Adverse Role of Shape and Size in Second Harmonic Scattering from Gold Nanoprisms

SUPPORTING INFORMATION

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Synthesis and characterization. *Chemicals.* All chemicals were commercially available and used without further purification. Gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), cetyltrimethylammonium chloride (CTAC), cetyltrimethylammonium bromide (CTAB), sodium borohydride ($NaBH_4$), L-Ascorbic acid (AA), sodium hydroxide (NaOH), potassium iodide (KI) and sodium iodide (NaI) were purchased from Sigma-Aldrich. Deionized water (Millipore Milli-Q grade, MQ) with resistivity of 18.2 MΩ·cm was used in all experiments.

Synthesis. Gold nanoprisms (sample #26, average edge length of 26 nm) were synthesized according to the literature protocol. [1] Briefly, to the solution containing 1.6 ml of 0.1 M CTAC, 8 ml of MQ and 0.075 ml of 0.01 M KI, 0.08 ml of 25.4 mM $HAuCl_4$ was added, followed by addition of 0.0203 ml of 0.1 M NaOH. The solution exhibited pale yellow color. Subsequently 0.08 ml of 0.064 M AA was injected and the mixture was moderately shaken, resulting in a colorless solution. Finally, 0.01 ml of 0.1 M NaOH was added, followed by quick shaking for 1-2 s. Within 10 min, the colorless solution turned red, purple and then blue.

Gold nanoprisms (samples #61, #78 and #87 with average edge lengths of 61, 78 and 87 nm respectively) were synthesized according to a modified literature protocol. [2] Briefly, the seed solutions typically used for the synthesis of gold nanorods [3] were prepared by reduction of 0.025 ml of 0.05 M $HAuCl_4$ with 0.3 ml of 0.01 M ice-cold $NaBH_4$ in 4.7 ml an aqueous 0.1 M CTAB solution under vigorous stirring. The mixture was left for 30 min under mild stirring. Subsequently, the growth solution was prepared according to, [2] namely to 9 ml of the aqueous solution containing 0.05 M CTAB and 0.050 mM NaI, 0.250 ml of 0.01M $HAuCl_4$, 0.050 ml 0.1 M NaOH and 0.050 ml 0.1M AA were added and the solution was gently mixed resulting in a color change from orange to colorless. Finally, the seed solution was added according to the nanoprisms average edge length targeted. The seed concentration in the growth solution was used as described in [2] to obtain nanoprisms with desired geometrical parameters.

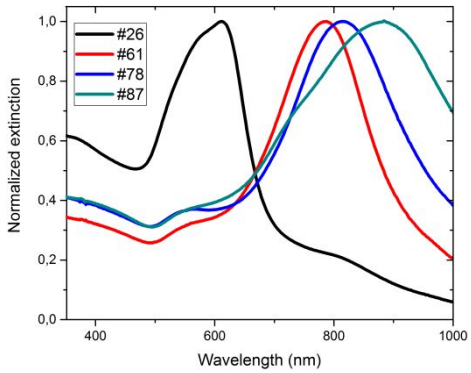

Figure S1. Normalized UV-Vis spectra of all samples.

Samples characterization. The samples were characterized by UV-Vis absorption spectroscopy and Transmission Electron Microscopy (TEM), see Figures S1 and S2(a-d) where all UV-Vis spectra and TEM images are presented.

The average values of the nanoprisms edge length were obtained from the TEM images as well as the nanoprisms content of the solutions that varied from 42% to 74% as shown in Table 1 in the manuscript, the remaining nanoparticles being assimilated as nanospheres. All data were corrected for linear absorption. Also, except for sample #26 for which the conditions are non-resonant, samples #61, #78 and #87 were performed with resonant conditions at the fundamental wavelength and non-resonant conditions at the harmonic wavelength where here resonance is considered with respect to the LSPR.

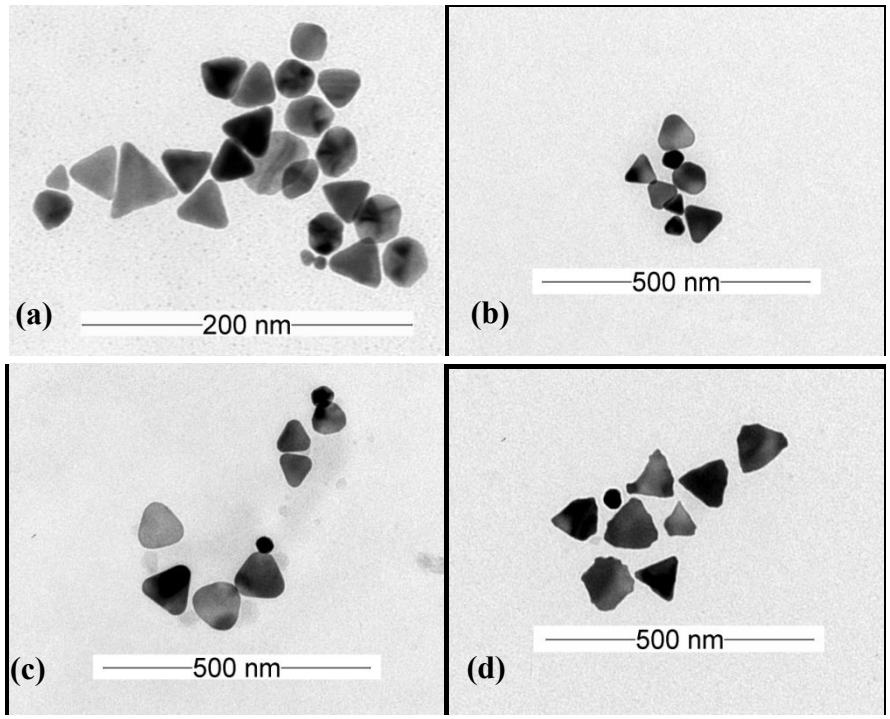

Figure S2(a-d). Transmission Electron Microscopy (TEM) pictures of samples #26 (a), #61 (b), #78 (c) and #87 (d). The deformation of edges of sample #87 is due to the surfactant centrifugation process performed prior to the screening.

Optical setup. The HRS arrangement was based on a Ti:Sapphire femtosecond laser operating at the wavelength of 800 nm with pulse length of 140 fs and repetition rate of 80 MHz. The average power was not exceeding 150 mW to avoid any sample damage. The beam was spectrally cleansed with a long-pass filter placed before it was gently focused into a fused silica cell containing the aqueous solution of nanoparticles with X10 magnification objective. The HRS intensity was collected at right angle by a single photon counting photomultiplier tube coupled with a spectrometer. A short-pass filter was inserted in the harmonic beam path in order to avoid detecting spurious light. For polarization analysis of the HRS intensity, a half-wave plate before the long-pass filter in front of the cell and an analyzer after the short-pass filter were installed on the set-up.

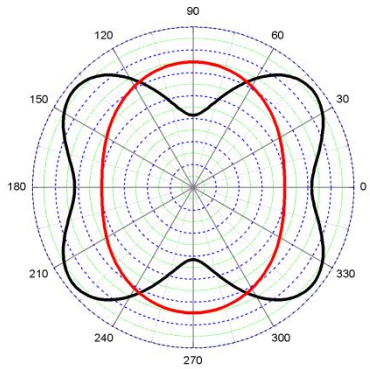

Figure S3. Theoretically simulated polar plots for 100nm edge length nanoprisms. Black represents vertically and red horizontally polarized HRS intensity respectively.

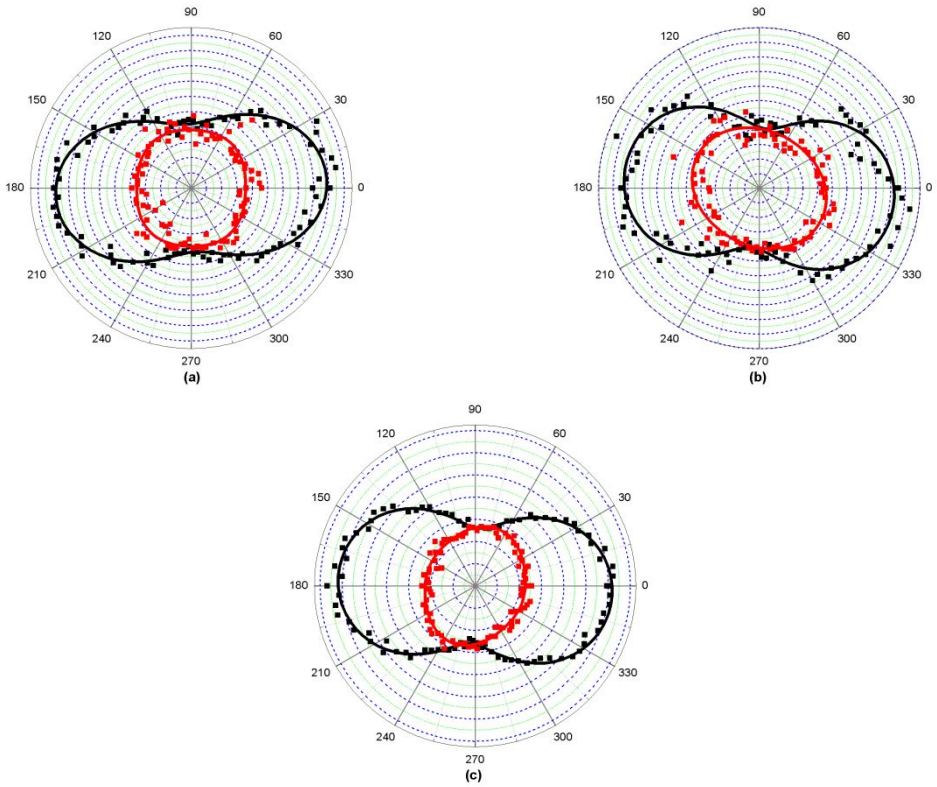

Figure S4(a-c). Polar plots of the polarization resolved HRS intensity for samples #61 (a), #78 (b) and #87 (c) and their fits using Eq.(2). Black represents vertically and red horizontally polarized HRS intensity respectively.

REFERENCES

(1) L. Chen, F. Ji, Y. Xu, L. He, Y. Mi, F. Bao, B. Sun, X. Zhang, Q. Zhang. High-Yield Seedless Synthesis of Triangular Gold Nanoplates through Oxidative Etching. *Nano Letters* **2014,** 14, (12), 7201-7206.

(2) M. R. Jones, C. A. Mirkin. Bypassing the Limitations of Classical Chemical Purification with DNA-Programmable Nanoparticle Recrystallization. *Angewandte Chemie International Edition* **2013,** 52, (10), 2886-2891.

(3) B. Nikoobakht, M. A. El-Sayed. Preparation and Growth Mechanism of Gold Nanorods (NRs) using Seed-Mediated Growth Method. *Chemistry of Materials* **2003,** 15, (10), 1957-1962.