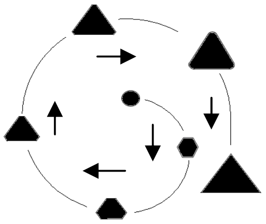
Supplemental Information

The shape evolution of photomorphic silver nanoparticles (AgNPs) was noticed in electron microscope images of samples prepared at various light excitation times and is depicted in Scheme S1. A comprehensive study was then conducted to elucidate the shape response that these particles had to light, as a function of time, using the following methods, images and spectra.



Scheme S1. The Shape Directed Growth of Photomorphic Silver Nanoparticles from Discs to Prisms.

Experimental Procedures. All solutions were prepared following the protocol reported in our previous paper.[1] All reagents were sourced from Sigma-Aldrich and used without any further preparation. The reagent concentrations were 50 μM $AgNO_3$, 200 μM Na_3Citrate, 200 μM $NaBH_4$ and 50 μM 4,4'-(phenylphosphinidene) bis(benzenesulfonic acid) dipotassium salt hydrate. Solutions were made in glass flasks to a total volume of 100 mL with reverse osmosis water. We cleaned all associated glassware for a minimum of 10 minutes with 10% HNO_3 wash. This was then followed by five rinses with DI water. The solutions were prepared using 4 hrs (±1 sec) of photodevelopment time in a Rayonet photochemical reaction chamber using sixteen 5750 Angstrom bulbs to produce photomorphic silver nanoparticles. Alternatively, the particles were driven to photo-ablation by continued photodevelopment for 6 hours. The synthesis of the 4 hour photodeveloped AgNPs was followed by 24 hrs of dark exposure for the conversion of light to dark-transformed particles.

TEI/SEM sample preparation. Transmitted electron images were collected using a JEOL 7500FA scanning electron microscope. A single drop with a volume of 8μL of the various nanoparticle suspensions were dried onto 200mesh TEM grids with a carbon support film (Agar Scientific). The dried preparations were then rinsed with EtOH and dried before being mounted on the appropriate SEM holder and placed in the SEM.

Transmitted electron images were collected in bright field mode at an accelerating voltage of 30kv with the specimen set at an 8mm working distance. These prepared samples were analysed within 2 hrs to avoid shape degradation.

Representative TEM Images (Size Analysis).

The particles were imaged for size determination as shown in Figure 2. The images were analysed using the software package Image ProPlus® (Version 6, MediaCybernetics) to determine the particle sizes.

Representative TEM Images (Shape Analysis).

The TEM images gave representative shape distributions of the AgNPs (Figure S1). Optical images are also shown as the insets for these samples. The color used for depicting the various particle shapes for the schematic in Figure 1 of the communication came from these images.

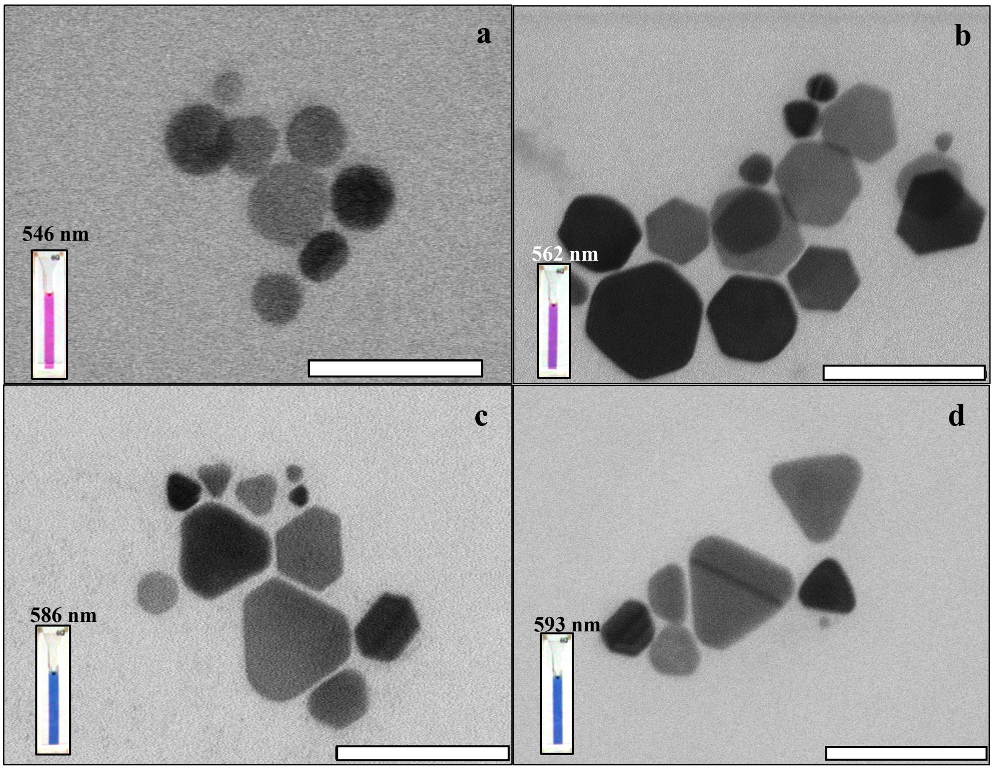


Figure S1. TEI and optical images of a) dark-transformed solution to b) 2 min, c) 8min, and d) 16 minutes of light excitation. The number shown is the position of the λ $_{max}$ of the in-plane dipoles of the solutions.

Light excitation longer than 16 minutes did not stop the photoconversion of the AgNPs in the solution (Figure S2). The sample solution was subjected to 120 minutes of light excitation. The in-plane dipole SPRB maximum was positioned at 611 nm after this exposure time. The significance of this continued red-shifting is beyond the scope and focus of this communication, but it does successfully answer what happens to solutions that are photodeveloped for excitation times longer than 16 minutes. It is logical to think that the tip corners of the particles sharpen with longer excitation times, thus greater red-shifting would be expected.

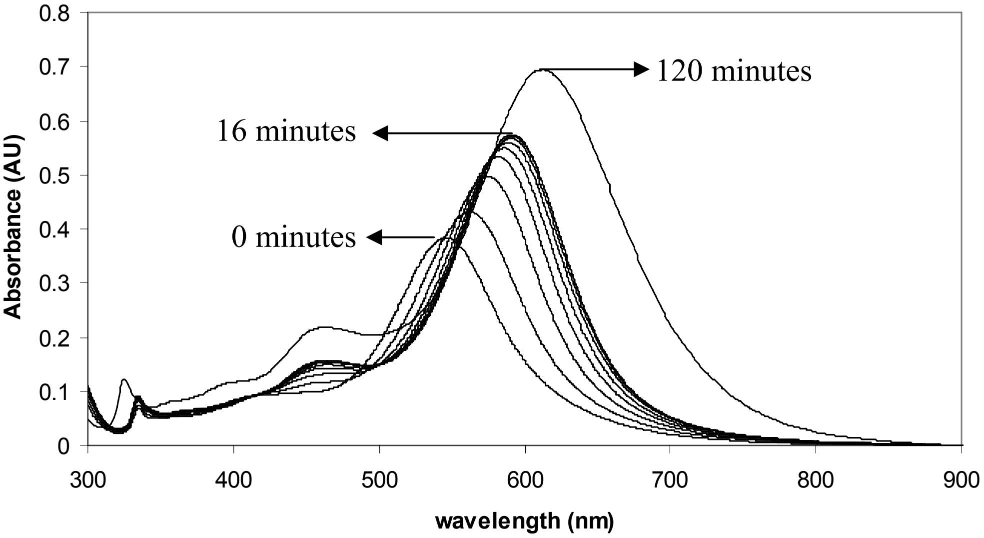


Figure S2. The overlapping spectra of a solution light excited for 0, 2, 4, 6, 8, 10, 12, 14, 16 and 120 minutes. The continued light excitation of solutions for 120 minutes caused a greater red-shift of the in-plane dipole SPRB compared to solutions that were irradiated for short timeframes.

Size Analysis of Transforming Particles

The sizes of prism-shaped particles are typically reported in the literature by side length measurements. However, we found that measuring side lengths was not practical with the numerous non-prism shapes that were developed. The sizes of the AgNPs were instead measured by height of the particles observed in the TEM images by measuring orthogonally from the flat base of the AgNPs to its top. The average sizes and standard errors are reported in **Table S1**.

Table S1. The absorption of λ_{max} and the average AgNP heights at these wavelengths.

λ_{max} (nm)	Average height (nm)	Standard Error (nm)
546	25	±1.2
562	36	±2.2
575	40	±2.1
586	50	±2.8
592	53	±2.1

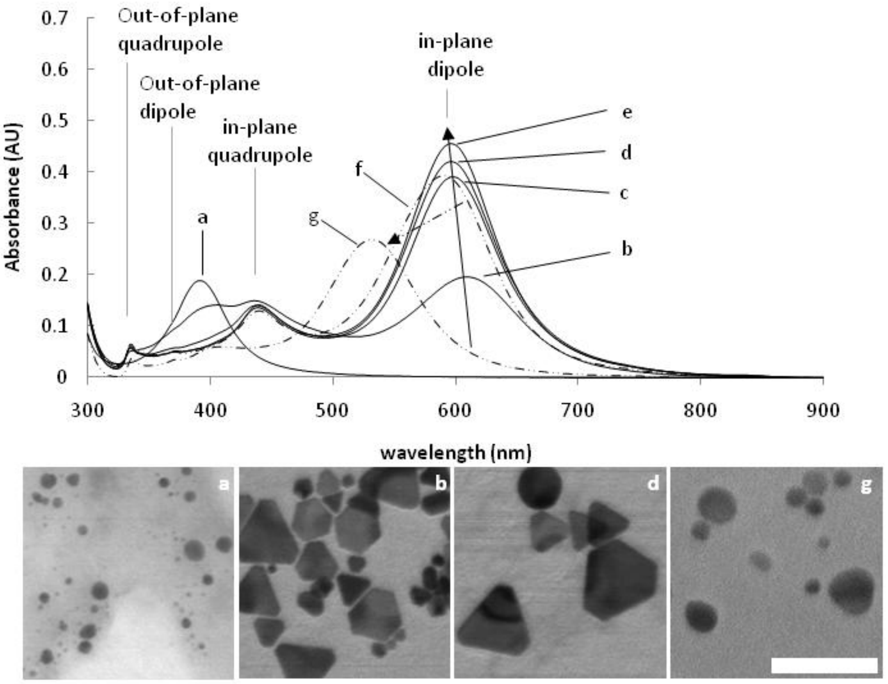


Fig. S3. The averaged UV-vis spectra of five photodeveloping solutions of AgNPs at irradiation times of 0, 1, 2, 3, 4, 5 and 6 hours (a-g, respectively). The solid black arrow indicates the direction of the developing in-plane dipole SPRBs during photoconversion, while the dotted arrows indicate the blue-shifting caused by photo-ablation. The position of λ max for the samples (a-g) during the time intervals are at 393, 609, 598, 597, 597, 591 and 531 nm, respectively. The TEM images are from the photodeveloping solutions of AgNPs at irradiation times of 0, 1, 4 and 6 hours (a, b, d and g). The scale bar is equal to 100 nm.

The photodevelopment characteristics of the AgNPs

The photoconversion of colloid spheres to prisms prepared via this synthesis method have a shape development which is characterisable by UV-vis and TEM analysis (Fig. S3).[2, 3] The plotted UV-vis spectral data are the average of five solutions that were photodeveloped separately. Initially, the UV-vis spectra have a single peak corresponding to that of spherical colloids peaking at ca. 393 nm. The initial colloidal peak eventually disappeared during the photoconversion process. Four peaks gradually appeared and increased in absorbance during the first 4 hours of photodevelopment. These peaks correspond to the in-plane dipole, in-plane quadrupole, out-of-plane dipole and out-of-plane quadrupole surface plasmon resonance bands (SPRB) associated with prism-shaped AgNPs. Prism-shaped particles have three tip corners which greatly enhances UV-vis absorption.[4-6] The in-plane dipole SPRB decreased in absorbance and slightly blue-shifted between 4 and 5 hours of photodevelopment. The UV-vis spectrum of the 6 hour photodeveloped solution had the in-plane dipole SPRB blue-shift and the entire spectral profile decreased in absorbance. The timeframe for these results were typical, however, the onset of this appreciable blue-shifting can be observed for solutions of identical chemical composition from 5 to 8 hrs of photodevelopment due to temperature variations and the distance the photodeveloping solutions are from the bulbs.

In Fig. S3, the shapes associated with the UV-vis spectra can be observed. The TEM images show that the initially synthesised particles are small spherical colloids. The initial synthesis method produced two populations of small colloids with average diameter sizes of 5 ± 1 nm and 14 ±11 nm. A few small colloid prisms with sharp tips were infrequently observed in TEM images without photoconversion. The smaller of the two populations of the initially synthesised colloids decreased in population during the photoconversion process. The smaller population of initially synthesised 5 nm colloids become negligible, while the larger 14 nm population were still observed; however, many of the particles in this size range grew to prism and hexagon shapes. The Mirkin research group has reported in the literature that colloid particles in the 2 to 6 nm size range are more susceptible to oxidation than the 10 nm size range.[7] Larger hexagon and prism shaped particles (42 ±5 nm) appeared in the TEM images after 1 hour of photodevelopment and are responsible for the absorbance at 609 and ca. 434 nm. The majority of observed nanoparticles in the TEM images after 4 hours of photodevelopment were hexagon and prism shapes (47 ± 10 nm), similar to those that appeared after 1 hour of photodevelopment. Some initial seed colloids remained in the solution throughout the entire synthesis but were infrequently observed. The shape of the majority of the particles in the 6 hour photodeveloped solution was disc-plates (35 ± 10 nm). These disc-shaped particles exhibit an in-plane dipole SPRB peak at 531 nm. The small spherical colloidal nanoparticles (17 ± 4 nm), similar to those observed in the 0 and 1 hour TEM images, reappeared. The extinction band that re-emerges at ca. 400 nm in the 6 hour UV-vis spectrum was attributed to the increased concentration of these small colloids.

The addition of Citrate of Photo-ablated Particles

The equivalent of 200 µM of trisodium citrate $_{(aq)}$ was added to a 1 mL solution of photo-ablated AgNPs. Then the solution was illuminated with 575 nm for 30 minutes **(Fig. S4)**. The in-plane dipole SPRB shifted as plotted in the figure insert. The TEM images revealed that the shape oriented growth mechanism was obeyed as the photo-ablated discs transformed to prisms.

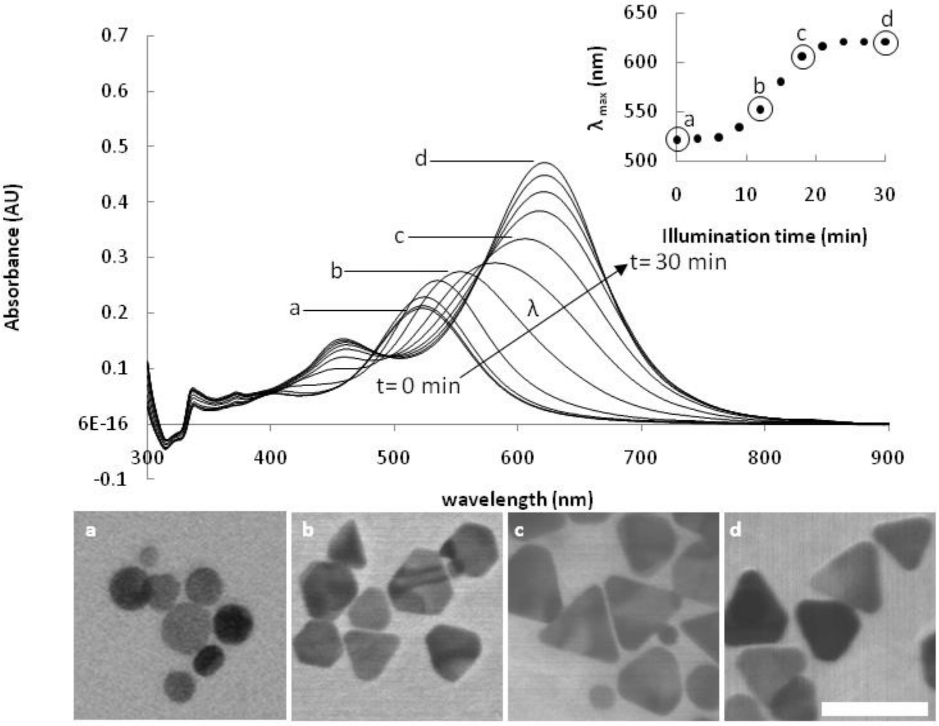


Fig. S4. UV-vis spectra of photo-ablated colloidal solutions taken after addition of 200 µM equivalent trisodium citrate and 0, 3, 6, 9, 15, 18, 21, 24, 27 and 30 minutes of 575 nm light exposure. The absorption of λ max of the in-plane dipole SPRBs are at 522, 523, 535, 553, 581, 606, 617, 621, 621 and 621 nm, respectively. TEM images of citrate treated photo-ablated colloids after 0, 12, 18 and 30 minutes of 575 nm light exposure.

The addition of 40 µM Citrate to Photo-ablated Nanoparticles and Their Response to Light Excitation.

The equivalent of 40 µM of freshly prepared citrate was added to a 1 mL solution of photo-ablated AgNPs. Then the solution was illuminated with 575 nm light for 200 minutes **(Fig. S5)**. During the first 40 minutes of light excitation the in-plane dipole spectra red-shifted **(Fig. S5a)**. A further 160 minutes of light exposure caused a blue-shift in the in-plane dipole as the spectra reverted back to the initial product **(Fig. S5b)**. A plot of λ_{max} more clearly shows the rate of change that occurred to the spectra as a function of light excitation time after the addition of the citrate **(Fig. S5c)**.

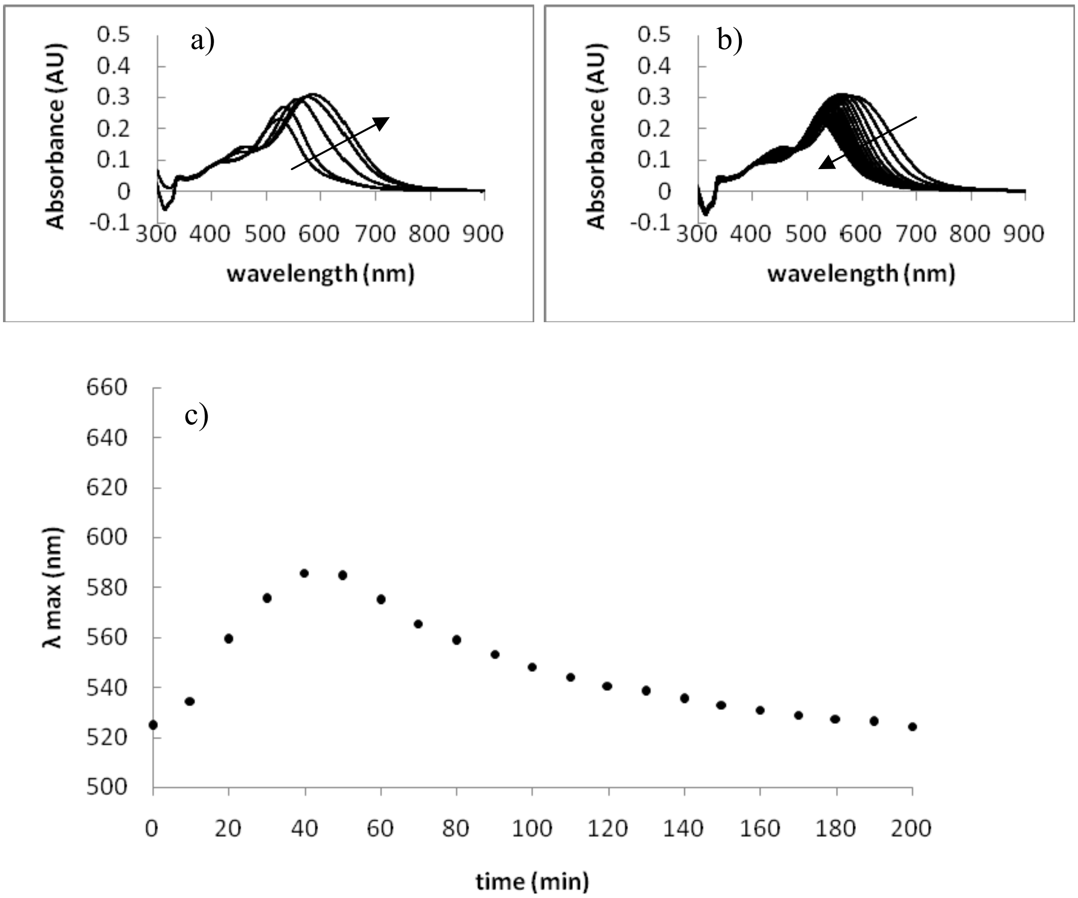


Fig. S5. a) The UV-vis spectra for the first 40 minutes of light excitation after the addition of 40 μM citrate. The arrow indicates the direction the in-plane dipole bands red-shifted. The measurements were recorded at 10 minute intervals at 0, 10, 20, 30 and 40 minutes of light exposure. b) The UV-vis for the continuation of light excitation from 50 to 200 minutes. The arrow indicates the blue-shifting of the in-plane dipole SPRB associated with light exposure during this time. c) The plotted values of λ_{max} position versus light excitation time.

References

1. G. P. Lee, A. I. Minett, P. C. Innis and G. G. Wallace, *J. Mater. Chem.*, 2009, **19**, 8294-8298.
2. X. Wu, P. Redmond, H. Liu, Y. Chen, M. Steigerwald and L. Brus, *J. Am. Chem. Soc.*, 2008, **130**, 9500–9506.
3. R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, *Science*, 2001, **294**, 1901-1903.
4. L. M. Liz-Marzan, *Materials Today*, 2004, **7**, 26 - 31.
5. P. Mulvaney, *Langmuir*, 1996, **12**, 788 - 800.
6. J. E. Millstone, S. J. Hurst, G. S. Metraux, J. I. Cutler and C. A. Mirkin, *Small*, 2009, **5**, 646 - 664.
7. C. Xue, G. Metraux, J. Millstone and C. Mirkin, *J. Am. Chem. Soc.*, 2008, **130**, 8337 - 8344.