

Supporting Information

Radiative cooling of surface-modified gold nanorods upon pulsed infrared photoexcitation

*Shao-Syuan Guo and Li-Kang Chu**

Department of Chemistry, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Rd., Hsinchu
30013, Taiwan.

Corresponding Author

*To whom correspondence should be addressed. Phone: 886-3-5715131 ext. 33396. Fax: 886-3-5711082. E-mail: lkchu@mx.nthu.edu.tw.

1. Materials preparations

1.1 Preparation of CTAB capped gold nanorods (AuNR@CTAB).

The synthesis of CTAB-capped gold nanorod (AuNR@CTAB) solution followed the seed-growth method reported by Vigderman and Zubarev with a slight modification.¹ *Solution A* contained 0.01 M sodium hydroxide (NaOH) and 0.01 M sodium borohydride (NaBH₄), achieved by mixing equal amounts of 0.02 M NaOH and 0.02 M NaBH₄ stock solutions. Then to 10 mL of 0.1 M cetyltrimethylammonium bromide (CTAB) solution in a water bath of 28 °C was added 172 µL of 0.029 M chloroauric acid (HAuCl₄) solution, followed by the addition of 920 µL of *Solution A* under mild stirring. The mixture was stirred until it turned dark brown and then retained for further use as the seeding solution. 1.44 g of the CTAB was dissolved in 34.87 mL of deionized water, after which 688 µL of 0.029 M HAuCl₄ solution, 2.8 mL of 0.01 M AgNO₃ solution, and 1.12 mL of 0.2 M hydroquinone solution were sequentially added. The mixture was shaken until it became a transparent light yellow color. Then 0.64 mL of the seed solution was quickly mixed with the aforementioned solution and the mixture was kept stationary for 24 hours until the solution became burgundy red. The residual chemicals and CTAB were removed by centrifugation. The solution was further divided equally into four 10-mL centrifuge tubes and subjected to 9,000 ×g centrifugation for 30 minutes. 9 mL of the supernatant in each tube was discarded, and to the remainder was added deionized water to a volume of 10 mL. The centrifugation was repeated and 9 mL of the supernatant was removed. The *ca.* 1 mL concentrate was treated as purified AuNR@CTAB for further time-resolved spectroscopic experiments and surface modifications. The aforementioned chemicals, HAuCl₄·3H₂O (Alfa Aesar, 99.9 %), CTAB (Alfa Aesar, 98 %), NaBH₄ (Sigma-Aldrich, ≥ 98 %), NaOH (J. T. Baker, ≥ 98.7 %), AgNO₃ (Sigma-Aldrich, 99.8 %), and hydroquinone (Merck-Schuchardt, >99 %), were purchased for use without further purification. The deionized water was prepared with a water purification system (SIPKSIA1, Merck Millipore) to achieve up to 18.2 MΩ-cm in resistivity.

1.2 Preparation of poly(sodium 4-styrenesulfonate) (PSS) capped gold nanorods (AuNR@PSS) upon surface modification of CTAB@AuNR.

The surface modification of AuNR@CTAB with PSS followed the method by Ma *et al.*² The concentrated AuNR@CTAB, mentioned in *Section. 1.1*, was re-distributed into deionized water

to 10 mL and 400 μ L of the PSS solution (10 mg/ mL in 6 mM NaCl) was added. The solution was aged for 10 hours under stirring, followed by centrifugation at 6,500 $\times$ g for 40 minutes. The supernatant was discarded and the AuNR@PSS was left in the concentrate form for further time-resolved experiments. PSS (Sigma-Aldrich, average molecular weight: 70 kDa) was purchased for use without further purification.

1.3 Preparation of mPEG capped gold nanorods (AuNR@mPEG) upon surface modification of CTAB@AuNR.

The surface modification of AuNR@CTAB with mPEG followed the method by Didychuk *et al.*³ with modification. The concentrated AuNR@CTAB was diluted to 5 mL with deionized water, followed by the addition of 0.2 mL of 5 mM poly(ethylene glycol) methyl ether thiol (mPEG) and stirring for 24 hours. The mixture was centrifuged at 7,600 $\times$ g for 20 minutes. 9 mL supernatant was discarded and the residual 1 mL concentrate, denoted as AuNR@mPEG, was used for further time-resolved experiments.

1.4 Preparation of SiO₂ capped gold nanorods (AuNR@SiO₂) upon surface modification of CTAB@AuNR.

The surface modification of AuNR@CTAB with SiO₂ followed the method by Cong *et al.*⁴ and Abadeer *et al.*⁵ with modification. The concentrated AuNR@CTAB was diluted $\times$ 10 with deionized water and centrifuged at 9,000 $\times$ g for 30 minutes. 9 mL of the supernatant was discarded and the residual concentrate was diluted with 225 μ L of 20 mM CTAB solution under stirring. A small amount of 0.1 M NaOH solution was added to adjust the pH of the mixture to *ca.* 10. Then 30 μ L of the v/v 25 % tetraethyl orthosilicate (TEOS) in alcohol was gradually added to the mixture under stirring and the mixture stirred for 30 minutes before further aging for 20 hours. The mixture was centrifuged at 5,500 $\times$ g for 25 minutes. 9 mL supernatant was discarded and the residual 1 mL concentrate, denoted as AuNR@SiO₂, was used for further time-resolved experiments.

1.5 Preparation of dried AuNR samples on a CaF₂ window.

The aforementioned samples were diluted until their corresponding optical densities at 1064 nm were *ca.* 1.0 for a 1-cm absorption length. Then 1 mL of each sample was centrifuged under the following conditions: AuNR@CTAB at 7,600 $\times$ g for 10 minutes, AuNR@SiO₂ at 4,000 $\times$ g for 10

minutes, AuNR@PSS at 5,300 ×g for 15 minutes, and AuNR@mPEG at 6,000 ×g for 20 minutes. The concentrates were deposited on the CaF₂ window drop-by-drop and dried within a controlled area of *ca.* 0.16 cm² (a diameter of about 4.5 mm).

2. Characterization methods

2.1 Steady-state spectroscopy.

A spectrometer from JASCO (V-670) was employed to collect the visible-near infrared (Vis-NIR) absorption spectra of the samples in aqueous solution. A Fourier-transform infrared spectrometer (Vertex 80, Bruker) operated in continuous scan mode, coupled with a multipass attenuated total reflection (ATR) from BioATR Cell II (Bruker), was utilized to collect the infrared (IR) absorption spectra of the ×50 diluted samples dried under N₂ purge on the sample compartment of the ATR.⁶ The spectral resolution was 16 cm⁻¹ with 60 scans for averaging in each spectrum. The steady-state infrared absorption spectra of neat capping materials X and AuNR@X are shown in **Figure 3**.

2.2 Electron microscopic images.

A high-resolution transmission electron microscope (JEM-2100, JEOL) was utilized to record the morphologies of the AuNR samples before and after laser irradiation. About 250 particles were counted to demonstrate the aspect ratios. The program (Nano Measurer, version 1.2.5, Jie Xu, Fudan University) was employed to measure the dimensions of the particles. We calculated the average aspect ratio (A.R.) using average length/average width and employed the following error propagation to account for the deviation.

$$\text{A.R.} \pm \sigma_{\text{A.R.}} = \frac{\text{average length} \pm \sigma_{\text{length}}}{\text{average width} \pm \sigma_{\text{width}}} = \frac{\text{average length}}{\text{average width}} \left(1 \pm \sqrt{\left(\frac{\sigma_{\text{length}}}{\text{average length}} \right)^2 + \left(\frac{\sigma_{\text{width}}}{\text{average width}} \right)^2} \right)$$

2.3 Time-resolved emission spectroscopy recorded with a step-scan Fourier-transform spectrometer.

The data acquisition followed a previous report.⁷ The sample was dried on the CaF₂ window and mounted at the focal point of the parabolic mirror on the side of the interferometer for collecting

the external emission, as shown in **Figure S1**. A sleeve was mounted to the sample compartment with a small amount of NaOH to adsorb the H₂O and CO₂ to reduce as much of the optical interference in the infrared propagation path as possible. A fundamental Nd:YAG laser (Quanta Ray INDI-40-10, Spectra-Physics) operated in long pulse mode provided *ca.* 70- μ s pulses at 1064 nm to excite the longitudinal plasmonic resonance bands of the AuNRs at a repetition rate of 10 Hz from the backside of the sample. A photodiode (DET10A/M, Thorlabs) was used to collect the scattering of the 1064-nm laser to serve as a trigger. The time-resolved infrared emission spectra were recorded with a Fourier-transform infrared spectrometer (Vertex 80, Bruker) operated in the step-scan mode. The temporal profiles at all the optical retardation points were collected using the ac-coupled method. A mercury cadmium telluride (MCT) detector (KMPV8-0.5-J1/DC, Kolmar Technologies) was employed to collect the infrared emission evolution and to transduce the photon signal to voltage, which was sent to an analog-to-digital convertor (20 MHz, 14 bits, Bruker) with further amplification ($\times 10$) and electronic filtering (10 Hz–10k Hz) by a voltage amplifier (SR560, Stanford Research Systems). An optical filter ($< 4,000\text{ cm}^{-1}$, LP-2500, Spectrogon) positioned in the midst of the optical path, the IR detector and other light-collection optical components defined the detection wavenumbers at 0–4,000 cm^{-1} . The spectral resolution was set at 16 cm^{-1} and the acquisition of the interferogram required 740 steps of the moving mirrors. The period for collecting one time-resolved spectrum was *ca.* 40 minutes, with 30 laser shots on average at a 10-Hz repetition rate at each mirror stop. Two identical experiments were performed to increase the ratio of signal to noise. After the completion of the data acquisition at all the optical retardations, the time-evolved emission spectra were derived via reverse Fourier transformation of the interferograms.

2.4 Infrared emissions of blackbody radiation at different temperatures.

A blackbody radiation simulator (IR-564, Graseby Infrared) provided the thermal irradiation at given temperatures, which was directed to the spectrometer at the same position where the dried AuNR samples were mounted, as shown in **Figure S2**. A mechanical chopper was mounted in the midst of the optical path of the blackbody radiation to modulate the emitting radiance, which was collected using the ac-coupled method with the interferometer (Vertex 80, Bruker) operated in step-scan mode. A mercury cadmium telluride (MCT) detector (KMPV8-0.5-J1/DC, Kolmar Technologies) was employed to collect the blackbody radiation evolution and to transduce the

photon signal to voltage, which was sent to an analog-to-digital convertor (20 MHz, 14 bits, Bruker) without further amplification and electronic filtering. The detection wavenumbers were defined using the same optics mentioned in *Section 2.3* as 0–4,000 cm^{-1} . The spectral resolution was set at 16 cm^{-1} . After completing the data acquisition at all the optical retardations, the time-evolved blackbody radiation spectra were derived via reverse Fourier transformation of the interferograms. The normalized emission spectra at different temperatures within the opening slot of the chopper are shown in **Figure S3**.

2.5 Temporal profile of 1064-nm laser.

The temporal profile of the 1064-nm laser (Quanta Ray INDI-40-10, Spectra-Physics) was monitored with a photodiode (DET10A/M, Thorlabs) upon averaging 128 laser pulses, as shown in **Figure S4**.

3. Infrared assignments of the neat capping materials.

The absorbance at 2300 cm^{-1} is attributed to the background CO_2 . The infrared assignments of four capping materials are discussed below.

3.1 CTAB (Figure 3a)

The bands at 3050–2800 cm^{-1} are attributed to the C–H stretching modes of methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2-$). 1481 cm^{-1} is attributed to C–H symmetric bending of the N^+-CH_3 moiety. Bands at 962 and 910 cm^{-1} are attributed to the C– N^+ stretching.⁸

3.2 PSS (Figure 3b)

The bands at 3000–2800 cm^{-1} are attributed to the C–H stretching mode of the methylene ($-\text{CH}_2-$). Three weak bands at *ca.* 1600–1500 cm^{-1} are attributed to C=C stretching modes of the benzene ring. Bands at 1195 and 1039 cm^{-1} are attributed to the S=O asymmetric and symmetric stretching modes of the SO_3^- moiety, respectively. 1128 and 1011 cm^{-1} are attributed to the in-plane skeleton vibration and bending of the benzene ring, respectively.⁸

3.3 mPEG (Figure 3c)

The intense bands at 2850 and 1100 cm^{-1} are attributed to the C–H stretching and C–O–C vibrational modes.⁹ Other bands at 1500–1250 cm^{-1} are mainly attributed to the CH₂ in-plane and out-of-plane bending.

3.4 SiO₂ (Figure 3d)

The intense peak at *ca.* 1080 cm^{-1} and a shoulder at *ca.* 1165 cm^{-1} are attributed to the transverse optical (TO) and longitudinal optical (LO) phonon modes of stretching of Si–O–Si bridges, respectively.^{10,11}

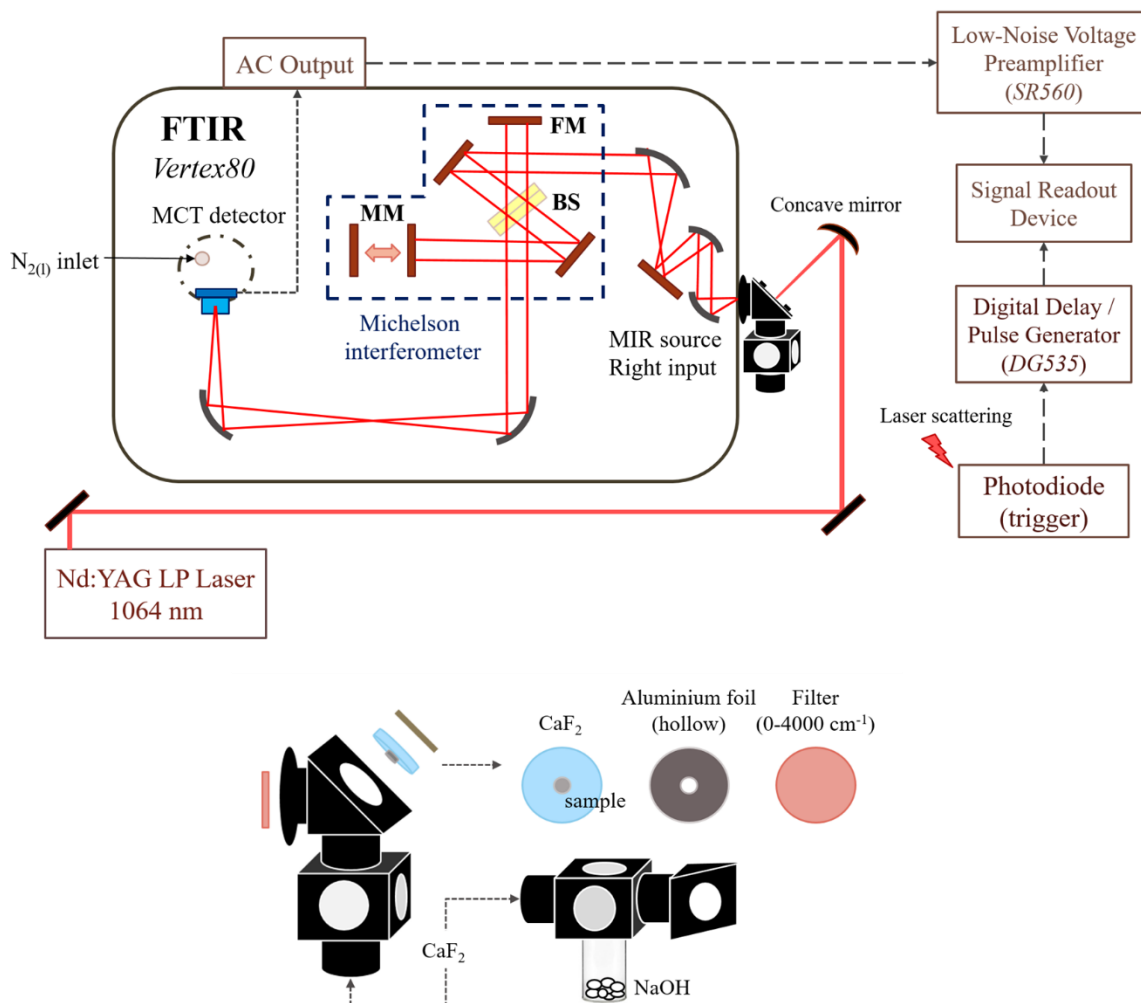


Figure S1. Experimental setup for monitoring the time-resolved infrared emission upon photoexcitation of AuNR@X with 1064 nm pulsed Nd:YAG laser.

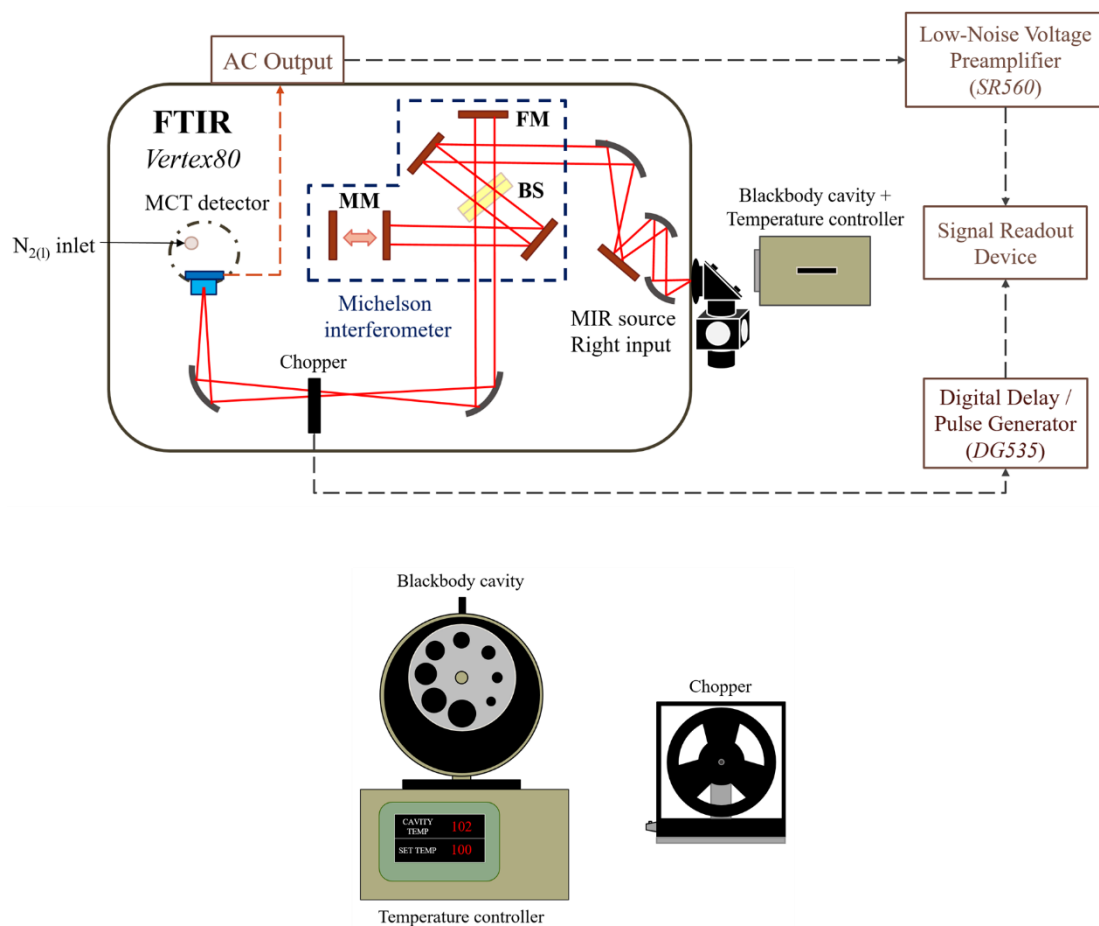


Figure S2. Experimental setup for detecting the modulated blackbody radiation at given temperatures.

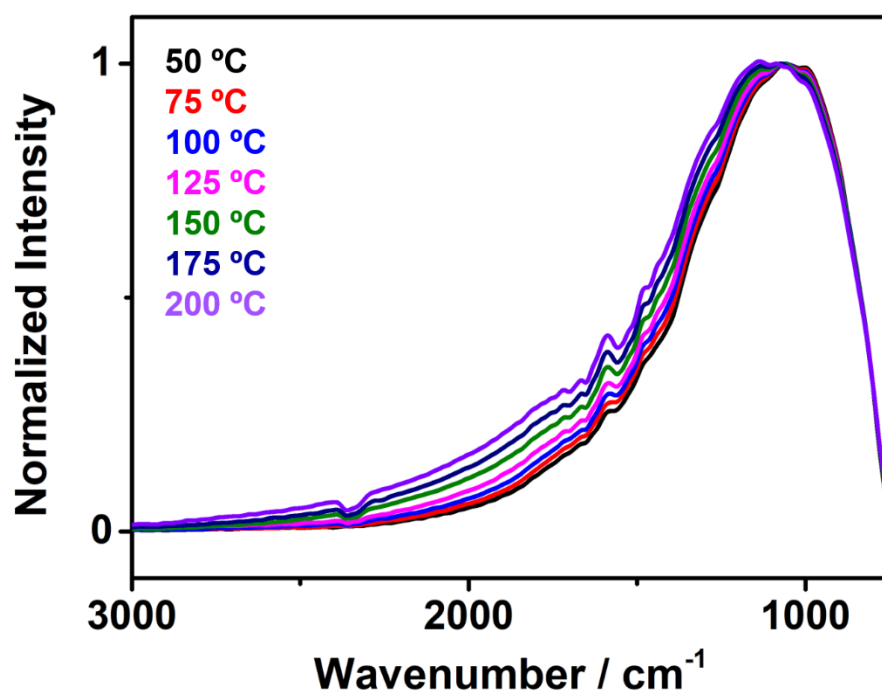


Figure S3. Normalized blackbody emission contours at different temperatures.

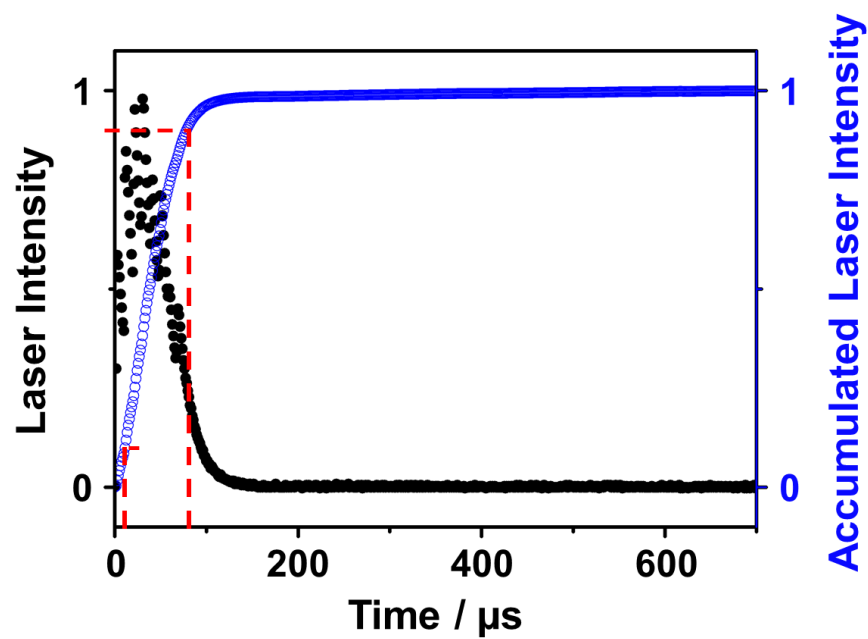


Figure S4. The temporal profile of the 1064-nm excitation pulse width. The corresponding 10–90% rise time of the accumulated laser intensity is roughly 70 μs .

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