Second Harmonic Scattering from Silver Nanocubes

Supplementary Information

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1   SEM images of the three nanocube samples

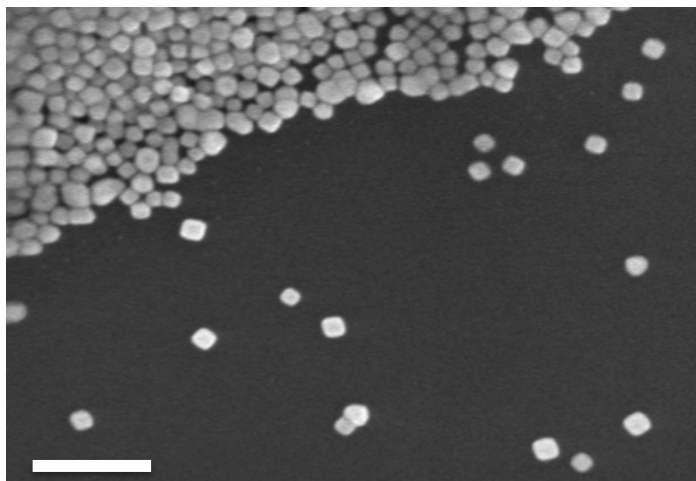Scanning electron microscopy images of the three different samples were obtained and are shown below.

Figure S1(a) :   Scanning electron microscopy of 39 ± 5.5 nm edge length silver nanocubes. Scale bar is 200 nm.
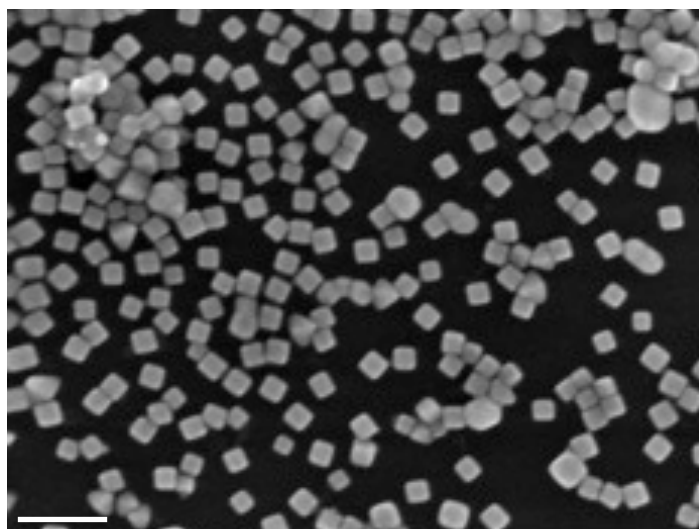

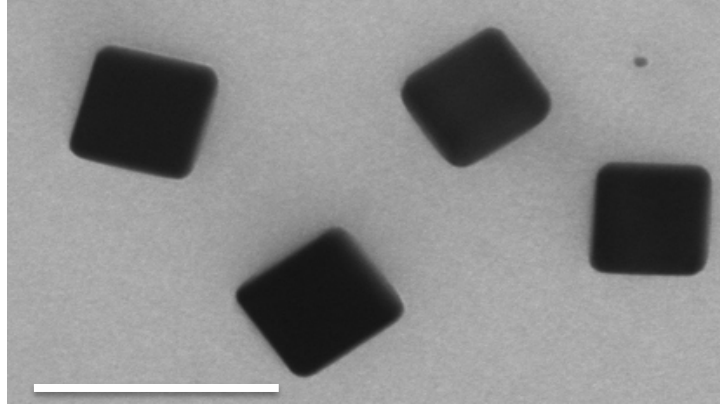**Figure S1(b) :**   Scanning electron microscopy of 48 ± 4.4 nm edge length silver nanocubes. Scale bar is 200 nm.

Figure S1(c) :   Transmission electron microscopy of 100 ± 9.0 nm edge length silver nanocubes. Scale bar is 200 nm.

2   Experimental hyper Rayleigh set-up.

The nonlinear optical experimental apparatus is described below. The right angle and forward geometries are emphasized.
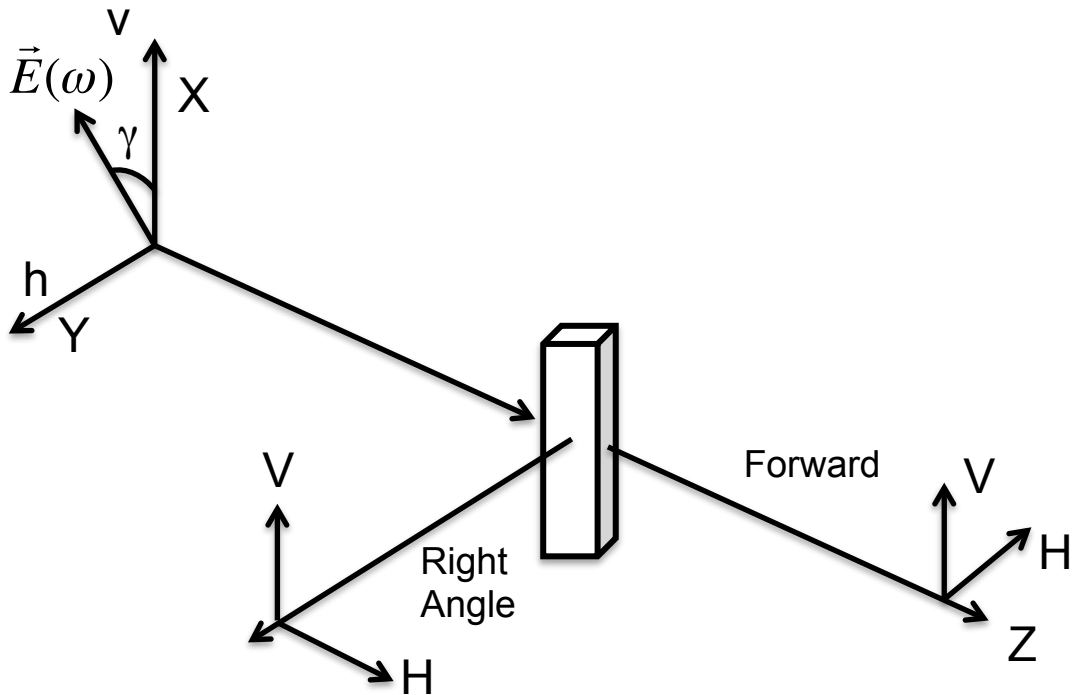

Figure S2 :   The experimental set-up for the right angle and forward geometries is described below. (v) and (h) stands for the vertical and horizontal polarization of the fundamental wave, respectively $\gamma = 0°$ and $\gamma = 90°$, and (V) and (H) stands for the vertical polarization of the harmonic scattered wave.

4 Simulation details

The details of the model used to describe the second harmonic scattering response from nanocubes are the following. Consider the eight nanocube corners as labeled from 1 to 8. Then, the first hyperpolarizability of the Ith corner is $\vec{\beta}_{m,I}(\vec{r}_I{}')$ in the corner reference frame and assumed here for simplicity to be reduced to its single zzz element $\beta_{zzz,m,I}(\vec{r}_I{}')$ where Oz is the axis going from the nanocube center through the nanocube corner. We then introduce the tensors describing the reference frame changes, namely $\overleftrightarrow{T}_{m \to C,I}(\vec{r}')$ accounting for the change from the corner frame to the nanocube frame and $\overleftrightarrow{T}_{C \to L}$ accounting for the change from the nanocube frame to the laboratory frame.

Then, as it is standard for second harmonic scattering from nano-objects dispersed in a liquid phase, the intensity at the second harmonic frequency is given by :

$$I^{\Gamma}(2\omega, \vec{r}) \propto \langle E^{\Gamma}(2\omega, \vec{r}) E^{\Gamma^*}(2\omega, \vec{r}) \rangle \tag{S1}$$

where the Γ stands for the output polarization and the brackets for the orientational average over all positions taken by the nanocube in the laboratory frame. The harmonic field amplitude of the Ith corner is itself given by :

$$\vec{E}(2\omega, \vec{r}, \vec{r}_I{}') \propto \frac{e^{[iK|\vec{r}-\vec{r}_{I'}|]}}{|\vec{r}-\vec{r}_{I'}|} \left\{ \hat{n} \times [\overleftrightarrow{T}_{C \to L} \overleftrightarrow{T}_{m \to C,I}(\vec{r}_I{}') \vec{\beta}_{m,I}(\vec{r}_I{}')] : \vec{E}(\omega, \vec{r}_I{}') \vec{E}(\omega, \vec{r}_I{}') \right\} \times \hat{n} \tag{S2}$$

where $\hat{n} = \vec{r}/r$ is the unit vector of the direction of collection and $K = 2\omega/c$, disregarding dispersion. Hence, the nanocube total harmonic field amplitude is :

$$\vec{E}(2\omega, \vec{r}) = \sum_{8}^{I=1} \vec{E}(2\omega, \vec{r}, \vec{r}_I') \tag{S3}$$

Therefore, retardation is simply introduced by the explicit consideration of their exact location within the nanocube. Indeed, a spatial phase appears at the fundamental frequency in the field amplitude $\vec{E}(\omega, \vec{r}_I')$ and at the harmonic frequency in the factor $e^{[iK|\vec{r}-\vec{r}_{I'}|]}/|\vec{r}-\vec{r}_I'|$. Finally, in the simulations, the first hyperpolarizability tensor element $\beta_{zzz,m,I}(\vec{r}_I')$ of the Ith corner may be equal to unity or differ from unity by the quantity $\pm\Delta\beta_{zzz}$ where $\Delta\beta_{zzz}/\beta_{zzz,m,I}(\vec{r}_I') = \pm0.1$ depending on the distribution selected.

5 Forward Scattering Polarization plots

The two crossed dipolar patterns recorded for the 39 and 100 nm edge lengths are provided in Figure S3 below. They are similar to the one obtained for the 48 nm edge length nanocubes reported in Figure 4 of the main text.
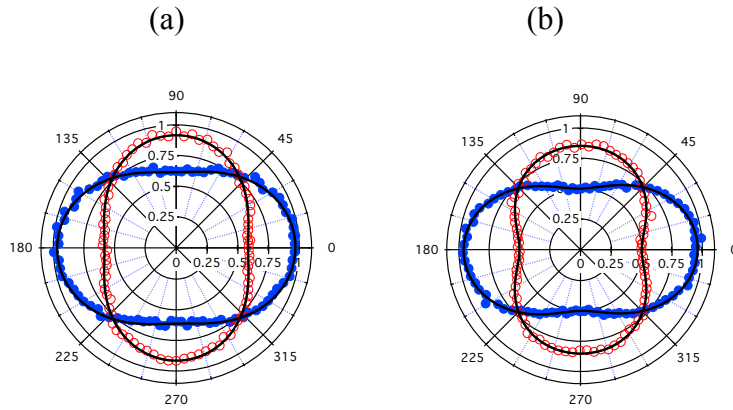

Figure S3 : Forward polarization plots of the HRS intensity excited at 800 nm for the (a) 39 nm and (b) 100 nm edge length nanocubes : (filled blue disks) V polarized harmonic intensity, (empty red disks) H polarized harmonic intensity.

6   Polar distribution

The polar distribution for the first hyperpolarizability tensor element is unlikely to occur for statistical reason of the corners element value. It is nevertheless provided below for comparison with the octupolar one given in the main text in Figure 6.
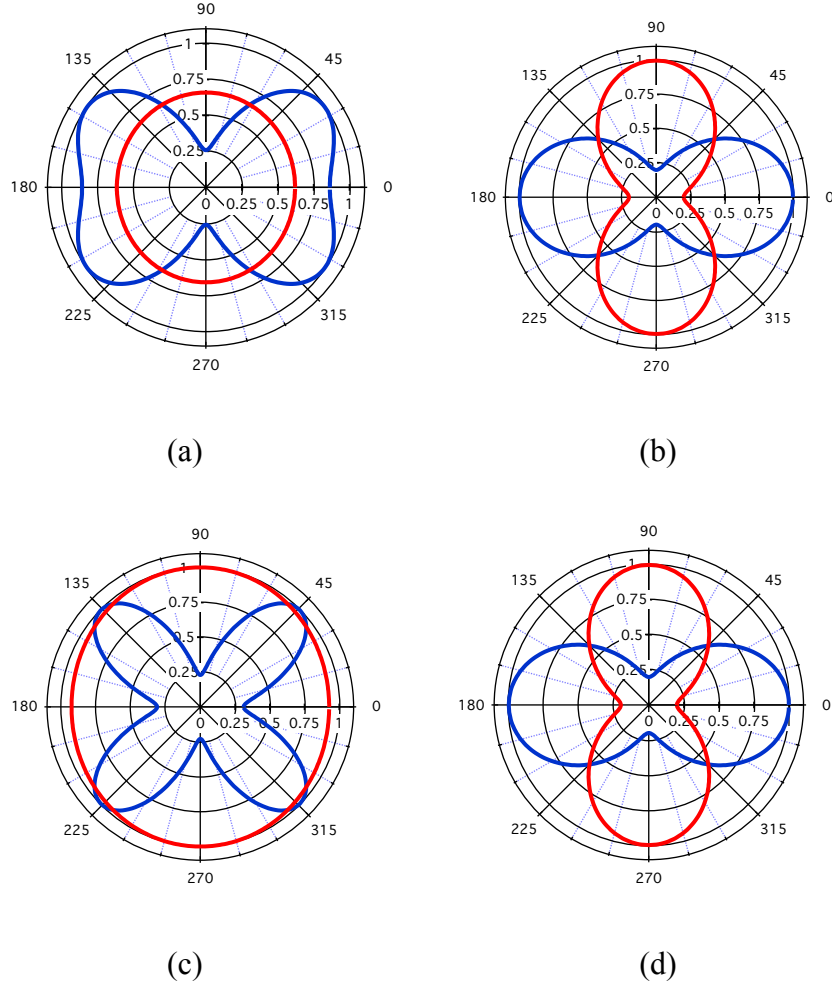

(a)   (b)

(c)   (d)

Figure S4(a-d) :   Simulated polarization resolved HRS plots for two different sizes of the polar distribution of the corners hyperpolarizability. (Blue) Vertically polarized harmonic intensity, (red) Horizontally polarized harmonic intensity. (a) 5 nm edge length, right angle configuration, (b) 5 nm edge length, forward configuration, (c) 80 nm edge length, right angle configuration, (d) 80 nm edge length, forward configuration.

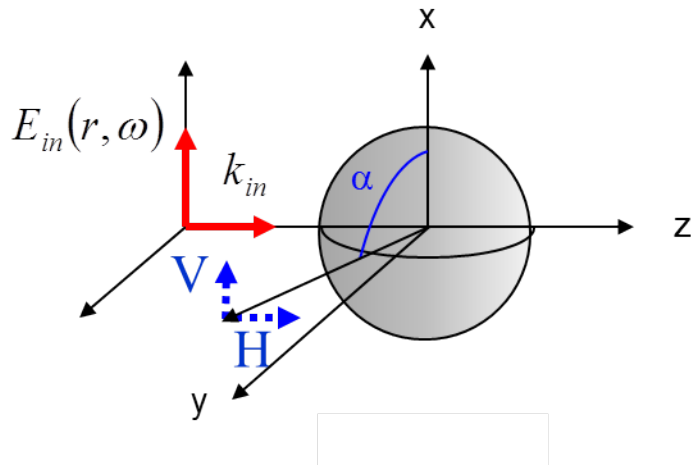## 7 Geometry for the SIE computations

Figure S5 :   For the SIE simulations, the nanostructures are driven by a planewave propagating along the z-axis. Contrary to the experiments, the incident polarization is fixed along the x-axis and the position of the field evaluation is given by the angle α, relatively to the x-axis. The field is always evaluated in the (O, x, y) plane. H denotes the polarization along the z-axis (perpendicular to the (O, x, y) plane) and V denotes the polarization in the (O, x, y) plane.