Supporting Information for

Color-coordinated approach to the flow synthesis of silver nanoparticles with custom morphologies

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Contents

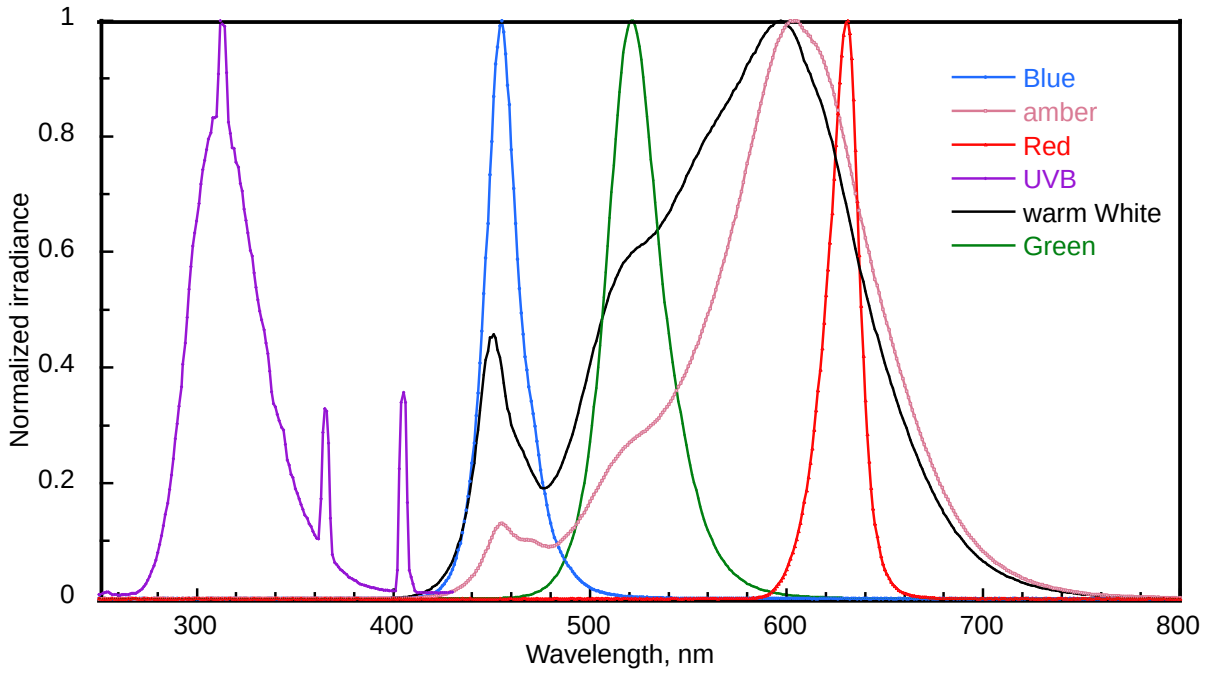

Fig. S1 Normalized lamp spectra. The UVB lamp is of the fluorescent type and all others are LED. Digital data courtesy of Luzchem Research, Inc. Additional lamps data can be found at: https://luzchem.com/pages/exposure-standards

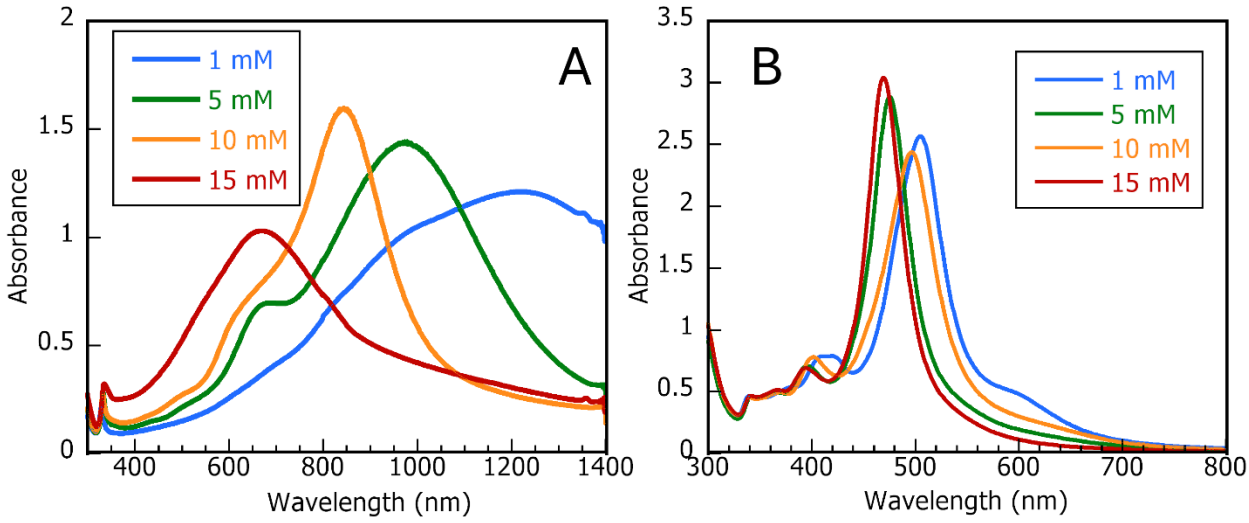

Fig. S2 Absorbance spectra of batch-scale AgNPs made using 1-15 mM of citrate. Legends indicates the [citrate] used to synthesize each batch of AgNPs. A) UV-Vis-NIR absorbance spectra of tAgNPs following 48h of 635 nm irradiation using a red WPI. B) UV-Vis absorbance spectra of dAgNPs following 24h of 450 nm irradiation using a blue WPI. See Figure S4 for images of AgNP batches and batch-scale illumination set up.

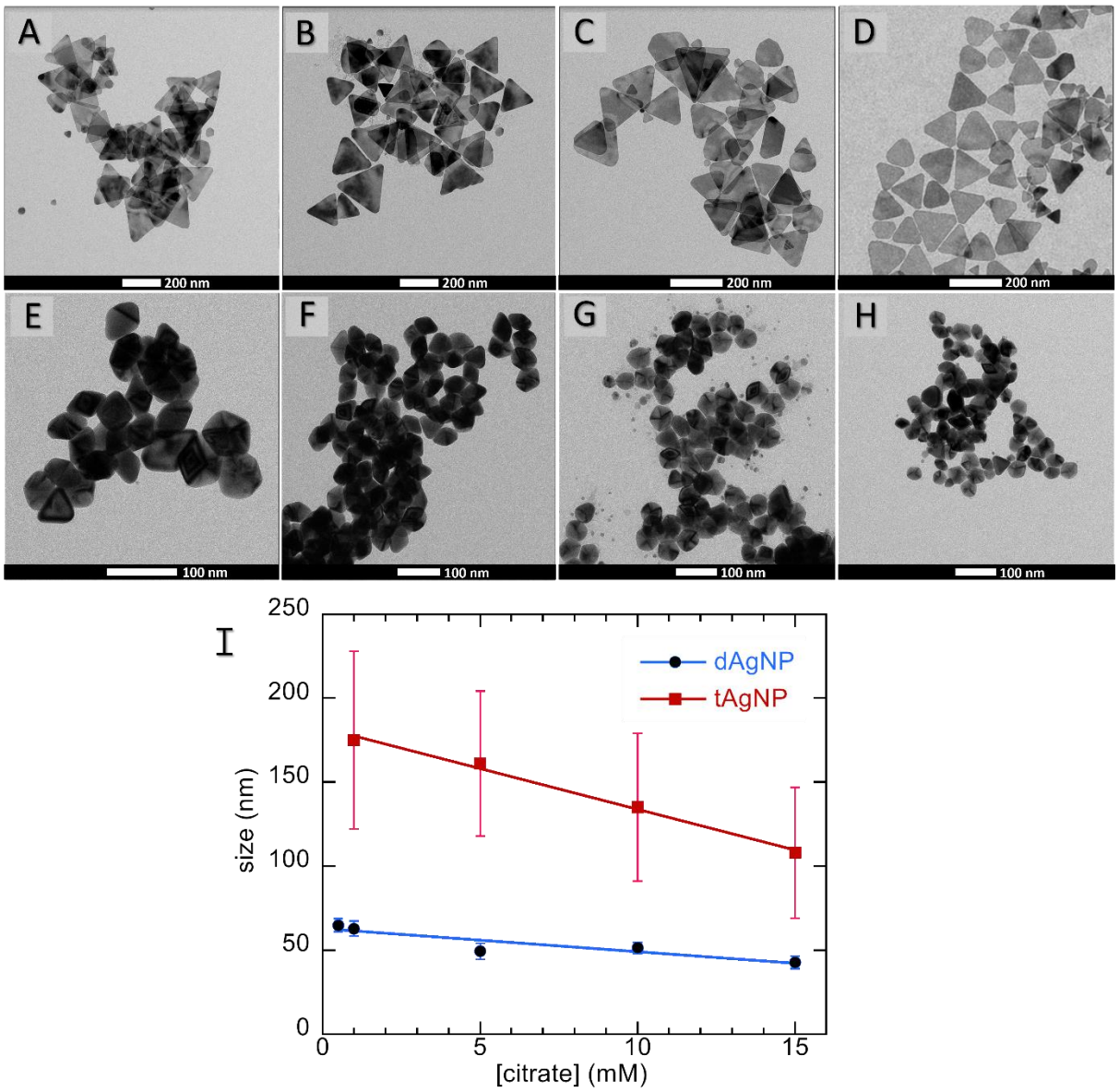

Fig. S3 TEM images of triangular (A-D), and decahedral (E-H) AgNPs, and corresponding size distributions for different [citrate] (I). Bars in the size plot represent standard deviation. Images correspond to the batch-scale syntheses of AgNPs using 1 mM (A,E), 5 mM (B,F), 10 mM (C,G), and 15 mM (D, H) of citrate. White scale bars represent 200 nm for A-D, and 100 nm for E-H.

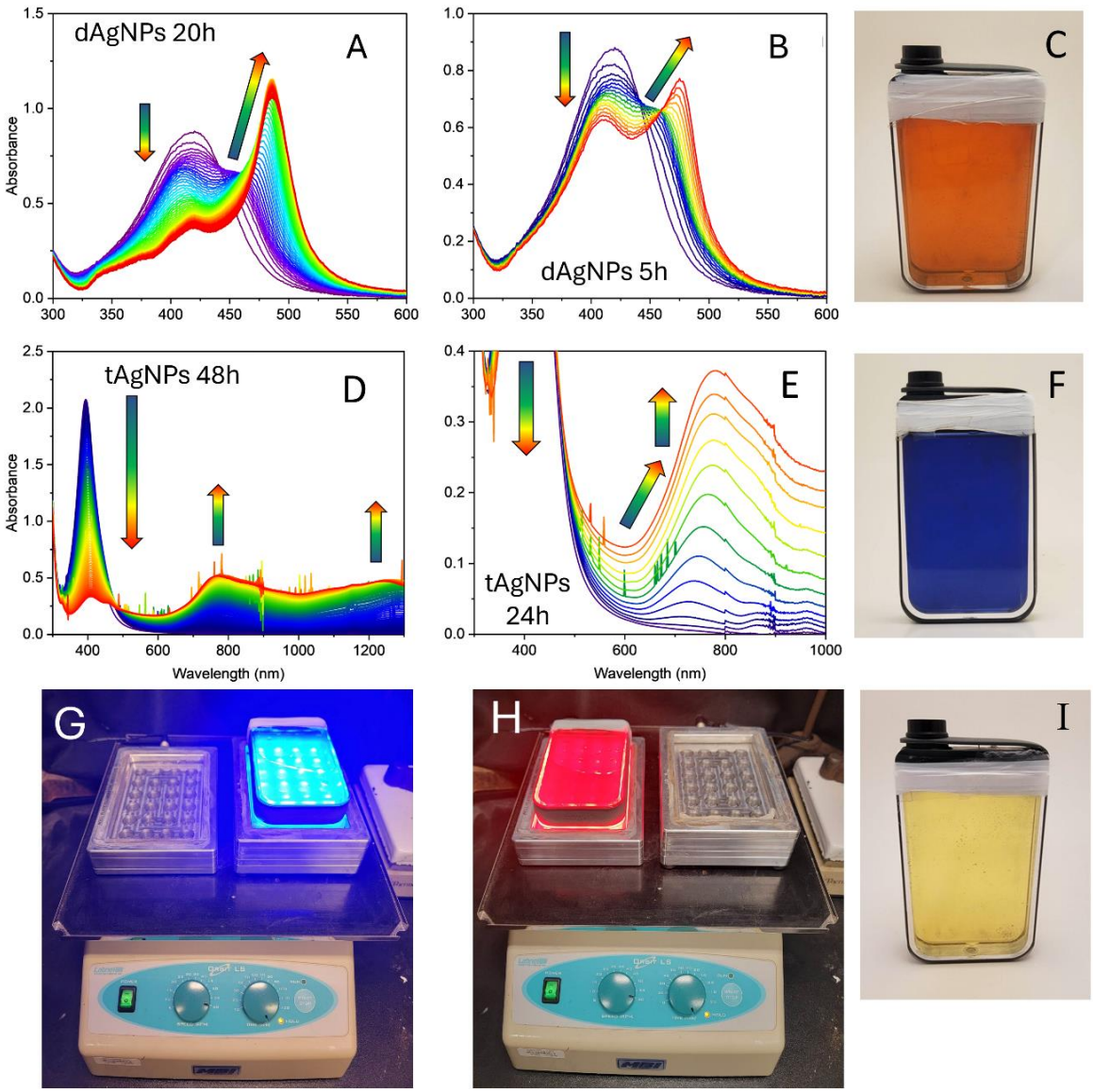

Fig. S4 Top row: UV-Vis absorbance shift over time of dAgNPs as particles grow under 450 nm batch-scale illumination for (A) 20h and (B) 5h. The final dAgNP suspension is shown in panel C. Middle row: UV-Vis-NIR absorbance shift of tAgNPs after (D) 48h, and (E) 24h of 635 nm batch-scale illumination. The final AgNP suspension is shown in F. Plots B and E were included to give a closer view of the "pushing" effect early in the reactions. Purple curves correspond to early timepoints, and shift to red as time progresses. Each trace is taken after 20 minutes of illumination in A&B, every 30 minutes in C, and every 2 hours in D. G and H show the 24 LED well-plate illuminators used for the batch-scale reactions, emitting at 450 nm (G, dAgNPs) and 635 nm (H, tAgNPs). Panel I shows the initial seed solution before illumination. The flasks used were Rabbit Leak-Free Discreet Flask (Black) - R4-06138 3.25" x 1.2" x 6" from Amazon.

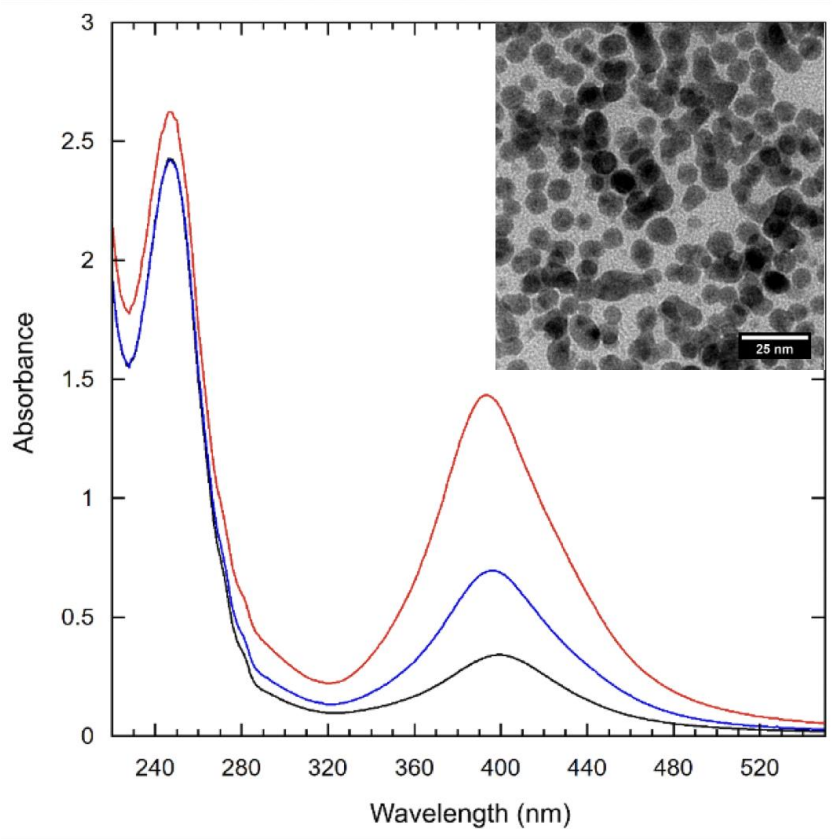

Fig. S5 UV-Vis absorbance spectra of bottle 3 seeds the day of synthesis (black), 6 days post synthesis (blue), and 14 days post synthesis (red). Inset: Selected TEM image of Bottle 3 seeds taken 16 days post-synthesis. Slight adjustments to contrast and brightness have been made for clarity

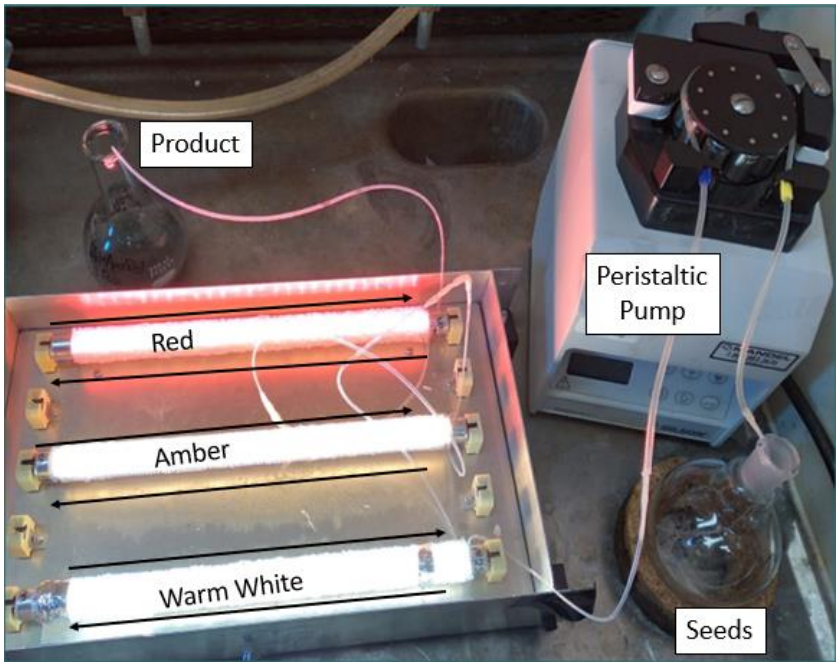

Fig. S6 In-Line setup of Warm White – Amber – Red LED (arranged bottom to top in picture) series used for tAgNP synthesis. System is uncovered for photo, but during synthesis aluminum foil is used to cover lamps, seed flask, and product flask. Black arrows represent net flow direction through double-wrapped lamps.

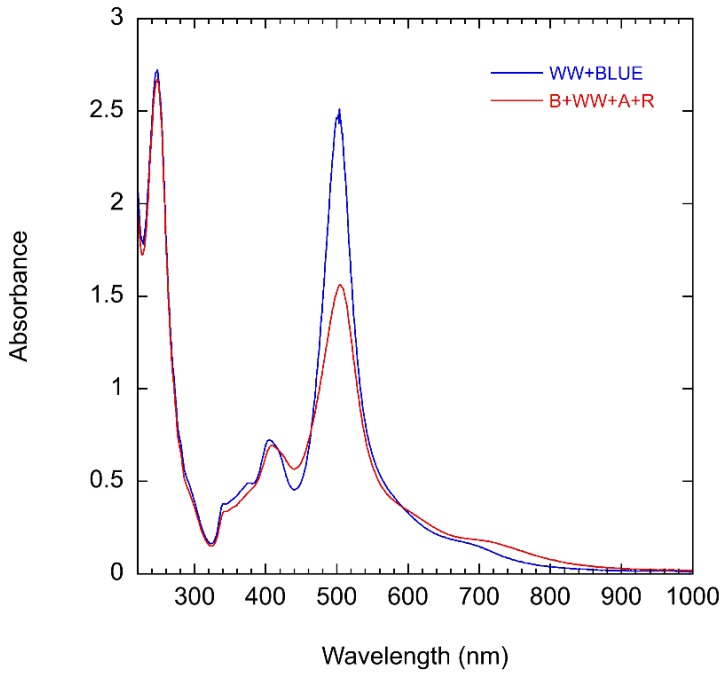

Fig. S7 Spectra collected from flowing a solution of AgNP seeds (green) slowly through a series of blue, warm white, amber, and red LEDs. A sample was taken after blue + warm white (shown in black), and after passing through all four lamps.

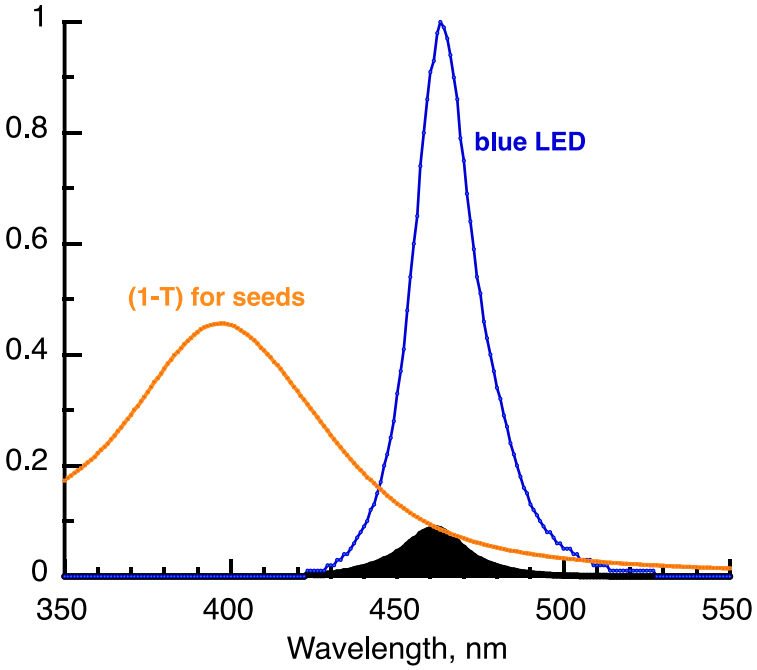

Fig. S8 Overlap of the normalized irradiance for the blue LED (blue) with the spectrum for the seed solution displayed as (1-T) for a 1.5 mm optical path (orange, not normalized) and the overlap of the two spectra shown in solid black. Comparison of the integrated irradiance with the overlap spectrum shows that the sample absorbs 8.6 % od the lamp emission. A similar calculation for a 1 cm optical path shows that 43.3 % of the LED light would be absorbed. LED emission spectrum, courtesy of Luzchem Research, Inc.

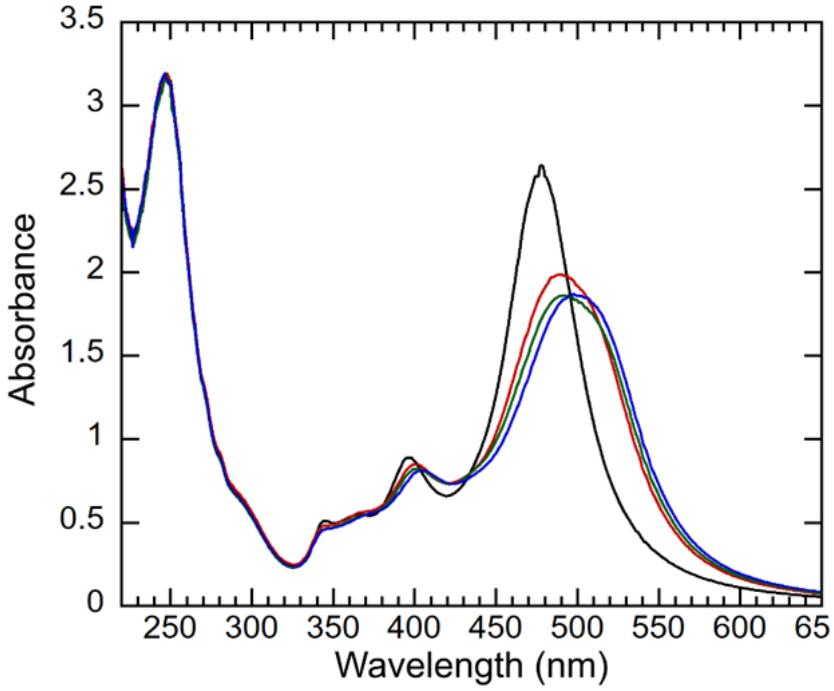

Fig. S9 Spectra collected from a solution of dAgNPs (black) being pumped slowly (recycling) through a series of 4 single wrapped green LEDs for exposure times of 3.5 hours (red), 10.8 hours (green), and 31 hours (blue).

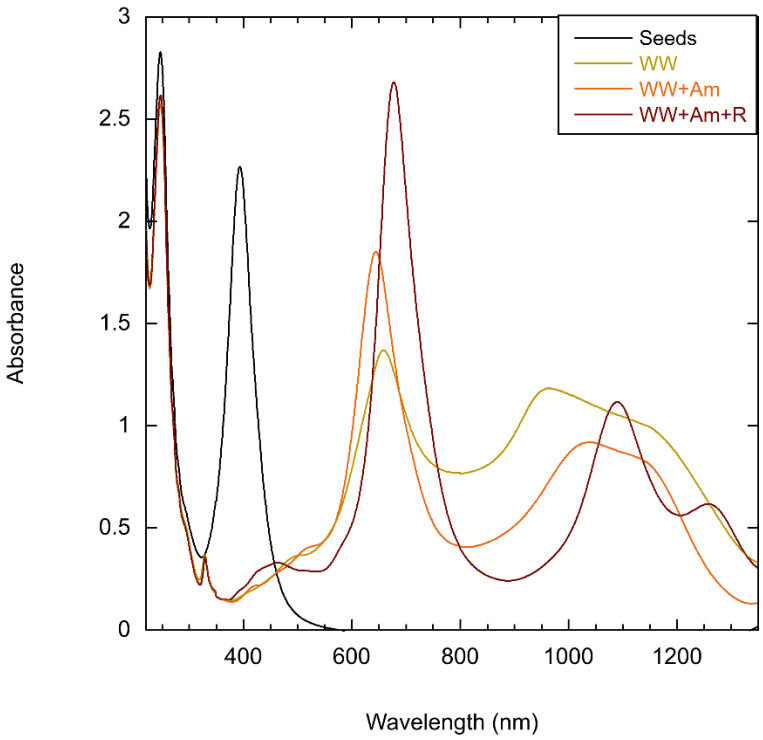

Fig. S10 Spectra collected from a modified warm white – amber – red LED series in which in-line sample valves were installed between each lamp and no temperature control was applied to any lamps. The displayed spectra were measured using the CARY-7000 the same day they were collected. At the time of collection for these samples, the maximum temperatures of the lamps were measured to be as follows: 61 °C (warm white), 67 °C (amber), 48 °C (red). The starting AgNP seed solution, shown in black, was pumped in a single pass through warm white (yellow), warm white and amber (orange), or warm white, amber, and red (red).

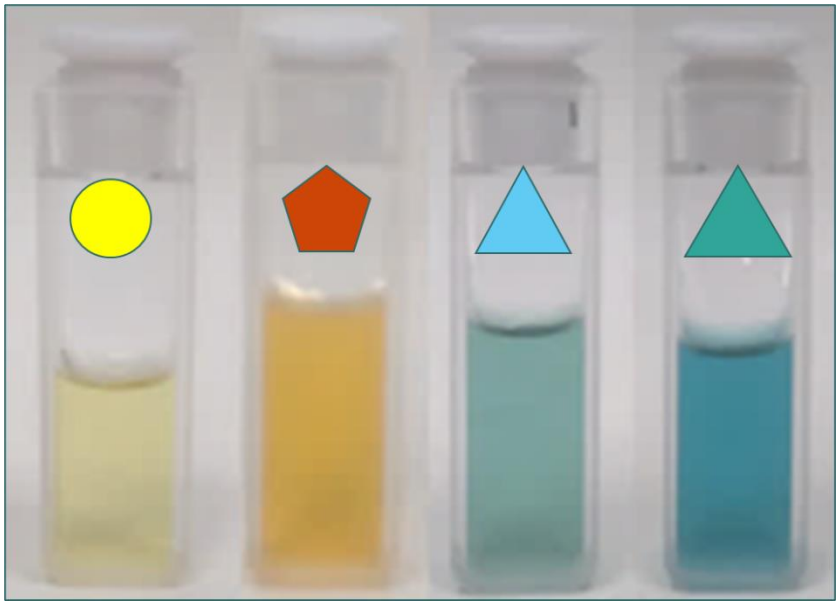

Fig. S11 Cuvettes containing solutions of synthesized AgNP seeds, decahedra, and triangles formed from warm white – amber and warm white – amber – red series. Two-dimensional representations of the major structure present in each solution are associated to each cuvette.

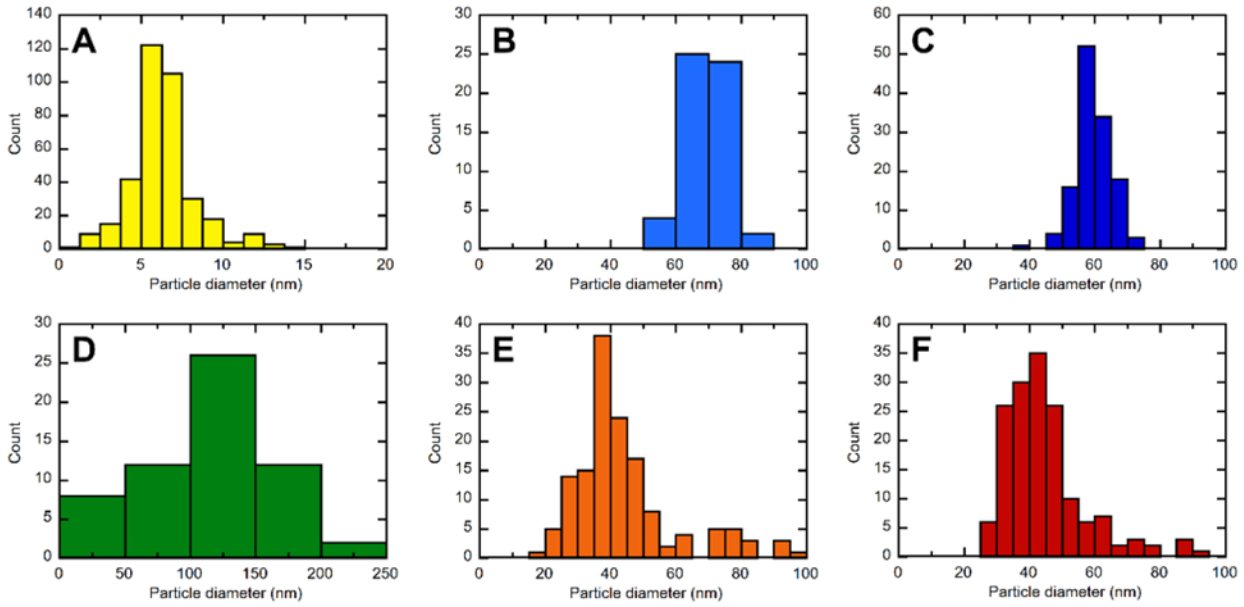

Fig. S12 Histograms of nanostructure dimensions obtained from measuring TEM images of (A) nanoparticle seeds, (B) decahedra made from flow recycle through blue LED, (C) decahedra made in a single pass through blue LED, (D) triangles made from slow flow recycle through green LED, (E) triangles made from a single pass through warm white + amber LED, and (F) triangles made from a single pass through warm white + amber + red LED. A minimum of 50 particles were counted for each histogram, with over 150 particles counted for graphs A, E, and F. Graphs have been formatted such that the highest bin contains a minimum of 20 particles. Seed diameters (A) were measured taking the particles as spheres. Decahedra (B, C) and triangles (D-F) were measured from the center of one side across to the opposite vertex, assuming facial symmetry. The average particle diameter and standard deviation of each were measured to be as follows: (A) 6 ± 2 nm, (B) 69 ± 7 nm (C) 56 ± 7 nm, (D) 110 ± 41 nm, (E) 47 ± 22 nm, and (F) 47 ± 19 nm

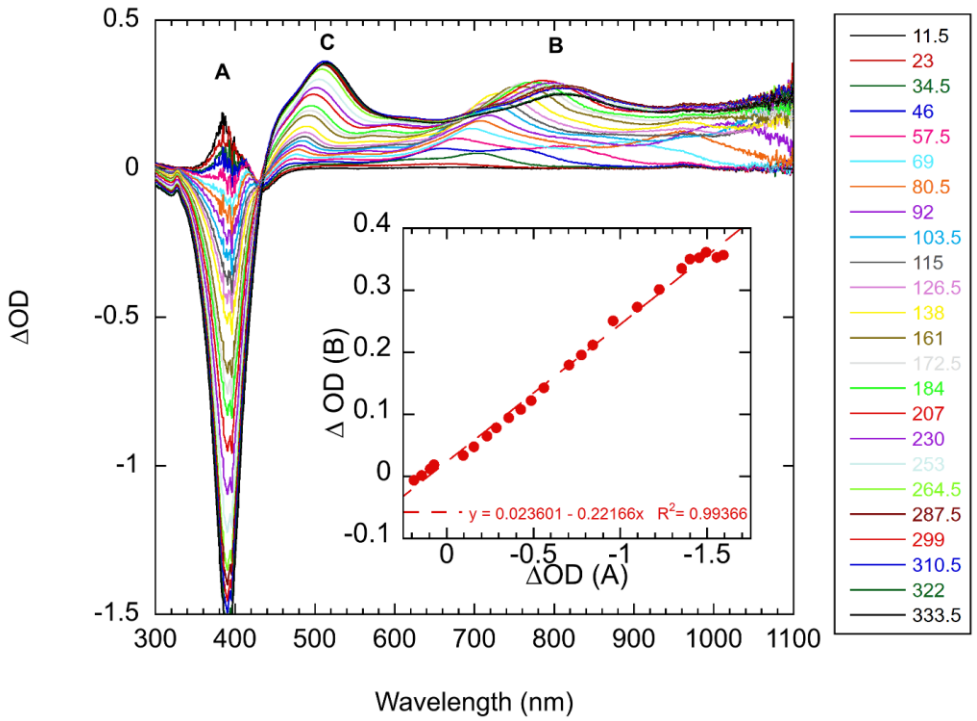

Fig. S13 Difference in optical density (ΔOD) in AgNP absorbance with respect to starting seed solution. Spectral measurements were taken using a flow cuvette during recycling of the solution through a double wrapped warm white LED. Intervals display the approximate cumulative irradiation time in minutes. Dead volume per cycle = 7 mL. This graph uses the same data and reflects the same experiment as Figure 10 in the main text. *Inset:* Change in optical density of region B peak with respect to that of the region A peak.

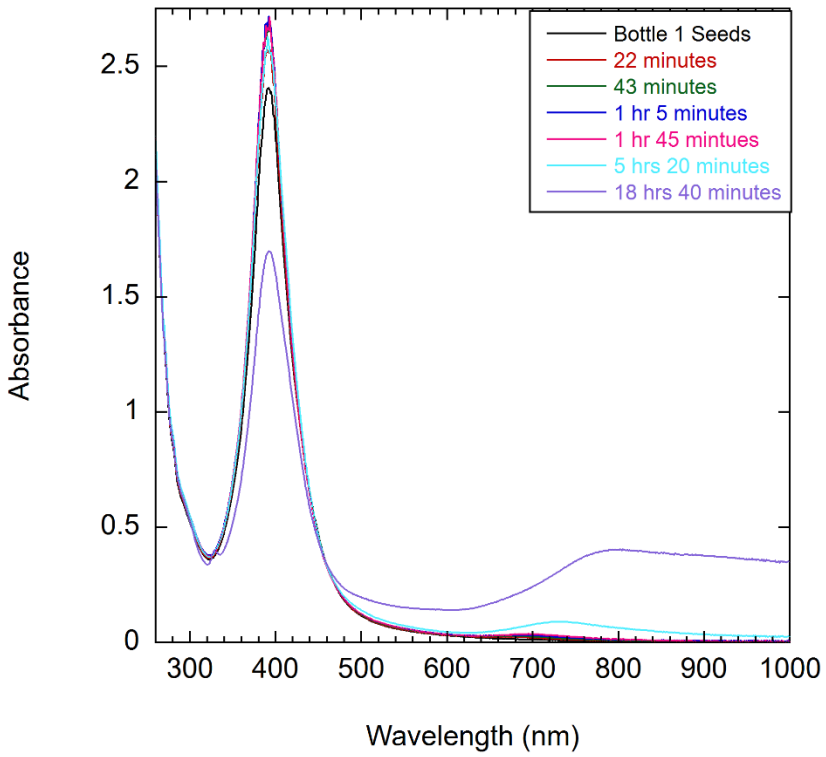

Fig. S14 Long-term flow recycling of seeds through a wrapped red LED. Note that no peak forms in the dAgNP region, but that transformation progress to tAgNP is extremely slow and the absorbance peak is poorly defined.

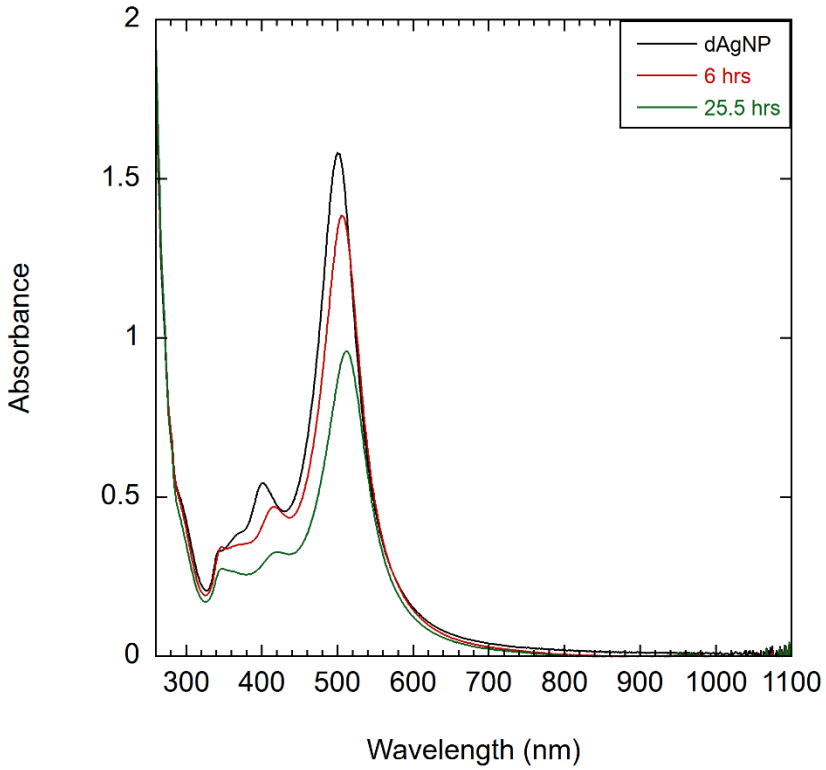

Fig. S15 dAgNP irradiated by a 406 nm lamp. A small portion of the lamp was wrapped with a single layer of Teflon tubing and dAgNP were cycled through with minimal dead volume as a proof of concept for the stability of dAgNP when irradiated with a higher energy wavelength.

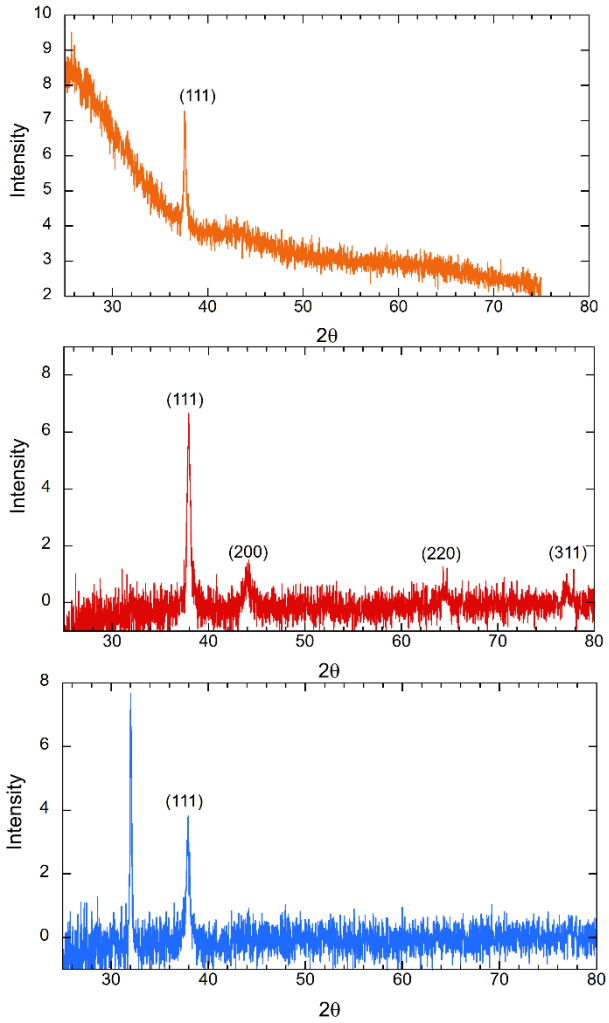

Fig. S16 XRD results of seeds (orange), dAgNP (red), and tAgNP (blue). For the dAgNP and tAgNP plots, the X-ray diffractograms of the baseline (glass microscope cover) have been subtracted. Planes were identified based on analysis of the angles at which maxima occurred and by comparison to published reference spectra of tAgNP and dAgNP [Ref. 2 and 34 in the main text].