Electronic Supplementary Information

Role of multipolar plasmon resonances during surface-enhanced Raman spectroscopy on Au micro-patches

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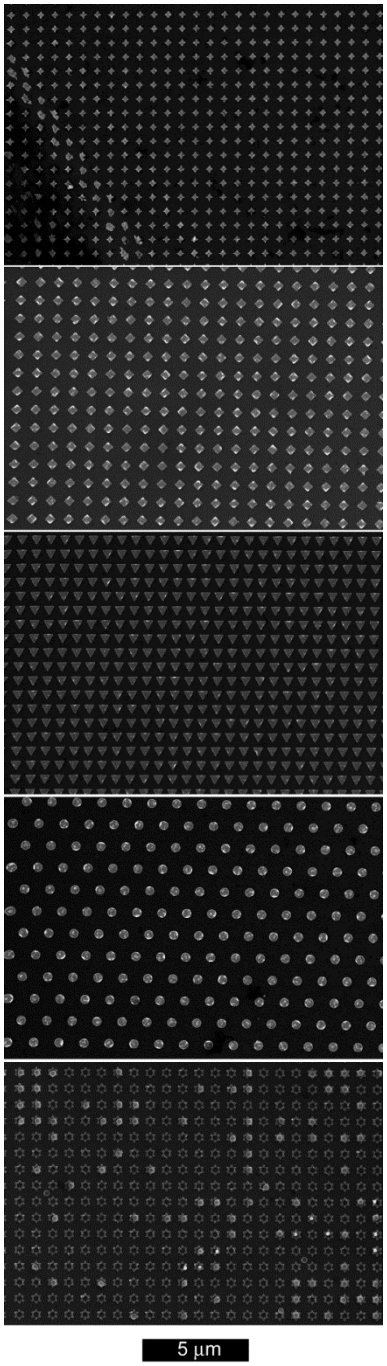

Fig. S1. Scanning electron microscope images showing some of the range of patch geometries investigated. Individual geometries were fabricated with widths ranging between 400 and 1000 nm. (a) Shurikens, (b) squares, (c) triangles, (d) circles, (e) 'hollow' stars.

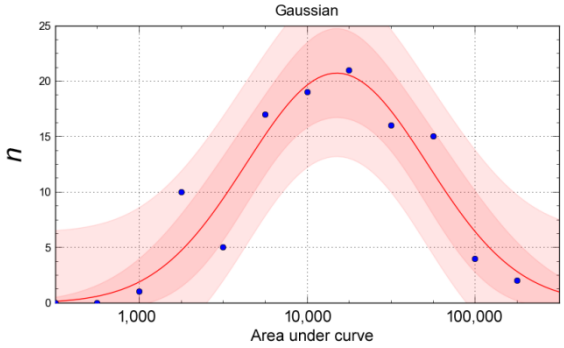

Fig. S2. Log-normal distribution of mean areas under peak at 1362 cm^{-1}.

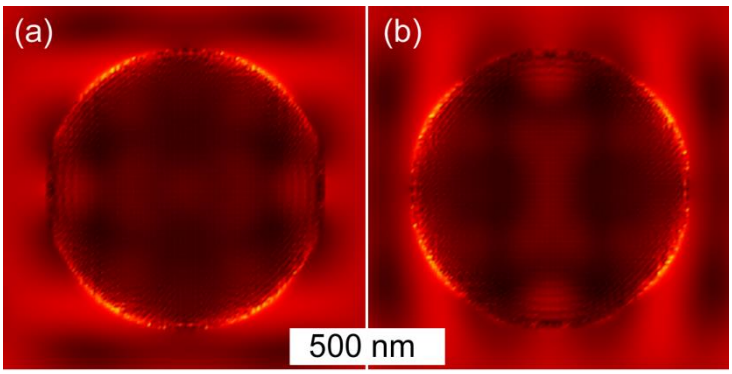

Fig. S3. Comparison of electric fields calculated for a 900 nm diameter gold disc on Si, (a) non-periodic simulation, (b) 2D periodic simulation. The $\|E\|^4$ parameter is 0.28 in both cases. This is because of the very short range nature of these multipolar resonances.

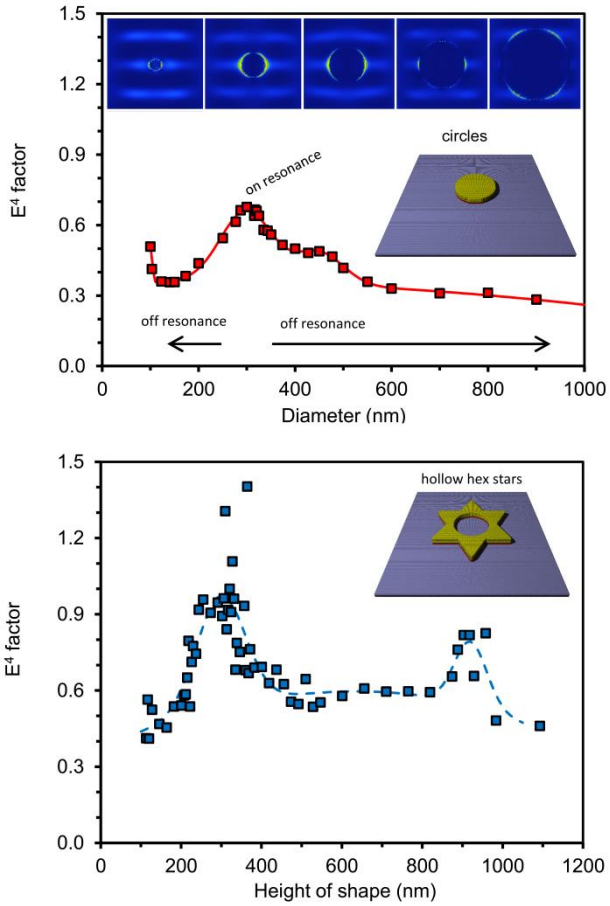

Fig. S4. Calculated values of E^4 for circles and hollow hexagonal stars excited at 633 nm. A series of maps of the local E^4 value is shown for selected circles along of the top of the upper diagram. Note how the area of the highest strength field (yellow regions in row of inserts along the top of the first figure) is greatest for the 300 nm diameter circle. The data for the stars (lower diagram) is quite noisy, due probably to the relatively coarse mesh used to render these quite complex shapes. Therefore, an empirical model was fitted to guide the eye. The insets show one example each of the geometric models that were simulated. The light is vertically incident.

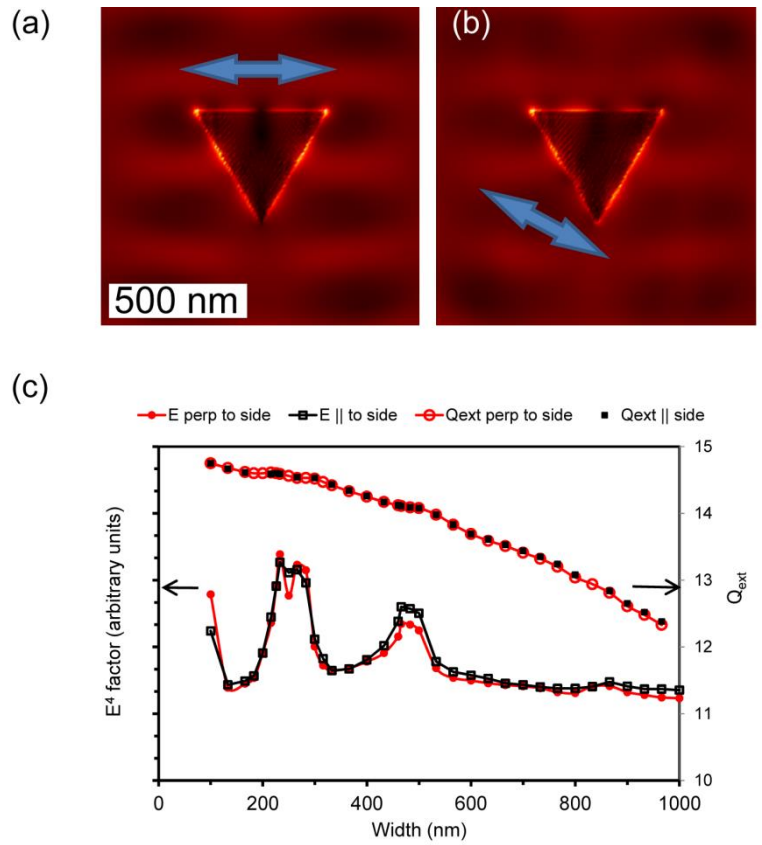

Fig. S5. (a) Electric field strengths on a plane 3 nm above the top surface of a equilateral triangle with 483 nm sides, for 633 nm excitation and a direction of electric field (blue arrow) parallel to one side of triangle. (b)As before but with electric field perpendicular to one side of triangle. (c) Although the direction of polarization in a triangle affects the distribution of the near-field [as seen in (a) and (b)] , it has no influence on Q_{ext} and little effect on the predicted efficacy of its Raman enhancement.

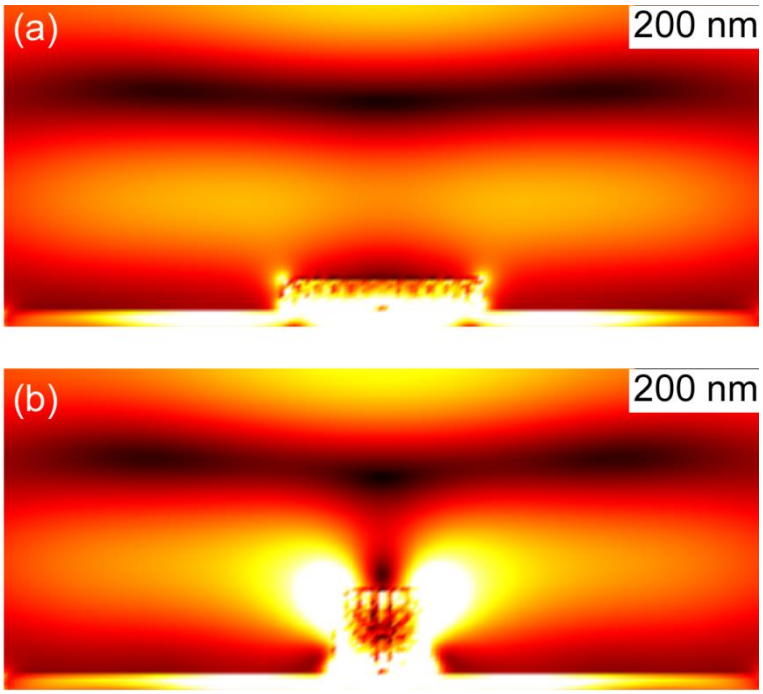

Fig. S6. Cross-sectional views of the electric near-field intensity of (a) the multimodal resonance on the 310 nm diameter gold disc, compared to (b) that of a gold cylinder of 150 nm x 120 nm height, both excited at 633 nm and both on a Si substrate. The oscillation in the latter is of a dipolar nature although not at peak resonance because that lies at a wavelength longer than 633 nm. It is clear that, in general, the electric field of a dipolar field is projected further out from the surface than for a multipolar field.