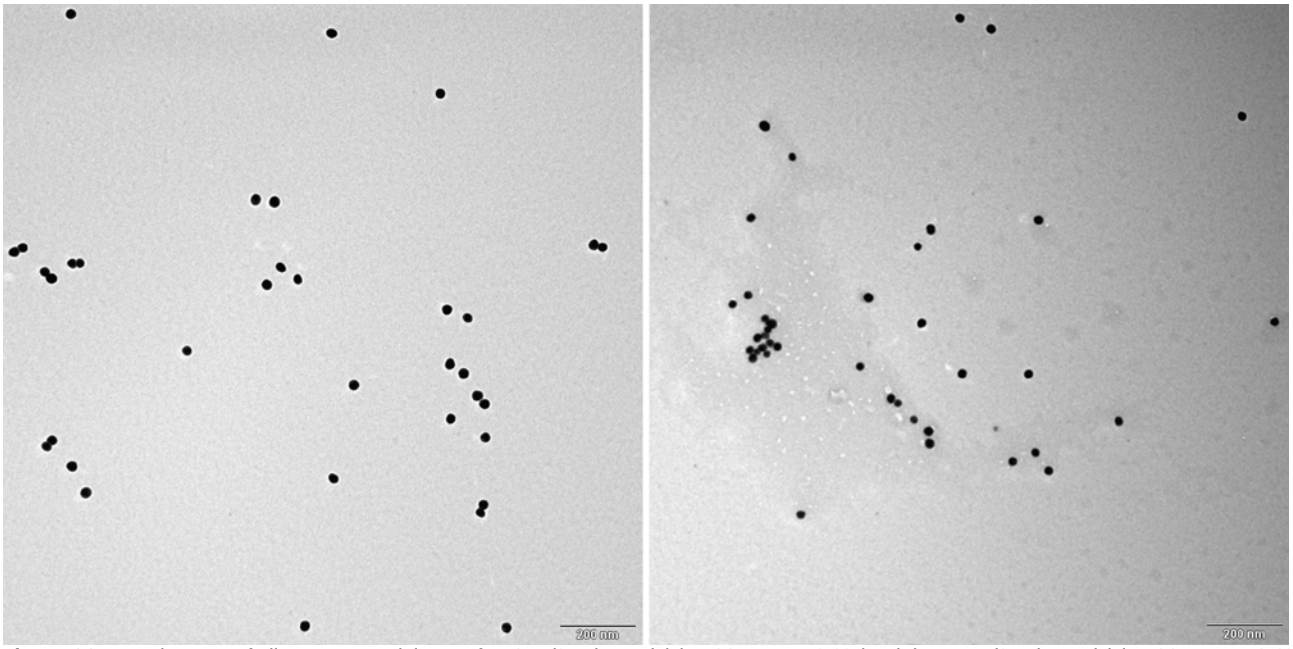

Figure 2S. TEM images of silver nanoparticles: Left: 50 vol% glycerol (size 28.1 nm ± 6.9%). Right: 75 vol% glycerol (size 23.7 nm ± 8.6%).

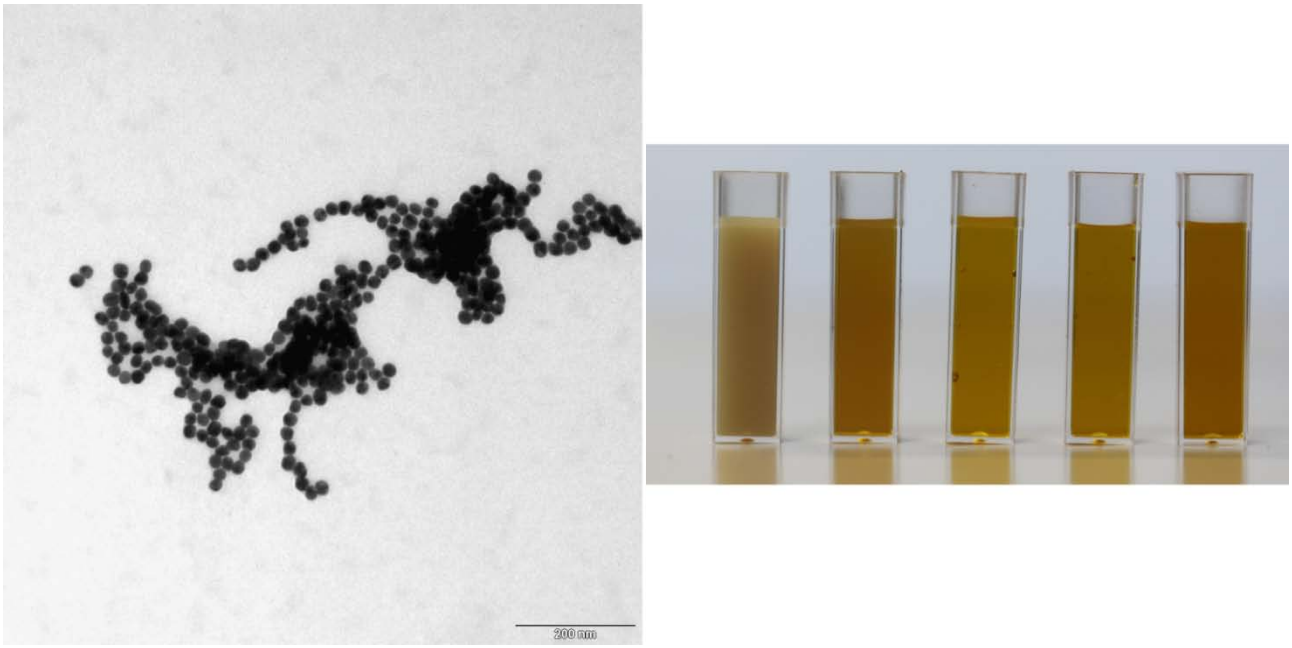

Figure 3S. TEM images of silver nanoparticles. Left: 100 vol% glycerol (size 22.6 nm ± 15.5%). The particles aggregated due to multiple centrifugation steps and high viscosity of the glycerol. Right: Photos of the colloids (from left to right: 0, 25, 50, 75, and 100 vol% glycerol).

Figure 4S. Photo of the gold samples in a cuvette. Left: Without glycerol (size 16.1 nm ± 12.2%). Right: With 40 vol% glycerol (size 49.5 nm ± 30.2%).

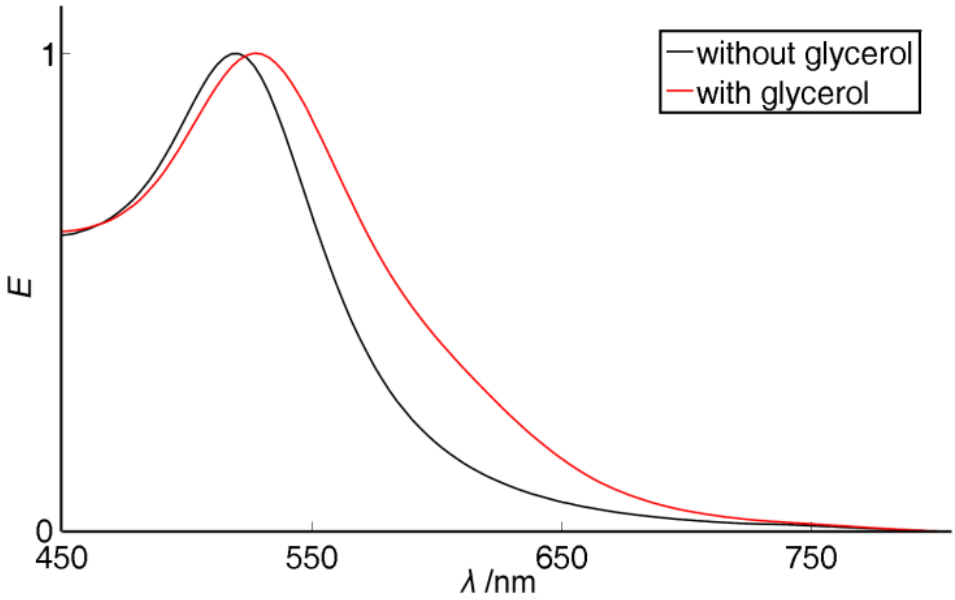

Figure 5S. Normalized LSPR spectra of the gold colloids. Maximum at 519 nm (without glycerol), and 527 nm (with 40 vol% glycerol).

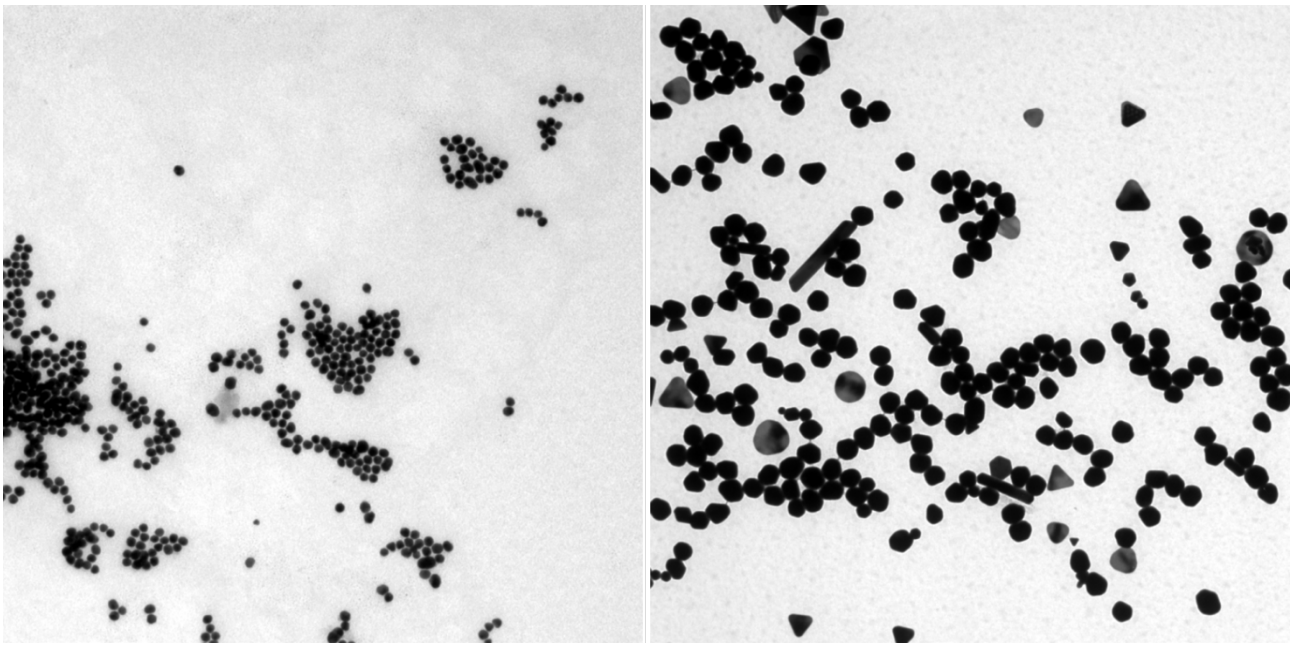

Figure 6S. TEM image of the gold colloids. Left: without glycerol. Right: with 40 vol% glycerol.

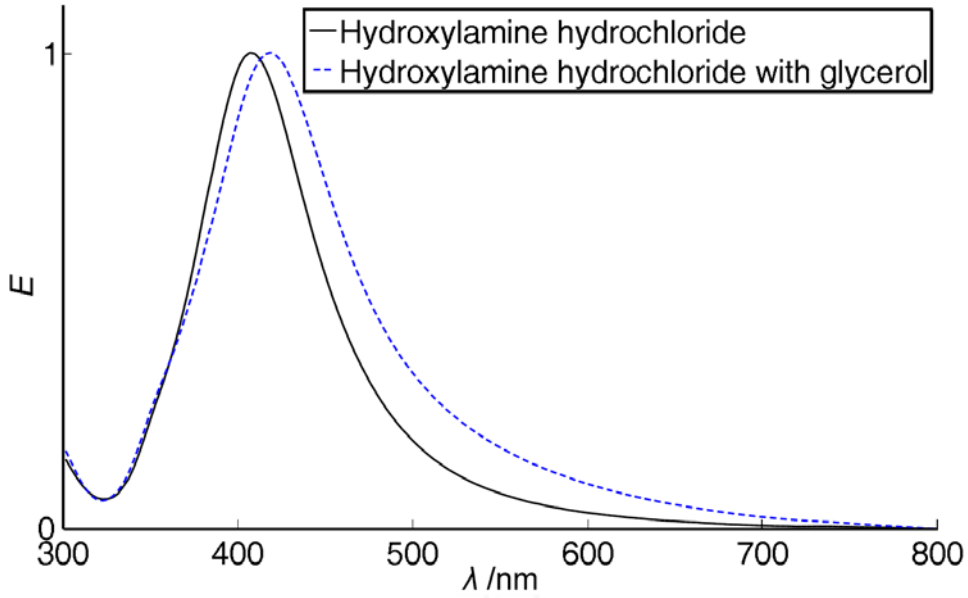

Figure 7S. Normalized LSPR spectra of the colloids. The silver nanoparticles were synthesized with and without the addition of glycerol.

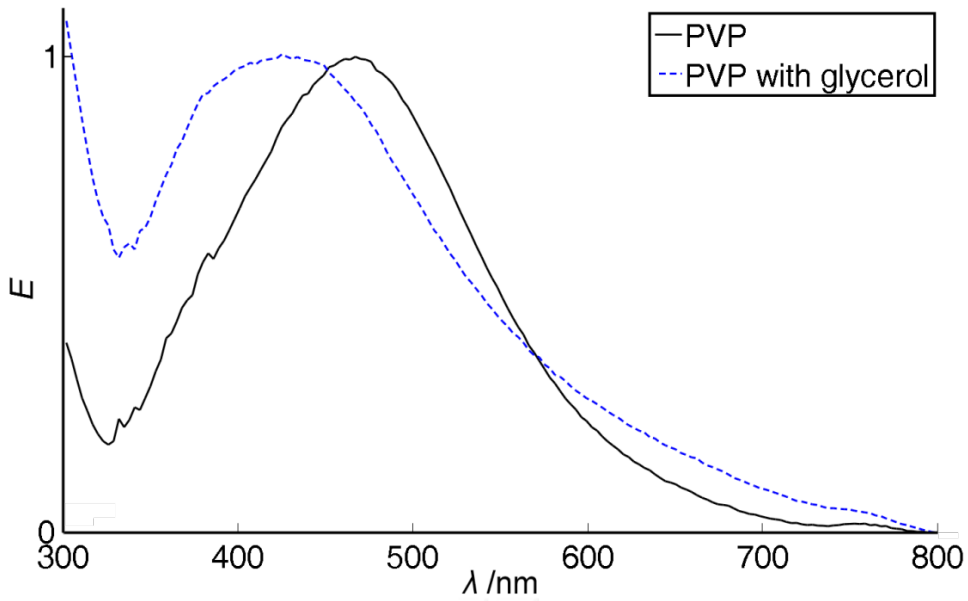

Figure 8S. Normalized LSPR spectra of the colloids. The silver nanoparticles were synthesized with and without the addition of glycerol.

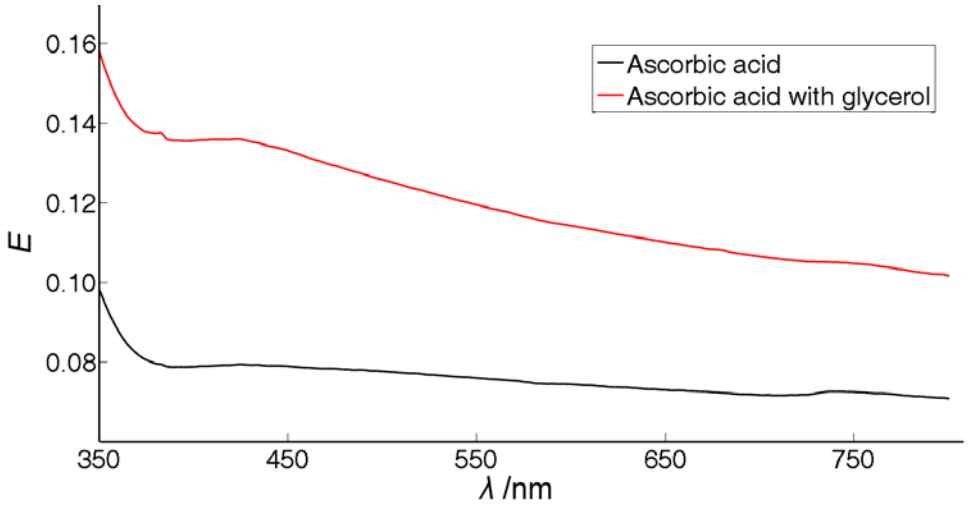

Figure 9S. LSPR spectra of the colloids. The silver nanoparticles were synthesized with and without the addition of glycerol.

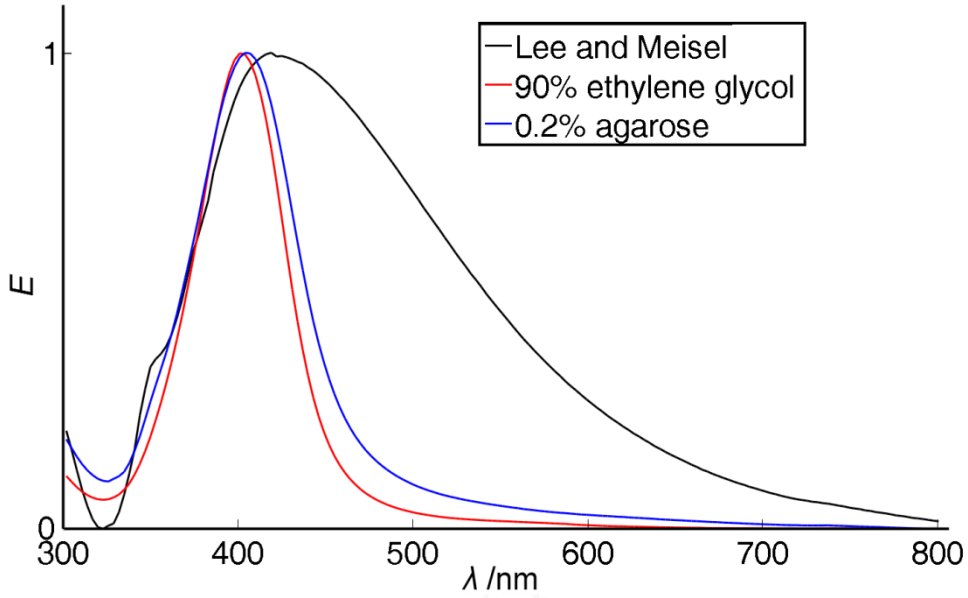

Figure 10S. Normalized LSPR spectra of the silver nanoparticles. Synthesis with the addition of agarose and ethylene glycol. Maximum at 420 nm (Lee and Meisel), 402nm (90% ethylene glycol), and 405 nm (0.2% agarose).

Figure 11S. Photos of the 0.2% agarose sample.

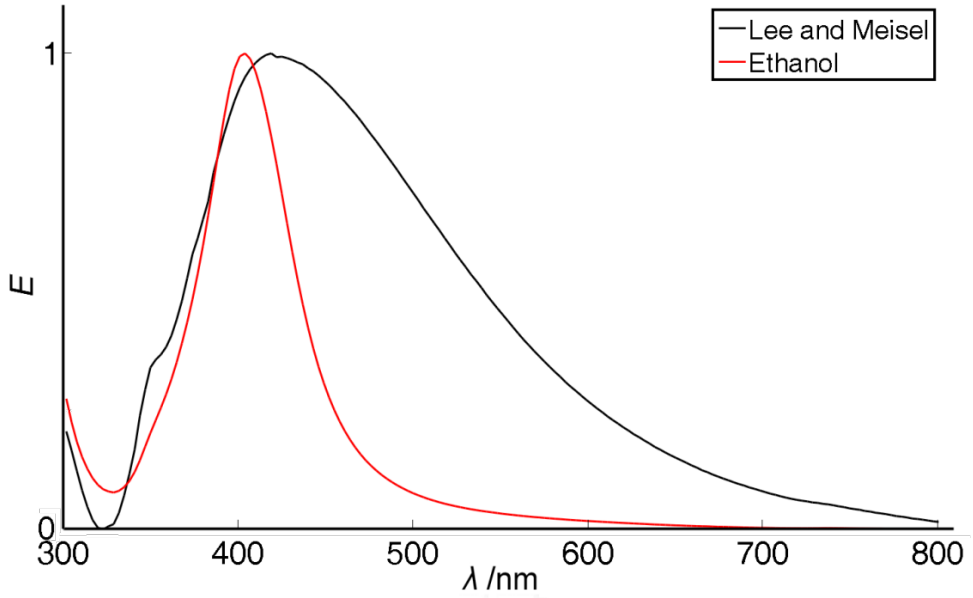

Figure 12S. Normalized LSPR spectra of the colloids. Synthesis with the addition of ethanol. Maximum at 420 nm (Lee and Meisel), 403nm (ethanol).

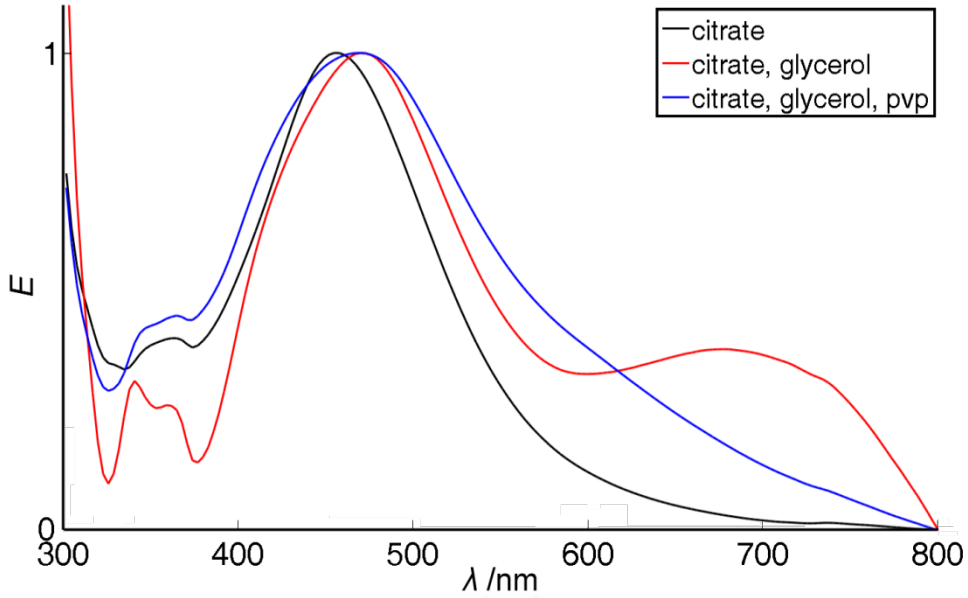

Figure 13S. Seed-mediated growth: Normalized LSPR spectra of the colloids, recorded after 36 hours. Maximum at 456 nm (60 mg sodium citrate, 161 mL water, 7 mL 27 nm silver colloid), 471 nm (60 mg sodium citrate, 138 mL water, 23 mL glycerol, 7 mL 27 nm silver colloid), 469 nm (60 mg sodium citrate, 138 mL water, 23 mL glycerol, 0.575 g PVP, 7 mL 27 nm silver colloid).

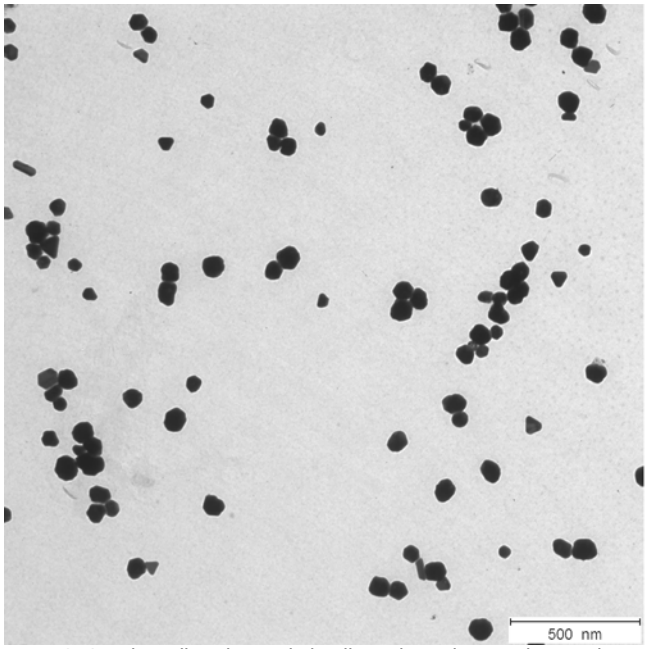

Figure 14S. Seed-mediated growth (sodium citrate in water): TEM image of the silver nanoparticles, recorded after 36h.

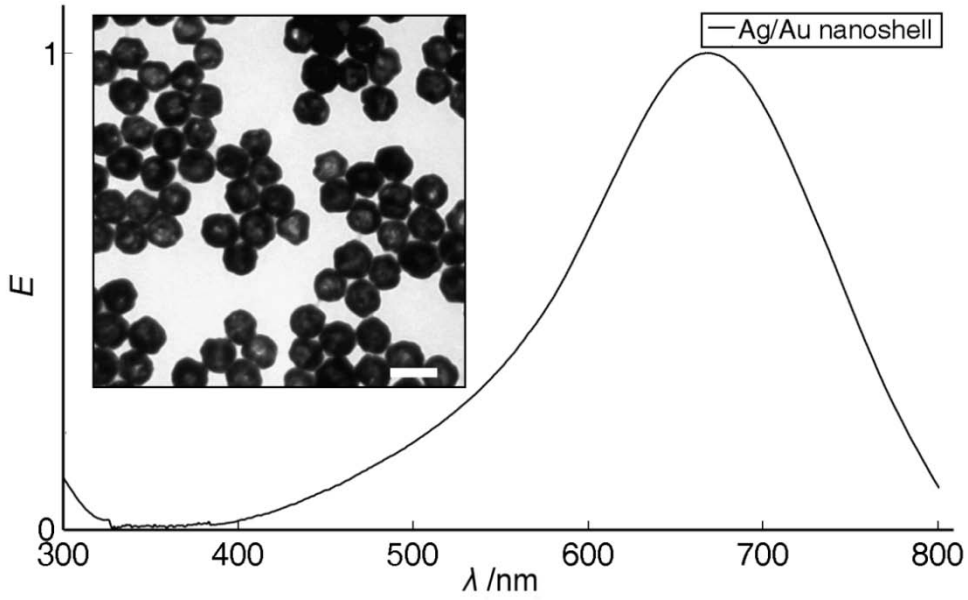

Figure 15S. Left: TEM image of the nanoshells. Scale bar: 100 nm. Right: Normalized LSPR spectrum of the silver colloid containing 60 nm nanoshells. Maximum at ~667 nm.