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Supporting Information

Optical Properties of Symmetry-breaking Tetrahedral Nanoparticle

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Section S1. Simulation construction for rounded gold tetrahedron

We adopted an approach reported in the literature [S1] to construct tetrahedral nanoparticles with rounded edges and vertices.

First, a gold tetrahedron is created in Lumerical FDTD software. The obtained gold tetrahedron, without rounded vertices and edges, is shown below:

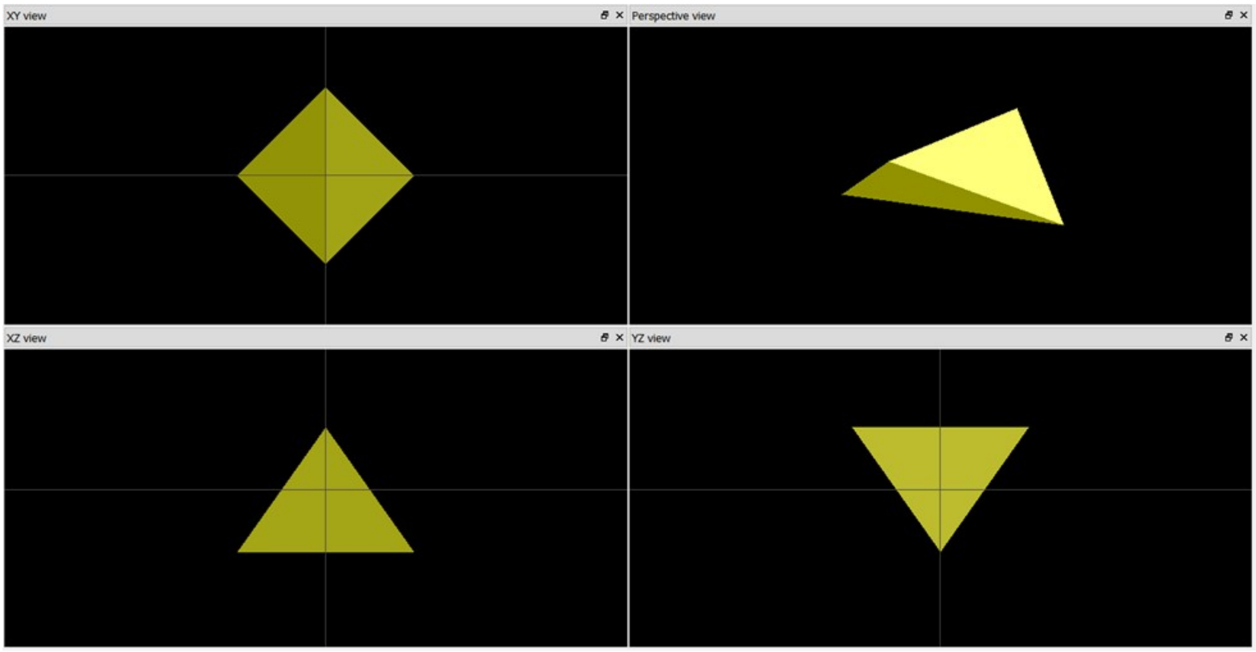

Figure S1. Schematic gold tetrahedral nanoparticle without rounding under different views.

Next, in order to round the gold tetrahedron by a radius r, six air cylinders are used to remove the sharp edges and vertices. The six air cylinders have a radius of $\sqrt{2}r$ and a length of (a+10 nm) where a is the tetrahedron edge length. The coordinates for the six air cylinders are listed below:

- Top: (0, 0, $\sqrt{2}$a/4) with a rotation around the x axis by 90°
- Bottom: (0, 0, -$\sqrt{2}$a/4) with a rotation around the y axis by 90°
- Left1: (-a/4, -a/4, 0) with a rotation around the y axis by 30° and the x axis by 35.26°
- Left2: (-a/4, a/4, 0) with a rotation around the y axis by 30° and the x axis by -35.26°
- Right1: (a/4, -a/4, 0) with a rotation around the y axis by -30° and the x axis by 35.26°
- Right2: (a/4, a/4, 0) with a rotation around the y axis by -30° and the x axis by -35.26°

The obtained gold tetrahedron with removed sharp edges and vertices is shown below: The cyan lines represent the air cylinders.

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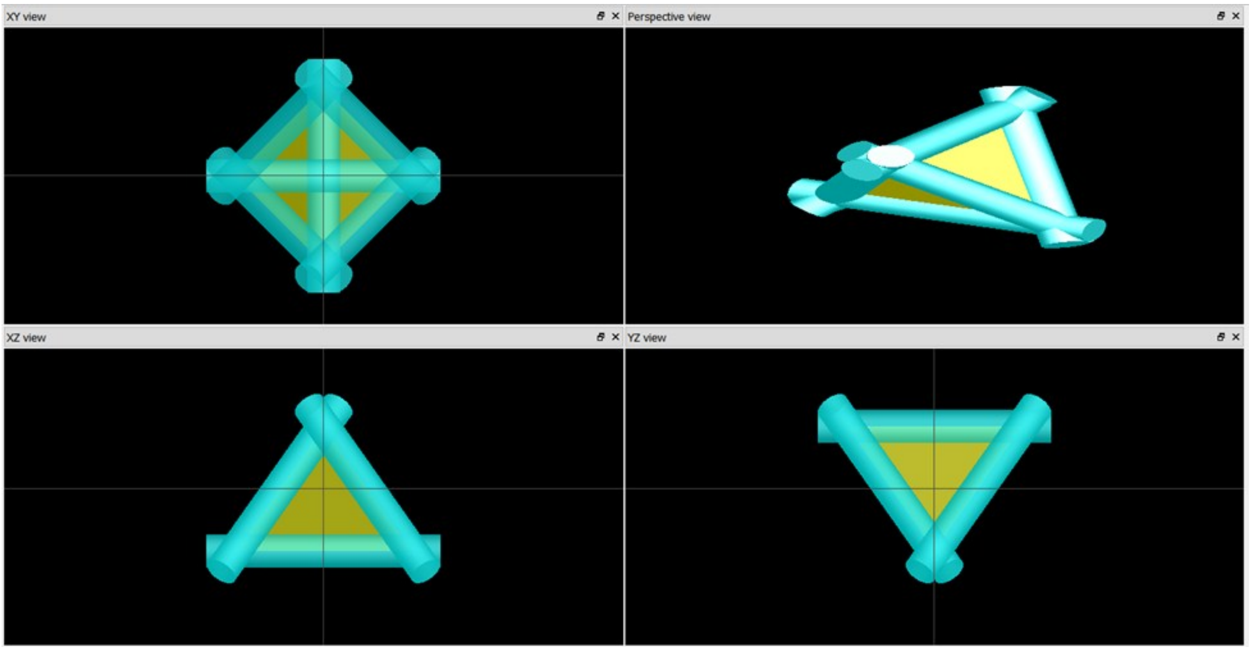

Figure S2. Schematic gold tetrahedral nanoparticle where edges and vertices are removed by six air cylinders under different views.

Subsequently, six gold cylinders with both ends rounded by a radius of r, which is the same as the rounded radius of the gold tetrahedron, are used to create rounded edges and vertices on the gold tetrahedron. The six gold cylinders have a radius of r and a length of ($a-8r/\sqrt{3}+2r$). The coordinates for the six gold cylinders are listed below: The cyan and the yellow lines represent the air cylinders and the main body of a gold tetrahedral nanoparticle.

- Top: ($0, 0, \sqrt{2}a/4-\sqrt{3}r$) with a rotation around the x axis by 90°
- Bottom: ($0, 0, -\sqrt{2}a/4+\sqrt{3}r$) with a rotation around the y axis by 90°
- Left1: ($-a/4+2r/\sqrt{3}, -a/4+2r/\sqrt{3}, 0$) with a rotation around the y axis by 30° and the x axis by 35.26°
- Left2: ($-a/4+2r/\sqrt{3}, a/4-2r/\sqrt{3}, 0$) with a rotation around the y axis by 30° and the x axis by -35.26°
- Right1: ($a/4-2r/\sqrt{3}, -a/4+2r/\sqrt{3}, 0$) with a rotation around the y axis by -30° and the x axis by 35.26°
- Right2: ($a/4-2r/\sqrt{3}, a/4-2r/\sqrt{3}, 0$) with a rotation around the y axis by -30° and the x axis by -35.26°

The obtained gold tetrahedron rounded by a radius of r is shown below:

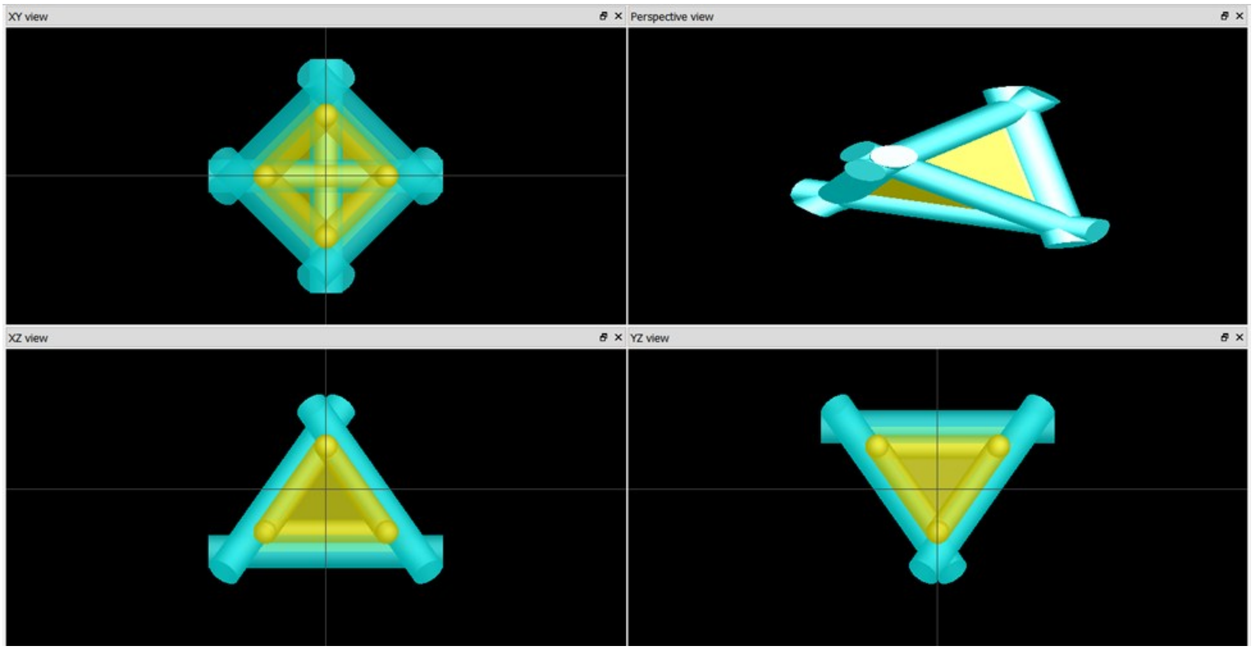

Figure S3. Schematic gold tetrahedral nanoparticle with rounded edges and vertices under different views.

The above process for the creation and rounding of the gold tetrahedral nanoparticle has also been added in detail to the supporting information section 1: "Simulation construction for rounded gold tetrahedron".

Section S2. Optimal mesh size determination

In order to identify the optimal mesh size for simulations, the extinction spectra for the gold tetrahedral nanoparticle with an edge length of 30 nm without any rounding under different mesh sizes were calculated. The optimal mesh size is identified to be 0.2 nm, as shown in Figure S4.

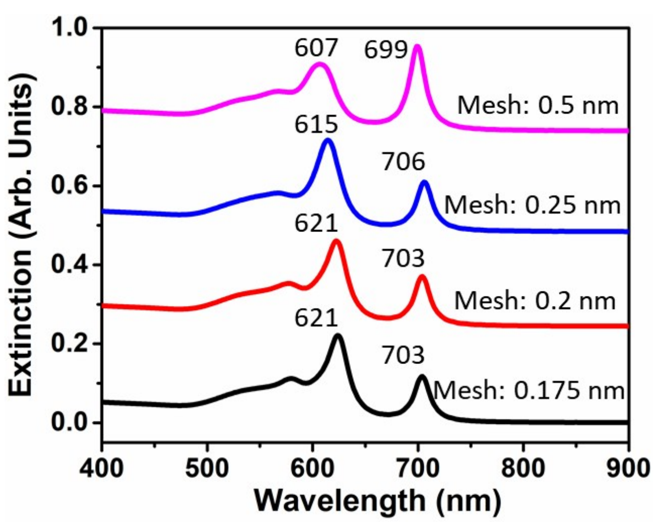

Figure S4. Extinction spectra for the gold tetrahedral nanoparticle with an edge length of 30 nm without any rounded under different mesh sizes. The optimal mesh size for simulation is thus identified to be 0.2 nm.

Section S3. Extinction spectra for a gold tetrahedral nanoparticle with varying edge lengths

The extinction spectra for a gold tetrahedral nanoparticle with an edge length of 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, and 70 nm are shown below as compared to the counterparts with a rounded radius of 0.5 nm.

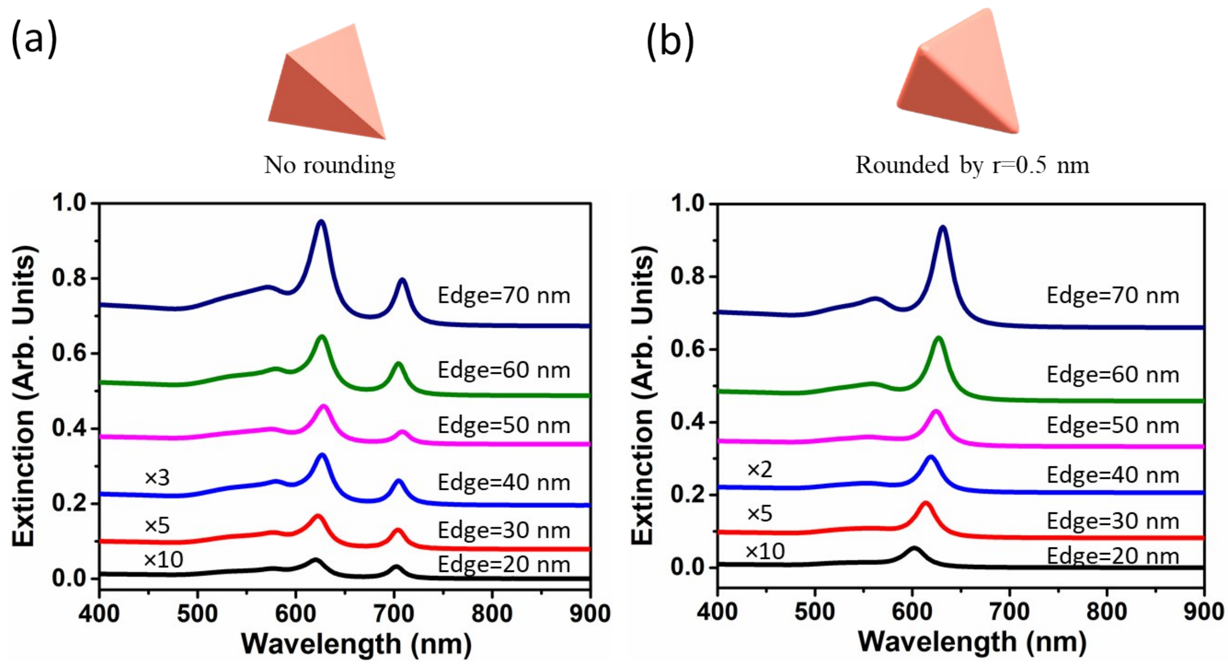

Figure S5. Extinction spectra for gold tetrahedral nanoparticles with a rounded radius of (a) 0 nm and (b) 0.5 nm. The edge length studied for the gold tetrahedral nanoparticles includes 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, and 70 nm.

Section S4. Surface polarization charge distributions of normal modes

The surface polarization charge distributions for the identified eleven normal modes on a gold tetrahedral nanoparticle with an edge length of 30 nm are shown below.

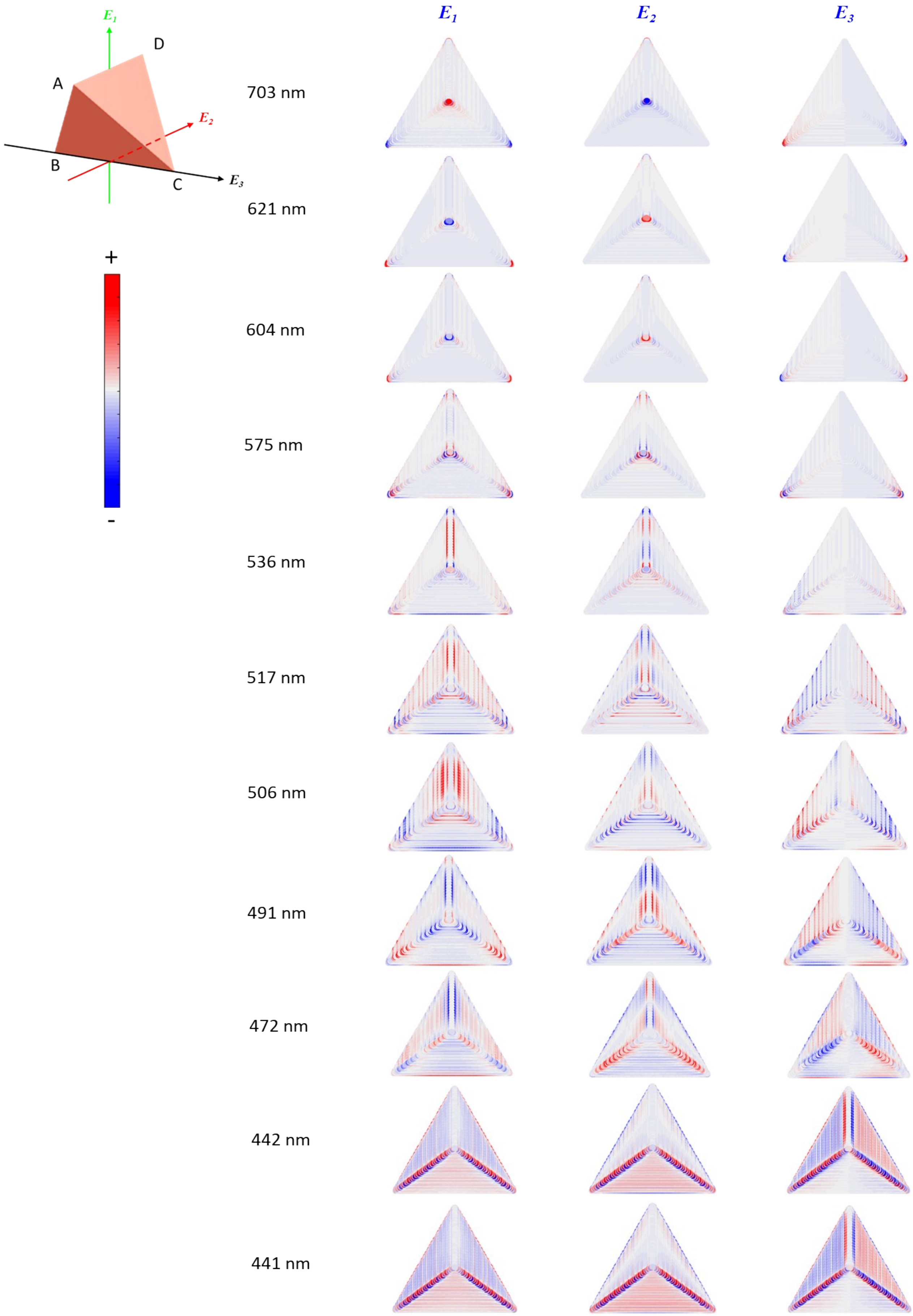
E1
D
A
E2
B
C
E3
+
-
E1
E2
E3
703 nm
621 nm
604 nm
575 nm
536 nm
517 nm
506 nm
491 nm
472 nm
442 nm
441 nm

Figure S6. Surface polarization charge distributions for the identified eleven normal modes on a gold tetrahedral nanoparticle with an edge length of 30 nm. The three orthogonal polarization directions along with the legend are shown on the left side of the figure.

Reference

S1. Zheng, Y.; Liu, W.; Lv, T.; Luo, M.; Hu, H.; Lu, P.; Choi, S.-I.; Zhang, C.; Tao, J.; Zhu, Y.; Li, Z.-Y.; Xia, Y., Seed-Mediated Synthesis of Gold Tetrahedra in High Purity and with Tunable, Well-Controlled Sizes. *Chemistry – An Asian Journal* **2014,** *9* (9), 2635-2640.