Supporting information

Configuration Modulated Hot Electron Dynamics of Gold Nanorod Assemblies

Megersa Feyissa Mideksa¹,², Hongyan Liu³, Fei Wang¹,², Wajid Ali¹,², Hongdong Li¹,², Xiaoli Wang¹,²*, Zhiyong Tang¹,²

1. CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, P. R. China

2. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, P. R. China

3. Beijing Institute of Aeronautical Materials, Beijing, 100095, P. R. China

*Corresponding author E-mail: wangxl@nanoctr.cn
**Part S1. Materials and Methods**

Tetrachloroauric acid hydrated (HAuCl₄·4H₂O, analytical grade) and silver Nitrate (AgNO₃, >99%) were purchased from Sinopharm. Cetyl trimethylammonium bromide (CTAB) and ethylenediaminetetraacetic acid (EDTA) were achieved from TCI America. Sodium borohydride (NaBH₄, 98%), and ascorbic acid (AA, 99%) were provided by Alfa Aesar. Hydrochloric acid (HCl, 37wt %), sodium hydroxide (NaOH, analytical grade) and ethanol (EtOH, analytical grade), analytical grade) were supplied by Beijing Chemical Reagent Company (China). The deionized water used in our experiments was obtained from the Milli-Q System. All the chemicals were used without further purification.

**Part S2. Preparation and Characterization**

**Synthesis of GNRs**

GNRs were synthesized by two steps seed-mediated growth method based on the reported literature with slight modifications.¹ Firstly, the seed solution was prepared by adding 0.25 mL of 10 mM HAuCl₄ into 7.5 mL of 100 mM CTAB solution. 1.65 mL of distilled water and 0.6 mL of 10 mM freshly prepared ice cold NaBH₄ was then quickly injected into the above solution under vigorous stirring. The obtained brownish yellow solution was stirred further for 1 min and aged at 30°C for 12 h before use. To prepare the growth solution with different aspect ratios (ARs), 50, 60 or 75 µL of 10 mM AgNO₃ was added to an aqueous mixture solution of 0.5 mL HAuCl₄ and 10 mL of 100 mM CTAB. While stirring the solution at 30°C, 0.6 µL of 100 mM AA was added under vigorously stirring until the color become colorless, and then 12 µL of seed solution was quickly injected. The obtained mixture was kept undisturbed over night at 30°C for growth. The AR of GNRs could be tuned by changing the amount of AgNO₃ solution. The obtained GNRs were isolated by centrifugation at 10,000 rpm for 10 min and washed with pure water two times to remove the excess surfactant. For further characterization the precipitate was re-dispersed in 10 mL of distilled water.
Assembly of the nanorods

Side-by-side assembly

The above synthesized solution was centrifuged at 10,000 rpm for 10 min. After decantation of the supernatant, the precipitate was re-dispersed in same volume of distilled water. To 1 mL of this solution, 100 µL of 1 mM EDTA \(^2\) was added and adjusted to 10 pH result in side-by-side assembly.

End-to-end assembly

To control the surface charge, the synthesized solution used without further centrifugation. To 1 mL of as-synthesized solution, 20 µL of 1 mM EDTA solution was added and stirred to mix well at 10 pH. Due to the number of cations on surface, the added anions linked the GNRs with their ends rather than the lateral side.

Instrument and characterization

To determine the size and the shape of the nanoparticles, TEM imaging was carried out on TecnaiG2T-20 U-TWIN under the accelerating voltage of 200 kV. The dilute solution of each AR of gold NRs and their assemblies were applied on cupper grid by using micropipette. UV-Vis absorption measurements were carried out using a Lambda 950 UV-Vis spectrometer. A 3 mL portion of each sample solution was added into a 1 cm quartz cell and measured at the scan speed of 300nm/min with a bandwidth of 1 nm. Femtosecond pump-probe spectroscopy was used to measure the transient absorption of the samples. The incident pump mean power is 13 mW with wavelength of 400 nm. The sample was placed in the overlapped focus of the probe beam and the pump beam with sample holder rotating during the measurement in order to get fresh solutions in each pass. Another reference beam was also collected to remove laser intensity fluctuations. The data of the measurements were analyzed by MATLAB to account for chirp of the “white light continuum” pulse.

Calculations

Three temperature model. In the model we assume a perfect contact at the interface and a purely diffusive thermal transport in the host medium water. The athermal regime is disregarded.
Due to the nonspherical shape of the nanoparticle, the coupled differential equations accounting for the energy exchanges between conduction electrons, metal lattice and host medium have been solved through a finite element method (COMSOL), providing the time evolution of the electron ($T_e$) and lattice ($T_l$) temperatures in the NR as well as the topography of the host medium temperature. The transient modification of the intraband susceptibility has been added to the interband one, determined through Lindhard’s theory and Rosei model, by calculating the dynamics of the electron collision rate.\textsuperscript{3}

**Supporting figures for characterization of the synthesized GNRs and their assemblies**

Figure S1. Statistic histograms for three different sizes of GNRs average aspect ratios. The scale bar is 50 nm.
Table S1. Statistics dimension of three different sizes of GNRs.

<table>
<thead>
<tr>
<th>AR</th>
<th>Length (nm)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>40.3</td>
<td>17.4</td>
</tr>
<tr>
<td>2.8</td>
<td>47.8</td>
<td>17.1</td>
</tr>
<tr>
<td>3.5</td>
<td>56.3</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Figure S2. TEM images of EE and SS assemblies. (a-b) are for GNRs with AR of 2.3, and (c-d) are for the GNRs with AR of 3.5.
Figure S3. UV-Vis absorption spectra of dispersed non-assembled GNRs (black curves), their SS (red curves) and EE (green curves) assemblies with AR of 2.3 (a) and 3.5 (b), respectively.

Figure S4. Field distribution of single nanorod, their EE and SS assemblies at transverse and longitudinal polarizations.
Figure S5. Transient absorption of GNRs with different ARs (2.3, 2.8 and 3.5) as well as their assemblies, (a) (d) and (g) dispersed non-assembled GNRs, (b) (e) and (h) SS assemblies, and (c) (f) and (i) EE assemblies, respectively.

Figure S6. Hot electron lifetime of T mode (left panel) and L mode (right panel) for dispersed non-assembled GNRs with AR of 2.8, their SS and EE assemblies, respectively. The solid curves are monoexponential decay fitting on the experimental data.
Figure S7. Hot electron lifetime of T mode (left panel) and L mode (right panel) for dispersed non-assembled GNRs with AR of 3.5, their SS and EE assemblies, respectively. The solid curves are monoexponential decay fitting on the experimental data.

Figure S8. Absorbance spectra of three dispersed non-assembled GNRs with different aspect ratios (GNR1: AR=2.3, GNR2: AR=2.8, GNR3: AR=3.5).
REFERENCES

