Supporting Information for:

Magneto-Optical Response of Cobalt Interacting with Plasmonic Nanoparticle Superlattices

Michael B. Ross*, Marc R. Bourgeois*, Chad A. Mirkin, George C. Schatz

Department of Chemistry and International Institute for Nanotechnology, Northwestern University, Evanston IL 60208.

Correspondence: chadnano@northwestern.edu (C.A.M.) and g-schatz@northwestern.edu (G.C.S.)

Materials and Methods

Magneto-plasmonic Fresnel Theory

The magneto-optical response of the superlattice-Co two-layer structure (pictured in Fig. 1a) to an incident plane wave was modeled using the transfer matrix method described by Qiu and Bader (which is described in detail in the Supporting Information).[1] In brief, a plane wave is incident on a multi-layer structure and within each layer the field is decomposed into forward and backward propagating s- and p- polarized waves. The interfaces are described by a matrix transfer operation such that the boundary conditions set by Maxwell's equations are satisfied. Non-magnetic material layers (Ag, Au, and dielectrics) are described by a diagonal, isotropic permittivity tensor εI_3 where I_3 is the identity matrix, and ε is the permittivity. Magnetic layers include off-diagonal components related to the Voigt vector **Q**.

$$\overleftrightarrow{\epsilon} = \epsilon \begin{pmatrix} 1 & iQ_z & -iQ_y \\ -iQ_z & 1 & iQ_x \\ iQ_y & -iQ_x & 1 \end{pmatrix} \quad (1)$$

These off-diagonal elements are proportional to the induced magnetization and are responsible for the various magneto-optic phenomena including Faraday rotation, Kerr rotation, and Kerr ellipticity. The diagonal components of the Co permittivity tensor were computed by interpolating the experimental dielectric function data of Johnson & Christy,[2] and the amplitude of the Voigt vector was taken to be $Q = 0.043 + i0.007$.[3] This value has given good agreement with experiments in the visible and near-infrared and was obtained by fitting measured Kerr ellipticity data as a function of Co thickness.[1]

Transverse Magneto Optical Kerr Effect

In the TMOKE geometry, whereby the applied magnetization **M** is oriented transverse to the plane of incidence, there is no mixing of s- and p-polarized field components for light reflected from the magnetized surface. The intensity of reflected p-polarized light does, however, depend on **M** and is given by $R(\vec{k},\vec{M}) = |r_{pp}E_0|^2$. When the direction of the applied magnetization is reversed in the sample, the sign of **Q** changes, altering r_{pp}. The change in reflected intensity upon reversal of the magnetization direction is quantified by the TMOKE parameter δ:

$$\delta = \frac{\mathrm{R}(+\mathrm{M}) - \mathrm{R}(-\mathrm{M})}{\mathrm{R}(+\mathrm{M}) + \mathrm{R}(-\mathrm{M})} \quad (2)$$

Maxwell-Garnett Effective Medium Theory

The macroscopic optical properties of the superlattice were modeled using Maxwell-Garnett effective medium theory. In this method, the effective dielectric function of the superlattice ε_{eff} is related to the polarizability of the inclusions α_i through the Clausius-Mossotti formula:

$$\frac{\epsilon_{\mathrm{eff}} - \epsilon_0}{\epsilon_{\mathrm{eff}} + 2\epsilon_0} = \frac{f\alpha_i}{3V\epsilon_0}$$

where *V* is the volume of an individual inclusion and *f* is the volume fraction of inclusions embedded in the background medium. For spherical inclusions with bulk dielectric function ε_i embedded in a medium with dielectric function ε_b, the polarizability is:

$$\alpha_i^{\mathrm{sphere}} = 3V\frac{(\epsilon_{\mathrm{i}} - \epsilon_{\mathrm{b}})}{(\epsilon_{\mathrm{i}} + 2\epsilon_{\mathrm{b}})}$$

For spheroidal inclusions, the polarizability is:

$$\alpha_i^{\mathrm{spheroid}} = V\frac{\epsilon_{\mathrm{i}} - \epsilon_{\mathrm{b}}}{\epsilon_{\mathrm{b}} + L(\epsilon_{\mathrm{i}} - \epsilon_{\mathrm{b}})}$$

where *L* is the geometric factor, which depends on the relative orientation of the incident light polarization and the spheroid principle axes. For light polarized along the longitudinal axis

$$L_{\mathrm{long}} = \frac{1-e^2}{e^2}\left(-1 + \frac{1}{2e}\ln\frac{1+e}{1-e}\right)$$

where the eccentricity *e* depends on the spheroid geometric parameters *a* (semi-major axis) and *b* (semi-minor axis):

$$e = \sqrt{1 - \frac{b^2}{a^2}}.$$

Because the sum of the geometric factors must equal 1, and the two transverse modes are degenerate, the transverse geometric factor can be determined from

$$L_{\mathrm{trans}} = \frac{1 - L_{\mathrm{long}}}{2}$$

To obtain an isotropic permittivity tensor, it is assumed that the spheroids are randomly oriented in the superlattice. To describe this situation an orientation averaged spheroid polarizability is used to compute the superlattice permittivity:

$$\bar{\alpha}_i^{\text{spheroid}} = \frac{1}{3}\alpha_i^{\text{long}} + \frac{2}{3}\alpha_i^{\text{trans}}.$$

Though Maxwell-Garnett effective medium theory does not account for interactions between inclusions, it has been shown to accurately describe the optical properties of nanoparticle superlattices for volume fractions up to ~ 20% when compared both with experiments as well as with numerical coupled dipole and analytic multiparticle Mie theory simulations.[4-6] Dielectric functions from Johnson & Christy were used for Au and Ag.[2] In all geometries, the Co layer was fixed at 100 nm, the total superlattice thickness was set to 100 nm, the angle of incidence was fixed at 30° from normal, and the background dielectric constant was fixed at 1.

Transfer Matrix Fresnel Theory

Here we provide a brief outline of the transfer matrix Fresnel theory - a detailed derivation may be found in ref.1 by Qiu and Bader. Within this framework a monochromatic plane wave is incident (from above) on a multi-layer stack structure, which is oriented such that the surface normals are directed along the z-axis. Within each layer the field is decomposed into forward (f) and backward (r) propagating s- and p- polarized waves:

$$P_m = \begin{pmatrix} E_s^f \\ E_p^f \\ E_s^r \\ E_p^r \end{pmatrix}_m$$

where P_m denotes the field components at the bottom of the m^{th} layer.

At the interface between two layers, the 4x4 medium boundary matrix (A_m) performs a change of basis such that

$$\begin{pmatrix} E_x \\ E_y \\ H_x \\ H_y \end{pmatrix}_m = A_m \begin{pmatrix} E_s^f \\ E_p^f \\ E_s^r \\ E_p^r \end{pmatrix}_m$$

This change of basis implicitly applies the boundary conditions imposed by Maxwell's equations, connecting the transverse field components on either side of the interface. Subsequent application of A_{m+1}^{-1} returns the field vector to the s,p polarization basis. A medium propagation matrix (D) connects the fields at the top and bottom interfaces of a layer such that the field at the top of the layer is equal to $D_m P_m$. The boundary condition at the interface is then satisfied by $A_m P_m = A_{m+1} D_{m+1} P_{m+1}$. The full solution for a multi-layer structure is constructed by repeated application of the A and D matrices:

$$A_i P_i = A_1 D_1 P_1 = A_1 D_1 A_1^{-1} A_1 P_1 = A_1 D_1 A_1^{-1} A_2 D_2 A_2^{-1} A_2 P_2$$
$$\vdots$$
$$= \prod_{m=1}^{N} (A_m D_m A_m^{-1})\, A_f P_f$$

This expression can be recast into the form $P_i = T P_f$ by defining matrix T as

$$T = A_i^{-1} \prod_{m=1}^{N} (A_m D_m A_m^{-1})\, A_f \overset{\text{def}}{=} \begin{pmatrix} G & H \\ I & J \end{pmatrix}$$

where the 2x2 sub-matrices G and I are used to determine the Fresnel reflection and transmission coefficients:

$$G^{-1} = \begin{pmatrix} t_{ss} & t_{sp} \\ t_{ps} & t_{pp} \end{pmatrix} \quad and \quad IG^{-1} = \begin{pmatrix} r_{ss} & r_{sp} \\ r_{ps} & r_{pp} \end{pmatrix}$$

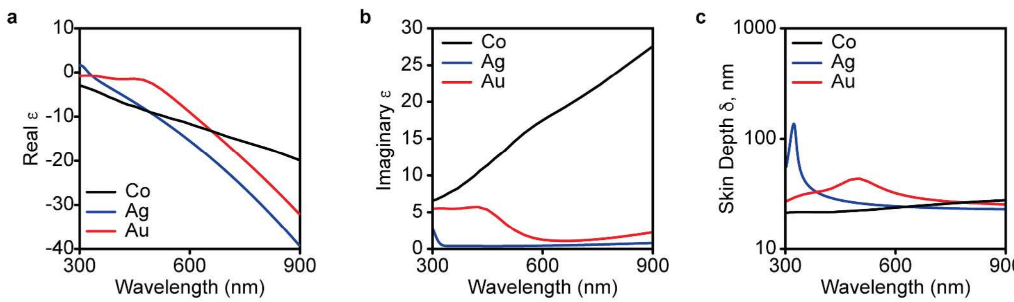
The material properties of each layer are incorporated into the A and D matrices through their dependence on the layer's permittivity tensor.

Supporting References.

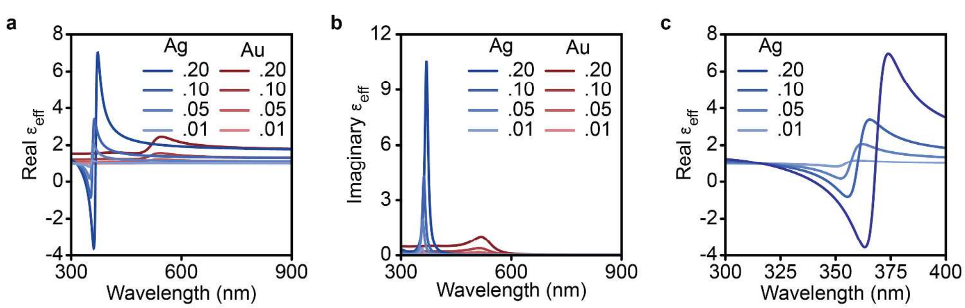
1. Qiu, Z. Q.; Bader, S. D., Surface Magneto-Optic Kerr Effect. *Review of Scientific Instruments* **2000,** *71*, 1243.
2. Johnson, P. B.; Christy, R. W., Optical Constants of the Noble Metals. *Physical Review B* **1972,** *6*, 4370-4379.

3. Osgood, R. M.; Riggs, K. T.; Johnson, A. E.; Mattson, J. E.; Sowers, C. H.; Bader, S. D., Magneto-Optic Constants of Hcp and Fcc Co Films. *Physical Review B* **1997,** *56*, 2627-2634.
4. Ross, M. B.; Blaber, M. G.; Schatz, G. C., Using Nanoscale and Mesoscale Anisotropy to Engineer the Optical Response of Three-Dimensional Plasmonic Metamaterials. *Nat. Commun.* **2014,** *5*, 4090.
5. Ross, M. B.; Ku, J. C.; Blaber, M. G.; Mirkin, C. A.; Schatz, G. C., Defect Tolerance and the Effect of Structural Inhomogeneity in Plasmonic DNA-Nanoparticle Superlattices. *Proc. Natl. Acad. Sci. U.S.A.* **2015,** *112*, 10292-10297.
6. Ross, M. B.; Mirkin, C. A.; Schatz, G. C., Optical Properties of One-, Two-, and Three-Dimensional Arrays of Plasmonic Nanostructures. *The Journal of Physical Chemistry C* **2016,** *120*, 816-830.

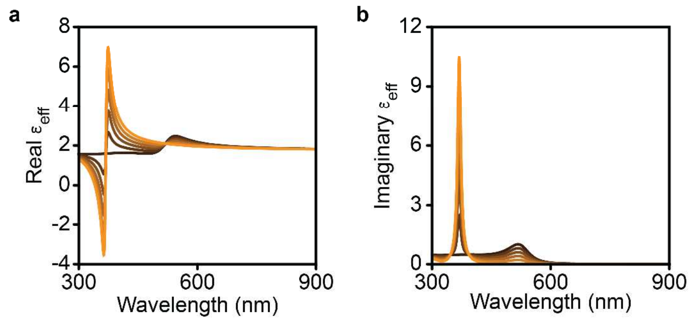
Supporting Figures



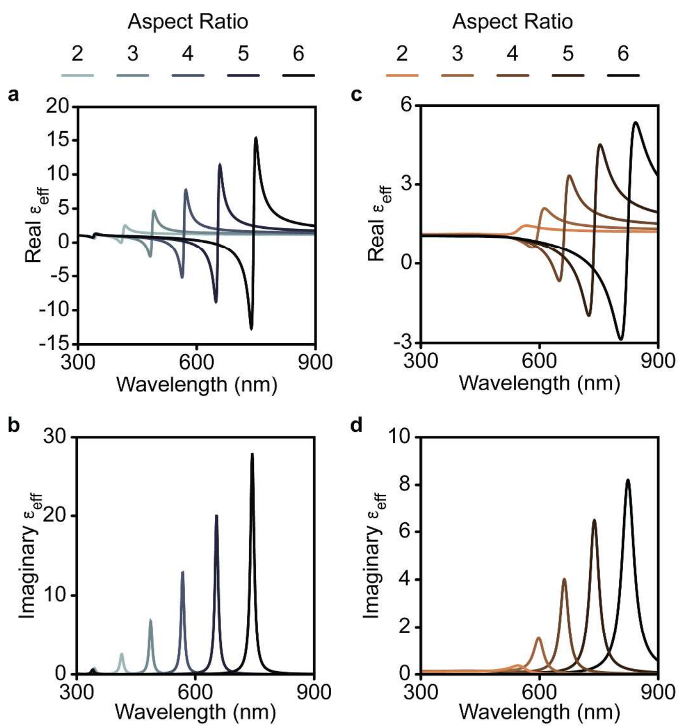
S1 Bulk optical properties of Ag, Au, and Co. Real (a.) and imaginary (b.) dielectric functions and (c.) skin depth penetration depth.



S2 Nanoparticle superlattice dielectric functions. Effective real (a.) and imaginary (b.) dielectric functions for Ag and Au as a function of volume fraction. (c.) Effective real dielectric functions for Ag superlattices between 300 – 400 nm.



S3 Effective dielectric functions for plasmonic alloys. Real (a.) and imaginary (b.) effective dielectric function for plasmonic alloys ranging from 100% Ag (lightest), to 100% Au (darkest) in increments of 20%. The total volume fraction for all materials is 20% (Ag%+Au%).



S4 Anisotropic nanoparticle superlattice dielectric functions. Orientation averaged ellipsoid-based effective dielectric functions for Ag (a., real, b. imaginary) and Au (c. real, d. imaginary) at 5% volume fraction.