

SUPPORTING INFORMATION

One-Dimensional Coupling of Gold Nanoparticle Plasmons in Self-Assembled Ring Superstructures

Wei-Shun Chang,^{1†} Liane S. Slaughter,^{1†} Bishnu P. Khanal,¹ Primit Manna,¹ Eugene R.
Zubarev,¹ Stephan Link^{1,2*}

¹Department of Chemistry, Rice University, Houston, TX, 77005

²Department of Electrical and Computer Engineering, Rice University, Houston, TX,
77005

[†]Authors contributed equally and in alphabetical order

*Corresponding author; email: slink@rice.edu

This document contains details regarding sample preparation and a description of the optical setup.

Sample preparation:

Gold nanoparticles with a polystyrene surface coating ($M_w = 10,000$ g/mol) were prepared following the procedure described elsewhere.¹ Cetyltrimethylammonium bromide (CTAB) stabilized nanoparticles were synthesized using a modified method introduced by Sau *et al.*^{2,3} This synthesis procedure typically results in a mixture of different shapes. Spherical nanoparticles are the most abundant (80 %) component of the mixture, followed by ~10 % of triangular prisms and 10 % of other shapes including cubes and rods.² The sample used in this study had an average diameter of 40 ± 5 nm as confirmed by transmission electron microscopy (JEOL 1230 HC-TEM operated at 120 kV). To functionalize the nanoparticles, CTAB was exchanged with p-mercaptophenol, to which biphenylcarboxy-terminated polystyrene ($M_w = 10,000$ g/mol) chains were attached via ester linkage, rendering the nanoparticles highly soluble in organic solvents. Purified polystyrene-functionalized nanoparticles were suspended and stored in chloroform. By allowing a drop of the functionalized NP solution to dry on an ITO-coated glass slide (Delta Technology, CG-51IN, $R_s = 8 - 12$ ohms), rings of various sizes were formed at the interface between the organic solvent and water droplets that condensed from the air due to evaporative cooling of chloroform.¹ A gold pattern was formed using an indexed copper TEM grid (Ted Pella, 79021C), allowing us to locate the exact same structures in scanning electron and optical microscopy (Figure S1). Samples for acquiring single nanoparticle spectra were prepared separately by replacing chloroform with tetrahydrofuran (THF) as the solvent. THF is miscible with water at any proportions and the interface between the water droplets and the organic solution does not form, thus preventing the self-assembly of the nanoparticles into rings. Before each

optical measurement, the rings and individual nanoparticles were characterized using an FEI Quanta ESEM2 scanning electron microscope operated under high vacuum at 15 kV.

Optical setup:

Scattering images were collected on a home-built microscope (Figure S2). Dark-field excitation was performed in a reflected light geometry using an inverted microscope (Zeiss, Axiovert 200) with a tungsten lamp as an excitation source. To allow for coarse and fine adjustments of the sample, a home-built sample holder was attached to a manual translational stage and mounted on a xyz piezo scanning stage (Physik Instrumente, P-517.3CL) connected to a surface probe microscope controller (RHK Technology, SPM 1000). Scattered light was collected using a Zeiss Epiplan-Neofluar 100X/0.9 objective and, after passing through 50 μm pinhole and a polarizing beam splitter, focused onto two avalanche photodiode detectors (Perkin Elmer, SPCM-AQR). Images were collected point by point by scanning the sample. We used filters of known optical density in the detection path as necessary to prevent saturating the detectors. No spectral correction for the quantum efficiency of the detectors was performed. Scattering spectra were acquired with a spectrometer (Princeton Instruments, Acton SP2150i) and a CCD camera (Princeton Instruments, PIXIS 400BR,). When taking a spectrum, the scanning stage moved the sample to the desired location so that only the scattered light from the selected location could pass through the pinhole. The scattered light was directed to the entrance of the spectrometer using motorized flipper mount (New Focus), dispersed by a grating (300 l/mm, blaze wavelength: 500 nm), and detected by the CCD camera. The spectra

were averaged over six frames, each having an integration time of 10 seconds. The background was measured at a region with no nanoparticles present, dark counts were measured with the lamp off, and we corrected for the scattering of the substrate using a clean glass slides. A polarizer was placed in the detection path after the pinhole to measure the polarization dependence of the scattered light. A depolarizer followed the polarizer to avoid any polarization bias due to the spectrometer. Matlab programs were written to correct for the efficiency of the lamp, collection efficiency of the spectrometer, any filters used in the detection path, compute intensity distributions, and calculate and fit the spectra.

References

- (1) Khanal, B. P.; Zubarev, E. R. *Angew. Chem, Int. Ed.* **2007**, *46*, 2195.
- (2) Sau, T. K.; Murphy, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 8648.
- (3) Sau, T. K.; Murphy, C. J. *Langmuir* **2004**, *20*, 6414.

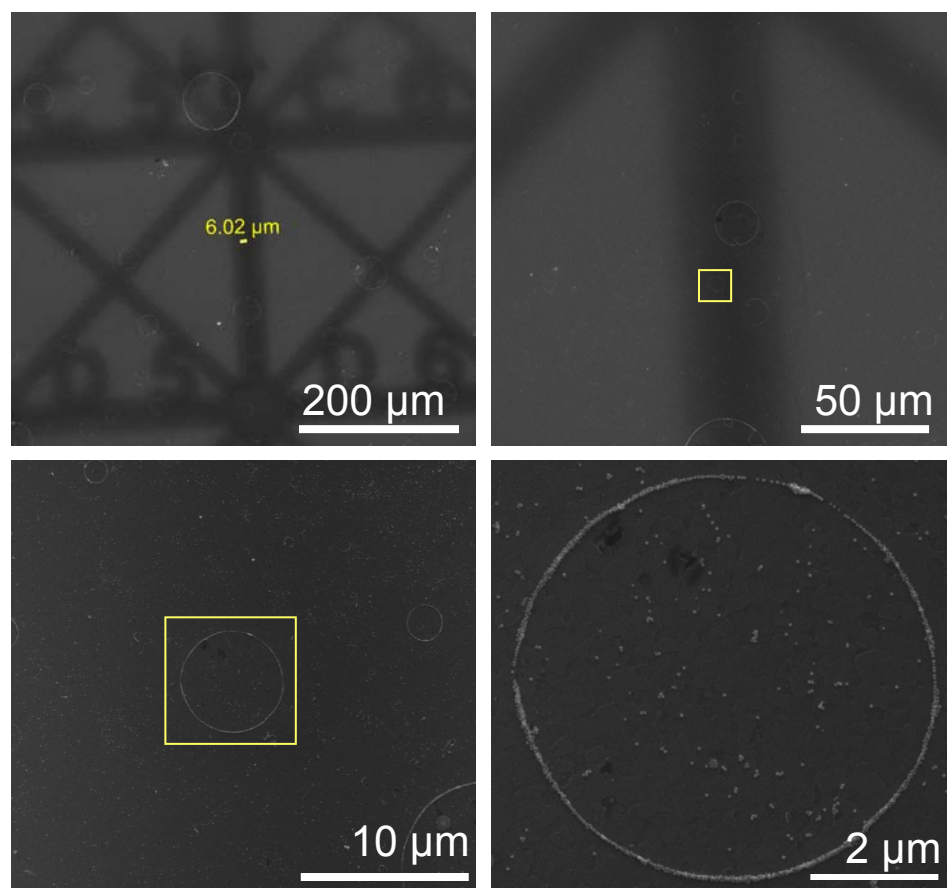


Figure S1: SEM images taken with different magnifications to show how individual rings can be located. Note that the light areas in the top left image correspond to the evaporated gold film.

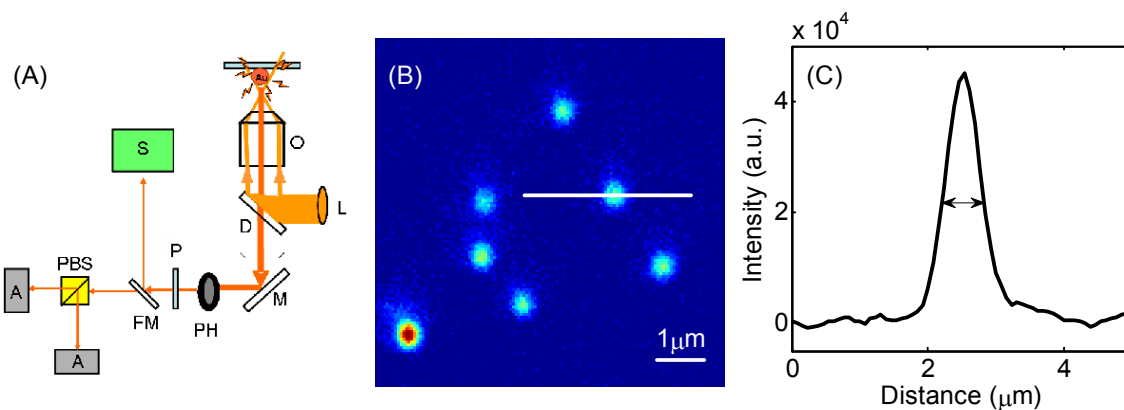


Figure S2: (A) Experimental setup of the dark-field microscope. L: Halogen lamp, O: Objective, D: Dark-field dichroic, M: Mirror, PH: 50 μm pinhole, P: Polarizer, FM: Flip mirror, S: Spectrometer and CCD camera, PBS: Polarizing beamsplitter, A: APD. (B) Dark-field image of 90 nm gold nanodots. (C) Cross section of the scattering intensity for the single gold nanoparticle marked by white line in (B). The FWHM of the peak is 560 nm.