Electronic Supporting Information (ESI):

Experimental section:

Reagents

Silver nitrate (99.9%), hydrogen peroxide (30-32 wt. % solution in water (ca.. 10.4 M), semiconductor grade, 99.99), L-arginine (TLC, 98%), sodium citrate tribasic dihydrate (99+%), and sodium borohydride (99%), polyvinylpyrrolidone (PVP, average $M_w = 10,000$; 40,000; and 1,300,000), poly(sodium 4-styrenesulfonate), (PSS, average $M_w = 70,000$) and poly(acrylic acid) (PAA, average $M_w = 1,800$; 100,000; and 1,250,000) were supplied by Aldrich and used as received. PVP with average $M_w = 55,000$ was supplied by Caledon Chemicals. High-purity deionized water (> 18.3 MΩcm) was produced using Millipore A10 Milli-Q.

Characterization

UV-vis spectra were recorded using both Ocean Optics QE65000 fiber-optic UV-vis spectrometer and Cary 50 UV-vis spectrometer. Both TEM and SEM imaging were performed with a Hitachi S-5200 using a copper grid with a formvar/carbon film (FCF-200, Electron Microscopy Science). AgNPs were centrifuged using Clinical 200 Centrifuge (VWR). Controlled uniform heating during pentagonal rods preparation was accomplished using a Heidolph MR 3004 safety heater with an aluminium heating block (VWR). Light exposure was performed using a set-up of royal blue (449 nm maxima) 1-watt 350 mA LEDs (LEDs Super Bright) powered by a TDC LED driver operating at 350 mA constant current.

Synthesis of silver decahedral nanoparticles (AgDeNPs)

AgDeNPs were synthesized using a new-generation photochemical synthetic protocol developed by our group.^{1,2} To a 20-mL vial containing 14.00 mL of high-purity deionized water, the following solutions were added in the listed order: 0.520 mL of 0.050 M sodium citrate, 0.0150 mL of 0.050 M of a steric stabilizer (total concentration of monomer units), 0.050 mL of 0.005 M L-arginine, 0.400 mL of 0.0050 M silver nitrate, and freshly prepared 0.200 mL of 0.100 M sodium borohydride. A pale yellow solution is first formed, which then turned to bright yellow upon continuing stirring (600 rpm). Subsequently, 0.300 mL of ca. 10.4 M hydrogen peroxide was added. The solution then has been kept stirring for further ca. 20 min. Finally, the produced solution was exposed to royal blue (449 nm) LED for 14 hrs.

Different steric stabilizers were investigated in the synthesis: PVP and PAA with different M_w , and PSS. All steric stabilizers were used at the same volume (0.150 mL) and total monomer concentration (0.050 M), as indicated above. For PVP different monomer concentrations were used in the range from 50:1 to 1:5 molar ratio to silver.

Synthesis of silver pentagonal rod nanoparticles (AgPRNPs)

Silver pentagonal rods nanoparticles with average length of ca. 120 nm are typically produced thermally using an adapted synthetic protocol that reported by our group.^{1,3} An aqueous preparation containing 6.00 mL of high-purity deionized water, 0.720 mL of 0.05 M citrate and 0.135 mL of 0.05 M steric stabilizer (PVP, PSS, or PAA) was heated at controlled temperature near boiling (ca. 98 °C) for 10 minutes. Subsequently, 1.00 ml of five-time concentrated AgDeNP dispersion, followed by a 0.800 mL of 0.005 M silver nitrate was added. Finally, the reaction mixture was heated for additional 15 minutes.

Supporting figures



Fig. S1 TEM images of AgDeNPs synthesized using (a) PVP, (b) PSS, (c) PAA as steric stabilizers, and (d) without steric stabilizers. The scale bars are 100 nm for all EM images.



Fig. S2 TEM images of AgDeNPs synthesized using PVP with different molecular weight (M_w) (a) 10,000, (b) 40,000 and (c) 1,300,000. The scale bars are 100 nm for all EM images.



Fig. S3 TEM images of AgDeNPs synthesized using PVP with different monomer unit concentrations (**a**) 0.048, (**b**) 0.096, (**c**) 0.24 and (**d**) 6.0 mM. The scale bars are 100 nm for all EM images.



Fig. S4 TEM images of AgPRNPs produced without using steric stabilizers after (a) one-time cleaning and (b) multiple cleaning (three times). The scale bars are 100 nm for all EM images.



Fig. S5 TEM images of AgPRNPs produced using (a) PVP, (b) PAA, and (c) PSS after multiple cleaning (three times). The scale bars are 100 nm for all EM images.

¹ N. Murshid, D.Keogh, V. Kitaev, *Part. Part. Syst. Charact.* 2013, **30**, DOI: 10.1002/ppsc.201300225.

² B. Pietrobon and V. Kitaev, *Chem. Mater.*, 2008, **20**, 5186–5190.

³ B. Pietrobon, M. McEachran and V. Kitaev, ASC Nano 2009, **3**, 21-26.