Circular magnetoplasmonic modes in gold nanoparticles

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Methods

Synthesis of colloidal gold nanoparticles. Spherical 12.8 nm gold nanoparticles were prepared according to a previously published method.[1] Briefly, 2.5 mmol of tetrachloroauric acid and 30 mmol of oleyalmine were dissolved in 100 ml tetralin. The mixture was kept at 80°C under magnetic stirring for 5 hours; the particles were then precipitated by adding ethanol, recovered by centrifugation and redispersed in hexane. Morphological analysis was carried out on a Philips CM12 transmission electron microscope with acceleration voltage of 100 kV; sample was prepared by depositing a drop of the colloidal nanoparticle suspension on a carbon coated TEM grid and allowing the solvent to evaporate. Statistical size distribution measured on over 200 particles gave an average diameter and standard deviation $D\pm\sigma$ of 12.8±0.7 nm .

Larger 17.7 nm gold nanoparticles were prepared using the same method but keeping the reaction temperature at 70°C; the particles were dispersed in tetrahydrofuran. Statistical size distribution measured on over 200 particles gave an average diameter and standard deviation $D \pm \sigma$ of 17.7±0.8 nm.

Smaller 3.4 nm particles were prepared following a modification of a previously published procedure:[2] 100 mmol of oleylamine were dissolved in 160 ml of chloroform at 40°C under nitrogen flow and vigorous magnetic stirring, followed by the quick addition of 23 mmol of tetrachloroauric acid dissolved in 5 ml chloroform. The mixture was heated to reflux; after 10 minutes, a solution of 34 mmol of tert-butylamine borane complex in 5 ml chloroform was quickly added. After one hour the mixture was allowed to cool down to room temperature. The particles were then precipitated by adding ethanol, recovered by centrifugation and redispersed in hexane. Statistical size distribution measured on over 200 particles gave an average diameter and standard deviation $D \pm \sigma$ of 3.4±0.4 nm.

Magnetic circular dichroism and optical absorption measurements. MCD spectra were acquired using a home-built setup using the polarization modulation technique:[3] to increase the signal to noise ratio dichroism is acquired by modulating the polarization of light between LCP and RCP at high frequency (50 kHz) using a photoelastic modulator and recovering the oscillating part of the signal of the photodetector via phase-sensitive detection; this in fact corresponds to alternatively acquiring the absorption of LCP and RCP light and subtracting one signal to the other, i.e. dichroism.[3] A static magnetic field is applied along the light propagation direction; a full MCD spectrum is obtained by acquiring two spectra, under positive and negative applied magnetic field, respectively. The negative field spectrum is then subtracted from the positive field one, thus filtering out spurious, non-magnetic dichroism. The magnitude of dichroism signal ($\Delta A = A_- - A_+$) is calibrated using a $Fe(CN)_6^{3+}$ solution for reference.

Optical extinction spectra were acquired on a commercial Jasco V-670 spectrophotometer. Optical and magneto-optical measurements were carried out on the same sample of gold nanoparticle dispersed in hexane using a standard quartz cuvette with 1 mm optical path. Optical absorption (A) is given in

normalized units at peak maximum (A/A$_{Max}$) and dichroism (ΔA) is scaled in accordance (ΔA/A$_{Max}$). All measurements were carried out at room temperature.

Simulation of absorption and dichroism spectra.

The absorption spectra were calculated starting from the generalized expression for polarizability in equation (2): for the scalar dielectric function of the gold nanoparticles $\varepsilon(\omega)$, we used the Johnson and Christy[4] experimental function, corrected for size with the procedure described in ref. 5. In the following, we adopted the convention of $\varepsilon(\omega) = \varepsilon_1(\omega) - i\,\varepsilon_2(\omega)$.

The helicity-dependent metal-field coupling function $f(\omega)$,[6] only takes into account Drude electrons, since the effect of the field is considered to be arising chiefly from free electrons:

$$f(\omega) = \frac{e}{m}\frac{\omega_P^2}{\omega}\frac{(\gamma - i\,\omega)^2}{(\gamma^2 + \omega^2)^2}$$

where

$$\omega_P^2 \equiv \frac{ne^2}{\varepsilon_0 m}$$

is the squared bulk plasma frequency and n the volume density of the free electrons.

In the present calculations we used the following experimental values for the solvent (hexane): $\varepsilon_m = 1.89$ and $f_m = 1.06 \times 10^{-6}\ T^{-1}$, for the dielectric constant and for the coupling constant, respectively. The value of f_m is related to the Verdet constant of the medium.[6] Considering the size of the gold nanoparticles used in the present work ($D \approx 13$ nm), the measured extinction cross-section is dominated by absorption,[5] so that the field- and helicity-dependent absorption cross-section $\sigma_B(\omega)$ was calculated from the generalized polarizability $\alpha_B(\omega)$ as:

$$\sigma_B(\omega) = k\sqrt{\varepsilon_m}\ Im[\alpha_B(\omega)]$$

with ε_m the dielectric function of the solvent and k the wave vector. The normalized simulated absorption spectrum at zero applied field is compared to the experimental one in Figure S7.

The magnetic circular dichroism spectrum was simulated by calculating two normalized absorption spectra under a positive and negative field of 1 T and subtracting the negative one to the positive one.

As reported in Figure 3, the field-dependent variation of the LSPR frequency is substantially different with respect to equation (2), when considering only the contribution of the free electrons in the dielectric function, i.e., by using instead of the full dielectric function its Drude approximation:

$$\varepsilon^D(\omega) = 1 - \frac{\omega_P^2}{\omega^2 + i\omega\gamma}$$

Indeed, it is easy to show that for Drude electrons one gets (see equation 4):

$$g^D(\omega) = -\frac{e}{2m}\frac{\gamma^2 - \omega^2}{\omega^2}$$

which, in the high-frequency approximation ($\omega \gg \gamma$), simplifies to $g^D(\omega) = -\frac{e}{2m}$, thus recovering the standard result that for Drude electrons the field-induced shift in the LSPR is given by half the cyclotron frequency ω_C.

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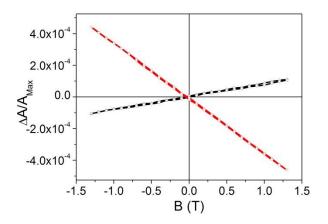2. Hou, X.; Zhang, X.; Fang, Y.; Chen, S.; Li, N.; Zhou, Q. J. Nanopart. Res. 2011, 13, 1929.

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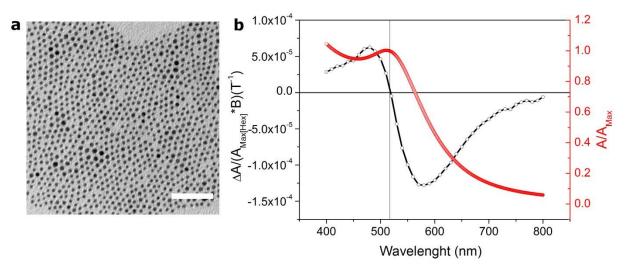4. Johnson, P.B.; Christy, R.W. *Phys. Rev. B* **1972,** *6* 4370-4379.

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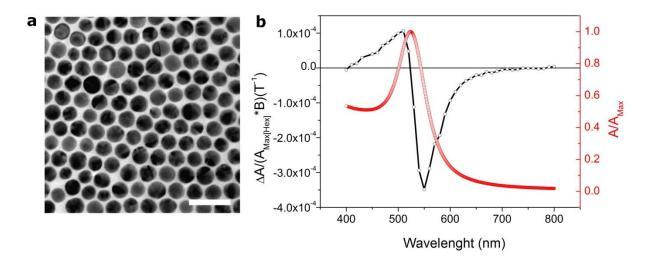6. Gu, Y.; Kornev, K. G. *J. Opt. Soc. Am. B* **2010**, 27, 2165-2173.
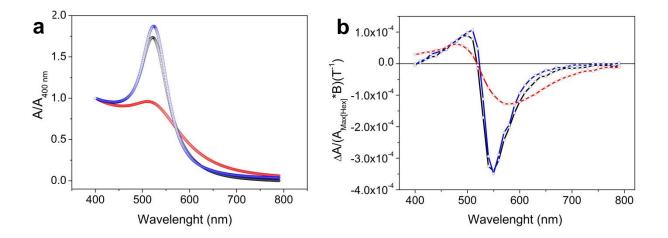
Supplementary Figures

Figure S1 Magnetic field dependence of the MCD signal of 12.8 nm gold nanoparticles. The field dependence was measured by fixing the probe wavelength at 500 nm (—o—) and 550 nm (—o—), corresponding to the MCD positive and negative lobes respectively, and scanning the field from 1.3 T to -1.3 T and from -1.3 T to 1.3 T.
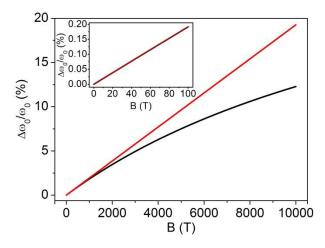

Figure S2 a, TEM micrograph of colloidal gold nanoparticles; scale bar is 40 nm. Average particle size is 3.4 ± 0.4 nm. b, Normalized optical absorption (—o—) and magnetic circular dichroism (—o—) spectra of the gold nanoparticles.
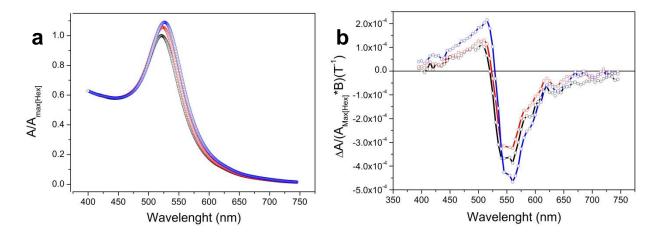
Figure S3 a, TEM micrograph of colloidal gold nanoparticles; scale bar is 40 nm. Average particle size is 17.7±0.8 nm. b, Normalized optical absorption (——o——) and magnetic circular dichroism (——o——) spectra of the gold nanoparticles.
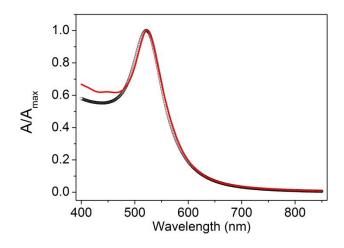

Figure S4 a, Normalized absorption spectra of 3.4 nm (——o——), 12.8 nm (——o——) dissolved in hexane and 17.7 nm (——o——) gold nanoparticles dissolved in tetrahydrofuran and b, the corresponding normalized MCD spectra. The comparison between the different samples shows the size-dependent trends in the absorption and MCD spectral features.

Figure S5 Comparison between the full equation describing the field-induced shift (——) and its linearized form (——). As can be seen from the inset, for realistic field values the approximation holds.

Figure S6 a, Normalized absorption spectra of 12.8 nm gold nanoparticles dissolved in hexane (——○——, RI=1.375), in chloroform (——○——, RI=1.446) and in toluene (——○——, RI=1.497) and b, the corresponding normalized MCD spectra.

Figure S7 Comparison between the experimental extinction spectrum (——○——) and the spectrum simulated using the quasi-static approximation (———).