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Second Harmonic Generation in Core (Shell) γ-Fe_2O_3 (Au) Nanoparticles

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Abstract. The films containing core (shell) γ-Fe_2O_3 (Au) nanoparticles that possess the plasmon resonance at the wavelength 550 nm are prepared. The second harmonic generation in these structures is shown to be diffuse and depolarized, that is typical for the hyper-Rayleigh scattering.. The studies of the magnetization-induced second harmonic generation shows that the ratio of the magnetic to nonmagnetic components of the hyperpolarizability of a single nanoparticle, $\gamma^M/\gamma^0 \sim 0.4$ in the field of about 3 kOe.

Introduction

Optical and nonlinear optical properties of metal nanostructures are the subject of intensive investigations during the last few decades. The studying of the coupling of light with the structures much smaller than the wavelength of light is very important for the fabrication of photonic devices on the nanometer scale. Previous studies of these optical interactions have been focused mostly on noble-metal nanoparticles and thin films which display resonances in the optical absorption spectrum dependent on the particles' size, shape, and inter-particle spacing. Magneto-optically active nanoparticles are very perspective as they can find applications in the emerging field of nanophotonics, data storage, or sensing [1].

In this work, magnetization-induced second harmonic generation (SHG) is applied for the studies of the nonlinear magneto-optical properties of magneto-plasmonic γ-Fe_2O_3 (Au) nanoparticles. The break of the structural inversion symmetry is combined with the broken time reversal symmetry in magnetic materials that creates the nonlinear magneto-optical sources with proper localization at surfaces and in nanostructures. Thus, among various probes of nanostructures, magnetization-induced SHG is known as an extremely sensitive one [2].

Preparation and characterization of samples

Synthesis of core (shell) nanoparticles has been reported previously [3]. In a typical synthesis 37.5 ml of ethylene glycol is mixed with 25 ml of oleylamine and heated to 150°C in a 100 ml round bottom flask. 4.0 g of $FeCl_3 \cdot 6H_2O$ is dissolved in a mixture of 10 ml ethylene glycol and 2.5 ml water and injected in the flask. After injection the reaction temperature is raised to 195°C and the solution is left to reflux for 18 hours. The resulting γ-Fe_2O_3 particles have an average diameter of 15 nm. After washing and drying, 100 mg of the particles is resuspended in 250 ml ethylene glycol and 50 ml octylamine and heated to 150°C. A solution of 500 mg $HAuCl_3 \cdot 3H_2O$ in ethyleneglycol is then slowly added to the mixture and left to react for 15 minutes. In this time the mixture changes colour from black brownish to blue. After the reaction, the mixture is left to cool and the coated nanoparticles are purified using a magnetic filtration system. Since this system only retains magnetic nanoparticles there is no contamination with pure gold nanoparticles should these be formed. Shell thickness can be controlled by varying the amount of $HAuCl_3 \cdot 3H_2O$ used. The

studied core (shell) nanoparticles consist of Fe_2O_3 core of 20-25 nm in diameter and Au shell of the thickness of about 2-4 nm. The size distribution of nanoparticles is very narrow, being about 10%. The resulting dry nanoparticle powder was resuspended in a solvent and deposited on a glass substrate. The thickness of the solid film was about 3 μm.

The absorption spectrum of these structures demonstrates the existence of the plasmon resonance in the gold shell at the wavelength of about 550 nm (Fig.1), that is the edge of the gold absorption band. At the same time the core (shell) nanoparticles possess the magnetic properties of γ-Fe_2O_3, that can be probably enhanced in the wavelengths range near the plasmon resonance.

The samples were characterized by atomic force microscope (Fig.2). The image proves that the average diameter of isolated nanoparticles is several tens of nanometers. One can see that the particles are randomly distributed on the substrate and that there are single nanoparticles and bunches of particles.

Magnetization curve of the sample demonstrates the absence of a hysteresis that proves the superparamagnetic state of nanoparticles. Magneto-optical effects in the composed samples could hardly be studied because the sensitivity of the experimental setup was not enough to detect the weak magneto-optical response from thin diluted layers of nanoparticles.

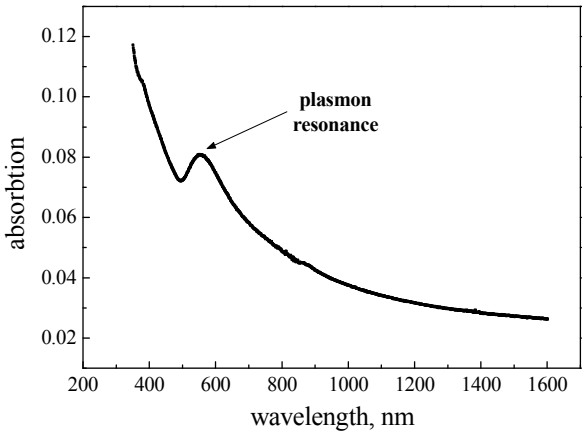

Figure 1. Absorption spectrum of the core (shell) nanoparticles

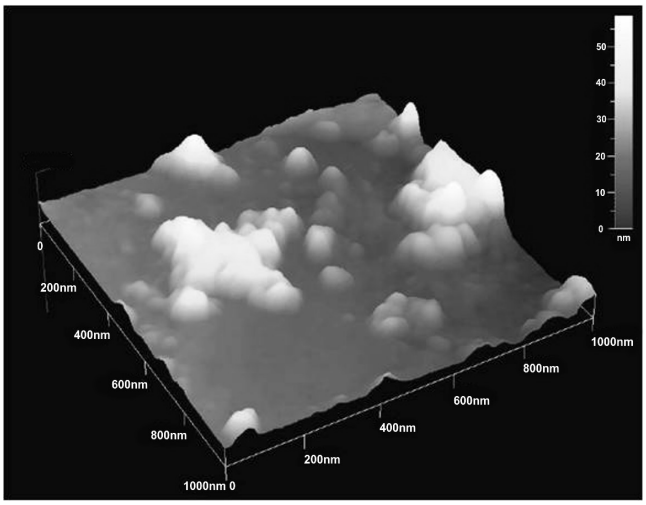

Figure 2. AFM image of the structure γ-Fe_2O_3 (Au) nanoparticles.

Nonlinear-optical studies

For the nonlinear-optical experiments, the p-polarized output of a YAG: Nd^{3+} laser at the fundamental wavelength of 1064 nm was used, with the pulse duration of 10 ns, repetition rate of 10 Hz, pulse power 5 MW. The second harmonic radiation generated in reflection from the samples at the angle of incidence of 45° was spectrally separated by an appropriate set of filters and detected by a photomultiplier and gated electronics. The SHG at 532 nm is close to the plasmon resonance spectral wavelength.

For the nonlinear magneto-optical studies the geometry of the transversal magneto-optical Kerr effect was used, as the magnetic field up to 4 kOe was applied to the samples. The measure of the magnetization-induced effect in SHG is the magnetic contrast of the SHG intensity:

$$\rho_{2\omega} = \frac{I_{2\omega}(\uparrow) - I_{2\omega}(\downarrow)}{I_{2\omega}(\uparrow) + I_{2\omega}(\downarrow)} \approx 2\frac{\chi^{odd}(M)}{\chi^{cr}}, \quad (1)$$

where $I_{2\omega}(\uparrow)$ and $I_{2\omega}(\downarrow)$ are the SHG intensities measured for the opposite directions of the applied magnetic field. The value of the SHG magnetic contrast characterizes the ratio of the magnetic to the nonmagnetic effective components of the second order susceptibility tensor $\chi^{odd}(M)$ and χ^{cr} [2].

Experimental results and discussion

The SHG indicatrix, i.e. the dependence of the SHG intensity on the angle of scattering at the fixed angle of incidence 45°, is shown at the figure 3. The angle of scattering is counted from the normal direction. The absence of the specular maximum proves that the SHG generated by the samples containing nanoparticles was diffusive, that is an intrinsic feature of the hyper-Rayleigh scattering (HRS) [4]. The average SHG intensity is proportional to the number of the nonlinear scatterers (nanoparticles). Inhomogeneities of the $\chi^{(2)}$ and the local field factor at the scale of several tens nanometers lead to incoherent scattering of SHG due to the inhomogeneous distribution of nonlinear polarization. The specular component is defined by the average value of the bulk nonlinear polarization. The diffusive component depends on the correlation of polarization's fluctuations.

The experimental data at the figure 3 were approximated by the function [4]:

$$I_{2\omega} \propto \exp(-(\frac{2\omega}{c})^2(\sin\theta - \sin\theta_0)^2 L_{corr}^2), \qquad (2)$$

where θ_0 is the angle of incidence, θ is the angle of SHG scattering, L_{corr} is the correlation length, that corresponds to the characteristic scales of spatial fluctuations of nonlinear polarization in the film structure. The calculated value of L_{corr} is approximately 30-40 nm, that is in a reasonable agreement with the value of the average nanoparticles' diameters.

Figure 4 shows the dependence of the SHG magnetic contrast on the value of the applied *dc* magnetic field measured for the core (shell) nanoparticles. One can see that the value of $\rho_{2\omega}$ increases continuously with the increase of the magnetic field and reaches the value of about 25% at the field 3.3 kOe. The magnetization-induced quadratic susceptibility is directly proportional to the value of magnetization of the sample. Therefore the absence of a hysteresis corresponds to the superparamagnetic state of the nanoparticles.

As the SHG magnetic contrast is a relative quantity, it is determined by the ratio of the magnetic to nonmagnetic components of the hyperpolarizability of a single nanoparticle and can serve for the characterization of its magnetic properties. One can evaluate the ratio of the magnetic to nonmagnetic components of the hyperpolarizability of a single nanoparticle, $\gamma^M/\gamma^0 \sim 0.4$ in the field of about 3 kOe. It is worth noting, that the relative value of γ^M is about two orders of magnitude larger than the typical values for the linear magneto-optical interaction.

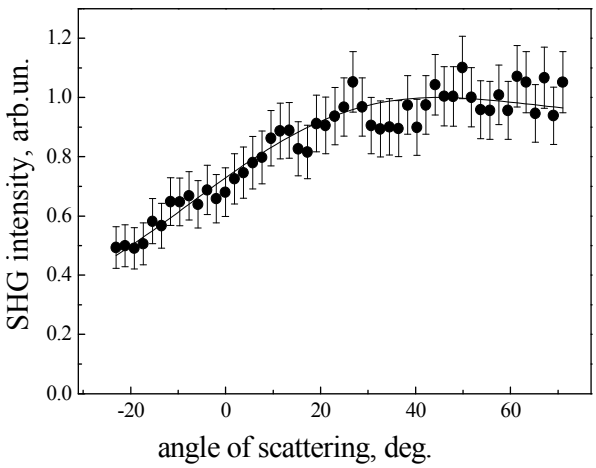

Figure 3. The SHG indicatrix of the (shell) nanoparticles. Angle of scattering is counted from the normal direction.

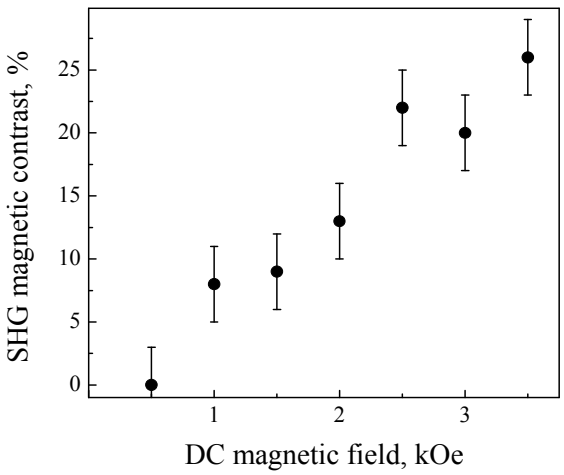

Figure 4. SHG magnetic contrast as a function of the magnetic field in plasmonic core (shell) nanoparticles.

Conclusion

To summarize, the nanoparticles with γ-Fe_2O_3 core and gold shell are fabricated and their nonlinear optical and nonlinear magneto-optical properties are studied. A plasmon resonance at the wavelength about 550 nm is attained in these structures. Nonlinear-optical studies at the fundamental wavelength of 1064 nm show that strong hyper-Rayleigh scattering yields the main contribution to SHG. Magnetization-induced SHG effect has been studied in different values of magnetic field that indicates the magnetic properties of the structure.

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