

Supporting Information for

Ultrafast Electron-Phonon Coupling in Hollow Gold Nanospheres

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Materials. Cobalt chloride hexahydrate (Puratronic, 99.998%) and chloroauric acid trihydrate (ACS reagent grade, 99.99%) were obtained from Alfa Aesar. Sodium citrate tribasic dihydrate (ACS reagent grade, >99%), sodium borohydride (99.99%), (+)-sodium L-ascorbate, hexadecyltrimethylammonium bromide (CTAB) and methanol were obtained from Sigma-Aldrich. All water used in the syntheses was 18.2 M Ω milli-Q filtered.

Hollow Gold Nanoparticle Synthesis.¹ Cobalt nanoparticles were prepared first as sacrificial templates for the resulting hollow gold particles. In a typical reaction (Sample A), 100 μ L of 0.4 M cobalt chloride solution and 400 μ L of 0.1 M sodium citrate solution were added to 100 mL of water. This solution was vacuumed for 30 minutes and then bubbled with argon gas for 10 minutes to ensure an air-free environment. In order to reduce the Co²⁺ to cobalt nanoparticles, 100 μ L of a freshly-made 1 M sodium borohydride solution was added with vigorous stirring. The cobalt nanoparticle solution was allowed to stir under constant argon flow until H₂ gas evolution ceased. Then, 30 mL of the cobalt nanoparticle suspension was quickly added to a gold solution containing 30 μ L of 0.1 M chloroauric acid diluted with water to a final volume of 10 mL. The solution was exposed to air, allowing complete oxidation of the cobalt nanoparticles until a thin shell of gold remained with water and dissolved salts inside.

Sample	Amount of 0.4M CoCl ₂ (μL)	Amount of 0.1M citrate (μL)	Amount of 1M NaBH ₄ (μL)	Amount of 0.1M HAuCl ₄ (μL)
A	100	400	100	30
B*	100	400	200	200
C	100	400	100	80
D*	100	400	200	100
E*	100	400	200	200
F	100	190	180	70
G	100	190	180	70
H	100	190	180	70
I	100	190	180	50
J	100	190	180	50

* Samples B, D, and E were prepared in a slightly different manner than described above. The cobalt nanoparticle suspension was prepared as stated above and allowed to stir until H₂ gas evolution ceased. Then, 50 μL of 0.1 M chloroauric acid was added to the stirring cobalt nanoparticle suspension (under constant Ar flow) every 60 seconds until a total volume of 200 μL of gold solution was reached. The entire solution was exposed to air, and hollow gold shells formed due to the reduction of gold and oxidation of cobalt. (Samples A and C were made from the same batch of cobalt nanoparticles. Samples H and J were made from the same batch of cobalt nanoparticles. Samples G and I were made from the same batch of cobalt nanoparticles.)

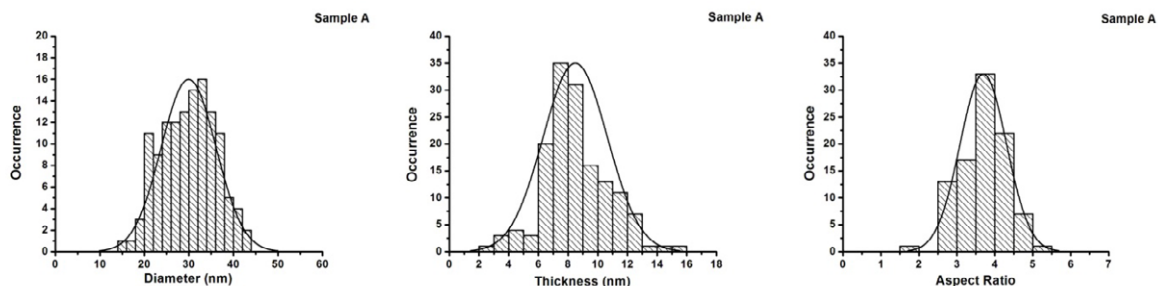
Solid Gold Nanoparticle Synthesis.^{2,3} Gold colloids having ~20-nm outer diameter (Sample K) were prepared by citrate reduction of gold, following the method reported by Ghosh *et al.*² Specifically, 50 mL of water containing 0.25 mM HAuCl₄ was heated to boiling. Then, 0.750 mL of 1% trisodium citrate was added to the boiling solution, reducing the Au³⁺ and forming the gold nanoparticles. Sample L and M were prepared following the seeding-growth approach reported by Jana *et al.*³ Gold seeds with approximately 4-nm diameter were formed by preparing a 20 mL aqueous solution of 2.5×10^{-4} M HAuCl₄ and 2.5×10^{-4} M trisodium citrate and then adding a freshly prepared ice-cold solution of 0.1 M NaBH₄ while stirring. A stock growth solution was prepared with 50 mL water and 2.5×10^{-4} M HAuCl₄. Then, 1.5 g of CTAB was added to the solution and this was heated until the solution turned a clear orange color. This solution was cooled to room temperature before further use. The seed solution was used within 3 hours of preparation to form the larger gold particles. First, 9 mL of the growth solution was mixed with 50 μL of freshly prepared 0.1 M ascorbate. Then, 1.0 mL of the seed solution was added while stirring vigorously. This solution was stirred for 10 minutes and then allowed to sit for 30 minutes before further use. Next, 9 mL of the growth solution was mixed with 50 μL of

0.1 M ascorbate and 1.0 mL of the previous gold colloid solution was added with stirring. The resulting gold colloids were stirred for 10 minutes and allowed to sit for 30 minutes before their further use. Again, 9 mL of the growth solution was mixed with 50 μ L of 0.1 M ascorbate and 1.0 mL from the previous gold colloid solution was added while stirring. The resulting gold colloids were stirred for 10 minutes and allowed to sit for 30 minutes before their further use (Sample L). Finally, 9 mL of the growth solution was mixed with 50 μ L of 0.1 M ascorbate and 1.0 mL from the Sample K solution was added with stirring. The resulting gold colloids were stirred for 10 minutes and allowed to sit for 30 minutes before their further use (Sample M).

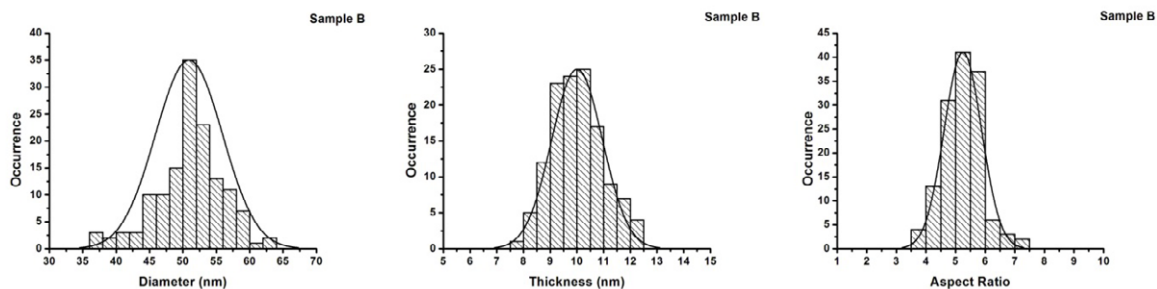
The resulting HGNs and SGNs were characterized by UV-Visible absorption spectroscopy and transmission electron microscopy (TEM). The absorption spectra for SGN samples K, L and M are provided in Figure S1. TEM images of these SGN samples are provided in Figure S2. TEM analysis revealed that the SGN samples J, K and L had outer diameters of 19.8 ± 3.7 , 37.7 ± 3.3 , and 83.3 ± 7.5 nm, respectively (Table S1). Detailed particle size and aspect ratio statistics for all HGN and SGN samples are included in the Supporting Information Figure S3.

Figure S1: HGN and SGN Size Distributions (d: diameter, t: thickness, and AR: aspect ratio)

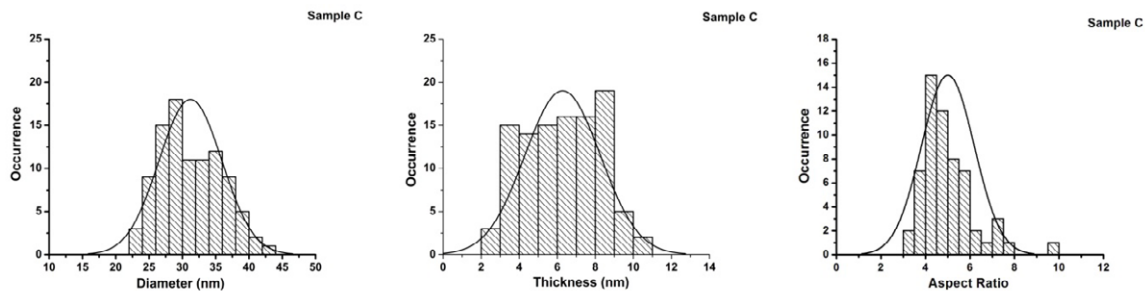
Sample A: $d = 29.9 \pm 6.2$ nm, $t = 8.5 \pm 2.2$ nm, $AR = 3.5 \pm 0.6$



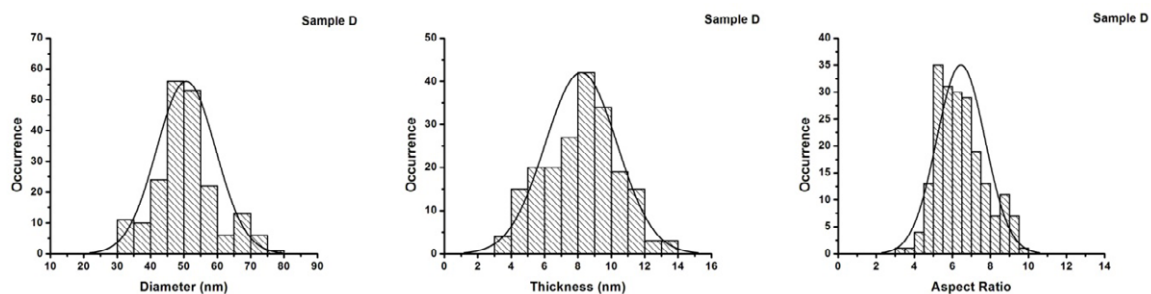
Sample B: $d = 51.1 \pm 5.1$ nm, $t = 10.0 \pm 1.0$ nm, $AR = 5.1 \pm 0.6$



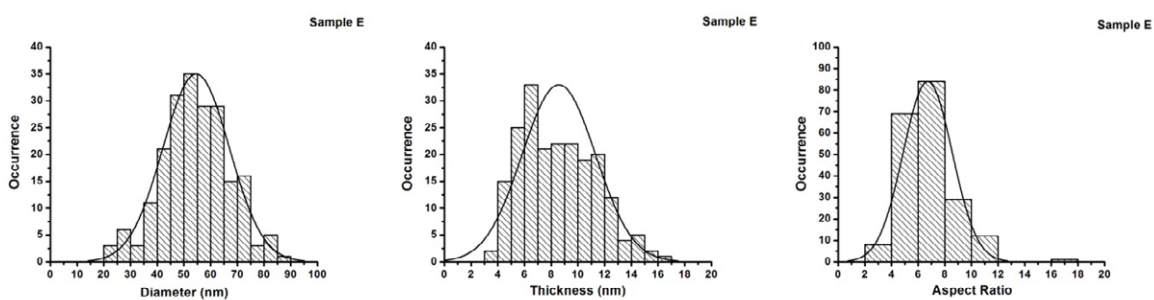
Sample C: $d = 31.2 \pm 4.6$ nm, $t = 6.3 \pm 2.1$ nm, $AR = 5.4 \pm 1.5$



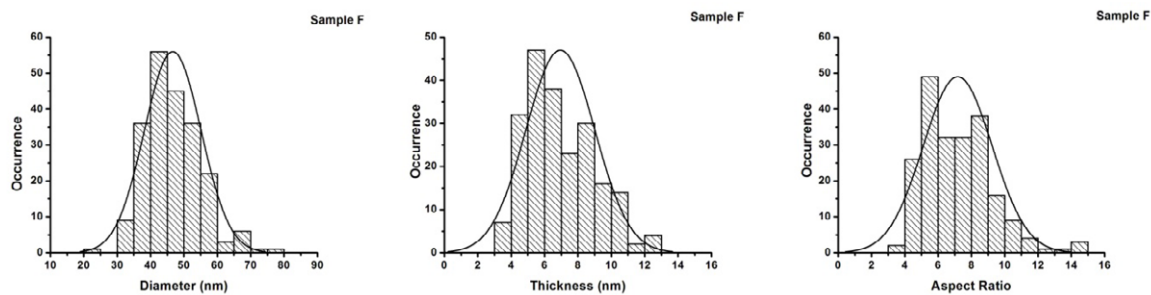
Sample D: $d = 50.7 \pm 8.9$ nm, $t = 8.2 \pm 2.2$ nm, $AR = 6.5 \pm 1.3$



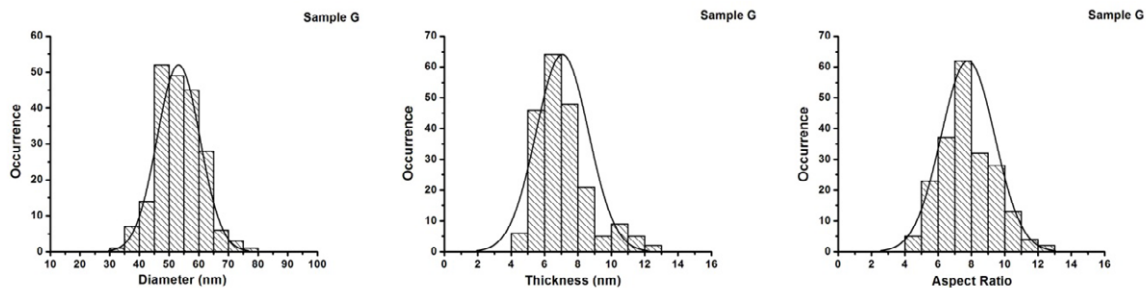
Sample E: $d = 54.6 \pm 12.5$ nm, $t = 8.6 \pm 2.9$ nm, $AR = 6.7 \pm 1.8$



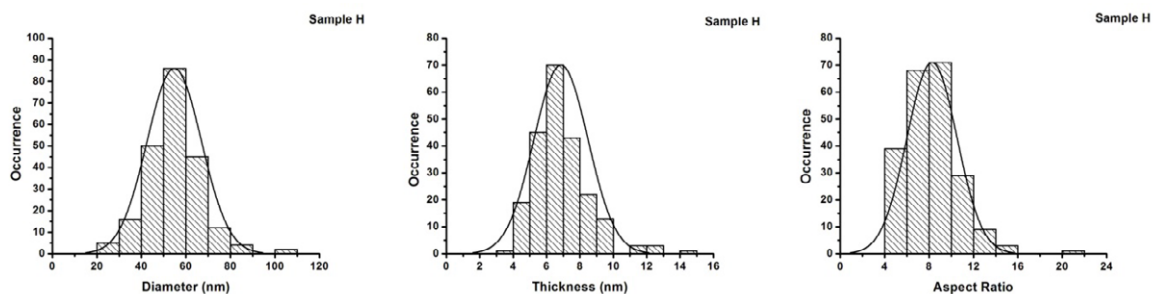
Sample F: $d = 46.7 \pm 8.5$ nm, $t = 7.0 \pm 2.1$ nm, $AR = 7.2 \pm 2.1$



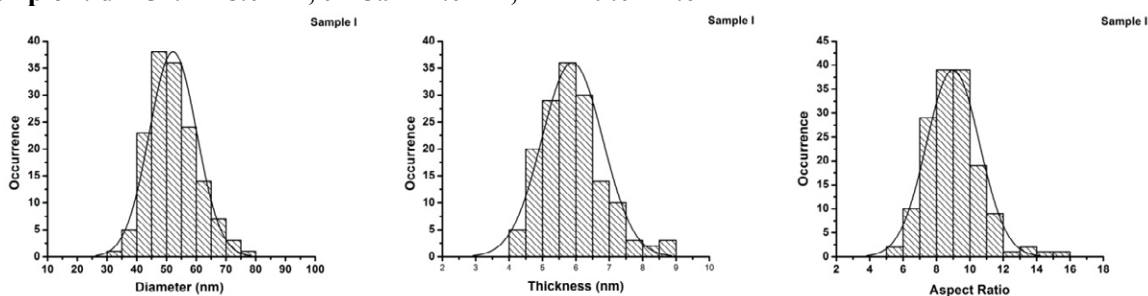
Sample G: $d = 53.2 \pm 7.2$ nm, $t = 7.1 \pm 1.7$ nm, $AR = 7.8 \pm 1.6$



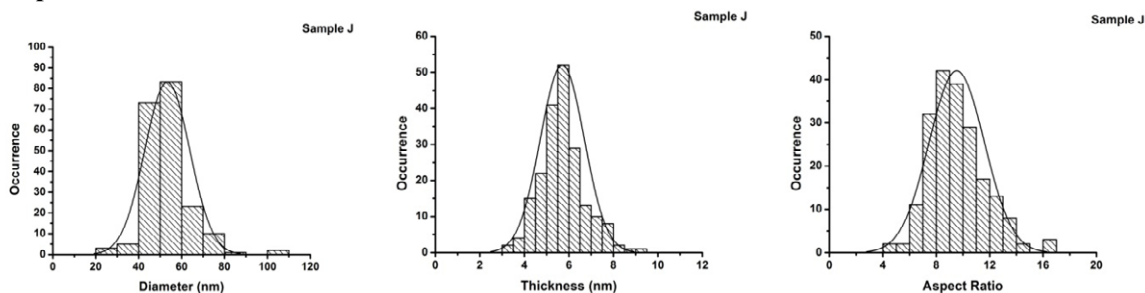
Sample H: $d = 54.8 \pm 12.2$ nm, $t = 6.9 \pm 1.6$ nm, AR = 8.3 ± 2.3



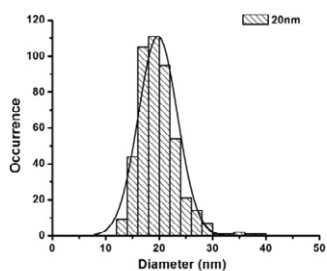
Sample I: $d = 52.2 \pm 8.0$ nm, $t = 5.9 \pm 1.0$ nm, AR = 9.0 ± 1.6



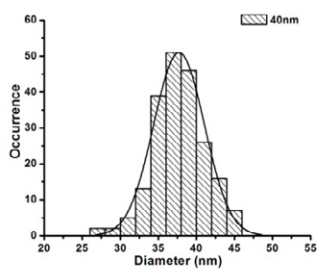
Sample J: $d = 53.3 \pm 10.5$ nm, $t = 5.7 \pm 1.0$ nm, AR = 9.5 ± 2.1



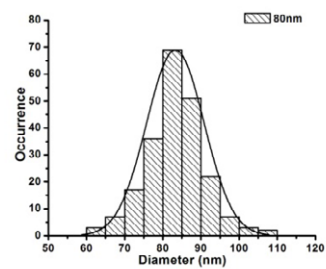
Sample K: $d = 19.8 \pm 3.7$ nm



Sample L: $d = 37.7 \pm 3.3$ nm



Sample M: $d = 83.3 \pm 7.5$ nm



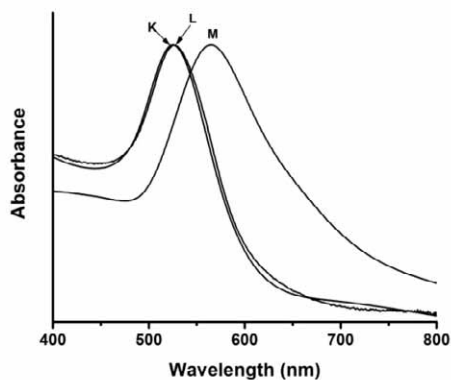


Figure S2: UV-visible absorption for solid gold nanoparticle samples K through M.

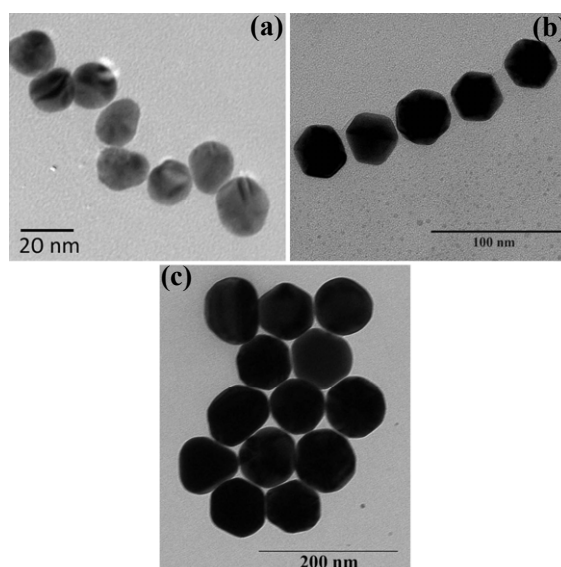


Figure S3: TEM images of the solid gold nanoparticle samples used in this study: (a) Sample K, (b) Sample L, and (c) Sample M, having diameters of approximately 20, 40, and 80 nm, respectively.

Table S1: Size distributions for SGN samples

Sample	Outer Diameter (nm)
K	19.8 (\pm 3.7)
L	37.7 (\pm 3.3)
M	83.3 (\pm 7.5)

Table S2: Electron-phonon coupling data for solid gold nanoparticles

Sample	Diameter (nm)	τ_0 (ps)	G [$10^{16} \text{ W m}^{-3} \text{ K}^{-1}$]
K	19.8 ± 3.7	1.00 ± 0.08	1.97 ± 0.16
L	37.7 ± 3.3	1.19 ± 0.08	1.64 ± 0.11
M	83.3 ± 7.5	1.01 ± 0.08	1.95 ± 0.15

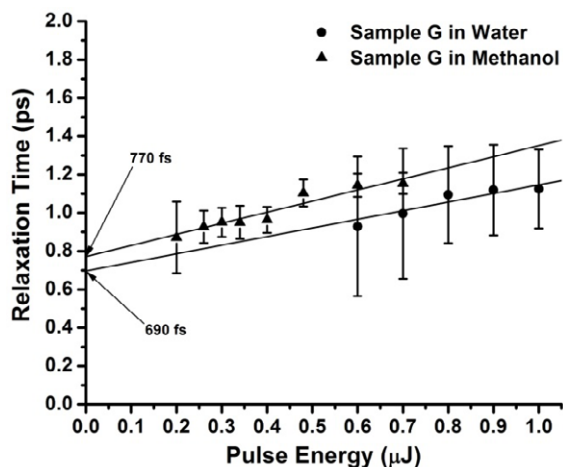


Figure S4: Electron-phonon coupling times as a function of the laser pulse energy for sample G in water (circles) and methanol (triangles).

References

- 1 A.M. Schwartzberg, T.Y. Olson, C.E. Talley and J.Z. Zhang, *J. Phys. Chem. B*, 2006, **110**, 19935.
- 2 S.K. Ghosh, A. Pal, S. Kundu, S. Nath and T. Pal, *Chem. Phys. Lett.*, 2004, **395**, 366.
- 3 N.R. Jana, L. Gearheart and C.J. Murphy, *Langmuir*, 2001, **17**, 6782.