

Magneto-Optical Characterization of Binding Ability of Magnetic Nanoparticles in Solution

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The magnetization profile of iron oxide magnetic nanoparticles (MNPs) and the binding ability of MNPs with metal ions in aqueous solutions were investigated by means of the magnetic linear dichroism (MLD) and the magneto-optical Kerr effect (MOKE) measurements. The ultra-visible MLD spectra of the non-modified and surface modified MNPs with -COOH showed a typical magnetization curve for a superparamagnetic particles. Also, the MLD spectra were changed drastically by the addition of dysprosium(III) ion and showed that MLD spectra can be used for the evaluation of metal-MNPs binding ability. Furthermore, the magnetization of MNPs solution was measured sensitively by the transversal MOKE measurements, where a polarized beam was reflected at the interface of prism/solution of MNPs.

Keywords: Magneto-optical effect, Magnetic linear dichroism, MOKE, Magnetic nanoparticles.

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1. INTRODUCTION

Magnetic nanoparticles (MNPs) have been widely used in bio-medical, mechanical and material technologies. Most widely used MNPs are the nanometer sized magnetite or magnetite and maghemite mixtures. Surface modified MNPs are also developed and used for various purposes [1,2].

Characterization of MNPs has been carried out usually by magnetometric methods and spectroscopic methods. Recent progress of magneto-optical methods, such as Faraday rotation [3,4], magneto-optical Kerr effect (MOKE)[5,6], magnetic linear dichroism (MLD)[7,8] and magnetic circular dichroism [9,10], opened new possibility to be applied for the characterization of MNPs. Especially, the interaction between the surface modified MNPs and small ions and molecules are fundamentally important subjects. However, these interdisciplinary subjects between chemistry and physics still require intensive study. In the present study, the MLD spectrometry was applied to the measurements of the magnetization of MNPs solution and of the chemical binding between MNPs and dysprosium(III) ion.

2. MATERIALS AND METHODS

2.1 Materials

Magnetic nanoparticles (MNPs) used in this study were an aqueous solution of magnetite, W-40 (40% magnetite, 8% oleic acid, 6% sodium dodecylbenzenesulfonate, 46% water) from Tauhokozai Co. Ltd. Tokyo, Japan and an aqueous solution of anionic surfactant coated magnetic nanoparticles, EMG707 (ca. 10 nm in diameter, COOH modified, 8.5-11.6% iron oxide, 5.7-7.8% surfactant, 80.6-85.8% water) from Ferrotec, Tokyo, Japan. The aqueous solution of Dy(III) ion was prepared by dissolving DyCl_3 with water. Water was purified by a Milli-Q system (Millipore, USA).

2.2 Methods

The magnetization of diluted MNPs and the interaction of the MNPs with metal ions in aqueous

solutions have been examined by MLD spectrometry. MLD spectra were measured by a spectropolarimeter (Jasco, J-820E) applying magnetic field with a pair of permanent magnets perpendicular to the propagating light through the sample in a 1 mm quartz cell. The magnetic field was changed in the range of 0-200 mT.

The transverse magneto-optical Kerr effect (TMOKE) of MNPs at the glass/solution interface was measured by TMOKE instrument, which was built in our laboratory by incorporating motor driven stage to move a permanent magnet which can apply magnetic field (0-97 mT) in the transversal direction. A vertically polarized green laser beam of 532 nm was incident on the prism/MNPs solution interface with 54.8° and the reflected beam was detected after another vertical analyzer.

3. RESULTS AND DISCUSSION

3.1 MLD measurements of magnetization

The MLD intensity of the diluted W-40 sample was increased with the increase of the magnetic field reversibly as shown in Fig. 1. This feature is understood as the typical magnetization curve for superparamagnetic materials. Then, it was concluded that MLD intensity can be used for the measurement of magnetization curve for diluted solution of MNPs.

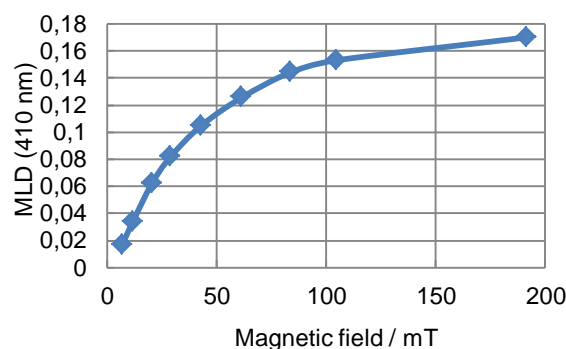


Fig. 1 – Correlation between the MLD intensity at 410 nm and the magnetic flux density (mT) for 0.1% magnetite (W-40) in aqueous solution with 1 mm cell.

3.2 Effect of Dy(III) ion on the MLD spectra

Dysprosium(III) ion is known to form the complex with -COOH group [11]. When a small amount of Dy(III) ion less than 10^{-4} M was added to the solution of EMG707, a drastic decrease of the MLD spectra was observed (Fig. 2). As the concentration of Dy(III) is increased, the MLD spectra decreased remarkably with the red-shift of the maximum wavelength from 330 nm to 379 nm.

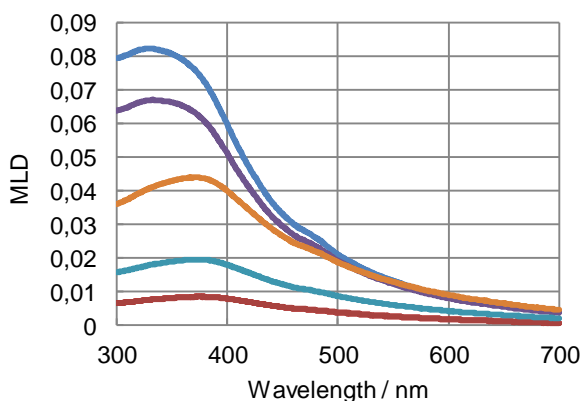
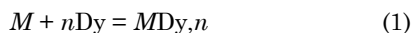


Fig. 2 – Decrease of MLD intensity with the concentration of Dy(III) for 0.0165% EMG707 MNPs solution. The concentrations of Dy(III) were, from top figure, 3.3×10^{-5} M, 6.7×10^{-5} M, 1.1×10^{-4} M, 1.5×10^{-4} M and 1.3×10^{-4} M.

In Fig. 2, the spectral decrease was somewhat affected due to the migration of MNPs complex toward the magnets in the higher concentration of Dy(III). Anyway, the decrease of MLD intensity with Dy(III) ion suggests the binding of the MNPs by the complexation of Dy(III) ion with the surface -COOH. Here, the value of pH was almost kept at 7.0 and the hydrolysis of Dy(III) is negligible. Therefore, the observed MLD intensity can be approximated to be the MLD of free MNPs remaining in solution.

To analyze the change of MLD spectra, we have postulated a chemical reaction between MNPs and Dy(III) as,



REFERENCES

1. B. Issa, I. M. Obaidat, B. A. Albiss, Y. Haik, *Int. J. Mol. Sci.* **14**, 21266 (2013).
2. H. Watarai, *Annual Rev. Anal. Chem.* **6**, 353 (2013).
3. H. Watarai, P. Gangopadhyay, R.A. Norwood, and N. Peyghambarian, *Chem. Lett.* **43** No10, 1651 (2014).
4. M. Suwa, K. Miyamoto, and H. Watarai, *Anal. Sci.* **29** No1, 113 (2013).
5. C.A. Herreño-Fierro, E. J. Patiño, *Phys. Status Solidi B* **252** No2), 316 (2015).
6. C.-Y. You, S.-C. Shin, *Appl. Phys. Lett.* **69** No9, 1315 (1996).

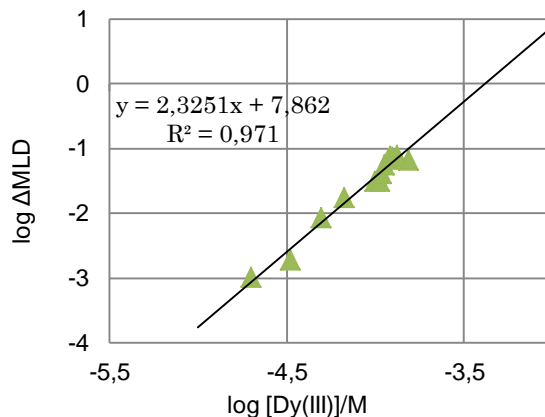


Fig. 3 – Linear correlation between logarithmic values of MLD intensity at the maximum wavelength and the concentration of Dy(III) ion

where M and MDy_n refer to the free MNPs and MNPs bound by n ions of Dy(III). Equation (1) suggests a linear relationship between $\log \Delta \text{MLD}$ and $\log [\text{Dy(III)}]$, in which ΔMLD means the decrease of MLD due to the addition of Dy(III). Figure 3 shows the plot of the observed data, which supported well the postulated relationship. The result of the present study demonstrated a high potential of MLD spectrometry for the evaluation of the binding ability.

3.3 TMOKE measurement of magnetization

TMOKE signal was measured for the diluted W-40 solution and EMG707 MNPs aqueous solution by the reflected beam of 532 nm at the prism/solution interface. It is interesting that the reflected light at the glass/solution interface gave a magnetization curve very similar to Fig. 1 observed by MLD spectra, and the curve suggested again the superparamagnetic property of W-40 and EMG707. In these measurements, the required volume was only 50 μL , which was put in the gap of a prism and a slide glass. Therefore, the sample volume could be reduced and it will be adaptable to green chemistry too. The interaction between the functional group bound to the glass surface and MNPs in solution will be measured by this technique. It will be conducted in our next study.

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7. A. Butykai, A. Orban, V. Kocsis, D. Szaller, S. Bordacs, E. Tatrai-Szekeres, L.F. Kiss, A. Bota, B.G. Vertessy, T. Zelles, I. Kezsmarki, *Sci. Rep.* **3**, 1431 (2013).
8. S. Taketomi, H. Takahashi, N. Inaba, H. Miyajima, *J. Phys. Soc. Jpn.* **60** No10, 3426 (1991).
9. J.T. Wang, S. Hall, Y. Zhen, D.S. Guo, *J. Supercond. Nov. Magn.* **23**, 1155 (2010).
10. O. Ohno, Y. Kaizu, H. Kobayashi, *J. Chem. Phys.* **99**, 4128 (1993).
11. T. Gushuchina and G. Kotenko, *Koord. Khim.* **12**, 325 (1986).