

# Multimode Resonances in Silver Nano-cuboids

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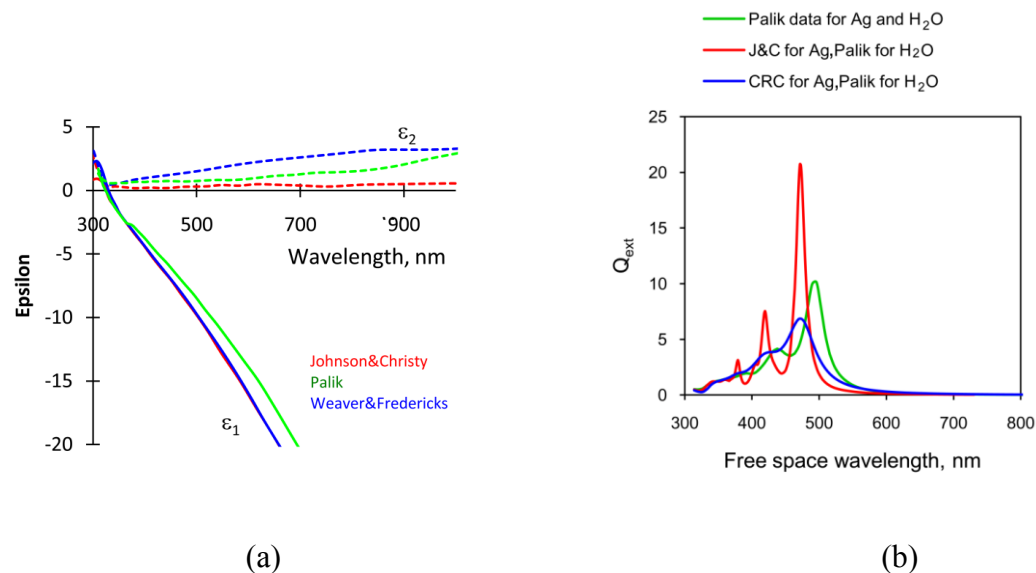


Figure S1. Influence of dielectric function used for silver (a) on the calculated extinction spectra (b) for a silver nanocube of 30 nm edge length suspended in water at 20°C. Here we have used the data from the compilations of Palik<sup>41</sup> and Weaver and Fredericks,<sup>39</sup> and the experimental data of Johnson and Christy.<sup>40</sup> The data listed by Palik<sup>41</sup> has been used for water. Note how the higher value of  $\epsilon_2$  for the Palik and Weaver & Fredericks data causes strong damping of the resonance peaks.

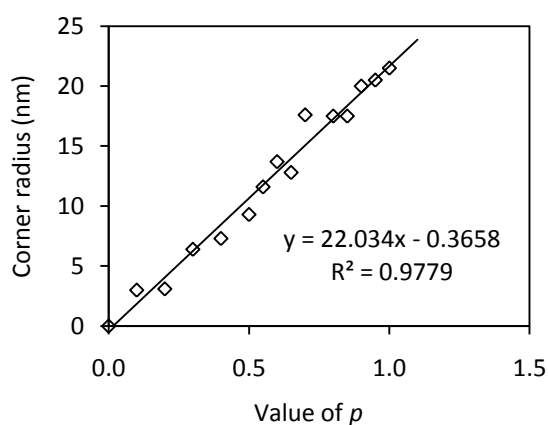


Figure S2. Corner radii measured for dipole targets generated for a range of  $p$  values.

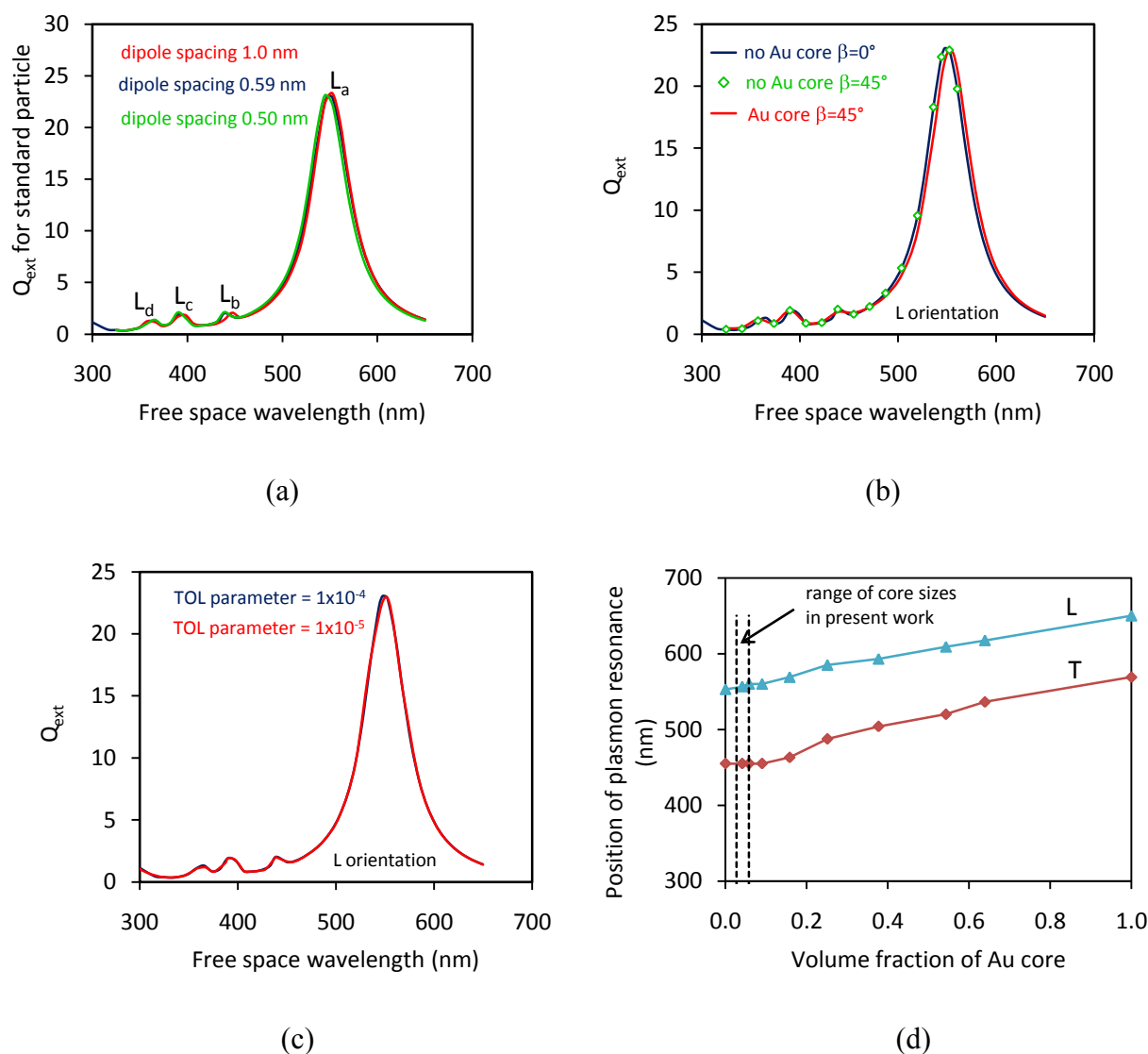


Figure S3. Effect of various parameters on the results of the DDA simulations. All of these calculations were performed with a surrounding medium with  $n=1.625$ ,  $k=0$  to make the individual extinction peaks easier to separate. Panels (a) to (c) are for targets in the longitudinal orientation only. Panel (d) includes the contribution of the transverse orientation as well. (a) Dipole spacing, (b) presence or absence of Au core and rotation of shape about long axis, (c) convergence tolerance parameter ('TOL'), (d) effect of the volume fraction of Au core on the position of the transverse (T) and longitudinal (L) plasmon resonances of the composite superellipsoid.

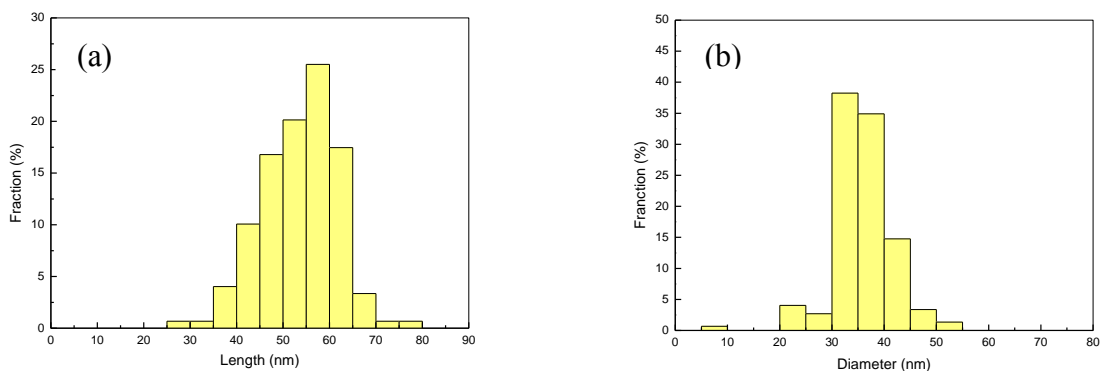


Figure S4. Histograms of (a) length and (b) diameter distribution of CTAC-wrapped Au-Ag core-shell nanorods.

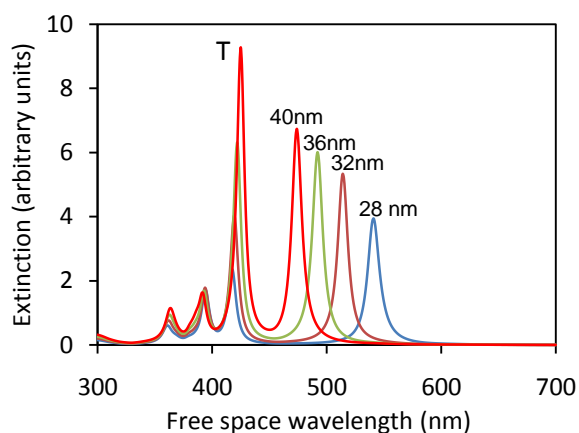


Figure S5. Effect of varying the width of a silver superellipse that is 53 nm long. Quasistatic calculations were performed for the case where the refractive index of the surrounding medium was 1.615. Note that the transverse resonances are far less affected by a change in aspect ratio but that the longitudinal resonances (which are labeled with the corresponding width of each target) are strongly shifted.

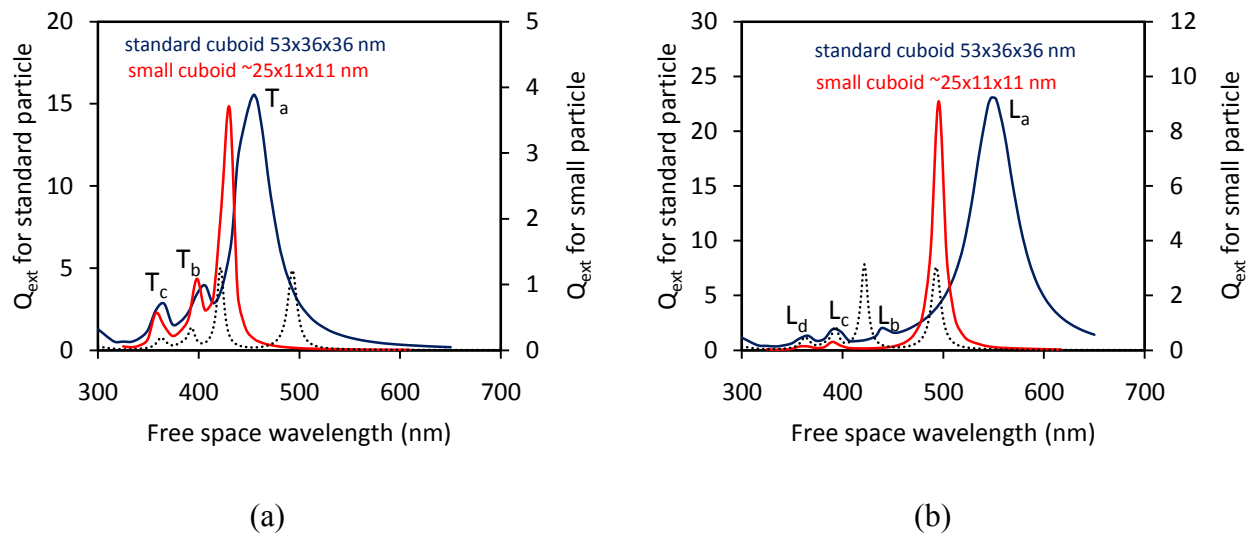


Figure S6. Effect of size on the development of plasmon resonances predicted by the DDA method. The silver nano-cuboid is of the standard shape and has been placed in a medium of  $n=1.625$ , (a) Transverse polarization (b) longitudinal polarization. The average extinction for both polarizations from the quasistatic calculation is shown as a dotted line with an arbitrary vertical scale. Note that the positions of the peaks of the small particle (red) correspond closely to those calculated by the quasistatic simulation, as expected. Observe also that DDA calculations on the larger particles predict broader peaks. This is the reason for the broader peaks of the DDA simulations of the standard particle compared to the quasistatic ones.

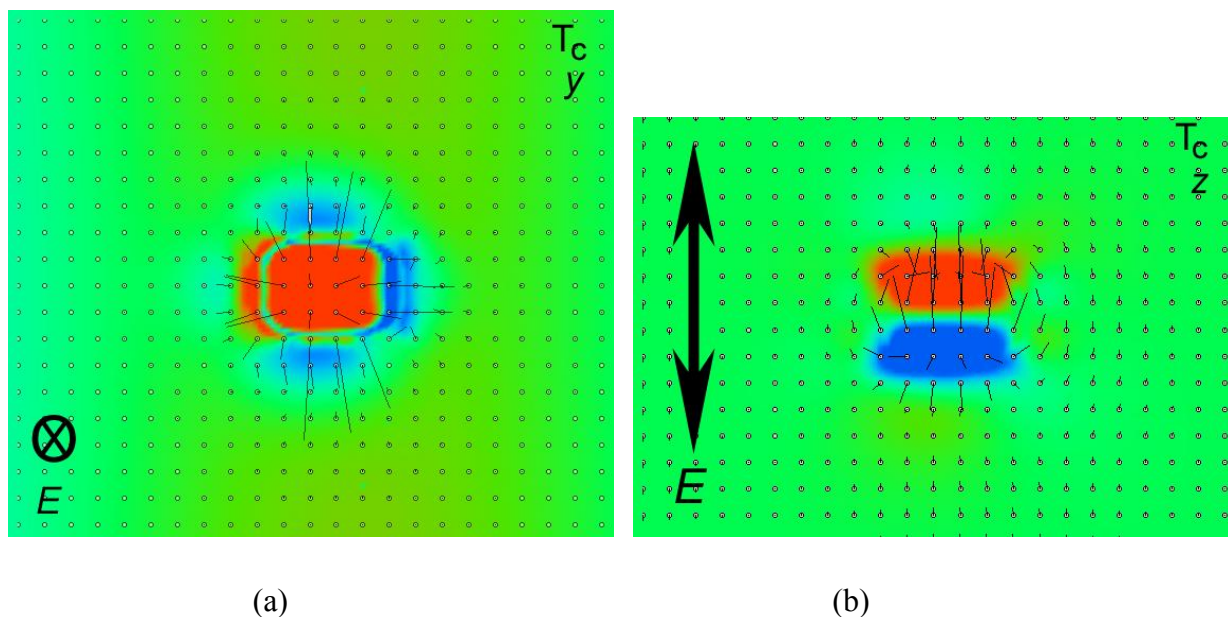


Figure S7. Electric field distributions of the  $T_c$  oscillation on (a) y and (b) z faces of the cuboid at  $\phi=90^\circ$ . Taken together with the cross-section in Figure 12 in the paper, these indicate the C5 cube mode.

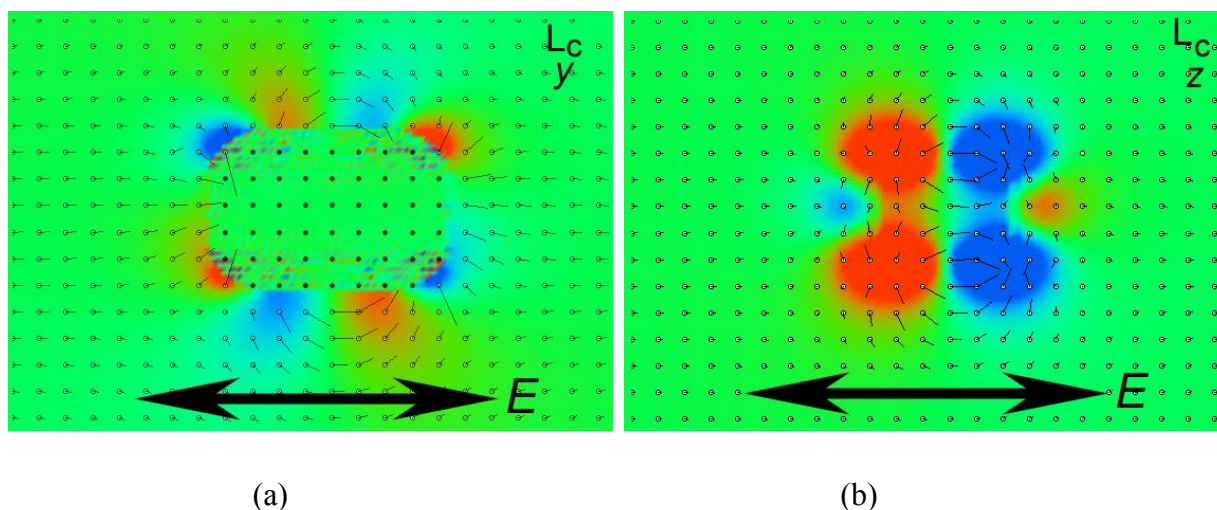


Figure S7. Electric field distributions of the  $L_c$  oscillation on (a) longitudinal cross section and (b)  $z$  face of the cuboid at  $\phi=330^\circ$ . Taken together with the cross-section in Figure 12 in the paper, these suggest the C3 cube mode although the corner components are very weak.

$\phi$	$L_a$ x component scale 0 to +5 mid-section	$L_b$ y component scale -1.5 to +1.5 mid-section	$L_c$ z component scale -1.5 to 1.5 above front z face	$L_d$ y component scale -1.5 to 1.5 mid-section
$0^\circ$				
$20^\circ$				
$40^\circ$				
$60^\circ$				

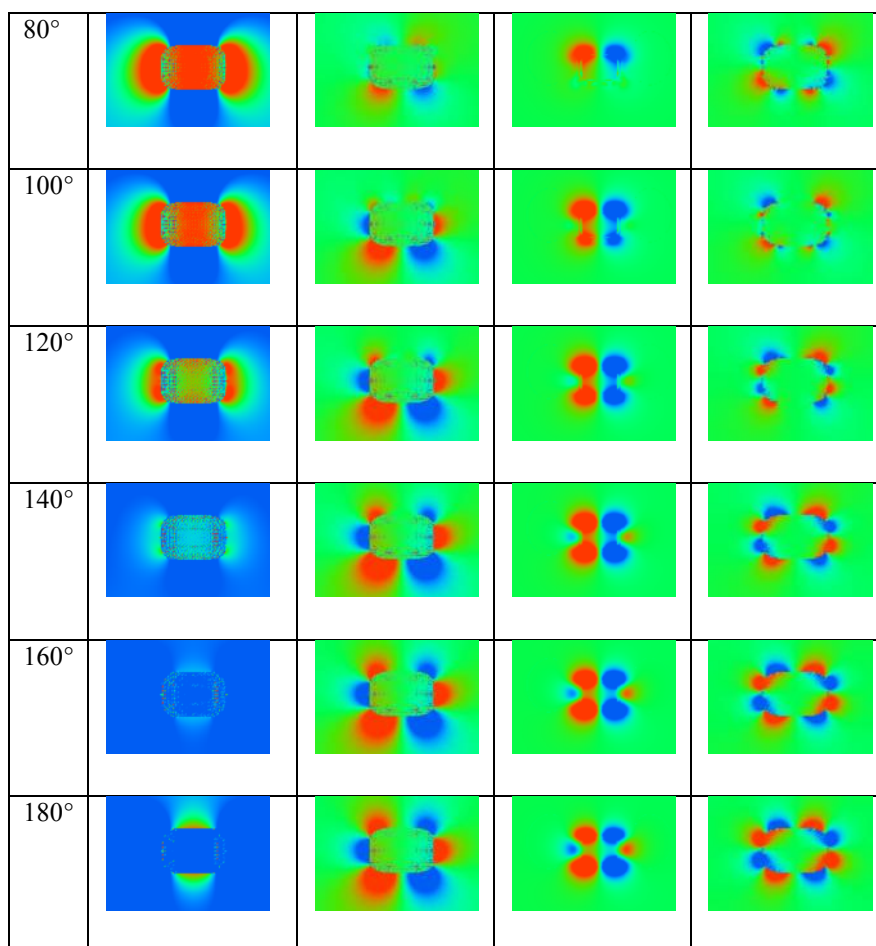
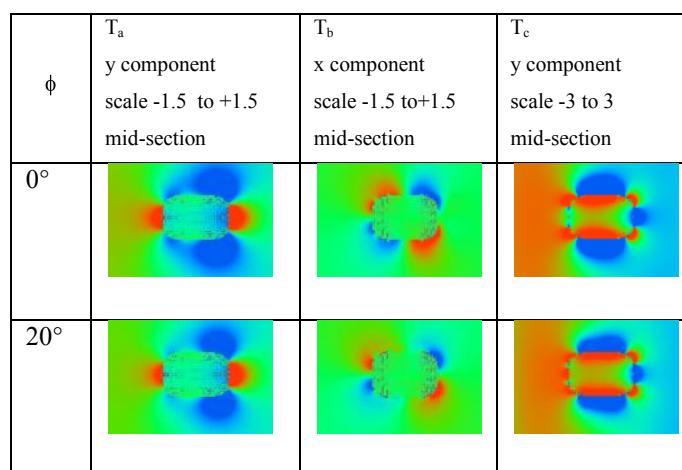


Figure S9. Snapshots of indicated electric field component through one half of a full 360° phase cycle (longitudinal resonances). Wave ( $k$ ) travelling from top to bottom,  $E$  left and right across page. Animations of these resonances are available on YouTube (search for ‘plasmon cortie’).



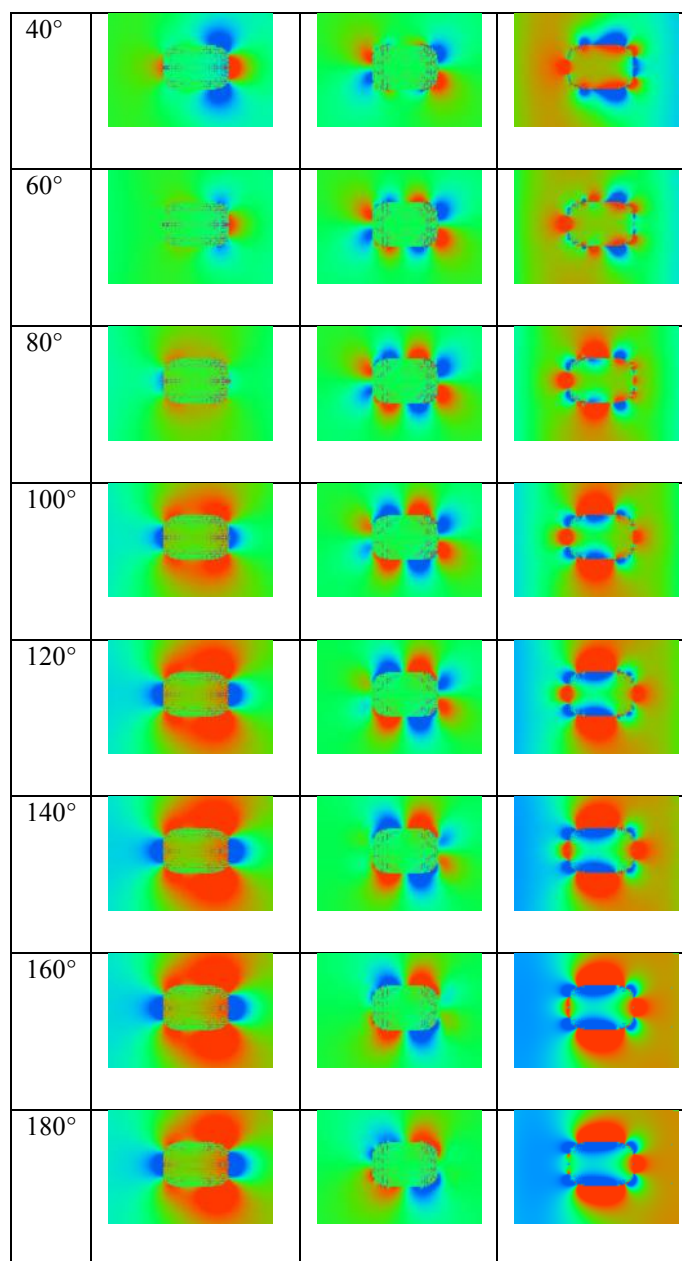


Figure S10. Snapshots of indicated electric field component through one half of a full 360° phase cycle (transverse resonances). Wave ( $k$ ) travelling from left to right,  $E$  up and down the page. Animations of these resonances are available on YouTube (search for ‘plasmon cortie’).

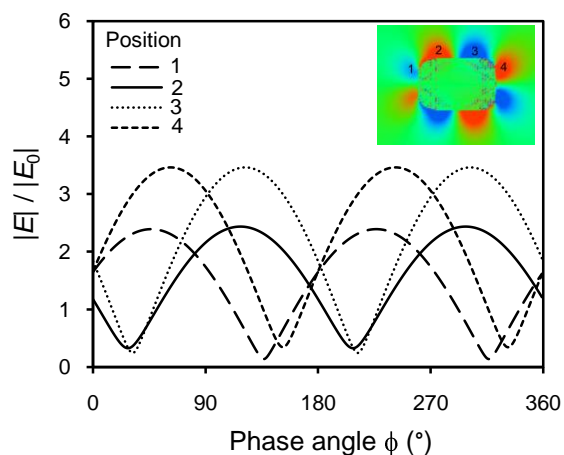


Figure S11. Illustration of the effect of retardation showing electric fields in the  $T_b$  resonance as a function of phase (equivalent to time) for edge and corner nodes. The electric field at the ends of the cuboid (positions 1 and 4) is approximately in phase while the electric field along the flanks (position 2 and 3) peaks about  $70^\circ$  later in the cycle. Similar effects occur on the other multimode resonances. The amplitude of the oscillations depends very closely on how far the probe point for  $E$  is placed from the surface of the nanoparticle so no inferences regarding the relative strength of the field around the perimeter of the nanoparticle should be made from this data.