Supporting Information for

Revisiting the Plasmon Radiation Damping of Gold Nanorods

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Materials and Methods
Figures S1 to S3 and Table S1.

Experimental details

1. Materials

All chemicals were obtained from commercial suppliers and used without further purification. Cetyltrimethylammonium bromide (CTAB, ≥98%) was purchased from Kermel. Sodium oleate (NaOL, >97%) was purchased from TCI. Tetrachloroauric (III) acid ($HAuCl_4 \cdot 3H_2O$) was purchased from Aladdin. L-ascorbic acid (AA), Sodium borohydride ($NaBH_4$, ≥98%), Silver nitrate ($AgNO_3$, ≥99%), Hydrochloric acid (HCl, 37 wt. % in water) were purchased from Sigma Aldrich. Ultrapure water obtained from a Direct-Q Water Purification System was used in all experiments.

2. Synthesis and characterization of gold nanorods

We have synthesized different gold nanorod batches to have a variety in aspect ratio and volume V (cf. Figure S1). The gold nanorods were prepared by a two-step seeded-growth process according to reference 1 with down-scale modifications. We have listed the details about the chemical amounts for each batch in Table S1. The dimensions of the synthesized gold nanorods were determined by scanning electron microscopy (SEM) using a Regulus 8100 microscope with a Cary 60 UV-Vis spectrophotometer. Figure S1 shows the representative SEM images of the gold nanorods. From those images, we obtained the diameter (D) and length (L) of thousands of nanorods and calculated with these values the particle volume by $V = \frac{\pi}{6} D^3 \left(\frac{3L}{2D} - \frac{1}{2}\right)$, which is also listed in Table S1. With such a data set, one could use artificial neural networks to design gold nanorods with certain geometry by varying the experimental condition [2].

Specifically, in the synthesis of gold nanorods, 0.28 g (0.037M in the final growth solution) or 0.36 g (0.047 M in the final growth solution) of CTAB and a certain quantity of NaOL were first dissolved in 10 ml of warm water (~50 °C) in a 50 ml centrifuge tube. The solution was allowed to cool down to 30 °C and 4mM AgNO3 solution was added. Following, 10 mL of 1 mM $HAuCl_4$ solution was added and mixed thoroughly, then the mixture was kept distilled at 30 °C for 15 min. The solution became colorless after 90 min of stirring (SPH-103D, 300 rpm) and a certain volume of HCl (37 wt. % in water, 12.1 M) was added (Table S1). After another 15 min of slow stirring (SPH-103D, 160 rpm), 0.05 mL of 0.064 M ascorbic acid (AA) was added and the solution was quickly stirred (SPH-103D, 200 rpm) for 30 s. Finally, a small volume of seed solution was injected into the growth solution (Table S1). The resultant mixture was stirred (SPH-103D, 200 rpm) for 30 s and then left undisturbed was put into a water bath at 28 °C for 12 h for gold nanorods growth. We have removed the growth reagents from the gold nanorods' solution by centrifuging the gold nanorods' solution for 30 min with 3214 g and re-dispersing the sedimentation into 10 mL of 0.05 M CTAB solution.

3. Single-particle spectroscopy characterizations

We used a home-built spectral imaging single-particle darkfield microscope to determine the radiation damping from the homogeneous plasmon line width of the gold nanorods with high statistics. The microscope setup consists of an upright microscope Zeiss Axioscope 5 with an EC-Epiplan 50x/0.75 Zeiss objective, a Plan-Apochromat 63x/1.4 Oil lris Zeiss objective, oil-immersion darkfield condenser (NA 1.2-1.4), a Halogen Lamp (OSL2, Thorlabs), and a liquid crystal tunable bandpass filter (KURIOS-VBI, Thorlabs). The scattered light of the gold nanorods under different wavelengths of excitation are collected by a COMS camera (Hamamatsu orca flash V4.0). we used a self-written MATLAB software program to determine the plasmon resonance energy (E_{res}) and linewidth (Γ) from all the particles.

4. Sample preparation for single-particle spectroscopy

To get sparsely distributed gold nanorods for single-particle measurements, we centrifuged 1 mL of gold nanorods solution (in 0.05 M CTAB) twice and redispersed the sedimentation in 1.2 mL ultrapure water. Following, we immobilized the particle on a piece of clean glass coverslip (Deckgläser, 24 x 60 mm) by drop-casting a centrifuged solution of gold nanorods (~50 μL), and then we rinsed the cover glass with ultrapure and ethanol separately. After dring the cover glass, we placed a piece of clean glass coverslip (Deckgläser, 24 x 24 mm) on the center of the glass coverslip (Deckgläser, 24 x 60 mm) with gold nanorods. We used four the small glasses (Deckgläser, 2 x 2 mm) as gap holders, which were placed at the four corners of the cover glass to (Deckgläser, 24 x 24 mm) so that a gap of about 0.2 mm thick was formed between the two pieces of glass. Finally, The glass coverslip (Deckgläser, 24 x 24 mm) was fixed with tape (0.5 cm wide and 3.5 cm long) along the long side of the glass coverslip

(Deckgläser, 24 x 60 mm), and then ultrapure water was injected to fill the interlayer, which allows us to measure the particle in water-immersion condition.

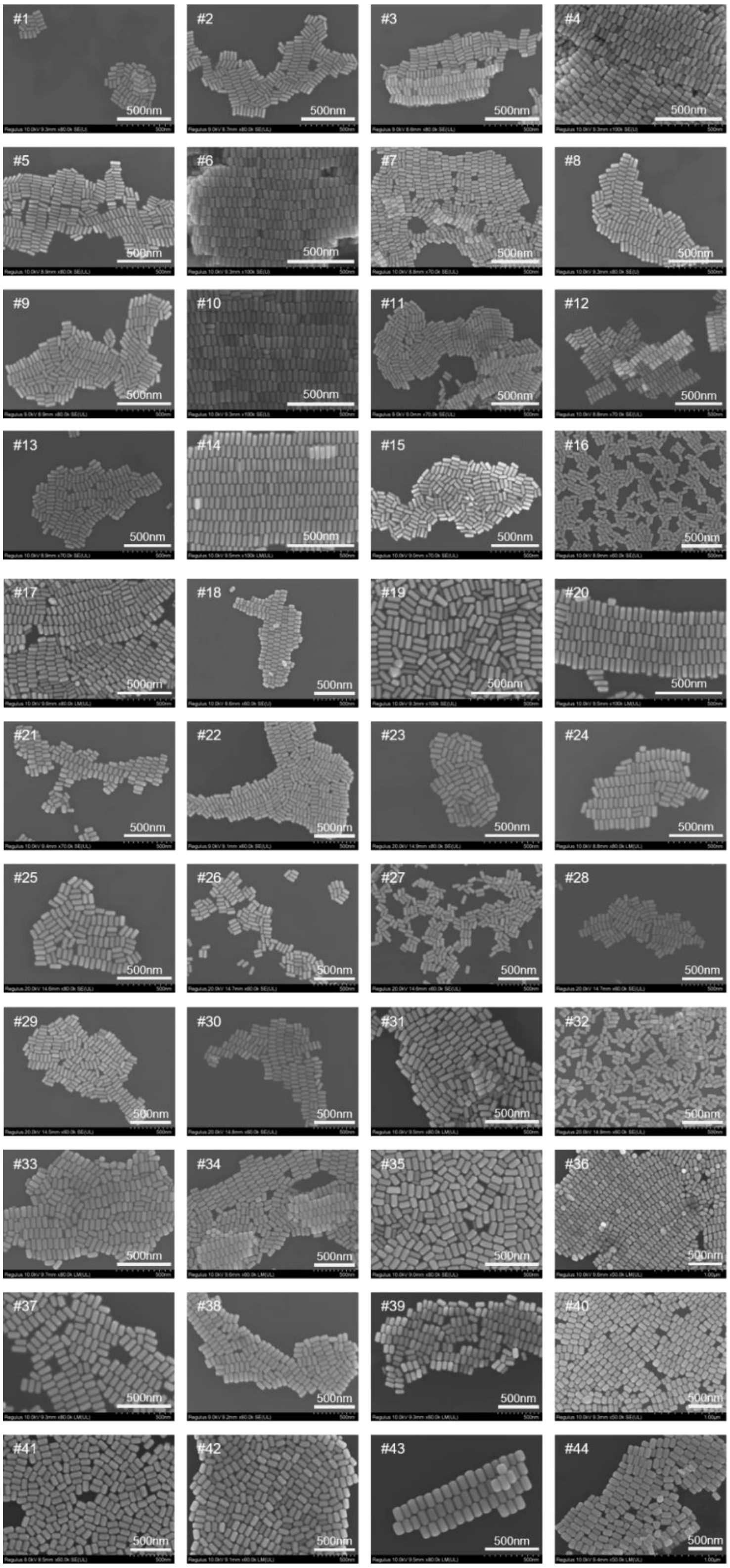

Figure S1. Representative SEM images of the 44 batches of gold nanorods used in this work. The scale bar is 500 nm and the sample number is indicated by the white number. The particles are ordered by their volume.

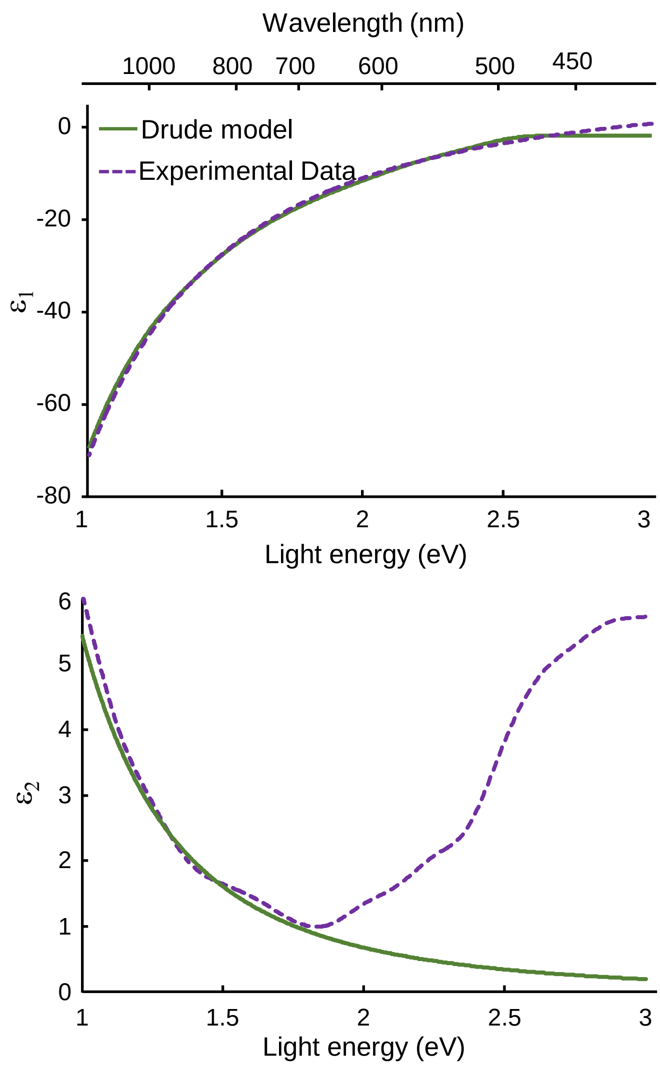

Figure S2. Experimental data and the Drude model for the real and imaginary parts of the dielectric function of bulk gold. Experimental data (purple dot line) were measured by Johnson and Christy, the Drude model (green line) was calculated from the given parameters.

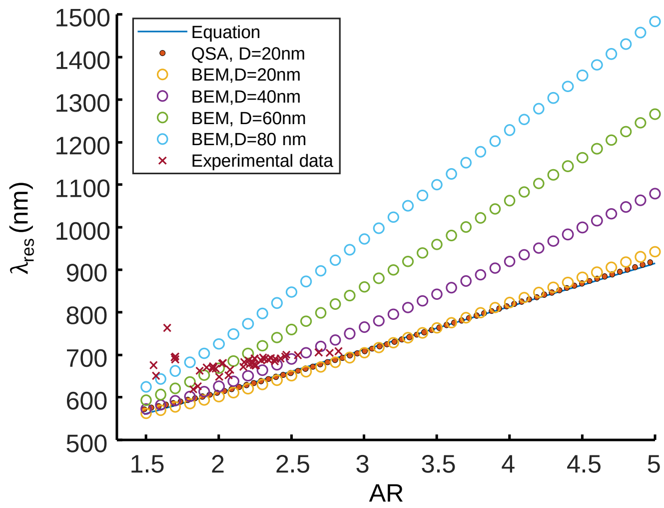

Figure S3. Predicted resonance wavelengths (λ_{res}) of gold nanorods by equation 10 (line) with Drude parameters. The QSA simulation (dot), BEM simulation (circle), and experimental data (cross) are used for comparison. In the case of QSA simulation, the data were calculated with the gold ellipsoidal nanoparticles for 20 nm diameter and different aspect ratios from 1.5 to 5 in 0.05 steps. For the BEM simulation, the data were simulated with the gold spherocylindrical nanoparticles with aspect ratios of 1.5 to 5 and diameters of 20 to 80 nm. We used tabulated optical constants (from Johnson and Christy) for all the simulations.

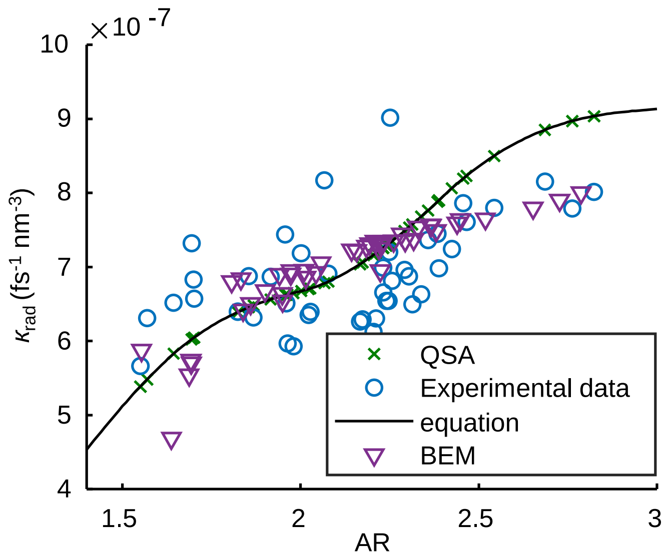

Figure S4. Comparison of experimental data to our mathematical model, QSA simulation, and BEM simulation. The radiation damping parameter from the experimental data and BEM simulation follows the same dependency on AR as our mathematical predictions. However, both of them demonstrate a lower value compared with the mathematical model for larger AR, which is due to the increase of retardation effects.

	CTAB (g)	$AgNO_3$ /4mM (ml)	Seed (ml)	HCl (ml)	NaOL (g)	Mean Length (nm)	Mean Diameter (nm)	Mean Volume (nm^3)	Aspect ratio
#1	0.36	0.4	0.08	0.06	0.06172	68.55±6.04	30.83±3.48	43928.70±10175.87	2.25±0.32
#2	0.36	0.72	0.064	0.06	0.06172	81.85±8.25	29.37±3.17	49107.33±10854.51	2.82±0.45
#3	0.36	0.72	0.08	0.06	0.06172	79.96±7.37	30.14±3.11	50113.35±10159.51	2.69±0.40
#4	0.36	0.32	0.08	0.06	0.06172	69.28±6.10	33.91±3.83	52969.09±12833.35	2.07±0.28
#5	0.36	0.72	0.08	0.06	0.06172	84.18±7.85	30.87±3.33	55652.37±11897.27	2.76±0.42
#6	0.36	0.48	0.08	0.06	0.06172	78.61±7.15	35.41±3.31	66146.37±13081.82	2.24±0.30
#7	0.36	0.36	0.08	0.06	0.06172	73.07±6.81	37.04±4.71	66372.81±17662.59	2.00±0.29
#8	0.36	0.56	0.08	0.06	0.06172	83.89±7.67	35.49±3.20	71609.03±13794.35	2.38±0.32
#9	0.36	0.72	0.048	0.06	0.06172	87.61±8.38	34.79±3.29	72567.79±14177.47	2.54±0.36
#10	0.36	0.64	0.08	0.06	0.06172	84.62±6.97	35.75±3.34	73380.55±14189.88	2.39±0.30
#11	0.36	0.72	0.032	0.06	0.06172	87.13±7.77	35.59±2.79	75041.66±12212.95	2.47±0.32
#12	0.36	0.44	0.08	0.06	0.06172	78.45±6.88	38.13±3.67	75465.06±15194.10	2.08±0.28
#13	0.36	0.52	0.08	0.06	0.06172	82.82±7.69	37.10±3.62	76449.47±14872.13	2.26±0.33
#14	0.36	0.72	0.016	0.06	0.06172	91.16±7.04	37.38±3.07	86707.67±14581.14	2.46±0.29
#15	0.36	0.68	0.08	0.06	0.06172	88.90±8.47	38.18±4.13	87812.06±19229.61	2.36±0.35
#16	0.36	0.6	0.08	0.06	0.06172	87.46±7.81	39.59±3.83	91817.63±17906.88	2.23±0.31
#17	0.36	0.48	0.096	0.04	0.06172	85.83±6.96	40.06±4.44	92350.45±21515.71	2.17±0.28
#18	0.36	0.24	0.08	0.06	0.06172	79.58±7.61	44.05±4.69	100096.39±23785.88	1.82±0.24
#19	0.28	0.72	0.096	0.06	0.04936	94.83±10.67	39.83±5.67	103953.99±30581.56	2.42±0.41
#20	0.28	0.72	0.048	0.06	0.04936	93.35±8.27	40.89±4.17	105769.08±23283.46	2.30±0.29
#21	0.36	0.28	0.08	0.06	0.06172	81.65±8.68	44.56±5.76	106577.12±31714.22	1.85±0.25
#22	0.36	0.72	0.016	0.06	0.06172	95.17±7.85	43.04±3.84	117984.80±21251.92	2.23±0.29
#23	0.36	0.64	0.08	0.06	0.06172	94.73±8.19	43.19±3.94	118406.99±22680.19	2.21±0.28
#24	0.28	0.72	0.032	0.06	0.04936	99.34±8.00	42.87±4.08	123658.03±24451.39	2.34±0.29
#25	0.36	0.72	0.08	0.06	0.06172	98.74±7.44	43.07±4.07	123761.43±24124.14	2.31±0.28
#26	0.36	0.7	0.08	0.06	0.06172	97.74±8.24	43.23±5.06	123762.59±28918.07	2.29±0.32
#27	0.36	0.71	0.08	0.06	0.06172	98.00±8.13	43.99±4.00	127228.04±23587.83	2.25±0.29
#28	0.36	0.69	0.08	0.06	0.06172	97.95±8.59	44.84±4.14	131678.86±25344.88	2.20±0.29
#29	0.36	0.74	0.08	0.06	0.06172	99.88±8.41	44.87±4.22	135042.17±25925.36	2.25±0.29
#30	0.36	0.68	0.08	0.06	0.06172	98.74±8.48	45.77±3.99	138018.62±25429.68	2.17±0.27
#31	0.28	0.48	0.048	0.084	0.06172	97.13±8.80	50.05±5.20	160279.17±37446.26	1.96±0.24
#32	0.36	0.66	0.08	0.06	0.06172	101.99±8.09	50.76±4.29	173264.93±31001.69	2.02±0.22
#33	0.28	0.48	0.016	0.084	0.04936	101.65±6.74	51.54±3.12	176677.89±23753.79	1.98±0.17
#34	0.36	0.72	0.008	0.06	0.06172	107.42±7.36	53.32±4.21	200909.70±32066.71	2.03±0.22
#35	0.28	0.48	0.096	0.084	0.06172	107.06±9.28	56.34±5.59	222518.42±48898.68	1.92±0.22
#36	0.28	0.48	0.008	0.084	0.04936	112.17±10.29	57.56±4.28	242863.59±41993.11	1.96±0.23
#37	0.28	0.48	0.008	0.084	0.06172	111.78±9.90	60.10±4.54	261926.79±47182.96	1.87±0.20
#38	0.36	0.72	0.008	0.06	0.06172	115.45±8.29	59.22±5.02	264887.68±46265.14	1.96±0.22
#39	0.28	0.48	0.064	0.084	0.06172	113.81±9.23	61.90±5.58	283171.64±57169.27	1.85±0.19
#40	0.36	0.2	0.08	0.06	0.06172	113.75±11.99	73.22±8.79	383387.23±105908.03	1.57±0.20
#41	0.36	0.72	0.004	0.06	0.06172	126.62±8.24	74.85±4.95	448231.62±61762.56	1.70±0.16
#42	0.28	0.48	0.032	0.084	0.06172	127.74±9.87	75.45±6.00	462263.15±84153.17	1.70±0.16
#43	0.28	0.48	0.008	0.084	0.06172	131.58±9.68	78.00±5.71	507412.31±84549.05	1.69±0.15
#44	0.28	0.72	0.008	0.06	0.04936	152.00±9.69	92.83±6.63	824252.22±128922.17	1.64±0.13

Table S1. Synthesis details and dimensions of gold nanorods. This table summarizes the dimension of gold nanorods characterized by SEM images and the amount of chemicals used for the gold nanorod synthesis.

Notes and references

1. X. Ye, *Nano Lett*. 2013, **13**, 765-771.

2. C.R. Rekha, *Optik*, 2018, **172**, 721-729.