Supporting Information for

A Wulff-Based Approach to Modeling the Plasmonic Response of Single Crystal, Twinned, and Core/Shell Nanoparticles

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Supporting Files (separate download). The full MATLAB graphical user interface code and the standalone MATLAB application are provided along with instructions. An example of a typical parameter file used for the simulations (ddscat.par) and the refractive index files of Au₁, Ag₁, Al², SiO₂³ and Al₂O₃² in the required DDSCAT format are also included to facilitate further calculations. Details about the variables included in the DDSCAT simulations and file formats can be found in the DDSCAT user manual⁴.
The user interface

The steps for the generation of the shape and input files are illustrated in Figure S1. The overall flow is as follows: first, the user sets the parameters in the four panels of the main window. Next, the shape geometry is calculated, followed by the definition of the shape size and optionally of the interdipole spacing and the creation of the shape and parameter files.

Specifically, the first step is to specify the Wulff model inputs in basic parameters, i.e. the surface growth velocities of the {100}, {110}, and {111} planes as well as the kinetic growth re-entrant surface, twin and disclination enhancements. Note that if one wished to do a thermodynamic approach, thermodynamic surface energies should be used instead of growth velocities, with no enhancement. The advanced parameters panel receives computational variables for the shape generation, which include the boundary of the dimensionless space in which the calculation takes place (boundary), the discretization step (step) and two smoothing parameters (smoothing beta and smoothing box). More specifically, smoothing beta smoothes the final growth front values matrix and the smoothing box is a factor in the exponential edge smoothing expression used in the calculation of growth velocity contributions of the facets in each grid point. The twinning type of the particle is defined in the homonymous panel and the user can select no twin plane (single crystal), one {111} twin plane (monotwin) or five non-parallel {111} twin planes (pentatwin). The last panel is used when calculating NPs with a shell, where shell thickness is defined as a percentage of the total thickness of the particle (shell percentage). When adding a shell, one must specify whether the shape is convex or concave since a different computational approach is needed to determine the points-dipoles that lie within a convex or concave shape. The shell generated is conformal, i.e. it has the same geometry as the Wulff NP without a shell.
After all the parameters are defined the shape can be calculated (create shape button). An isosurface is then displayed in the right panel and an array of dipoles approximating the volume of the nanoparticle is created and temporarily saved for the next steps. The displayed shape can be saved as a Matlab supported file (.fig) or an image file (e.g. bmp).

The shape is dimensionless until the user defines a size. In the DDSCAT the size of the studied target is introduced in the parameter file as the effective radius:

\[ a_{\text{eff}} = \left( \frac{3}{4\pi} V \right)^{\frac{1}{3}} \]  

where \( V \) is the volume of the target. To calculate \( V \) and the effective radius (calculate effective radius), the user is prompted to select two arbitrary points on the shape and input the distance between them as shown in Figure S1b.

When performing the DDSCAT calculations the choice of dipole number or equivalently dipole size is important for the accuracy of the obtained result. Therefore, the user is given the option to define the interdipole distance (define interdipole distance) through the dialog box (Figure S1c). In order to satisfy the given interdipole distance and NP size, the boundary and step input in the advanced parameters panel are automatically updated.

The first DDSCAT input file generated is the shape file (create shape file), which contains the array of dipoles that represent the NP as well as information about its orientation and composition. The orientation is specified in a dialog box by defining the target axes\(^4\) (Figure S1d). When the shell percentage is given a non-zero value, the core material will be assigned the reference number 1 and the shell material the reference number 2; an example of the first few lines of the shape file, including this information, is shown in Figure S1g.
The second DDA input file generated is the DDSCAT parameter file (*create ddscat file*), Figure S1f. This file includes details about the computational setup of the calculations, the material and effective radius of the target, the incident field and the output files. The dialog box shown in Figure S1e allows the user to define all the parameters under the tabs *preliminaries, computational, composition & target orientation, incident beam & scattering* and *output & save*. When a shell is defined it is automatically assigned to the second refractive index parameter. A detailed description of the parameter file and its variables can be found in the DDSCAT manual⁴, and a typical parameter file can be found in the Supporting Information.

**Figure S1.** Flow chart of the Wulff construction tool steps (a) - (e) required to generate the (f) parameter file and (g) shape file for the DDSCAT calculations.
Figure S2: Calculated (a) absorption and (b) scattering for Au cube with different interdipole distances (dd). Insets show a magnification of the area outlined in red. Edge length (black solid arrow) is 50 nm.

Figure S3: Calculated (a), (c) absorption and (b), (d) scattering for Ag cube and Au sharp decahedron respectively with different interdipole distances (dd). Edge length (black solid arrow) for both shapes is 50 nm.
Figure S4: Calculated (a), (c) absorption and (b), (d) scattering for Al octahedron and bipyramid with different interdipole distances (dd). Edge length (black solid arrow) for both shapes is 50 nm.
**Figure S5:** Calculated (a) absorption and (b) scattering for Au@SiO₂ cube with a 5 nm shell for 1 nm and 2 nm interdipole distance (dd) corresponding to the dipole shape representations shown in (c) and (d) respectively. Cube core edge length is 50 nm.
Figure S6: Calculated (a), (c) absorption and (b), (d) scattering for Au and Ag sharp decahedra with different polarization conditions as illustrated on the right. The orthogonal polarization components are as shown, along the y and z axis.

Table S1: Interdipole distance, corresponding number of dipoles and size for the modelled shapes used for the absorption and scattering simulations shown in Figures 2 and 4.

| Shape                | Interdipole distance (nm) | Number of dipoles | Interdipole distance (nm) | Number of dipoles | Interdipole distance (nm) | Number of dipoles | $a_{el}$ (nm) | Edge length (nm) |
|----------------------|---------------------------|-------------------|---------------------------|-------------------|---------------------------|-------------------|---------------|------------------|
| Cube                 | 1.9                       | 19683             | 1.9                       | 19683             | 0.9                       | 148877            | 31            | 50               |
| Decahedron (Dh)      | 0.6                       | 655980            | 0.6                       | 655980            | -                         | -                 | -             | -                |
| Marks Dh             | 0.6                       | 700217            | -                         | -                 | -                         | -                 | -             | -                |
| Octahedron           | -                         | -                 | -                         | -                 | 0.5                       | 1083459           | 31            | -                |
| Bipyramid (Bp)       | 1                         | 128735            | 1                         | 128735            | 0.3                       | 5162401           | 31            | -                |
| Nanotriangle (Nt)    | 0.7                       | 543467            | 0.7                       | 543467            | -                         | -                 | 18            | 75               |
**Table S2:** Interdipole distance, corresponding number of dipoles and size for the modelled shapes used for the absorption and scattering simulations shown in Figure 3.

| Interdipole distance (nm) | Number of dipoles | Interdipole distance (nm) | Number of dipoles | Interdipole distance (nm) | Number of dipoles | Interdipole distance (nm) | Number of dipoles |
|---------------------------|-------------------|---------------------------|-------------------|---------------------------|-------------------|---------------------------|-------------------|
| Au@SiO$_2$ Dh 0 nm       | 655060            | Au@SiO$_2$ Marks 0.6 nm   | 702217            | Ag@SiO$_2$ cube 1.9 nm    | 19883             | Al@ALO$_3$ Bp 0.5 nm     | 128735            |
| Au@SiO$_2$ Marks 0.5 nm  | 1166804           | Au@SiO$_2$ Marks 0.5 nm   | 1346756           | Ag@SiO$_2$ cube 2.1 nm    | 19883             | Al@ALO$_3$ Bp 0.5 nm     | 330900            |
| Au@SiO$_2$ Marks 0.7 nm  | 609025            | Au@SiO$_2$ Marks 0.8 nm   | 392184            | Ag@SiO$_2$ cube 2.6 nm    | 19883             | Al@ALO$_3$ Bp 0.5 nm     | 465542            |
| Core edge length (nm)    | 50                |                          | 20                |                          | 50                |                          | 50                |

**Table S3:** GUI input parameters used to model the studied shapes.

| Twinning type | $a_{(100)}$ | $a_{(110)}$ | $a_{(111)}$ | $\Psi_{\text{<enter>}}$ | $\Psi_{\text{<twinc}}$ | $\Psi_{\text{<rotation}}$ | Shell percentage t = 5 nm / t = 10 nm |
|---------------|-------------|-------------|-------------|--------------------------|-------------------------|-----------------------------|-----------------------------------|
| Cube          | single      | 5           | 10          | 10                       | 0                       | 0                           | 18.7 / 28.6                       |
| Decahedron (Dh) | pentatwin | 8           | 15          | 6.93                     | 1                       | 0                           | 19.6 / 32.4                       |
| Marks Dh      | pentatwin   | 11          | 20          | 9                        | 0                       | 0                           | 18.6 / 28.0                       |
| Octahedron    | single      | 10          | 10          | 5                        | 0                       | 0                           | 18.6 / 28.0                       |
| Bipyramid (Bp) | monoclinic | 5           | 10          | 10                       | 1                       | 0                           | 29.9 / 46.0                       |
| Nanotriangle (Nt) | monoclinic | 9.61        | 22          | 0.9                      | 12                      | 12                          | 0 / -                             |

**References**

(1) Johnson, P.B., Christy, R. W. Optical Constants of Noble Metals. *Phys. Rev. B* 1972, 6, 1–10.

(2) Palik, E. D. *Handbook of Optical Constants of Solids*; San Diego: Academic Press, 1998.

(3) Rodríguez-de Marcos, L. V.; Larruquert, J. I.; Méndez, J. A.; Aznárez, J. A. Self-Consistent Optical Constants of SiO$_2$ and Ta$_2$O$_5$ Films. *Opt. Mater. Express* 2016, 6, 3622.

(4) Draine, B. T.; Flatau, P. J. User Guide for the Discrete Dipole Approximation Code DDSCAT 6.1. 2004.