Switchable Light Reflectance in Dilute Magneto-Optical Colloids 
Based on Nickel Ferrite Nanowires

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Optical properties of diluted narrow band gap magnetic semiconductor nanowire colloids are controlled by modest magnetic fields under 100 Oe. High aspect ratio NiFe$_2$O$_4$ nanowires are used to achieve responsiveness to magnetic field, light absorption and -scattering. Visible light reflectance of the diluted colloids can be either increased or decreased depending on the nanowire alignment relative to the direction of the light propagation. The prepared colloids can be applied as magneto-optical switches or as smart window devices. [DOI: 10.1380/ejssnt.2018.119]

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I. INTRODUCTION

Recently we demonstrated smart window devices based on the dilute colloids of relatively large-size ZnO nanowires (diameter below 200 nm and length of up to 3 μm) in amino-terminated polydimethylsiloxane (PDMS) where transmittance of the device was modulated by means of changing the scattering cross-section during the electrophoretic alignment of nanowires in the direction of electric field, also coinciding with the direction of the light propagation [1]. We found that high aspect ratio nanowires with diameters smaller than 200 nm exhibit anomalously low scattering in the chaotic state and despite the obvious decrease in the geometrical cross-section upon nanowire alignment parallel to the direction of light propagation, the scattering efficiency increases during the alignment and light undergoes diffuse multiple scattering inside the colloid. The reversible transmittance change from 70% to 20% can be reached by colloids at nanowire concentrations of as low as ~0.25 wt%.

Furthermore, we investigated colloids prepared by using visible light absorbing transition metal doped ZnO nanowires [2]. The obtained colloids visibly change appearance from vivid colored state to black upon nanowire alignment towards light propagation. The origin of the observed optical behavior has not been explained yet but the effect is clearly related to multiple scattering and -adsorption in the complex dielectric media where the alignment of the visible light absorbing nanowires induces complex changes in scattering and adsorption intensity.

In the case of high optical path length (mm length scale and higher), the combination of these complex effects result in strong visible changes of the appearance of the colloid.

Here we synthesize NiFe$_2$O$_4$ nanowires and stabilize them in methanol solution of amino-terminated PDMS. Dilute colloids exhibit switchable visible light reflectance in magnetic field which can be either increased or decreased depending on the nanowire alignment relative to the direction of light propagation. Magnetic colloids and suspensions with tunable optical properties are important for magneto-optical applications where optical properties can be varied by magnetic field [3].

II. EXPERIMENTAL

Nickel ferrite nanowires were synthesized by using nitriloacetic acid (NA) as complexant and for directing one-dimensional nanocrystal growth under hydrothermal conditions. In typical procedure 1 mmol of Ni(NO$_3$)$_2$·6H$_2$O and 2 mmol of Fe(NO$_3$)$_3$·9H$_2$O are dissolved in 40 mL of the solution of water and 2-propanol (1 : 1 volume ratio). After obtaining clear solution, 6 mmol of the NA was added and mixture was kept under magnetic stirring at 60°C for 3 h. During mixing solution colour changes from brown to light green which can be attributed to metal-organic complex formation. After stirring, a mixture was poured into a 50 mL Teflon lined stainless steel autoclave and heated at 180°C for 24 h. The obtained white precipitates were washed with water and methanol by using filtering method, dried and annealed at 450°C for 3 h. After annealing, precipitates turned brown and exhibited ferrimagnetic behavior.

Crystalline phases of synthesized materials were determined by using Ultima+ X-ray diffractometer (Rigaku, * This paper was presented at the 8th International Symposium on Surface Science, Tsukuba International Congress Center, Tsukuba, Japan, October 22-26, 2017.
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Japan) with Cu Kα radiation and the microstructure was analysed by using high resolution scanning electron microscopy (SEM, Helios Nanolab, FEI). Light reflectance of samples was measured by Shimadzu UV-vis spectrophotometer, UV-3700 (Shimadzu Scientific Instruments Kyoto, Japan) with barium sulphate coated integrating sphere ISR-240A. A Kubelka-Munk conversion was applied to a diffuse reflectance spectrum to obtain absorption. Magnetic properties were measured by a vibrating sample magnetometer (Lake Shore Cryotronic Co., Model 7404 VSM, USA).

Nanowire colloids were prepared by mixing nanowires (0.25 wt%) into the solution of amino-terminated polydimethylsiloxane (amino-PDMS Gelest, AMS-1203) and methanol (mixed in ratio 1 : 1). To achieve higher quality dispersion and good amino-PDMS bonding to nanowire surface, the nanowire mixture was ultrasonicated by ultrasonic device (Hielscher, UP200H, Germany) at maximum power in volume 20 mL for 5 min.

Magneto-optical properties for colloids were measured in the sample cell attached to the integrating sphere of the UV-vis spectrophotometer. Nanowires were oriented in different directions parallel and perpendicular to the light propagation by applying magnetic field 45 Oe.

III. RESULTS AND DISCUSSION

The XRD diffractogram of synthesized NiFe₂O₄ is demonstrated in Fig. 1(a). The XRD reveals two different phases—NiFe₂O₄ (ICDD 00-010-0325) and hematite (ICDD 00-033-0664). We performed Rietveld analysis on measured XRD diffractogram, which show that the dominant phase is NiFe₂O₄ (63 ± 1 % by weight) and secondary phase is hematite Fe₂O₃ (37 ± 1 % by weight). Figure 1(b) shows SEM image of synthesis products. During the synthesis a high aspect ratio nanowires formed with length of up to 10 μm and diameter below 250 nm. NA, used as chelating agent during the synthesis, forms ion-based coordination polymer nanowires and crystallizes into the one-dimensional structures during the hydrothermal treatment [4]. These structures can be turned into the inorganic compounds by annealing [4].

Optical properties of nanowires were analyzed by performing UV-vis reflectance measurements. Measured reflectance was converted to absorption by using Kubelka-Munk function. The absorption spectrum [Fig. 2(a)] of semiconductor nanowires shows typical steep edge of band gap absorption at around 600 nm. The indirect band gap was observed from \((A\nu)^{1/2}\) versus photon energy plot [Fig. 2(b)]. Two absorption edges can be observed from Fig. 2(b), from which one (1.93 eV) corresponds to hematite indirect band gap [5], but other (1.63 eV) to NiFe₂O₄ indirect band gap [6]. Overall, measurements show that nanowires exhibit visible light absorption, which is important to observe optical effect described below.

The vibrating sample magnetometer hysteresis curve of the synthesized nanowires measured at room temperature is demonstrated in Fig. 3. Material shows soft magnetic behavior with narrow hysteresis loop. Saturation magnetization \((M_s)\) of the sample reaches 18.6 emu/g. The \(M_s\) is smaller than reported before for NiFe₂O₄ nanoparticles [7, 8], which is due to the presence of antiferromagnetic hematite phase. Nanowires also exhibit some coercive force up to 122 Oe and remanence up to 3.56 emu/g. Although particles has some remanent magnetization and coercive force, the nanowires in colloid used for

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**FIG. 1.** (a) XRD diffractogram of synthesized NiFe₂O₄; (b) SEM images of NiFe₂O₄ nanowires.

**FIG. 2.** The Kubelka-Munk UV-vis absorption spectra (a) and \((A\nu)^{1/2}\) versus photon energy plot (b) of synthesized nanowires.
FIG. 3. Magnetization versus magnetic field curves at room temperature for synthesized NiFe$_2$O$_4$ nanowires.

FIG. 4. Baseline corrected reflectance spectra for diluted nanowire colloids at different orientations; chaotic, parallel, and perpendicular to light direction.

optical switch is protected from agglomeration caused by magnetic attraction, because device (as demonstrated below) can be operated in magnetic fields weaker than coercive force. Nanowires are also protected from agglomeration because of amino-PDMS stabilization. Amino groups strongly adsorb on oxide surfaces, thus prohibiting agglomeration [9].

From the synthesized NiFe$_2$O$_4$ nanowires magnetic field responsive colloids were prepared. Colloids were filled in measurement cell and placed directly in front of the integrating sphere in UV-vis spectrophotometer to measure magnetic field switchable reflectance. The optimal concentration of nanowires in colloids (0.25 wt%) was chosen by taking into the account results from our previous studies [1, 2], where the highest optical contrast was observed for this particular nanowire concentration. The reflectance spectra measured for three different nanowire orientations (chaotic, parallel, and perpendicular to light direction) are demonstrated in Fig. 4. The reflectance in visible range either increases or decreases upon nanowire alignment perpendicular or parallel to the light direction, respectively. The lower reflectance for nanowire colloids where nanowires are aligned parallel to the light direction can be explained by the deeper light penetration into the aligned nanowire colloid where light undergoes multiple reflections in between nanowires and some portion of light is absorbed upon each light-nanowire interaction, thus decreasing total reflectance [10].

IV. CONCLUSION

Performed synthesis technique yield high aspect ratio magnetic nanowires composed of NiFe$_2$O$_4$ and α-Fe$_2$O$_3$ crystalline phases. Nanowires exhibited visible light absorption and soft magnetic properties. Nanowire colloids in the solution of methanol and amino-PDMS exhibit switchable reflectance in magnetic field which can be either increased or decreased by switching between perpendicular or parallel orientation of nanowires towards the direction of light propagation. The device can be operated in magnetic fields lower than coercive force of nanowires, thus ensuring stability of nanowire colloids. The prepared colloids could be applied as magneto-optical switches.

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