Supplementary Information (SI) for Journal of Materials Chemistry C.


**Supporting information**

# Thermally Driven Resonance Tuning in Nanobipyramid Plasmonic Substrates

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## S1. Characterization of AuNBP

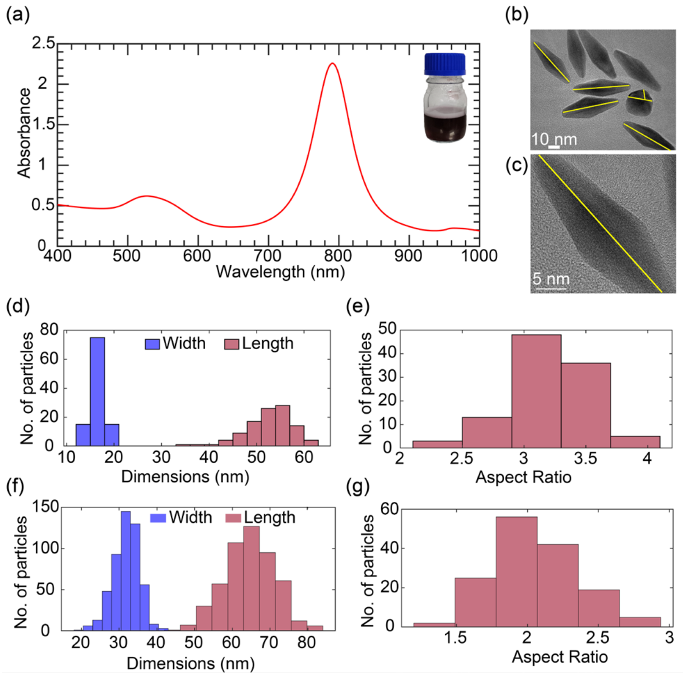


**Figure S1: Synthesis and characterization of AuNBP.** (a) UV-Visible spectrum of AuNBP. The inset shows the dark violet colour of AuNBP after synthesis. (b) & (c) shows the TEM images of the AuNBP at different magnifications. (d) AuNBP measurement distribution of length and width from TEM micrographs. (e) Aspect ratio (AR) distribution of the AuNBP calculated from TEM micrographs. (f) Length and width distribution of AuNBP from SEM image. (g) Aspect ratio distribution of AuNBP calculated from SEM images.

| Dimensions | Dimensions from SEM | Dimensions from TEM |
|---|---|---|
| **Length** | 64.5±6.5 nm | 52.6 nm ± 4.9 nm |
| **Width** | 31.9±3.4 nm | 16.5 ± 1.3 nm |
| **Aspect Ratio** | 2.02 | 3.2± 0.2 |
| **Radius of curvature** | | 6.8 ± 0.2 nm |

**Table S1: Dimensions of AuNBP**

## S2. Isothermal spectrums

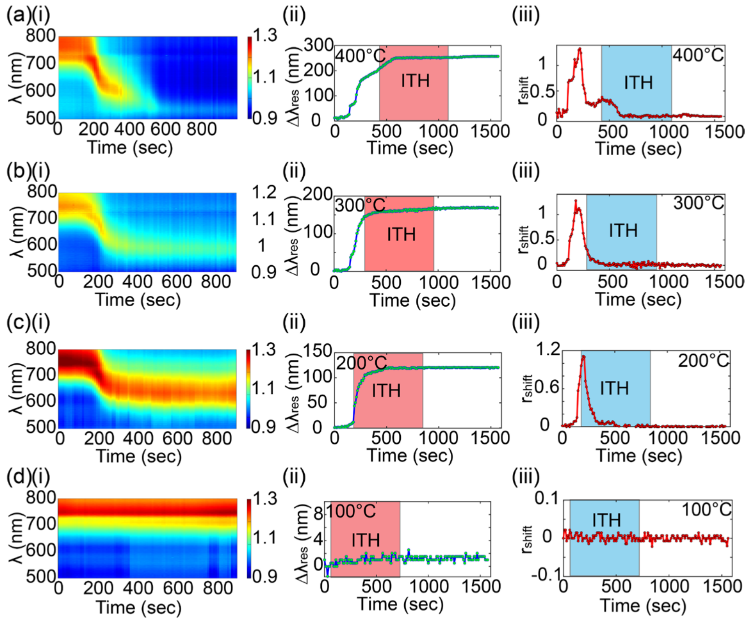


**Figure S2: *Real-time* spectrum of iso-thermal holding substrates.** (a, b, c, d) Shows the data set for isothermally heated substrates at 400°C, 300°C, 200°C, 100°C. (i) Shows the surface plot of wavelength shift as a function of time. (ii) Resonance shift as a function of time. (iii) Rate of change of resonance shift as a function of time during the different isothermal heating processes.

We can see from the images Figure S2(a)(i) that at 400°C isothermal the spectrum shifts fast from 750 nm to 530 nm with in first 600 sec of heating cycle. From the Δλ as a function of the time plot in Figure S2(a)(ii), we see the major shift in peak position happened during the ramp-up cycle. Figure S2(a)(iii) Shows the rate of peak shift as a function of time. The shaded region marks the isothermal holding region at the respective temperatures. The blue region on the surface plot shows the spectrum intensity with low or no change at specific wavelengths. The red colour indicates the regions with the highest change in intensity at certain wavelengths. Figure S2(b)(i) shows the surf plot for the 300°C isothermal heating sample. It shows the spectrum shift from 750 to 580 nm within the first 300 sec, and it remains the same throughout the cycle. We can confirm the same from the change in the peak position plot in Figure S2(b)(ii) and also from the rate of change of the peak plot in Figure S2(b)(iii). Figure S2(c) shows the surface plot for the 200°C isothermal heating cycle. We see the peak resonance shift happens in the initial 300 sec only and remains constant throughout the remaining heating cycle duration. The Δλ plot as a function for time (Figure S2(c)(i)) shows that the change in peak position happens during the isothermal heating at 200°C. In the later half of the cycle, it becomes stable, and no change is observed. We see from Figure S2(c)(iii) the rate of change is highest at the beginning of the isothermal holding cycle at 200°C. From Figure S2(d)(i) we see that there is no change in the longitudinal LSPR peak shift from 750 nm during the 100°C isothermal heating cycle. Figures S2(ii) & (iii) also confirm that the change in peak position remains barely minimal throughout the 100°C heating cycle duration.

## S3. Size and aspect ratio calculation for isothermal heated substrates

The table below shows the lengths, widths, calculated in-plane aspect ratio (from SEM images) and the measured resonance wavelengths.

| Sample | Length (L) | Width (W) | In-plane Aspect Ratio (L/W) (from SEM) | Measured resonance wavelength (nm) |
|---|---|---|---|---|
| 100°C | 51.02 ± 6.86 | 28.13 ± 3.23 | 1.82 ± 0.25 | 750 nm |
| 200°C | 54.29 ± 8.09 | 35.10 ± 5.77 | 1.56 ± 0.23 | 630 nm |
| 300°C | 56.81± 12.88 | 44.66 ± 6.48 | 1.27 ± 0.22 | 580 nm |
| 400°C | 52.27 ± 12.62 | 43.86 ± 9.40 | 1.19 ± 0.15 | 529 nm |

**Table S2: Size analysis and resonance wavelength of isothermally heated samples.**

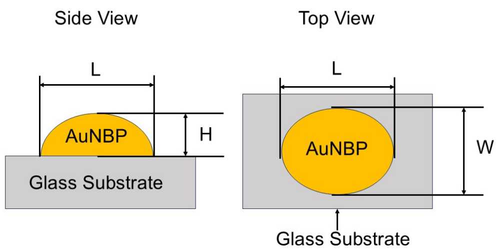


**Figure S3: Schematic explaining aspect ratio measurement method from SEM image**

The out-of-plane aspect ratio can be calculated using the following calculations. The volume of the oblate hemi-spheroid is given by $V_o = \frac{1}{8} * \frac{2}{3}\pi * L * W * H$, where *L*, *W* and *H* are the length, width and height of the oblate hemi-spheroid. Assuming that the average volume of the particles remains constant at both 300°C and 400°C and using the length (L) and width (W) calculated from the SEM images, we can calculate the height (H) of the spheroid. The length and width are provided in the Table given above. From this analysis, the ratio of height of the 300°C sample to the 400°C sample is given by

$$\frac{H_{300}}{H_{400}} = \frac{\langle L_{400} * W_{400} \rangle}{\langle L_{300} * W_{300} \rangle},$$

where the mean of the product of length and width at the respective temperatures are used. For the current case, $H_{300}/H_{400}$ is equal to 0.87. This indicates that the height of the particle increases on increasing heating temperature.

## S4. *In-situ* heating of AuNBP in TEM

The AR was calculated from five single particles. A consistent trend in AR change is observed in all particles. All the particles are colour-coded and can be correlated to the AR change plots as a function of time and temperature. From in-situ TEM analysis we see a change in aspect ratio. Figure S3(a) shows all the TEM images at different temperature cut points. From the images, we clearly see a loss in the tip sharpness of the bipyramid nanoparticle and becoming round. The Figure S3(b) shows the aspect ratio as a function of time for five different particles analysed from the TEM data. This plot gives us a statistical understanding of how the aspect ratio is changing following the same trend for all the particles. We see a major change in the aspect ratio occurs during the S-A cycle which is the ramp-up duration between 50°C to 200°C. Slowly the aspect ratio change settles down around 200°C and remains same during the A-B holding duration at 200°C. The ratio starts to change sharply during B-C the 300°C ramp-up cycle. This change in aspect ratio continues during the C-D the 300°C holding cycle. The change in the aspect ratio become stable in the D-E cycle during the 400°C ramp-up cycle. This stability in the aspect ratio change remains constant throughout the duration of 400°C holding cycle E-F. We can conclude that the particles reach a thermodynamic stability between 200°C to 300°C where there is no significant aspect ratio change. Similar stability is observed in the region between 300°C to 400°C.

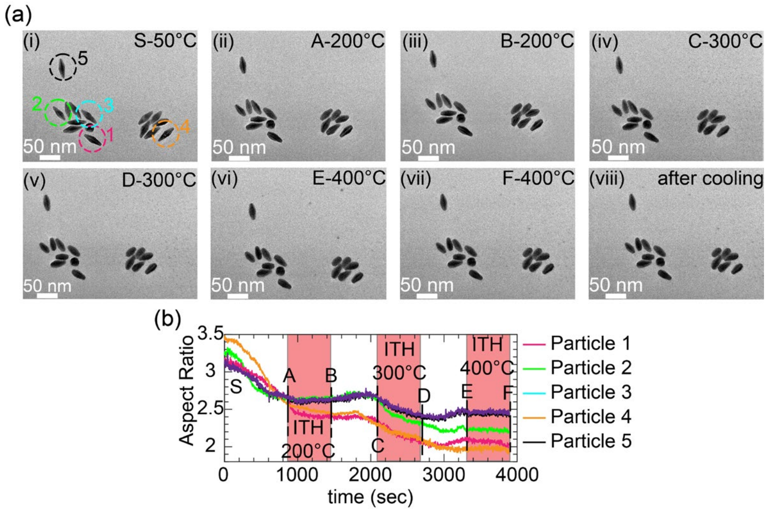


**Figure S4:** ***In-situ* TEM.** (a) Shows the TEM images at the different temperature cut points. (b) Aspect ratio as a function of time graph shows more particles with similar trends.

## S5. Thermally driven pattern fabrication

We performed two other patterning based on the heating of the AuNBP substrates. Pattern 2 is a modified version of pattern 1, where a significant portion of the substrate is in contact with the Cu plate, whereas a little portion is hanging out. Figure S4(a) shows the schematics of the experimental setup. The goal of the experiment was to observe the change in colour only in the region with contact. From Figure S4(b), a clear colour change is observed in the region in contact with the Cu plate. The surface plot Figure S4(c) shows the spectral mapping of the substrate where the red region shows a higher spectral wavelength as it was not in contact with the Cu plate. Whereas the portion in green is the area with a lower peak resonance wavelength. The reflection vs wavelength plot in Figure S4(d) confirms the higher peak resonance of point 1 compared to point 2. Figure S4(e) shows the SEM at the respective point 1 having more particles with longitudinal length. Whereas Figure S4(f) shows that most of the particles are spherical and correlate well with the measurement of the peak resonance around 530nm and its red colour.

Figure S5(a) shows the schematics of the experimental used for making pattern 3. In pattern 3, the substrate was held with one edge touching the hotplate so that we could see a clear colour gradient as the heat dissipated along the substrate. In Figure S5(b), we see that at point 1, the edge has got a thin red colour, and the colour change slowly fades away at point 4. The surface plot Figure S5(c) shows the spectral mapping of the substrate where the red region shows higher spectral wavelength as it was far away from the heating plate. The blue colour represents point 1, where we see the maximum colour change towards a lower wavelength. The four points 1 to 4 shows a gradual peak shift from higher to lower wavelength in the reflection Vs wavelength plot in Figure S5(d). In Figure S5(e) we see more spherical particles proving its correspondence with the red colour and lower wavelength. Gradually the shape changes along points 2, 3 and 4 Figure S5(f-h). We see more bipyramid particles in Figure S5(h) as it is the farthest from the hot plate and lesser or no effect of temperature is found in this region. For this reason, the shape of the nanoparticles has not changed as well as the spectrum.

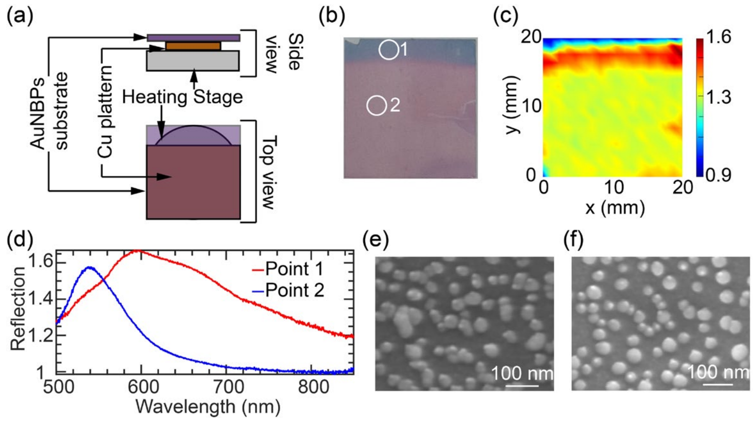


**Figure S5: Patterning using copper plate.** (a)Schematics of pattern 2 where a small portion of the substrate is hanging out the Cu plate which is in contact with the stage. (b) Shows the colour change in the substrate after heating. (c) Shows the spectral mapping of the substrate. (d) The reflection spectrum in the two positions 1 and 2 where we see visibly 2 different colours. (e) and (f) shows the respective SEM images at point 1 and 2.

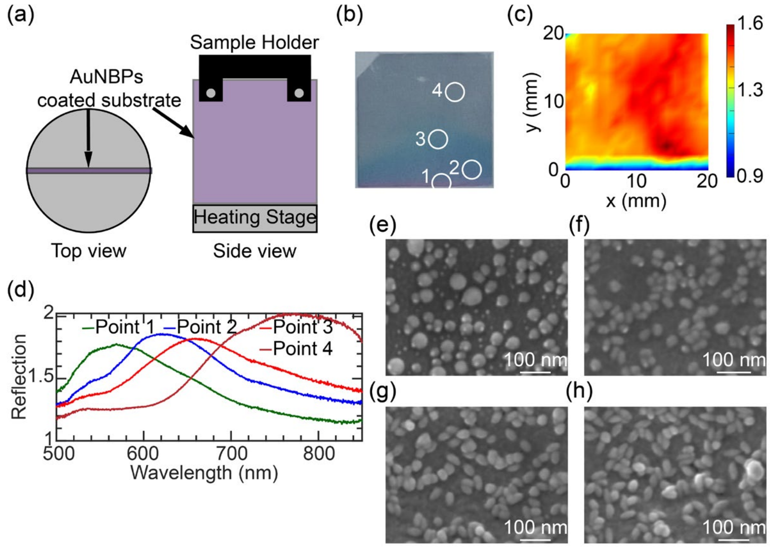


**Figure S6: Colour gradient on heating from one edge.** (a)Schematics of pattern 3 where one edge of the substrate is placed perpendicular to the stage. (b) Shows the colour change in the substrate after heating. (c) Shows the spectral mapping of the substrate. (d) The reflection spectrum in four different points where point 1 is at the edge in contact with the heating stage and 4 is the farthest point from the heating stage. (e-h) shows the respective SEM images at point 1,2,3 and 4.