Supplementary Information

Silver Nanoparticles with Planar Twinned Defects: Effect of Halides for Precise Tuning of Plasmon Absorption from 400 to >900 nm

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Experimental:

Materials

Sodium borohydride (99%), silver nitrate (99%+), sodium tricitrate tribasic dehydrate (99.0%), hydrogen peroxide, 30 wt% (99.999%), potassium chloride (ACS grade), potassium bromide (ACS grade) were supplied by Sigma-Aldrich and used as received. High purity deionized water (>18.3MΩ·cm) was produced by Millipore A10 Milli-Q.

Prism Preparation

Two routes for control of plasmonic absorption (PLA) of silver nanoparticles with planar twinned morphologies (AgNPRs) through the visible and near infrared regions have been developed. The first includes direct formation of the nanoparticles upon addition of bromide and chloride. The second is based upon formation of large AgNPRs, and then further transformation by addition of bromide or chloride. Dual-stage protocol based on combination of the two approaches was used for precise tuning of plasmon adsorption: addition of halides upon prism formation (direct formation route) and post-synthetic modification with halides.

A typical synthesis was performed in a 20 mL scintillation vial (VWR) in aqueous solutions under ambient conditions, adapted from the preparation reported by Mirkin's group.[1] Polyvinylpyrollidone (PVP), used in the original procedure has been excluded to shorten reaction time from 20-30 to 1-3 minutes and to enable easy modification of electrostatically (citrate) stabilized AgNPRs. Absence of PVP did not negatively affect the size distribution evidenced by the plasmonic absorption (Figure S1). Citrate protected AgNPRs are stable for many months, and if required, PVP can be introduced after AgNPR formation.

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[1] Metraux, G. S.; Mirkin, C. A. *Adv. Mater.* **2005**, *17,* 412

For the direct formation route, sodium citrate 2.4 mM, silver nitrate 0.12 mM, and hydrogen peroxide 26 mM were dissolved in high purity deionized water. To this solution, varying amounts of potassium bromide (0.0002-0.0065 mM) (for reduction of size) or potassium chloride (0.01-0.22 mM) were added before reduction with sodium borohydride (1.2 mM). Upon sodium borohydride addition, the solution goes through visible colour changes through nucleation (pale yellow) and growth (yellow, orange, red, purple, blue, light blue with scattering). Increasing amounts of bromide hinders the growth of nanoprisms and shifts plasmon peaks to higher energies. Chloride addition causes red-shift of plasmon peaks up to the point where formation of silver chloride becomes visible by cloudiness and silver NP formation can no longer be accomplished.

Therefore, the more bromide added – the smaller the resultant prisms. Chloride promotes growth of NPs, yielding enlarged prisms. Since higher concentrations of chloride are used, its addition is accompanied by cloudiness indicating formation of silver chloride. At higher chloride concentrations (>0.23-0.25 mM) silver can no longer be reduced to stable nanoparticles.

The post-synthetic transformation protocol starts with appropriate AgNPRs (enlarged with chloride, if necessary). AgNPRs synthesis can be easily performed on a larger scale. We usually used a 250 mL round bottom flask. Reaction mixtures were typically around 80 mL with 2.4 mM sodium tricitrate, 0.13 mM silver nitrate, 60 mM hydrogen peroxide (larger amounts of peroxide improve reproducibility of scaled-up preparations), and 0.02 to 0.14 mM potassium chloride were added. The solution was then reduced with 1.2 mM sodium borohydride. The large scale prisms underwent the same growth transformation as the direct reduction route. The synthesized batch was then characterized by UV-vis spectroscopy (and electron microscopy, if necessary). For the optimally reproducible post-modification, the prisms were aged overnight (approximately 16 hrs). 2-5 mL portions were typically used for the transformation, where various amounts of potassium bromide were added to cause plasmon shift to lower wavelength. Added potassium bromide amounts varied from 1.0×10^{-5} to ca. 1.5×10^{-4} mM, which respectively yield prisms with the maximum of the plasmonic absorption in the range from ca. 900 nm to 400 nm depending on the starting AgNPRs described.

Utilizing a two-stage protocol based on combination of the two methods proved to enable increased control over AgNPR plasmon absorbance. By preparing samples with coarsely tuned plasmon absorption using the direct formation route, the maxima of plasmon resonances can be subsequently fine-tuned to the desired wavelength by small additions of bromide.

Characterization

Electron microscopy (both TEM and SEM) was performed using Hitachi S-5200. Operating voltage was 30.0 kV. Nanoparticle solutions were deposited on carbon-coated formvar grid (EMS Corp.). The average sizes and standard deviations were determined from SEM and TEM images by averaging diameters of at least 100 particles. The thickness of AgNPRs was measured from TEM images of their stacked arrays, where perpendicular orientation of the particles was mostly assured. UV-vis spectra were acquired with either Ocean Optics QE65000 fibre-optic UV-vis spectrometer or Cary 50Bio UV-vis spectrophotometer. IR spectra were acquired with Perkin Elmer Lambda 900 spectrometer.

Table S1. Description of AgNPR samples shown in Figure 3a.

λ_{max} (nm)	Formation	Modification	Aging
402.2	1.6×10^{-6} M KBr	3.2×10^{-7} M KBr	24 hr
450.1	1.6×10^{-6} M KBr	1.9×10^{-7} M KBr	24 hr
503.8	None	1.2×10^{-4} M KBr	None
551.9	None	1.1×10^{-6} M KBr	48 hr
603.5	1.3×10^{-6} M KBr	6.5×10^{-8} M KBr	1 hr
654.8	2.5×10^{-5} M KCl	6.5×10^{-8} M KBr	1.5 hr
704.8	None	None	None
745.5	8.4×10^{-5} M KCl	1.9×10^{-7} M KBr	3 hr
794.3	1.31×10^{-4} M KCl	None	None
852.4	8.4×10^{-5} M KCl	2.5×10^{-7} M KBr	1 hr
897.5	1.2×10^{-4} M KCl	1.3×10^{-6} M KBr	1 hr
>1000	1.5×10^{-4} M KCl	None	None

Samples were prepared using a combined method of direct formation and post-synthetic modification. Concentrations of KBr or KCl adder prior to the silver reduction are listed under formation; concentration of KBr added to AgNPRs ([Ag] = 0.12 mM) for fine tuning of plasmon absorption is listed under modification.

Table S2. Description of AgNPR samples shown in Figure 3b.

λ_{max} (nm)	**Formation**	**Modification**	**Aging**
403.79	4.17×10^{-6} M KBr	9.9×10^{-8} M KBr	2 hr
404.58	4.17×10^{-6} M KBr	9.9×10^{-8} M KBr	2 hr
404.58	4.17×10^{-6} M KBr	9.9×10^{-8} M KBr	2 hr
500.78	2.28×10^{-6} M KBr	6.1×10^{-7} M KBr	22 hr
500	2.28×10^{-6} M KBr	6.1×10^{-7} M KBr	22 hr
500.78	2.28×10^{-6} M KBr	6.1×10^{-7} M KBr	22 hr
599.65	1.3×10^{-6} M KBr	4.8×10^{-8} M KBr	30 min
599.65	1.3×10^{-6} M KBr	4.8×10^{-8} M KBr	30 min
598.88	1.3×10^{-6} M KBr	4.8×10^{-8} M KBr	30 min
700.27	7.28×10^{-5} M KCl	4.8×10^{-7} M KBr	23 hrs
700.27	7.28×10^{-5} M KCl	4.8×10^{-7} M KBr	23 hrs
699.51	7.28×10^{-5} M KCl	4.8×10^{-7} M KBr	23 hrs

Samples were prepared using a combined method of direct formation and post-synthetic modification. Concentrations of KBr or KCl adder prior to the silver reduction are listed under formation; concentration of KBr added to AgNPRs ([Ag] = 0.12 mM) for fine tuning of plasmon absorption is listed under modification. Samples were aged 24 hours prior to modification. Aging time after modification with bromide is listed. Samples reach endpoint wavelength within 24 hours, and remain stable at said wavelength for 2-5 days.

Table S3. Statistical details of the four series of three samples shown in Figure 3b (see Table S2 for more details)

Wavelength	400nm	500nm	600nm	700nm
λmax vial 1 (nm)	403.8	500.8	599.6	700.3
λmax vial 2 (nm)	404.6	500.0	599.6	700.3
λmax vial 3 (nm)	404.6	500.8	598.9	699.5
Standard Deviation (%)	0.46	0.45	0.45	0.44
Average (nm)	404.3	500.5	599.4	700.0
Precision (%)	1%	0.1%	0.1%	<0.1%

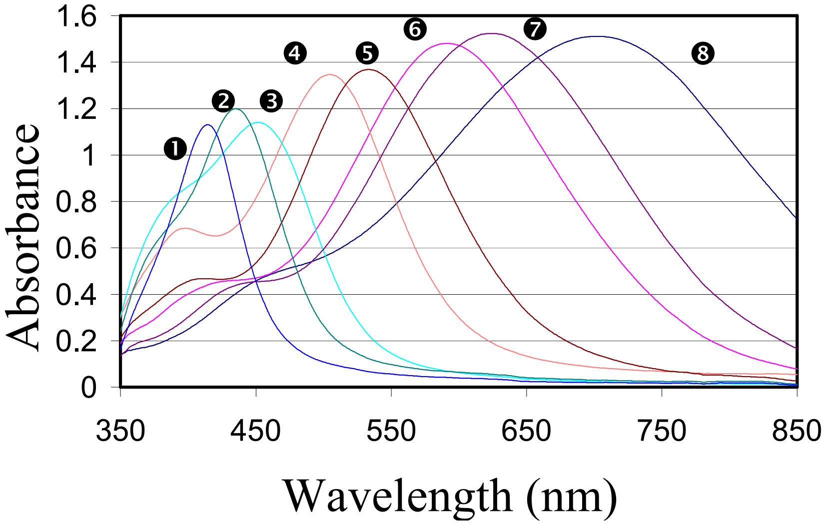

Figure S1. UV-vis spectra of AgNPRs prepared via direct formation route with and without PVP. Samples prepared without PVP (as per experimental described earlier) are ❸❹❻❽, which contain 2.7×10^{-6} M, 2×10^{-6} M, 1.3×10^{-6} M and 6.5×10^{-7} M of KBr respectively. Samples ❶❷❺❼ are prepared with 0.9 mM PVP and 2.7×10^{-6} M, 2×10^{-6} M, 1.3×10^{-6} M and 6.5×10^{-7} M of KBr respectively. Samples without PVP developed within 3 minutes, where as PVP containing samples took between 20-30 minutes for complete growth.

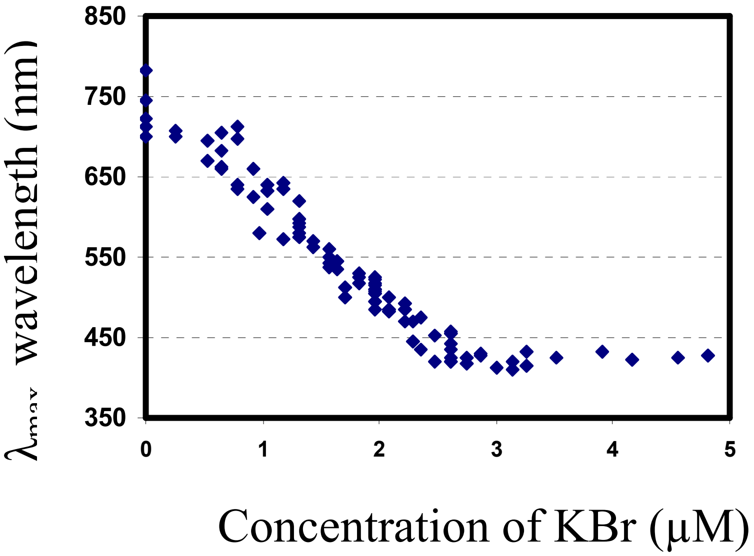

Figure S2. Wavelength of the maxima of plasmon absorption, λ_{max}, vs. increasing concentration of KBr during Ag-t-NP formation. Each point represents an individual sample.

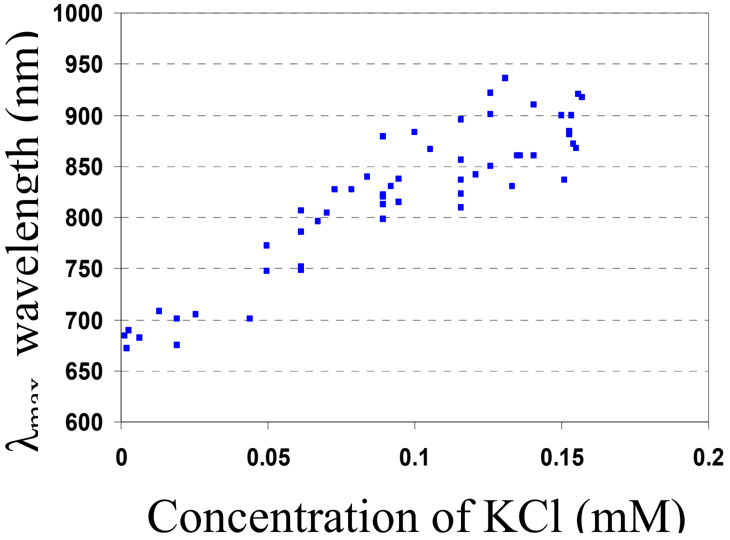

Figure S3. Wavelength of the maxima of plasmon absorption, λ_{max}, vs. increasing concentration of KCl during Ag-t-NP formation. Each point represents an individual sample.

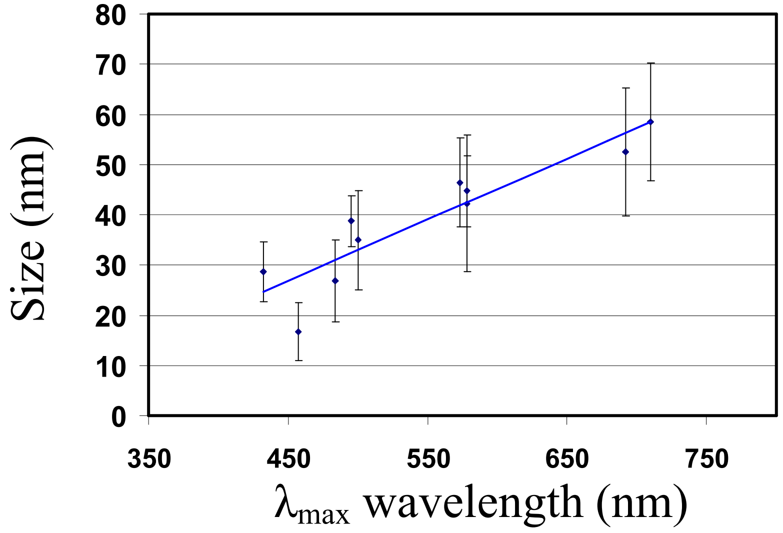

Figure S4. Average size (largest lateral dimension of AgNPRs) measured plotted against λ_{max} wavelength of the maxima of plasmonic absorption.

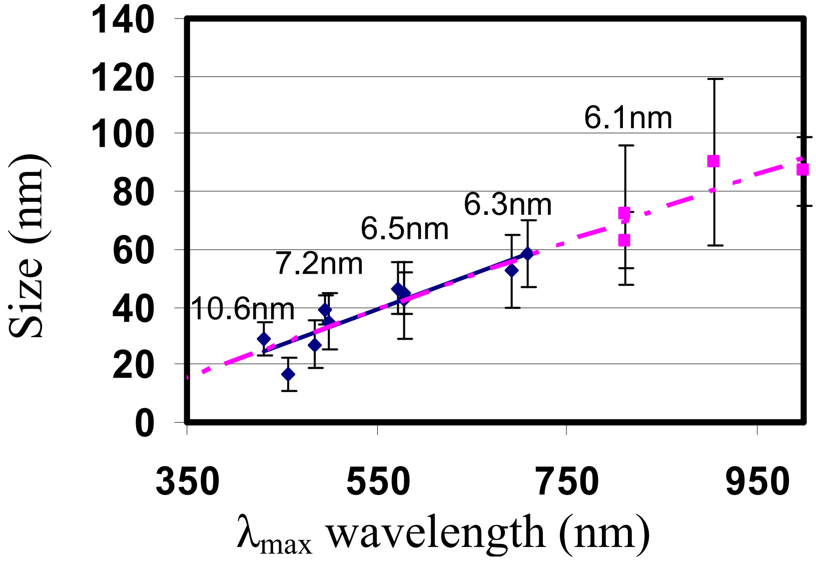

Figure S5. Average size (largest lateral dimension of AgNPRs) measured from EM images for bromide (blue) and chloride (magenta) samples plotted against wavelength of the maxima of plasmon absorption, λ_{max}. Average thicknesses of AgNPRs are listed on the graph for above samples. A trend line shows size continuum between AgNPRs prepared using both bromide and chloride.

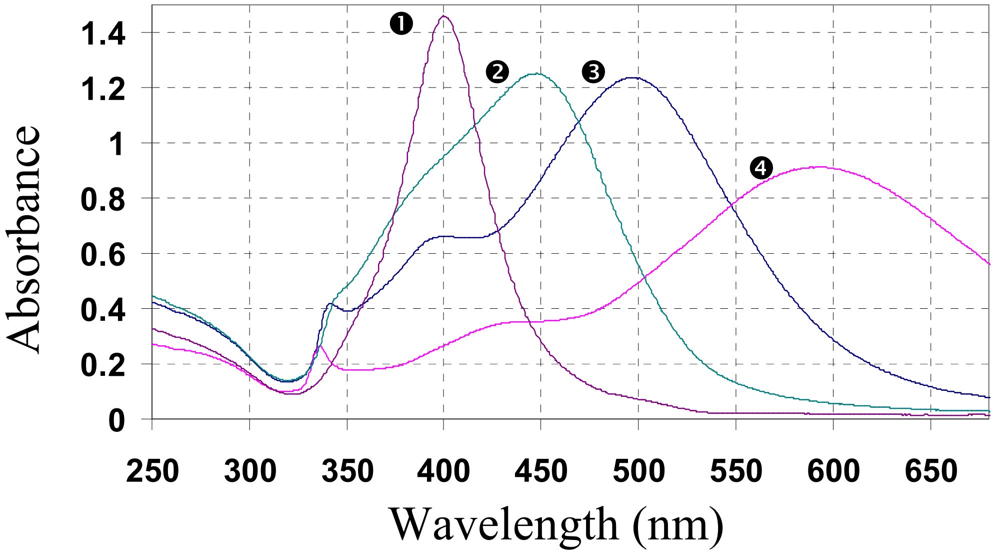

Figure S6. UV-vis spectra of samples prepared with ❶ 3.9×10^{-6} M, ❷ 3.3×10^{-6} M, ❸ 2.3×10^{-6} M and ❹ 1.4×10^{-6} M KBr added in one stage and aged prior to fine-tuning showing changes in out-of-plane quadrupole resonance at 330-340 nm

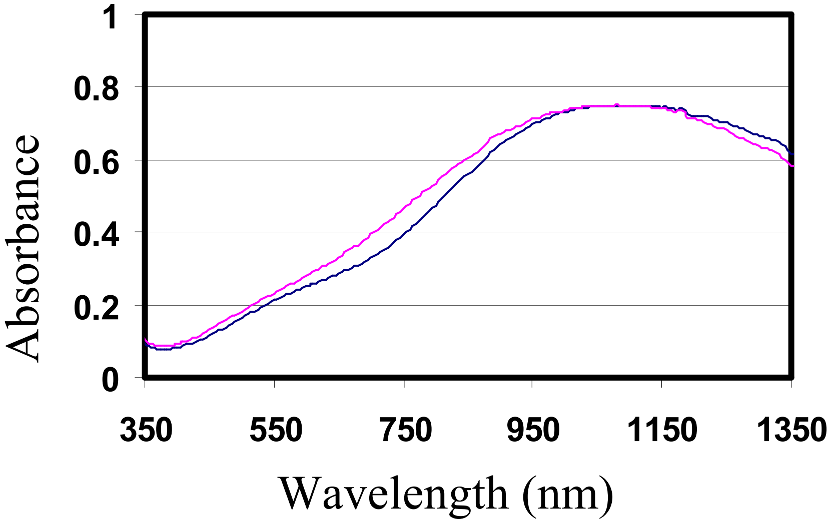

Figure S7. UV-vis-NIR spectra of AgNPRs prepared with large amounts of chloride. KCl concentration is ca. 0.2×10^{-3} M.

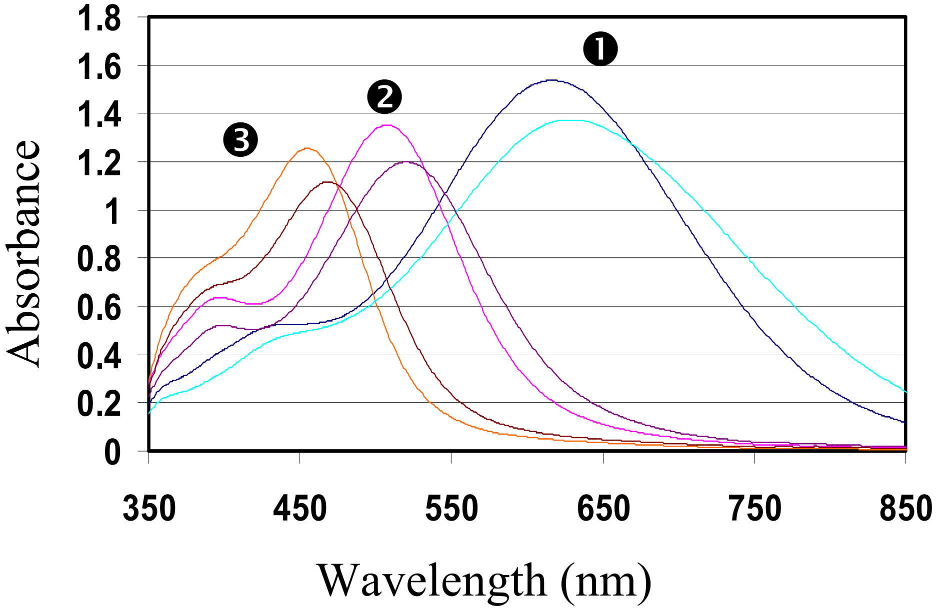

Figure S8. Comparison of UV-vis spectra of samples prepared with KBr with those prepared with the same concentrations of dodecyltrimethylammonium bromide (DTAB). In each three couples of spectra, bromide samples have higher intensity, whereas spectra of DTAB samples are noticeably more broad and red-shifted relative to bromide samples. ❶ – 1.3×10^{-6} M; ❷ – 2×10^{-6} M; ❸ – 2.7×10^{-6} M.

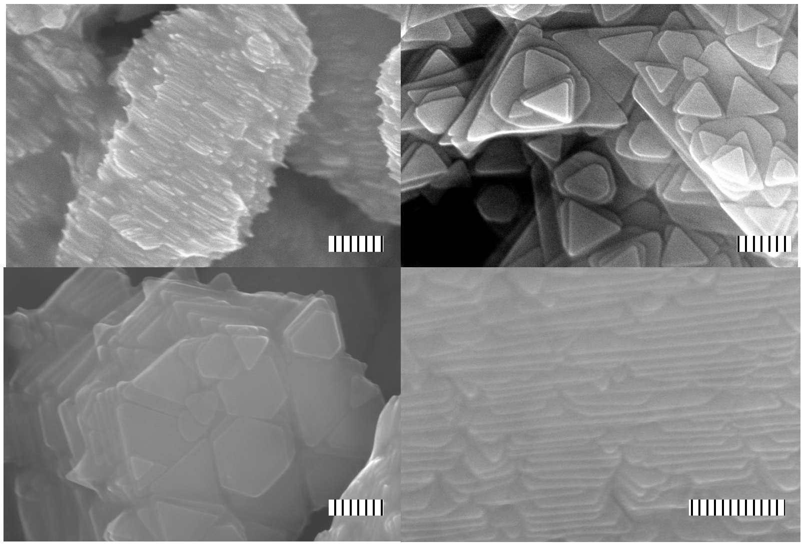

Figure S9. Scanning electron microscopy images of AgNPRs prepared using the direct formation route with KCl (1.4×10^{-4} M) as an enlarging agent. Scale bars are 200nm for all images. Representative IR spectra of AgNPRs imaged are shown in Figure S7.

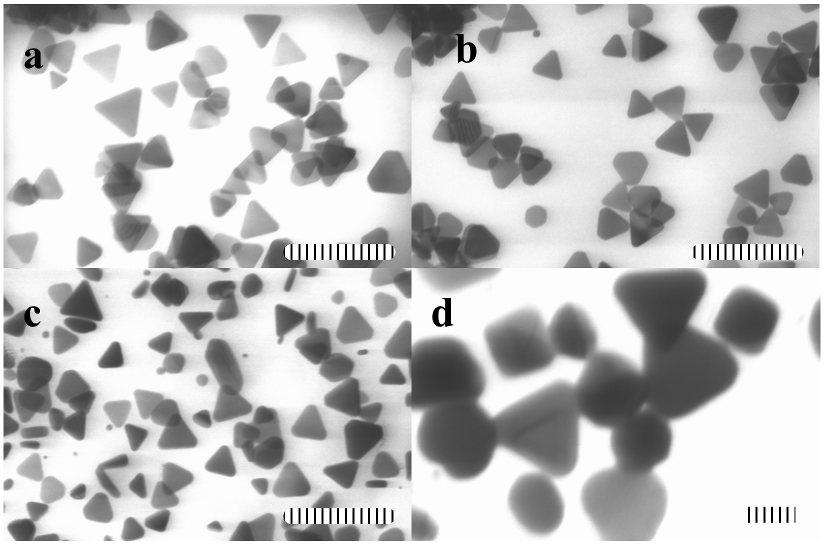

Figure S10. TEM images representative of AgNPRs prepared with bromide via the direct formation method. **a)** 6.5×10^{-7} M; **b)** 1.3×10^{-6} M; **c)** 2×10^{-6} M; d) 3.2×10^{-5} M KBr. Scale bars are 200nm for all images.