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Supporting Information

Low-Energy, Nanoparticle Reshaping for Large-Area, Patterned, Plasmonic Nanocomposites

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Table of Contents

SI 1.0 Relation between L, d, [Au] and [CTAB] for Isovolumetric transformation2
SI 2.0 Estimate of Aspect Ratio via L-LSPR (nm)4
SI 3.0 Reshaping Rate5
SI 4.0 Heat-Induced Chemical Reshaping: L-LSPR (nm) Evolution for Varying Temperatures and Environments
SI 5.0 Heat-Induced Chemical Reshaping: Degradation of PVA7
SI 6.0 Heat-Induced Chemical Reshaping: Arrhenius behavior of reshaping rate for AR, CTAB concentration and T <tg< td=""></tg<>
SI 7.0 Activation Energy of Chemically Induced Reshaping Relative to Curvature Induced Reshaping9
SI 8.0 AuNR Reshaping in Propylene Carbonate at 220 $^{\circ}\mathrm{C}$ 10
SI 9.0 Heat-Induced Chemical Reshaping: Confirmation of Oxidation with Solution Studies11
SI 10.0 Heat-Induced Chemical Reshaping: Au salt reduction in PVA12
SI 11.0 Heat-Induced Chemical Reshaping: Effect of Matrix and Graft on Reshaping13
SI 12.0 Models for estimating the rate of change in aspect ratio14
SI 13.0 Thermal Equilibrium Model17
SI 14.0 Changing Temperature of PVA film Under Broadband Irradiation
SI 15.0 Photo-Induced Chemical Reshaping: Sample Details for Fig 4b22
SI 16.0 Photo-Induced Chemical Reshaping: Shape and volume distrubtion of AuNRs23
SI 17.0 Photo-Induced Chemical Reshaping: AuNR Dissolution of PS-grafted AuNRs in poly(styrene) (PS)24
SI 18.0 Photo-Induced Chemical Reshaping: Arrhenius behavior of reshaping rate for $T < T_g$ 25
SI 19.0 Photo-Induced Chemical Reshaping: AuNR Etching Under Broadband Irradiation26
SI 20.0 Photo-Induced Chemical Reshaping: AuCl ₄ PVA NP formation27
SI 21.0 Photo-Induced Chemical Reshaping: In-plane Narrowing of Optical Pattern
SI 22.0 References

SI 1.0 Relation between L, d, [Au] and [CTAB] for Isovolumetric transformation

In order to evaluate the validity of making the assumption that $\Delta V = 0$, theoretical calculations of potential dimensions were calculated. A new monolayer of Au (added thickness equivalent to nearest neighbor distance, 0.288 nm) deposited from the ends to each side would result in an adjusted diameter and length as such:

$$d = d_o + 0.576 (nm)$$
$$L = \frac{V}{\pi (\frac{d}{2})^2}$$

Where d is the diameter of the AuNR with a monolayer added to each side, d_0 is the previous diameter, L is the new length associated with the diameter d, and V is the conserved volume of the AuNR. This calculation was reiterated until an aspect ratio of 1 was reached and plotted with respect to experimentally determined dimensions in Figure 2.



Figure S1. Example Size Analysis from thermal reshaping of 50 nM CTAB coated AuNRs of L/d = 2.8. Histograms of length (a), width (b), and volume (c) illustrating change in AuNR dimension while conservation of volume.

In addition to estimating theoretical AuNR dimensions with conserved volume, the number of gold atoms migrating from ends to side was estimated (which is directly related to the number of gold atoms being oxidized, [Au_{ox}])

$$[Au_{ox}] = \frac{4}{a^3} [AuNR] [\pi(\frac{d}{2})^2 (L_o - L)]$$

Where *a* is the unit cell length (0.408 nm for bulk gold), 4 is the number of atoms per unit cell (4 for FCC lattice) *d* is the original diameter (nm), L_0 is the original length (nm), *L* is the final length (nm), and *D* is the final diameter resulting in an isotropic structure. Using the original dimensions as well as the difference in length that renders an isotropic structure, it is possible to estimate the number of gold atoms in a nanorod that migrate during reshaping. When this number is multiplied by the total gold nanorod concentration, *[AuNR]*, the total concentration of gold atoms undergoing oxidation can thus be estimated and put into context with the concentration of CTAB.

SI 2.0 Estimate of Aspect Ratio via L-LSPR (nm)



Figure S2. Estimation of aspect ratio (AR) via L-LSPR when AuNRs are dispersed in water. Line is the emperical linear relationship between AR and L-LSPR taken from reference (gray squares). ¹ After reshaping, PVA-AuNR films were dissolved in water (red circles) and UV-Vis spectroscopy as well as TEM image analysis was conducted for particle characterization. The blue shift of L-LSPR and corresponding decreasing in AR determined from TEM image analysis show good agreement with the emperical linearlity.

SI 3.0 Reshaping Rate

Given the impractic clity of measuring reshaping rate through physical quantification of AuNR dimension via TEM image analysis over every AuNR system, the rate of geometric shape change was instead quantified through tracking the L-LSPR peak. Under conditions of volume conservation, it is possible to equate shifts in L-LSPR directly to aspect ratio (See SI 2.0) and conclusions on dimension were directly inferred for most cases and confirmed in selected systems. The L-LSPR was thus put into units of energy (eV) and the shift over time in units of Δ (L-LSPR)/t = eV / s.

To calculate these rates, L-LSPR was plotted in units of eV and initial reshaping slopes were calculated as such

$$\frac{\frac{hc}{\lambda} - \frac{hc}{\lambda_o}}{t} = \Delta LSPR \text{ (eV) rate}$$

Where λ is L-LSPR peak wavelength (nm), λ_0 is initial L-LSPR peak wavelength (nm), and t is time (s)





Figure S3. The L-LSPR vs time graphs of AuNRs in PVA (~100 μ m thick, 50 nM AuNR, AR ~2.8) as a function of varying temperature (a) and environment. The films in (a) (>2CTAB:1Au, ca. 50 nM AuNR) were subject to ambient environment from temperatures varying from 90 °C to 140 °C. The films in (b) (>2CTAB:1Au, ca. 50 nM) were subject to varying flow pressures of N₂ in a controlled temperature chamber at 140 °C. All films used in b were subject to identical aging conditions outside of environment, and were aged for 4 days.



Figure S4. AuNR reshaping effects with respect to varying atmospheric condition. L-LSPR evolution as a function of time for a single AuNR/PVA film (>2CTAB:1Au, ca. 50 nM AuNR) subject to varying flow rates of N₂ at 140 °C. By replacing oxygen with nitrogen, it is seen that even at elevated temperatures, reshaping is significantly retarded. These AuNRs were aged four days under inert (Ar) conditions.

SI 5.0 Heat-Induced Chemical Reshaping: Degradation of PVA



Figure S5. Degradation of PVA. The PVA (wt% black line, derivative in wt% red dashed line) used in this study displayed an onset of degradation begins at ca. 200 °C, in agreement with prior literature. ^{2,3} The drop off around 100 °C is indicative of removal of residual water followed by degradation through condensation (ca. 250 °C) and oxidation (ca. 380 °C & 450 °C).



SI 6.0 Heat-Induced Chemical Reshaping: Arrhenius behavior of reshaping rate for AR, CTAB concentration and T<Tg

Figure S6. Arrhenhius plots of AuNRs under varying parameters. a) For all AuNRs of varying CTAB content, AR, and volume, it is seen that the reshaping rate below T_g falls under expected values according to extrapolated values from Arrhenius fits, suggesting further impact of matrix mechanical properties on reshaping. Reshaping rate of AuNRs with varying CTAB content (b) and ARs (c). The purple stars and pink pentagons show samples of AuNR of L/d = 3.3 and L/d = 6 respectively, with less than critical CTAB concentration while the red triangles have an AR of L/d = 2.8 and approximately 2CTAB to 1 Au atom oxidation. It is seen that there exists identical slopes (despite absolute rates of reshaping) suggesting the same mechanism of reshaping occurs over all AuNR volumes, ARs, and surfactant concentration.

SI 7.0 Activation Energy of Chemically Induced Reshaping Relative to Curvature Induced Reshaping



Figure S7. Taylor *et. al* previously demonstrated there exists a relationship between curvature and activation energy for thermally induced reshaping.⁹ Using this relationship, the activation energies of AuNRs used in this study are plotted versus predictions for thermal reshaping as a function of AR. It is seen that across all ARs, the activation energy of thermally induced chemically reshaped AuNRs remains consistent.

Taylor *et. al.*⁹ previously established a relationship curvature and activation energy:

$$E_A = \frac{2\left(\frac{L}{2}\right)C}{AR^2 + 1}$$

where $C = 2.6 \times 10^8$ eV/m, L is length, and AR is aspect ratio. It was seen throughout all aspect ratios used in this study, the activation energy for a given form of reshaping was consistently the same value.

SI 8.0 AuNR Reshaping in Propylene Carbonate at 220 °C



Figure S8. Thermally induced reshaping of AuNRs (L/d = ca. 2.8, ca. 1 nM,, [CTAB] < 0.05 mM.) Upon replacing polymer matrix serving as a reducing agent with a thermally stable surrounding medium (propylene carbonate), it is seen that AuNRs initially undergo thermally induced reshaping at much slower rates (ca. 8 ev/10⁵s at 220 °C) than rates that incorporating chemically facilitated reshaping (ca. 80 eV/10⁵s at 180 °C). Additionally, at this elevated temperatures (220 °C) without reductant, it is seen that AuNRs eventually are oxidized in presence of CTAB which can be confirmed by the increasing intensity around 300nm which is the characteristic peak from gold salt.

SI 9.0 Heat-Induced Chemical Reshaping: Confirmation of Oxidation with Solution Studies In order to confirm oxidation of the gold nanorods, solution studies of varying bromine / chrlorine content as well as varying oxygen levels were evaluated. Solutions were heated at 90 °C in 100 mM CTAB (1 nM AuNR) in ambient condition and dissolution was evaluated by measuring intensity peak shifts at the L-LSPR as well as monitoring absorption values at the Au(I) peak at approximately 265 nm.



Figure S9. Solution studies exploring the effects of varying parameters such as oxygen and bromine content. a) A typical UV-Vis spectra showing the eventual dissappearance of the AuNR (L/d ~2.8) L-LSPR (through etching) and formation of the Au(I) peak at 262 nm. b) L-LSPR evolution as a function of time comparing CTAB and CTAC grafts as well as Argon and ambient environments. c) The effect of etching rate as a function of CTAB:Au ratio, showing peak values at 100CTAB:1Au atom oxidation.

It was found that AuNRs in a solution of bromide (CTAB) and oxygen were most readily oxidized, where AuNRs in inert environments (Ar) and with chloride (CTAC) were the least readily oxidized/etched. After 15 minutes, Au NRs dispersed in CTAB were readily dissolved in solution compared to AuNRs in CTAC solution & inert environments (Ar) were more likely to sediment than reshape. The L-LSPR of these solutions were monitored through UV-Vis for as long as a signal could be acquired. It can also be seen that increasing CTAB concentration to render a ratio of 200 CTAB: 1 Au also resulted in a maximum etching rate. The 100 fold increase in CTAB necessary to reach maximum etching is likely associated with CTAB micelle formation in water.

SI 10.0 Heat-Induced Chemical Reshaping: Au salt reduction in PVA



Figure S10. Heat inducted AuNP formation from gold salt in PVA. It was found after ten minutes at 180 °C, gold salt dispersed in PVA made AuNPs. UV-Vis spectra evolution shows gold salt (red curve), gold clusters (blue line), and gold nanoparticles. This is in good agreement with the polyol method previously reported in literature.^{4,5}



SI 11.0 Heat-Induced Chemical Reshaping: Effect of Matrix and Graft on Reshaping

Figure S11. Effect of ligands and matrix on chemical reshaping of AuNRs. A typical CTAB stabilized AuNR- PVA film (L/d = 2.8, ca. 50 μ m, [AuNR] ca. 50 nM) was compared with a) PEG(5k)-AuNRs in PVA and b) PS(53k) functionalized AuNRs in PS film. The films were subject to 150 °C heating up to an hour. Compared to those of CTAB coated AuNRs in PVA, it is seen that shape change occurs at significantly lower rates.

SI 12.0 Models for estimating the rate of change in aspect ratio

A comprehensive analytical solution for isovolumetric transformation from rod (or ellipsoid) to a sphere can not be postulated with simple functions. Analytical approach is developed for transformation of cylinder to sphere and numerical approach is developed for transformation of spherocylinder, cylinder and ellipsoid to sphere below. Both provide the same general relationship between the initial rate of change of aspect ratio (AR = α), the AR and particle volume.



Figure S12. Postulate the intersecting volume between a sphere of radius, r, and a cylinder of radius, R, with length, $L = 2\alpha R$, whose centroids are coincident.

To derive an analytical solution, consider the intersecting volume between a sphere of radius, r, and a cylinder of radius, R, with length, L = 2 α R, whose centroids are coincident and where α is the aspect ratio, AR. Assuming the transformation is isovolumetric, $V = \left(\frac{R}{r}\right)^2 = \left(\frac{3}{2}\alpha\right)^{-\frac{2}{3}}$. To calculated the fractional volume δ V/V, that has to be transported to transformation from a cylinder to a sphere, the volume of intersection, V_I, and volume to be transported δ V, are:⁶

$$V_I = \frac{4}{3}\pi r^3 - \frac{4}{3}\pi (r^2 - R^2)^{\frac{3}{2}},$$
(1)

$$\delta V = V - V_I = \frac{4}{3}\pi (r^2 - R^2)^{\frac{3}{2}}$$
(2)

$$\frac{\delta V}{V} = \frac{\frac{4}{3}\pi (r^2 - R^2)^{\frac{3}{2}}}{\frac{4}{3}\pi r^3} = \left[1 - \left(\frac{R}{r}\right)^2\right]^{\frac{3}{2}} = \left[1 - \left(\frac{3}{2}\alpha\right)^{-\frac{2}{3}}\right]^{\frac{3}{2}} = f(\alpha)$$
(3)

Note that $\delta V/V$ does not approach zero as $\alpha \rightarrow 1$, rather it approaches ~0.1. This is due to the assumption that the initial structure is a truncated cylindar of radius R, which does not smoothly transform to a sphere nor have the same volume of a sphere when r=R. This issue is considered

acceptable given the goal of establishing a general relationship between the initial rate of change of aspect ratio (AR = α), AR and volume, rather than developing a quantitative model.

Since the initial reshaping rate can be described as the initial rate of change of the fraction volume, $\frac{\delta V}{V}$, then:

$$\frac{d}{dt}\left(\frac{\delta V}{V}\right) = \frac{d}{dt}f(\alpha) \tag{4}$$

$$V^{-1}\frac{d(\delta V)}{dt} = f'(\alpha)\frac{d}{dt}(\alpha)$$
(5)

$$\frac{d}{dt}(\alpha) = (f'(\alpha) \cdot V)^{-1} \cdot \frac{d(\delta V)}{dt}$$
(6)

Note that the local volume transfer rate is constant (i.e. redox chemistry is uniformly occurring on all surfaces), then $\frac{d(\delta V)}{dt} = A$, a constant, and

$$f'(\alpha) = \left[\frac{\left(\frac{3}{2}\alpha\right)^{5/3}}{\left(1 - \left(\frac{3}{2}\alpha\right)^{-2/3}\right)}\right]$$
(7)

Therefore, the initial rate of changing aspect ratio can be described as a function of initial aspect ratio as:

$$\frac{d}{dt}(\alpha) \sim A V^{-1} \left[\frac{\left(\frac{3}{2}\alpha\right)^{5/3}}{\left(1 - \left(\frac{3}{2}\alpha\right)^{-2/3}\right)} \right]$$
(8)

Numerically, the transformation can also be modeled using the framework discussed in SI 1.0. Figure S13 summarizes the results of iteratively removing mass (Au monolayer) from all surfaces, and then depositing this mass on the particle sides. This simple mechanism reduces AR with iteration step.

Overall, both Eqn (8) and model results in Fig S13 show the initial reshaping rate should be greater with larger AR, and inversely related to particle volume.



Figure S13. a) Numerical solution of intersecting volume between ellipsoid/spherocylinder/cylinder and sphere as a function of initial aspect ratio(α). b) Numerical solution of rate changing aspect ratio as a function of initial aspect ratio (α).

SI 13.0 Thermal Equilibrium Model

The bulk temperature rise in the AuNR-PVA composite is modeled with a simple thermal equilibrium model:

$$m C_p \frac{d\Delta T}{dt} = Q_{in} - Q_{out} \tag{1}$$

$$Q_{out} = -hA(T - T_{\infty}) \tag{2}$$

where m is sample mass, C_p is heat capacity, Q_{in} is heat in, Q_{out} is heat out, and Q_{st} is the stored heat, hA is the lumped cooling constant, T is temperature, and T_{∞} is ambient temperature.

The relationship of ΔT vs power absorbed gives insight into the lumped constant, hA, such that at steady state, when $Q_{in} = Q_{out}$, this constant can be determined and is the inverse slope of ΔT vs power absorbed. After stopping irradiation the AuNR-PVA film, and $Q_{in} = 0$, it is possible to equate both equations 1 and 2 to further model the time dependent cooling. Using known sample dimensions and assuming PVA material properties, this thermal equilibrium model is used to determine:

$$\frac{d\Delta T}{dt} = \frac{-hA(T-T_{\infty})}{m C_{p}}$$

$$(3)$$

$$-hA[T - T_{inf}] = m C_{p} \frac{dT}{dt} = \rho V C_{p} \frac{dT}{dt}$$

$$Substituting [T - T_{inf}] = \theta; and \ \theta_{i} = [T_{i} - T_{inf}]:$$

$$-hA\theta dt = \rho V C_{p} d\theta$$

$$dt = -\frac{\rho V C_{p}}{hA\theta} d\theta$$

$$t = -\frac{\rho V C_{p}}{hA} \ln \left(\frac{\theta}{\theta i}\right) = \frac{\rho V C_{p}}{hA} \ln \left(\frac{\theta i}{\theta}\right)$$

$$(4)$$

It is seen in Figure 4a that the expected cooling of the film agrees with predicted values from classic models.

The Xe lamp used in this study was measured both with a Thor Labs powermeter (S302C) to estimate overall broadband power as well as experimentally calibrated at individual wavelengths

from 350 nm to 1100 nm to determine power output at each wavelength as displayed in Figure S14.

All AuNRs were embedded in ~0.2 cm³ of PVA. In order to determine the molarity of AuNRs in the film, the thickness of each film is measured using a micrometer. Using beer-lamberts law, $A_{\lambda} = \epsilon lc$, it is possible to determine the AuNR concentration from the experimentally measured UV-Vis spectra. The extinction coefficient is estimated from empirical studies previously determined as a function of AuNR dimension.¹ The absorbance value is taken at the optical density value of the L-LSPR and then extrapolated to give a certain concentration in molarity. From this value, an average AuNR number density and subsequent inter-particle interdistance can be calculated as follows:

$$\left(\frac{[AuNR]N_A}{.001}\right)^{-\frac{1}{3}}10^9 = IPD_{AuNR}$$

where [AuNR] is the molarity of AuNR [M], N_A is avagradro contant and IPD_{AuNR} is the average inter-particle distance of each AuNR (in nanometers).

Additionally, the average number of AuNRs being irradiated can be estimated as follows:

$$\left(\frac{[AuNR]N_A}{.001}\right) * \pi R^2 * tl = AuNR_{spot}$$

where [AuNR] is the molarity of AuNR [M], N_A is avagradro contant and R is the radius of light irradiation spot size [m], tl is the thickness of the irradiated film [m] and AuNR_{spot} is the average number of AuNRs irradiated

Using these approximations, the number of AuNRs in a given volume can be determined and subsequently used to estimate the average power absorbed per nanorod.

By experimentally measuring the power difference between a blank slide and a slide with an AuNR film, it is possible to determine the average power absorbed from the AuNR film, and this value can be divided by the total number of AuNRs in the light spot size, leading to estimates of ca. 10's pW/AuNR.

An alternative method to determine Q_{in} can also be done according to:

$$Q_{\rm in} = I_{\rm abs} \eta_{\rm NR}$$

Where I_{abs} is the intensity of light absorbed at each wavelength and η_{NR} is the fraction of energy absorbed that is transmitted to heat. Using this equation, power absorbed by the AuNRs was calculated and found to be in good agreement with experimentally determined results.



Figure S14. Calculation of Q_{in} Under the assumption of a photo-thermal efficiency close to one, the overall power absorbed in a typical film (AR ~ 2.8, 100 μ m, 50 nM AuNR) can be estimated, and through integration across the broadband spectra, a value of ca. 10's pW/AuNR was found.

Local Steady State Temperature Profile around Isolated AuNRs

Knowing each nanorod emits ca. pW of heat, it is possible to classically predict the local temperature profile expected at the surface of the each AuNR. Using spherical coordinates and assuming a roughly isotropic structure for each AuNR (effective radius calculated through: $(Vol_{AuNR}/(4p/3))^{1/3})$ a simple one dimensional analysis of heat transfer follows as:

$$q' = -kA \frac{dT}{dr}$$
where $A = 4\pi r^2$

$$\frac{dT}{dr} = -\frac{q'}{4\pi r^2 k}$$
 $T = \frac{q'}{4\pi r k} + C$

results in

where k is the thermal conductivity of PVA ($k_{PVA} \sim 0.2 \text{ W/mK}$), r is the radial distance from the surface of the AuNR, and L is the midpoint between two AuNRs

$$\Delta T = \frac{q'}{4\pi k} \left(\frac{1}{r} - \frac{1}{L}\right) = 0.001 \, K$$

To determine the temperature of the AuNR and the profile of the near surface region, all the parameters are known except for the interface thermal conductivity. It was previously demonstrated in the literature by Losego et. al.⁸ that the interface conductance of a gold surface ranged from ca. 34 MW/m²K to 65 MW/m²K for ligands interacting with the Au covalently to ionic or van der Waals. Using this as an estimated for interface conductance, the thermal model yields an estimate temperature rise of ca. 0.0007K - 0.0015 K for the optical power, PNC absorption spectra and molar absorptivity of the AuNRs. Assuming an average estimate of 50 MW/m²K, the temperature increase ca. 0.001K

It is useful to note that some experiments have demonstrated steam generation of AuNRs in water.^{9,10} However, the irradiation power density ca. 10^4 W/cm² in these experiments are 3-orders of magnitude greater than in ours (power density ca. 10 W/cm²).



SI 14.0 Changing Temperature of PVA film Under Broadband Irradiation

Figure S15. Given the electrically insulating and optically transparent nature of the PVA matrix, it is expected that the increase in temperature due to irradiation with broadband light to be negligable. As seen up to power densities of approximately 13 W/cm² the temperature increase less than 5 °C

	CTAB (mM)	AuNP (nM)	tl (μm)
Blue Triangle	50	60	180
Red Square	50	75	42
Blue Circle	5	126	47
Purple Diamond	0	257	47
Green Circle	5	80	65
Pink Circle	0.5	10	50
Orange Circle	0.5	100	58
Grey Circle	3.4	35	70
White Circle	0	31	100

SI 15.0 Photo-Induced Chemical Reshaping: Sample Details for Fig 4b

Table 1. Table of temperature increase vs power absorbed. Details from symbols showing varying CTAB molarity, gold nanostructure molarity, and thickness.

It is noted that regardless of film thickness, CTAB content, or AuNR molarity, the overall temperature increase seen in the composite is linear with overall power absorbed.



SI 16.0 Photo-Induced Chemical Reshaping: Shape and volume distrubtion of AuNRs

Figure S16. Isovolumetric Photo-chemical reshaping of AuNRs. AuNR films (L/d = 2.8, >2CTAB:1Au) irradiated with ca. 10 W/cm² light up to complete reshaping (15 minutes) in supporting Figure 5. While the length (a) decreased, and width (b) increased, the volume (c) remained unchanged. d) The average AuNR dimensions agree well with predicted L-LSPR peaks for conserved volume.

SI 17.0 Photo-Induced Chemical Reshaping: AuNR Dissolution of PS-grafted AuNRs in poly(styrene) (PS)



Figure S17. PS-AuNR (graft 10k) in PS (35k MW) matrix undergo etching without conservation of volume under broadband irradiation (AuNR L/d = 2.8, 50 nM AuNR, light power density 10 W/cm².) With the significantly lower molecular weight of the PS matrix and elevated temperatures (180 °C), it is hypothesized that etched salts will more readily diffuse away from the NR surface and conservation of volume becomes less feasible.

SI 18.0 Photo-Induced Chemical Reshaping: Arrhenius behavior of reshaping rate for $T < T_g$



Figure S18. Arrhenius plot of Photo-Induced Reshaping of AuNR (L/d ~ 2.8, ca. 50 nM AuNR, <2CTAB:1Au) in PVA. Much like heat induced reshaping trends, it is found that below the softening temperature of the matrix, reshaping rates fall significantly below predicted values extrapolated from Arrhenius fits. This is attributed to the subsequent confinement effects associated with the matrix. Nonetheless, it is seen that activation energies are similar, though slightly higher, in light activated processes as with thermally activated processes.



SI 19.0 Photo-Induced Chemical Reshaping: AuNR Etching Under Broadband Irradiation

Figure S19. Oxidation of AuNRs in presence of 0.05 M CTAB. The AuNR solution was kept in 1mm quartz cell and placed on a) quartz slide (no filter), b) glass slide (cut off light below 250 nm) c) 500nm long pass. a-c) The change in absorbance spectra. Shaded block indicates the range of wavelength which is filtered. The spectrum was taken every 10 min. The peak intenstiy decreases significantly on quartz slide indicating oxidation of AuNRs. e) Control experiment showing that the same solution annealed in oven at 45 °C does not show any sign of reshaping.





Figure S20. Reduction of AuCl4 via light assisted polyol process. a-c) 0.5 mM AuCl₄ in 100 um thick PVA film. The film was placed on a) quartz slide (no filter), b) glass slide (cut off light below 250 nm) c) 500nm long pass. Shaded block indicates the range of wavelength which is filtered. The spectrum was taken every 15 min. Initially, the film shows peak around 300 nm from AuCl₄. The peak intenstiy decreases as the reduction proceeds. As the AuNPs forms, overall peak increases back due to interband and intraband absorption from reduced Au. When the particlel size increases larger than 2nm, plasmon resonance peak emerged. The reduction was faster in a), no reduction in c). d-f) 0.5 mM AuCl4, 1.0 mM CTAB in 100 um thick PVA film. The film was placed on d) quartz slide , e) glass slide f) 500 nm long pass. The spectrum was taken every 15 min. In this case, the initial film shows the two peaks at 300 nm and 400 nm which are due to the formation of CTAB-AuCl₄ complex which also slowed down overall reduction rate. No reduction when 500 nm long pass filter was used.

Au(III) (AuCl₄) containing PVA film is seen here in to form Au clusters and nanoparticles within 15 min when illuminated with unfiltered or 300 nm long pass filtered Xe lamp. Films under irradiation reached ca. 70 °C However no nanoparticles form when illuminated with a 500 nm long pass filtered Xe lamp. Although AuNPs would inevitably form at elevated temperatures due to thermal processes, it is seen that upon implementing a 500 LP filter, such temperatures cannot be reached using photo-driven processes.



Figure S21. Au (0) formation through heat and light irradiation in a PVA matrix. In order to evaluate the reductive capabilities of PVA, gold salt in a PVA matrix was both heated and irradiated with light. It was confirmed that gold salt in the presences of PVA will form Au(0) (through emergence of an SPR indicative of gold nanoparticles)



SI 21.0 Photo-Induced Chemical Reshaping: In-plane Narrowing of Optical Pattern

Figure S22. Cross-section image of AuNR film. A cross sectional image of a AuNR Film (L/d \sim 2.8, 50 nM, ca. 400 mm) illustrating the heat diffusion profile and subsequent reshaping profile through thickness using broadband light.

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