Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

Structure-Specific Chiroptical Responses of Hollow Gold Nanoprism

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1. Schematic diagram of the simulation configuration

The following diagram shows the used simulation configuration for this work.

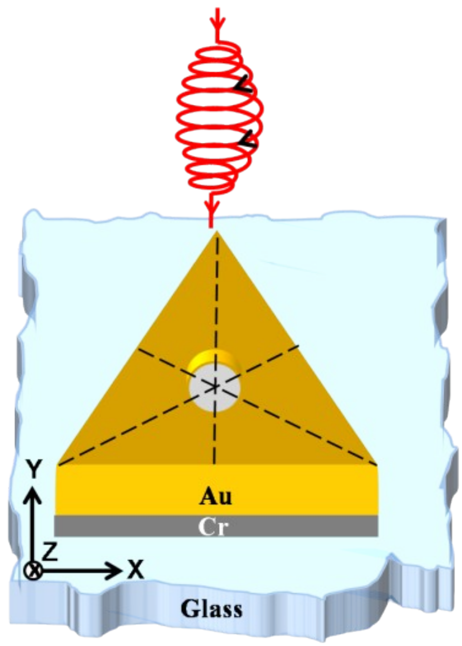

Figure S1. Schematic representation of the numerical simulation set up. An HGN, having 150 nm edge length, 40 nm thickness and 28nm cavity diameter is placed on a 4 nm thick Cr substrate which is already placed on a 20 nm thick glass. The whole system is excited either by linearly polarized (X or Y) or circularly polarized (LCP or RCP) light coming from the +ve Z-direction.

2. Absorption and scattering spectra of free-standing symmetric HGN for linearly polarized light

Absorption and scattering spectra of free-standing symmetric HGN were also calculated using linearly polarized (Either along X or along Y-direction) light. Spectral position is rather insensitive toward the state of the linear polarization.

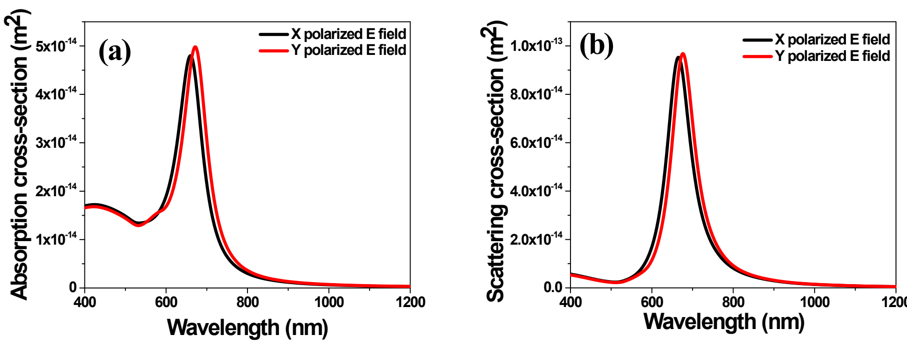

Figure S2. (a) Absorption spectra and (b) scattering spectra of free-standing HGN (L=150 nm, T=40 nm and cavity diameter 28 nm) excited by a plane wave having electric field along X (black lines) and Y (red lines) direction.

3. CD spectra of SGN and symmetrical HGN

The following figures show that symmetrical HGN and SGN interact with two circularly polarized light similarly and do not show any CD signature. The CD signature is absent even after placing them on the Cr and glass layer. This is not surprising as both the structures, SGN and symmetrical HGN, have multiple σ-plane and hence are achiral.

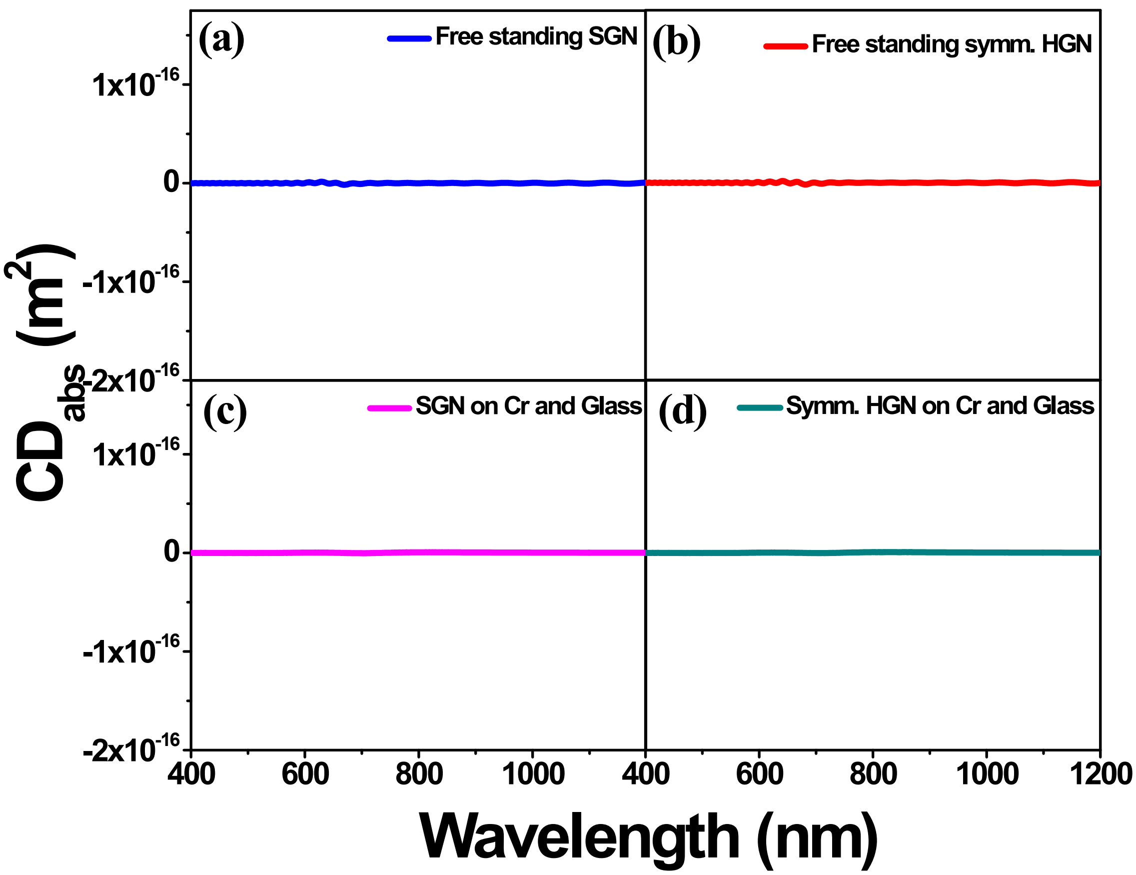

Figure S3. CD_{abs} spectra for (a) free-standing SGN, (b) free-standing symmetrical HGN, (c) SGN on glass and Cr and (d) symmetrical HGN on glass and Cr. Both the SGN and HGN have same edge length (150 nm) and thickness (40 nm). The symmetrical HGN has a cavity (diameter 28nm) at its centroid.

4. Schematic diagram of the gold nanoprism consist of six equivalent triangles

Geometrically, for a prism, three medians of a triangular face intersect each other to generate 6 smaller triangles which are all identical. One of those six smaller triangular sections is highlighted in the figure below. For hollow gold nanoprism structure, if the cavity-center is moved from the centroid of the main triangle to the inside of any one of the smaller triangles (and strictly not on the medians), then we obtain a new HGN whose symmetry is C_1 (when there is a substrate beneath the gold structure). Thus, any HGN having its cavity-center anywhere inside one (say the one highlighted in the below figure) of the six smaller prisms is chiral. Therefore, the best way to find the structure with maximum enhancement in CD is to position the cavity-center at various different points within the smaller prism and determine the CD for each of the corresponding chiral HGN. That is what we have done in this study. Note that we made sure that cavity center never lies on any median as that would lead to achiral structures with C_s symmetry. Now, since all the 6 smaller prisms are identical, it is sufficient to check the cavity-center position dependency within only one of them. Doing the same study by placing the cavity-center in any of the rest five smaller prisms will not generate new structure: either it will repeat the same set of structures or their mirror images.

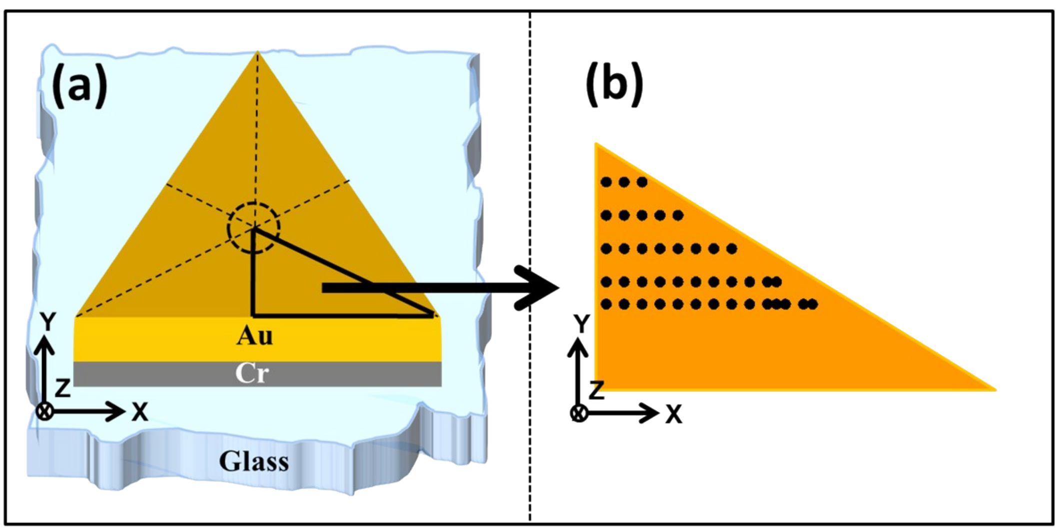

Figure S4. (a) All the six equivalent smaller triangles, created by the intersection of the medians are shown. The highlighted triangle is the region where the cavity-center position dependence of CD has been probed in this study. (b) The exact positions of cavity centers accessed are shown. Each black dot refers to one cavity center. Note that the number of chiral HGN structures studied here is equal to the number of the dots. However, all the cavity-center positions are shown together as an array within a single structure, just for simplicity.

5. Differential electric field for chiral HGN structures

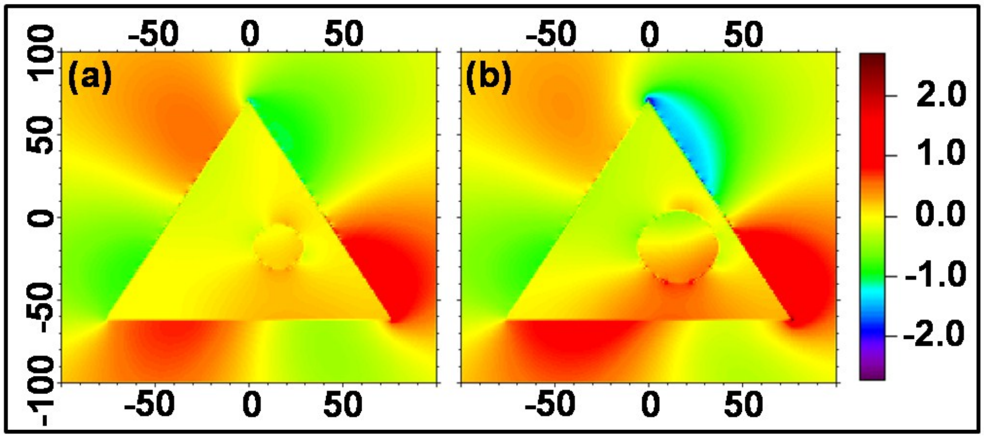

Figure S5. Differential electric field distribution(|E_{RCP}|-|E_{LCP}|) of a chiral HGN (L = 150nm, T= 40nm and 16nm offset) of having cavity of (a) 28nm and (b) 44nm diameter.

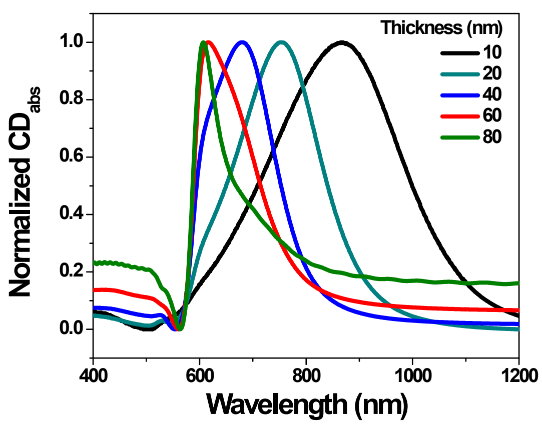

Figure S6. Dependence of the CD spectra of the chiral HGNs of edge length 150nm and a 28nm cavity having 16nm offset on the thickness. In the figure CD_{abs} of HGN having thicknesses 10nm (black), 20nm (cyan), 40nm (blue), 60nm (red) and 80nm (olive) are shown. It should be noted that since the depth of cavity is equal to the prism-thickness, this plot implicitly shows they effect of the cavity-depth as well.

7. Comparison between the CD intensities obtained for a chiral HGN and gold gammadion

We have compared the CD spectra obtained for a chiral HGN (28 nm cavity diameter and 32 nm cavity offset from the centroid to the +X direction) to that for a gold gammadion nanostructure. Both the nanostructures have similar volume. Following plots clearly show that CD intensity is higher for the HGN compared to the gammadion. We note that the CD intensity (absorption as well as scattering) of HGNs can be further enhanced by choosing proper cavity diameter, cavity position and prism thickness.

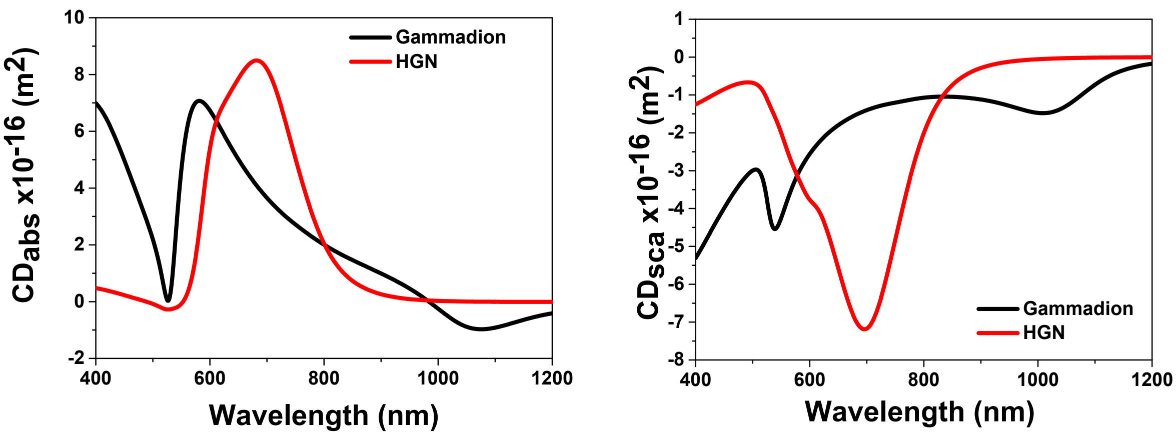

Figure S7. Comparison between the CD spectra obtained for a chiral HGN and gold gammadion; left: CD_{abs}, and right: CD_{sca}.