Near-Field Thermal Imaging of Optically Excited Gold Nanostructures: Scaling Principles for Collective Heating with Heat Dissipation into the Surrounding Medium

Susil Baral[1], Ali Rafiei Miandashti[1] and Hugh H. Richardson[1]*

[1]Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701

Supporting Information for Publication

Er^{3+} Energy Level Diagram

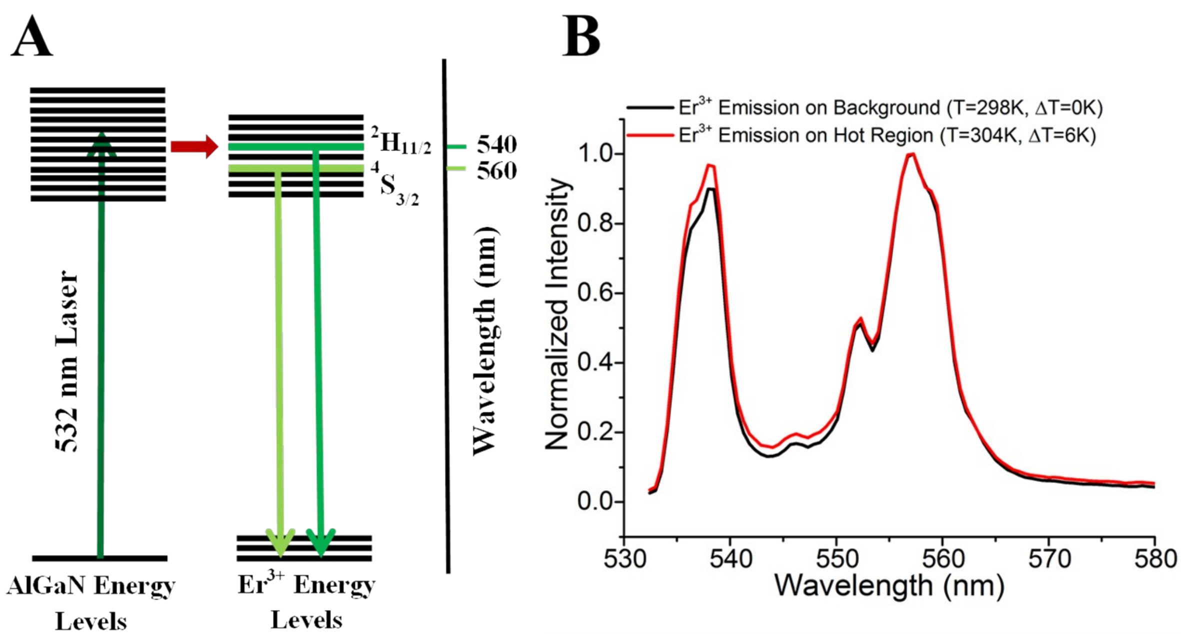

Figure S1. (A) Energy level diagram of Er^{3+} embedded on AlGaN matrix and the corresponding temperature dependent photoluminescence from Er^{3+} excited states to the ground state. (B) Representative Er^{3+} photoluminescence spectra for hot and cold region (room temperature) on the substrate.

Estimation of Diameter and Radius (Rc) of a Cluster of Gold Nanoparticles

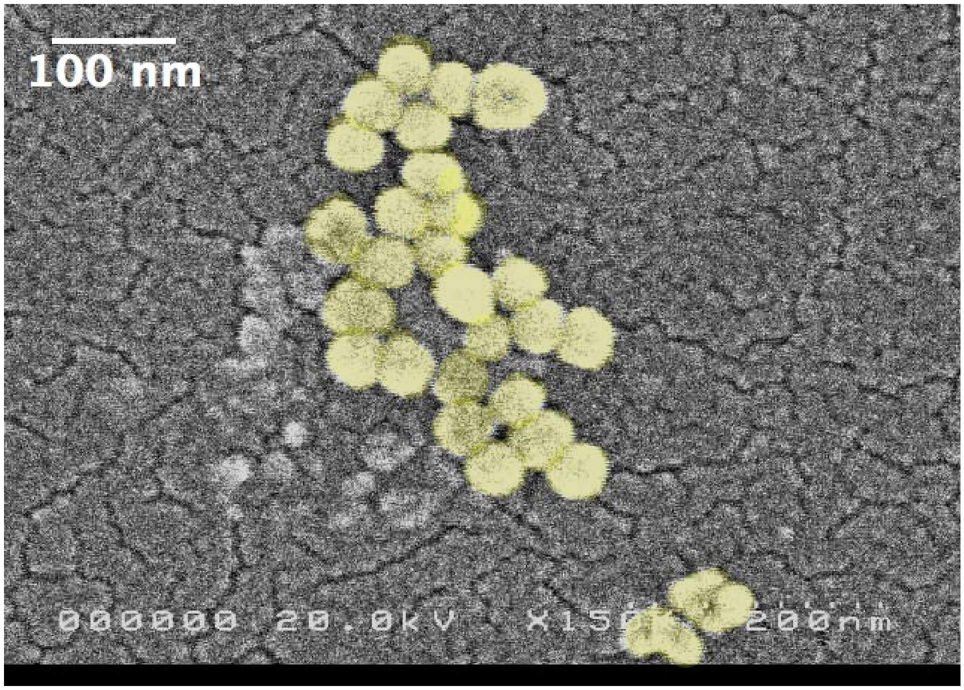

Figure S2. Representative SEM image of a cluster of 40 nm gold nanoparticles drop-casted onto the Silicon substrate. The substrate was made hydrophilic by plasma treatment before drop-casting the dilute colloidal solution of gold nanoparticles.

Characterization of NSOM tip

The NSOM tip was characterized using scanning electron microscope. Figure S3 shows the SEM image of NSOM tip and the approximate size of aperture in our temperature measurements. The aperture is a rectangular shape with a size of ~100 and 120 nm. The size of the hole becomes larger after a few times of usage and the resolution of the images can no longer be below the diffraction limit of light when the aperture size gets bigger therefore it needs to be replaced.

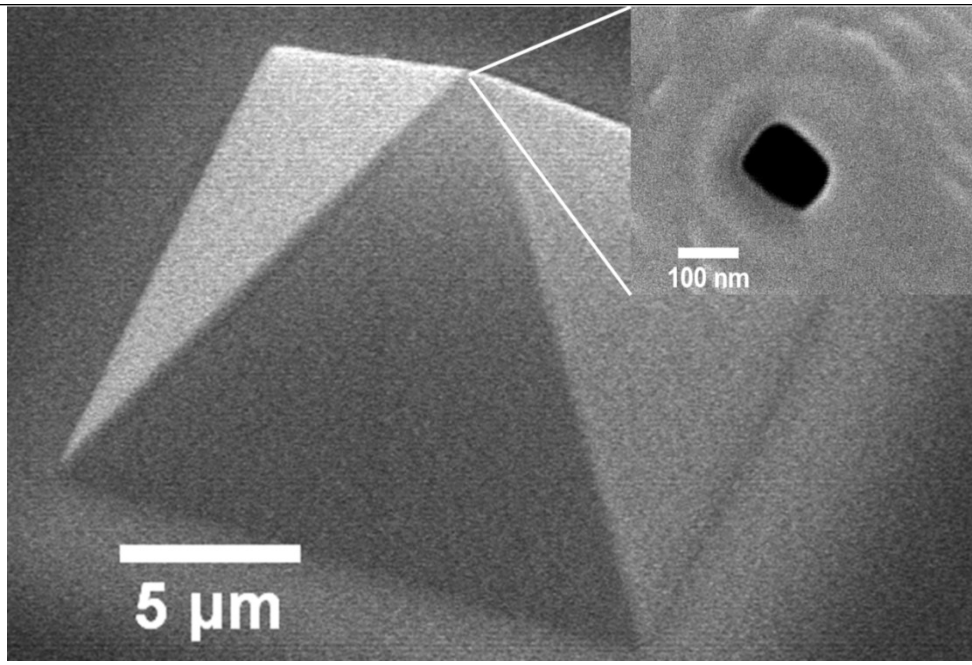

Figure S3. Characterization of NSOM tip and aperture size. NSOM tip has a pyramidal shape with a size of approximately 15×15 um baser. Insert shows an aperture size of 100 nm by 120 nm rectangular hole at the apex of the pyramid.

Transmission and Scattering Images

The data collected in figure 2a in the manuscript is produced from the inverse of transmission of 532 nm laser illuminated through the gold nanostructure and collected through NSOM tip from the top. Because the transmission shows as a dip instead of a peak, we plotted the inverse of transmission profile. Figure S4 a and b show the images of the gold nanoparticles onto glass coverslip and AlGaN:Er^{3+} on sapphire respectively.

To further characterize the potential of the NSOM tip map the temperature from nanostructures, we studied the thermal image and profiles from 40 nanometer gold nanoparticles. We used the 532 nm laser to illuminate nanostructures either in transmission or scattering through an NSOM tip. The spatial resolution of the tip is close to the aperture size of NSOM tip which is about 120 nm. Figures S5 a and c shows thermal image produced from 532 nm illumination and back collection of photoluminescence of the surface. Figures S5 b and d shows the corresponding profile from the line drawn through the nanostructures and the FWHM is ~125 nm and ~170 nm.

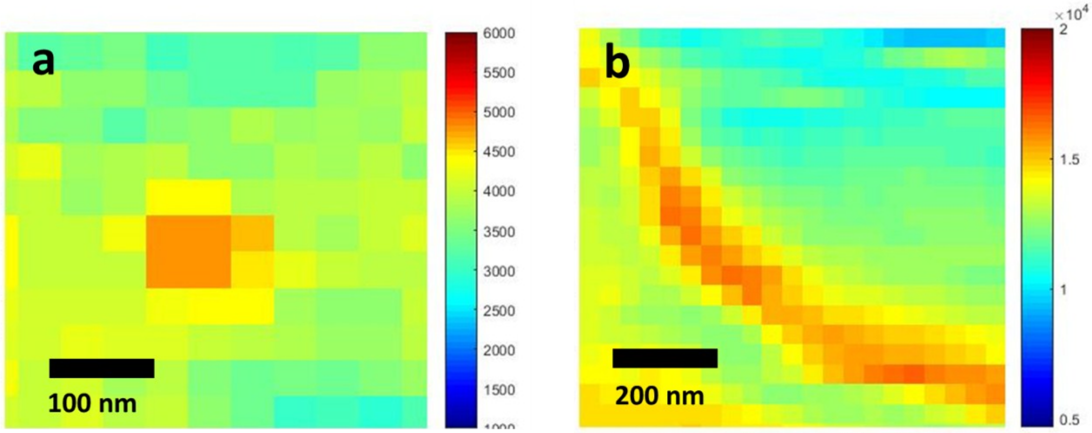

Figure S4. Characterization of NSOM tip and aperture size. Inverse of transmission (a) and scattering (b) images of the gold nanoparticles on glass coverslip and AlGaN:Er^{3+} on sapphire respectively. The transmission/scattering profiles show the spatial resolution of less than 150 nm for the gold nanodot and line of gold nanoparticles.

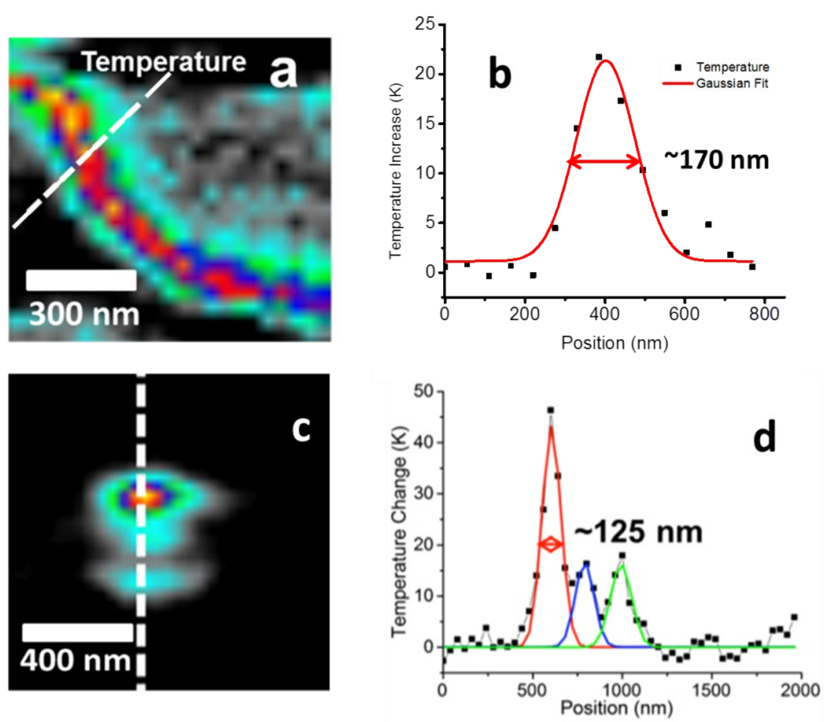

Figure S5. a and c) Thermal image of 40 nanometer gold nanoparticles. We used the 532 nm laser to illuminate nanostructures through an NSOM tip. Thermal image produced from 532 nm illumination and back collection of Er^{3+} photoluminescence from the surface. b and d) The corresponding profile from the line drawn through the nanostructures and the FWHM is ~125 and ~170 nm.

i) Estimation of Cluster Radius (R_c) from Thermal Profile

The diameter of a cluster of nanoparticles is estimated from the experimental thermal profile generated by drawing a cross section across the thermal image as represented in Figure 4d. On this thermal profile, diameter of a cluster is the region (length) where ΔT_{max} is relatively constant and from one inflection point of the profile to the other. The radius (R_c) of a cluster is then half this length (diameter). Some experimental thermal profiles and their estimated radius are shown in Figure S6.

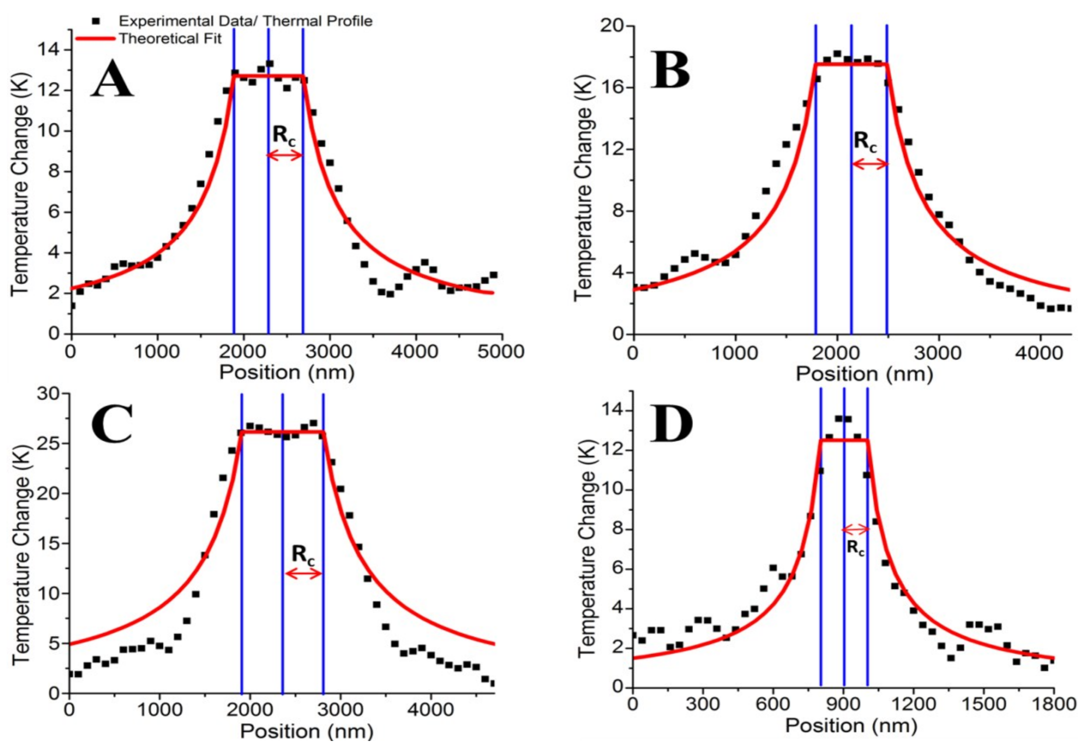

Figure S6. Illustration of estimation of cluster radius (R_c) from thermal profile generated by drawing a cross section across the steady state thermal image of a cluster of 40 nm gold nanoparticles.

ii) Comparison Between Estimation of Cluster Radius (R_c) from Thermal Profile, AFM, and Changes on Er^{3+} and 532 nm Intensities

Figure S7. Comparison between estimation of cluster radius from (A) thermal profile (B) AFM profile and (C) total Er^{3+} photoluminescence intensity. The AFM profile (Figure S7B) is generated by drawing a cross section across the AFM image of a cluster generated during near field imaging. The AFM profile shows the height of ~33 nm suggesting the 2-D cluster of the nanoparticles (40 nm diameter). The FWHM of the AFM profile is approximately 780 nm which is very close to the cluster diameter of 800 nm estimated from the thermal profile shown in Figure S7A. The Er^{3+} intensity profile is generated by drawing a cross section across the Er^{3+} intensity image. The Er^{3+} intensity image is generated by applying a filter for Er^{3+} emission peaks (H and S band) on an original image/ spectrum. As the measurement is performed by bringing the 532 nm CW laser from the bottom and collecting the Er^{3+} emission from the film on transmission mode (see materials and methods), the region with gold nanoparticles cluster shields the Er^{3+} emission. The Er^{3+} intensity profile (Figure S7C) shows the drop in Er^{3+} intensity with the plateau of approximately 800 nm, in close agreement with the cluster diameter of 800 nm estimated from the thermal profile (Figure S7A).

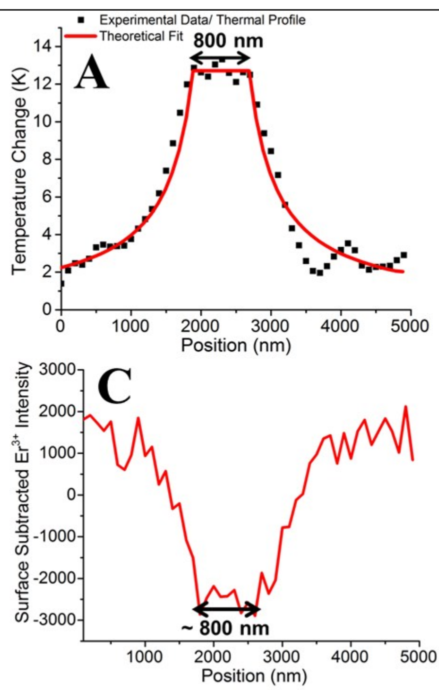

Figure S7. Comparison between estimation of cluster radius from (A) thermal profile (B) AFM profile and (C) total Er^{3+} photoluminescence intensity.

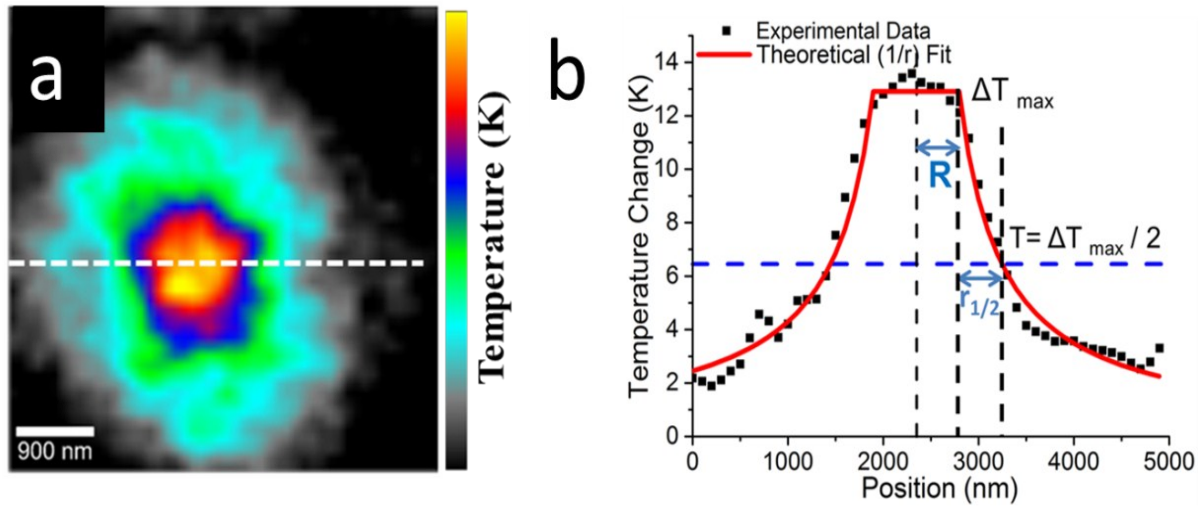

Figure S8. Steady state thermal image of a cluster of gold nanoparticles drop-casted onto the thermal sensor film of AlGaN:Er^{3+} on sapphire glass substrate in Near-Field imaging mode. (b) Illustration of estimation of cluster radius (R_c) from thermal profile generated by drawing a cross section across the steady state thermal image of a cluster of 40 nm gold nanoparticles. R_c is the radius of the cluster and $r_{1/2}$ is the distance starting from the edge of the cluster until a distance where the temperature reaches half of its maximum.

Two Laser Steady State Data Collection Experiment

Figure S9 shows the thermal image of drop casted gold nanoclusters under near-field thermal measurement. The cluster is excited through the tip with 532 nm CW laser (4.5 mW power). The near-field thermal image calculated from luminescence ratio thermometry shows the hot-spot in the center and cooler areas around the cluster. Figure 4b also shows the thermal image of the same cluster excited by 532 nm CW laser (4.5 mW power) through the tip and 980 nm CW laser from bottom (50mW). Figure 4c shows the thermal image produced from subtraction of the thermal images of fig.S9a and fig.S8b. Figure S9d is the thermal profile for the horizontal white dashed line drawn across the hot spot shown in Figure S9a, b and c.

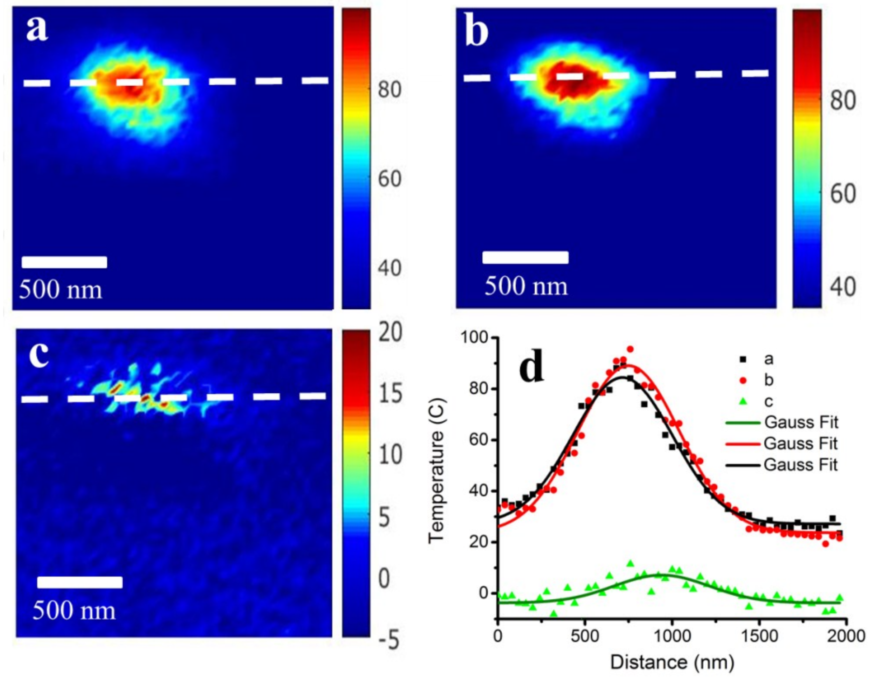

Figure S9. Two laser temperature profile data collection from 40 nm drop casted gold nanoparticles (a) Scanning near-field optical image of a cluster of gold nanoparticles illuminated by 532 nm CW as excitation laser through the SNOM tip. (b) Scanning near-field optical image of cluster of gold nanoparticles illuminated by 532 nm CW as excitation laser through the SNOM tip and 980 nm as heater from bottom. (c) Thermal image produced from subtraction of b from cluster of 40 nm gold nanoparticles. (d) Thermal profile from white dashed lines drawn across the cluster from images of illumination under 532 nm laser, 532 nm and 980 nm lasers and subtracted temperature image.

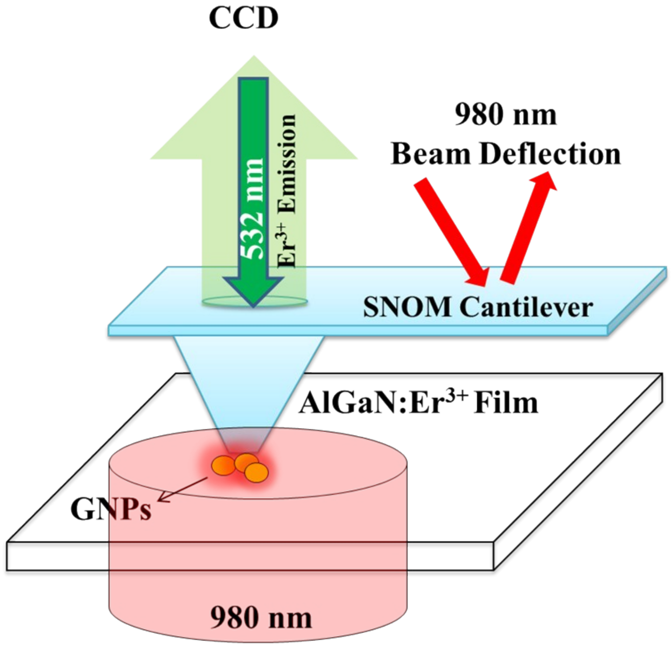

Figure S10. Schematic diagram of luminescence thermometry with two laser experiments where 980 nm laser is excited from bottom and 532 nm from the top using an upconverting film.