Enhancement of Magneto-Optical Effects in Magnetite Nanocrystals Near Gold Surfaces

Gabriel Shemer and Gil Markovich*

School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

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Magnetic circular dichroism (MCD) was measured at Langmuir−Blodgett films of magnetite (Fe_3O_4) nanocrystals. The measurements of the effect were preformed in two different configurations, transmission and reflection. When a nanocrystal monolayer was deposited on a rough gold surface, the MCD signal was enhanced significantly in comparison to the signal obtained for a monolayer deposited on a hydrophobic glass substrate. The effect was found to be sharply dependent on the separation distance of the magnetite monolayer from the gold surface. This surface enhanced magnetooptical (SEMO) effect is probably caused by the enhancement of the electric field component of the electromagnetic waves at rough features of the gold surface.

Studies of thin magnetic films through magneto-optical (MO) effects are important for the understanding of basic magnetization properties of materials and for the development of MO storage media.[1] MO microscopy, especially scanning near-field MO microscopy,[2,3] provides a valuable characterization tool for magnetic storage media and magnetic micro- and nanostructures. To further push down the resolution limit of this technique, it would be essential to locally enhance the MO effects. A possible method would be to use rough noble metal surfaces to obtain large enhancements of optical phenomena such as in single molecule surface enhanced Raman scattering (SERS) experiments.[4]

In MO studies of ferromagnetic materials joined with noble metals, either as multilayer films[5] or granular films[6] a signature of the MO effects (Kerr rotation) was observed in light scattered by the noble metal surface plasmons. These effects are basically attributed to changes in the effective complex optical dielectric constant of the system due to excitation of metal surface plasmons.

In addition, it was demonstrated in pioneering experiments by Schultz and co-workers[7,8] and calculated by Kosobukin[9] that a small metallic sphere on top of a ferromagnetic surface can enhance MO effects in the light scattered from this system. This may eventually lead to increased resolution of the apertureless near-field scanning magnetooptical microscope and allow imaging of magnetic structures on scales well below 100 nm.[8]

In this Letter we show that the MCD effect in magnetite (Fe_3O_4) nanoparticle films is enhanced when the films are placed in proximity to gold surfaces. MCD was measured in both transmission and reflection configurations, where magnetic field and incident light are both perpendicular to the surface. The dependence of the enhancement on the separation between the magnetite monolayer and the gold surface was explored to better understand the enhancement mechanism.

The substrates used in the experiment were 1 cm^2 polished microscope glass slides that were cleaned in Piranha solution (4:1 H_2SO_4:30%H_2O_2) and rinsed with distilled water. The slides were coated with gold by thermal evaporation. Colloidal heptane solutions of magnetite nanocrystals coated with oleic acid molecules were used to deposit nanoparticle monolayers either by the Langmuir−Blodgett (LB) technique, as described elsewhere,[10] or by spin-coating submonolayer films on the substrates. The average diameter of the nanocrystals was determined by TEM to be 7 nm with about 20% size distribution and interparticle separation of the order of 1−2 nm. Bare glass substrates used as reference samples were coated with a LB monolayer of stearic acid prior to deposition of the magnetite nanoparticle monolayer. To obtain increasing separation distances from the gold-coated substrate, LB films of either stearic acid or pentadecanoic acid were stacked on top of the surface before depositing a magnetite monolayer. Exchanging the oleic acid coating layer to dodecenoic acid reduced the separation to the minimal distance possible using the LB technique. All surfaces were imaged by an atomic force microscope (AFM), P47-NTMDT, after gold deposition and after magnetite nanocrystal deposition.

The MO measurement setup employed a green (543 nm) 1 mW HeNe laser as the light source. A temperature controlled photoelastic modulator (Hinds, PEM-90) was used to sensitively measure the small polarization changes by the ferrite nanoparticle monolayer. To avoid random laser interference effects in the modulator, which would introduce noise into the measurement, the beam was diffused by a rotating diffuser and then re-collimated. Prior to the modulation the beam was linearly polarized with a Glan-Thompson polarizer at 45° to the modulator axis. After a 50 kHz phase modulation of $\lambda/4$ amplitude, the light was passed through (or reflected from) the sample located between the poles of an electromagnet at normal incidence (or slightly off-normal by ∼5° for specular reflection). The light beam was detected by a photodiode and the preamplified signal was split to dc and ac components. The ac component was lock-in amplified at the first harmonic. The amplified ac signal is proportional to the MCD effect for small rotation angles.[11] The ac signal was normalized by dividing it by the dc signal to eliminate the differences in the transmittance and reflectance of the different samples. This normalized signal was recorded as a function of the magnetic field applied by the electromagnet perpendicular to the substrate.

The MO signal is proportional to the local magnetization in the particles; hence the obtained MCD vs field curves represent

* Corresponding author. E-mail: gilmar@post.tau.ac.il.

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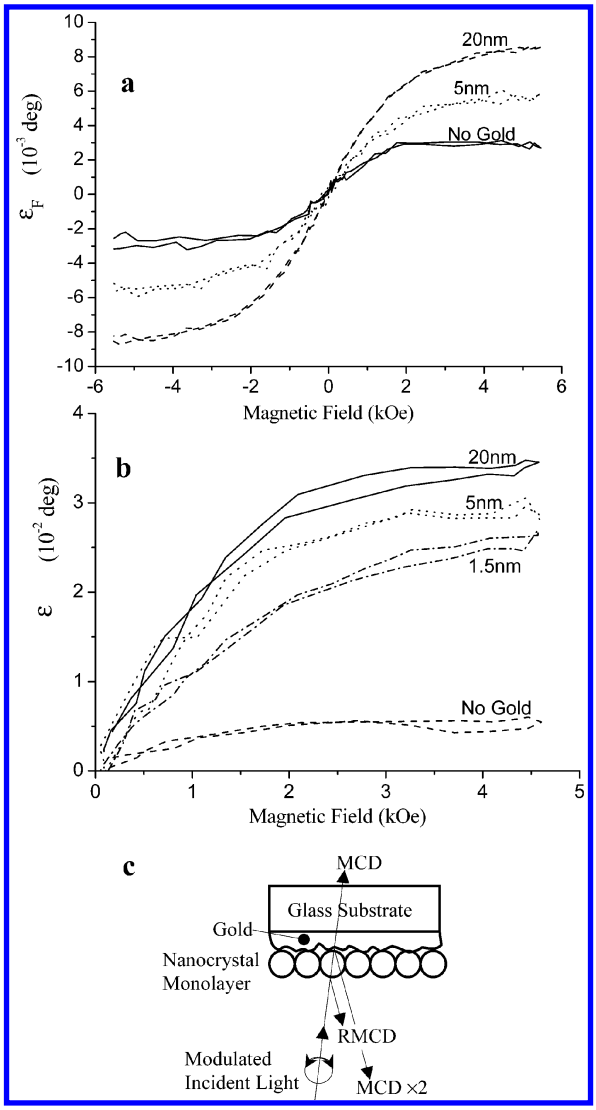

Figure 1. Comparison between MCD magnetization curves for magnetite nanocrystal monolayers with and without a gold film measured in transmission (a) and reflection (b) configurations. MCD is proportional to the plotted Faraday ellipticity (ϵ_F). The numbers on the curves indicate the average gold film thickness. (c) Specular reflected light consists of two contributions: RMCD (Kerr ellipticity) coming from the face of the thin magnetic film, and the transmitted beam, which is reflected from the magnetite−gold interface, passing twice through the magnetic film ($\sim 2\epsilon_F$).

the true average perpendicular magnetization curve of the magnetite nanocrystal monolayers. Because the magnetite nanocrystals are in the superparamagnetic state at room temperature, the magnetization curves displayed paramagnetic behavior, saturating at a field of about 3−4 kOe.[10]

Figure 1 displays MCD magnetization curves of the transmission (a) and reflection (b) configurations measured at 543 nm for the magnetite nanoparticle layers deposited on gold-coated and bare hydrophobic glass substrates. The graphs show the Faraday ellipticity, ϵ_F, in degrees, as a function of the external magnetic field. Faraday ellipticity is proportional to $\Delta\alpha$, which is the difference between the left-hand (α_-) and right-hand (α_+)-circular polarization absorption coefficients. A clear enhancement of the MO effect by a factor of 2−6 in the presence of gold films of varying thickness is observed. The reflection configuration typically exhibited enhancements larger by a factor of 2−3 relative to the transmission for the same samples. AFM imaging confirmed that samples on bare glass and on gold surfaces had the same density of magnetite nanoparticles to

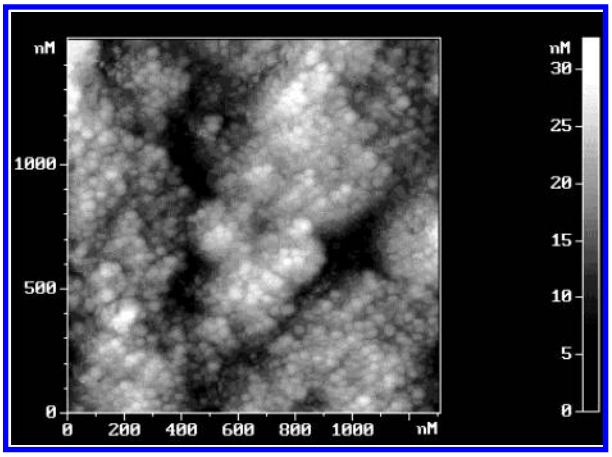

Figure 2. AFM image of a magnetite nanocrystal LB monolayer deposited on an evaporated gold film of 20 nm average thickness.

within 20% accuracy. Figure 2, displaying a typical AFM image of a monolayer deposited on a 20 nm thick evaporated gold film, shows that the magnetite particles cover uniformly the gold surface in a close-packed array.

The overall signal in the reflectance configuration consists of two contributions, as illustrated in Figure 1c. The first is the direct reflection by the magnetic nanoparticles film, commonly termed reflectance-MCD (RMCD[12]), and the second contribution comes from the light passing through the film and reflected from the film−gold interface. Because the optical density of the nanoparticle monolayer is low ($\sim$0.04), it is reasonable to assume that the second contribution is the major one in the case of the gold-coated substrates and it is not significant for the magnetite on bare glass reference sample. This contribution should increase the enhanced reflection MCD signal by a factor of 2 relative to that of the transmission. The second effect was probably responsible for the larger enhancement observed in the reflection configuration. This indicates that the enhanced MCD effect originates in enhanced absorption of the circularly polarized light at the magnetite nanocrystals.

It is difficult to assign the transitions participating in the absorption of the magnetite nanocrystals at a wavelength of 543 nm. Fontijn et al. have used MO spectroscopy to identify various transitions in bulk Fe_3O_4,[13] whereas Taketomi et al. have identified a blue shift of about 0.12 eV in the absorption spectra of 7 nm diameter Fe_3O_4 nanoparticles relative to the bulk absorption.[14] On the basis of those results and the magnetite nanocrystal film absorption spectrum, it is estimated that in the nanocrystals there is a relatively strong intervalence $Fe^{2+}-Fe^{3+}$ charge-transfer absorption band centered below 600 nm that is responsible for the absorption at the wavelength of the experiment. According to ref 13, this absorption line has a "paramagnetic" nature; i.e., it is a transition from a degenerate ground state where the oscillator strengths for transitions to the excited state caused by left and right circularly polarized light are not equal, leading to the appearance of the MCD effect.

Figure 3 displays the decrease in the enhancement with increasing separation between a 20 nm thick gold film and the magnetic nanoparticles monolayer. The distance values appearing in Figure 3 are estimates based on the length of the fatty acid molecules. The relative error for the short separations is large due to uncertainty in the determination of thickness of the oleic or dodecenoic acid coating of the particles. There appears to be a sharp decrease in the enhancement at a separation distance of the order of about 30 Å. Distance-dependent SERS experiments performed on molecules bound to gold substrates showed a similar decrease of signal with increasing separation

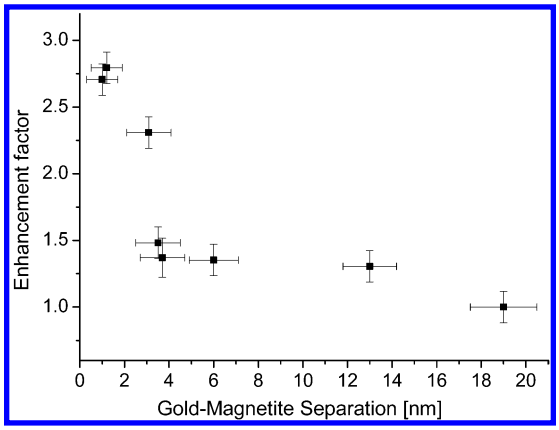

Figure 3. Dependence of the enhancement factor on the gold−magnetite nanocrystals separation distance. The distances were estimates based on oleic or dodecenoic acid coating thickness (from TEM) + length of pentadecanoic or stearic acid molecules used as spacer LB films.

between a chromophore and the surface.[15] The SERS results gave a simple power law dependence on $r + a$, where r is the separation distance and a is a typical gold surface curvature.[16] In the present study a power law behavior was not obtained.

One should note a significant difference between previous experiments on multilayer and granular ferromagnetic−noble metal systems[5−8] and the present work. In the previous experiments a rotation of the plane of polarization of light was observed for light scattered off the noble metal spheres or films (MO Kerr effect). In the present case it is the direct absorption of transmitted circularly polarized light by the magnetic material itself that produces the enhanced MO effect. Thus, the present results appear to pertain to the same class of other surface-enhanced phenomena where the spectrum of the scattered light is primarily affected by the energy levels of the enhanced material.

The prevalent model that is suggested for surface-enhanced phenomena such as SERS, surface-eenhanced infrared absorption (SEIRA),[17] surface-enhanced fluorescence,[18] and also surface-enhanced photochemistry[19] attributes the enhancement to an amplification of the electric field component of the radiation when resonant with the surface plasmons of the curved noble metal surface. It is our assumption that the same mechanism applies in the present study. Extensive information acquired recently on the microscopic details of SERS active sites in granular metal films[20,21] implies that the extent of MCD enhancement varies between the magnetic particles in a film, depending on the local increase of the electric field produced by the gold surface features. Thus, it is expected that by optimizing the noble metal−magnetic nanocrystals configuration it would be possible to significantly increase the scale of MO enhancement.

From the symmetry of the positive and negative sides of the magnetization curves measured in transmission it can be deduced that the MCD absorption coefficient, $\Delta\alpha = \alpha_+ - \alpha_-$, was enhanced due to overall enhancement of the unpolarized absorption coefficient α; i.e., both α_+ and α_- were enhanced by the same factor. Because the visible light absorption of the magnetite monolayer is weak relative to the absorption of the underlying gold film, it was not possible to determine directly whether α was also enhanced in the presence of the gold film.

The new type of SEMO effect that has been demonstrated for the ferrite nanoparticle−gold system could be utilized for development of novel magneto-optical storage media. This effect would be a useful tool for studies of the magnetic properties of low-dimensional magnetic nanostructures. In addition, the circular dichroism experiment was found to be a sensitive tool to measure the absorption enhancement in the visible region, somewhat similar to surface-enhanced fluorescence, which may also be a sensitive indicator to enhanced absorption (or decreased excited-state lifetime).

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