Supplementary Information

Enhancing Circular Dichroism by Chiral Hotspots in Silicon Nanocube Dimers

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I. Dependence of chirality on the dimer's geometric parameters.

(1) Dependence of chirality enhancement on the particle shape.

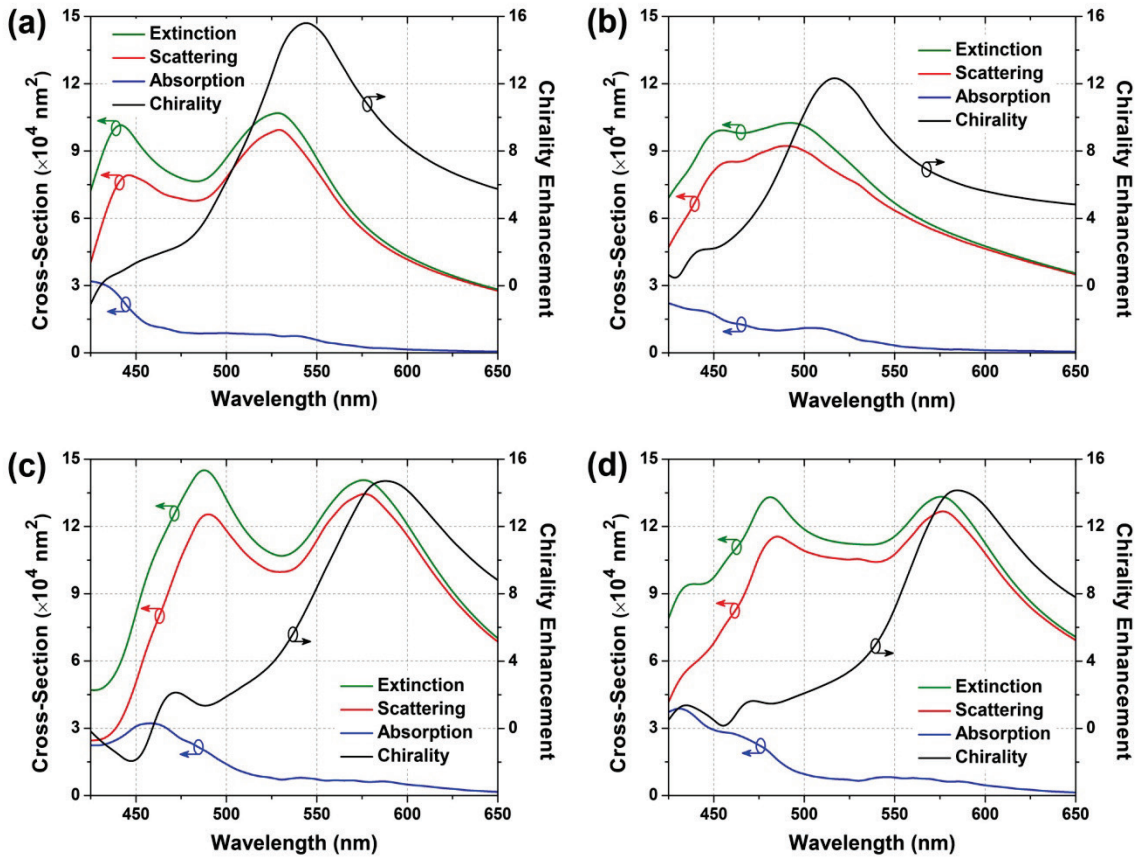

Figure S1. Extinction and chirality spectra with varying particle shape. Unless specified otherwise, the edge lengths of the nanocubes in all directions are 100 nm as in the main text. The gap size is fixed to be 10 nm, and the corner/edge roundedness is 15 nm. (a) The nanocubes are shortened in *y*-direction (along the dimer axis; see Figure 2c and 2d for the coordinates) to an edge length of 80 nm. Elongated dimers show similar results except a red-shift. (b,c) The nanocubes are flattened (b) or lengthened (c) in *z*-direction to 80 nm (b) and 120 nm (c), respectively. (d) The nanocubes are widened in *x*-direction to 120 nm. Narrowed dimers show similar results except a blue-shift.

(2) Dependence of chirality enhancement on the gap size.

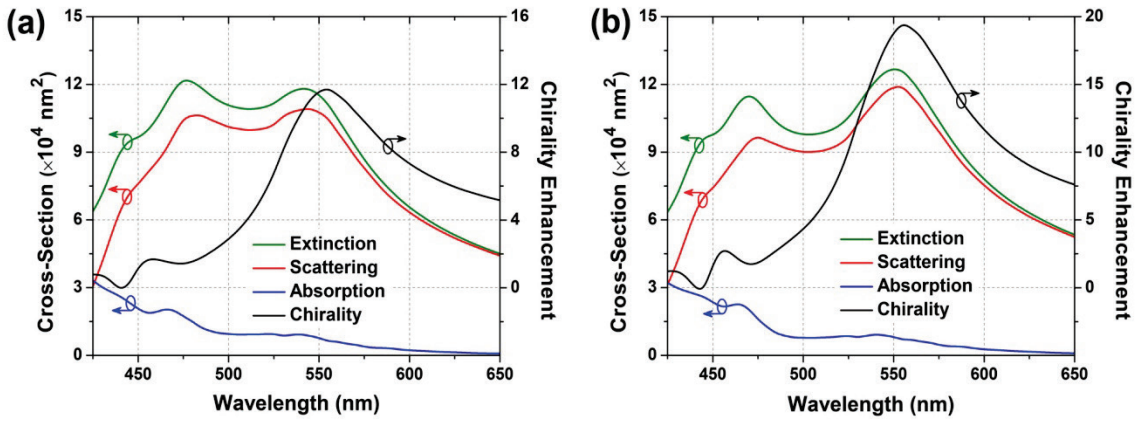

Figure S2. Extinction and chirality spectra with varying gap size *g*. The edge lengths of the nanocubes in all dimensions are 100 nm as in the main text. (a) *g* = 15 nm. (b) *g* = 6 nm.

II. Influence of native oxide layer on chirality enhancement.

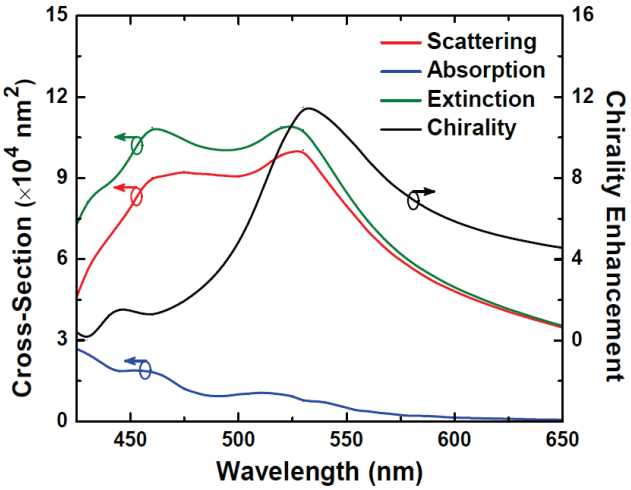

Figure S3. Extinction and chirality spectra of a silicon nanocube dimer with native oxide. The edge length of the silicon particles is 95 nm, and the oxide is modeled as a uniform coating layer with a constant refractive index n_{oxide} = 1.47 and thickness t = 2.5 nm. The gap size is 10 nm. Corner/edge roundedness is included in simulations. Compared with the curves in Figure S2(a), the slightly decreased Si particle size causes additional blue-shifts, while the chirality enhancement in the gap remains over 10 around the resonance wavelength.

III. Modeling of chiral molecules as a bulk medium.

For a single chiral molecule, its extinction and CD spectra can be described (in the cgs units) by[1]

$$\varepsilon_{ext} = \frac{4\pi}{n\cdot c_0}\frac{\omega\cdot N_A\cdot 10^{-4}}{0.23}\left(\frac{\Gamma}{(\hbar\omega-\hbar\omega_0)^2+\Gamma^2}-\frac{\Gamma}{(\hbar\omega+\hbar\omega_0)^2+\Gamma^2}\right)\frac{{\mu_{12}}^2}{3}, \quad \text{(S1)}$$

$$\varepsilon_{CD} = \frac{16\pi}{c_0}\frac{\omega\cdot N_A\cdot 10^{-4}}{0.23}\left(\frac{\Gamma}{(\hbar\omega-\hbar\omega_0)^2+\Gamma^2}+\frac{\Gamma}{(\hbar\omega+\hbar\omega_0)^2+\Gamma^2}\right)\frac{\mathrm{Im}(\boldsymbol{\mu_{12}}\cdot\boldsymbol{m_{21}})}{3}. \quad \text{(S2)}$$

Here n is the refractive index of the background medium, c_0 is the speed of light in vacuum, N_A is the Avogadro constant, Γ is the broadening or full width at half maximum (FWHM), and $\boldsymbol{\mu_{12}}$ and $\boldsymbol{m_{21}}$ are the matrix elements of the electric and magnetic dipole moments, respectively. At

spectral peaks where $\varepsilon_{ext,max}$ and $\varepsilon_{CD,max}$ are reached and with broadening Γ determined from the extinction spectrum, the dipole moments can be calibrated from experimental data. Subsequently, the coefficients γ and β in Equations (7) and (8) are given by:

$$\gamma = 4\pi n_0 \frac{{\mu_{12}}^2}{3} \tag{S3}$$

and

$$\beta = \mathrm{i} \cdot 4\pi n_0 \frac{\mathrm{Im}(\boldsymbol{\mu_{12}} \cdot \boldsymbol{m_{21}})}{3} \tag{S4}$$

with n_0 the effective density of the dipole pairs which each corresponds to an amino acid. For a macroscopic protein or chiral molecule containing many amino acids, the size of a single amino acid is estimated based on the molecule size and structural information. In the main text, the molecule in Figure 4 is calibrated from simplified spectra of bR trimers with n_0 = (0.7 nm)$^{-3}$, taking account of the monomer size (~2.5×3.5×4.5 nm^3), the number of amino acids (248) in a monomer and possible size expansion during aggregation.

References

[1] A. O. Govorov and Z. Fan, *ChemPhysChem*, 2012, **13**, 2551-2560.