Magnetophoretic detection of photo-induced spin transition†

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Magnetophoretic velocimetry detected the spin transition of a single Co–Fe Prussian Blue analogous micro-crystal in water induced by a single-shot pulse laser.

Innovative principles for the migration of micro-particles like colloids, DNAs, and cell composites have been greatly required in analytical separation sciences, being necessary for the further development of colloidal chemistry, medical science, biotechnology and so on.[1,2] It has recently been demonstrated that novel migration phenomena generated by various external fields are useful for the separation and characterization of micro-particles.[3–5] Especially, magnetophoresis, which utilizes an inhomogeneous magnetic field, has been applied to some cell sorting techniques, *e.g.*, field-flow fractionation (FFF),[6] and split-flow thin fractionation (SPLITT).[7,8] One of the specific properties of a magnetic field different from an electric field is that there is no magnetic monopole, hence $div\mathbf{B} = 0$, which causes the difficulty of shielding. This seems to be a disadvantage. However, in the case of separation of micro-particles, this feature can become an advantage. The magnetophoretic velocity of micro-particles reflects their intrinsic magnetism in contrast to electrophoretic velocity, which mainly depends on the surface charge of the particle that is neutralized by electrolyte in the medium, because their electric properties are easily shielded by ions. Another advantage of magnetophoresis is that the magnetism of a transition metal complex is changeable by controlling the spin state induced by ligand or crystal field and valence number. Recently, we have developed a novel technique called "magnetophoretic velocimetry". This technique can measure not only the volume magnetic susceptibility of a migrating particle, but also the amount of paramagnetic ions including in and adsorbing on the micro-particle, from the magnetophoretic velocity under an inhomogeneous magnetic field.[9,10] The purpose of this paper is to show a new applicability of magnetophoresis as an analytical technique. We report here for the first time that the photo-induced spin transition of the single crystalline particles of Co–Fe Prussian blue analogues can be detected from a sudden change of magnetophoretic velocity.

Recently, Hashimoto *et al.* demonstrated the interesting photomagnetic properties of Co–Fe Prussian blue analogues.[11] According to their report, Co–Fe Prussian blue analogues had a face-centered cubic structure composed of Fe, Co and CN. At low temperature, the spin states of both Co and Fe were low spin state ($t_{2g}^6 e_g^0$, $S = 0$), called low temperature phase (LT phase). By heating the LT phase, an electron of Fe(II) transferred to Co(III), and then the high spin state Co(II) was produced, because the Co–N bond length was increased and hence the crystal field was weakened. As a result, at high temperature (HT phase), the spin states of Co and Fe became $t_{2g}^5 e_g^2$ ($S = 3/2$) and $t_{2g}^5 e_g^0$ ($S = 1/2$), respectively. This thermal process was reversible, although the transition had a hysteresis loop that the transition temperature in cooling process was lower than that in a heating process. The transition temperature region in the hysteresis loop was dependent on the composition of Co and Fe. Moreover, they reported that Co–

Fe Prussian blue analogues exhibited bistability between HT phase and LT phase, and one-shot pulse laser of 532 nm could induce the phase transition from LT to HT phase at the temperature in the hysteresis loop.[12]

Co–Fe Prussian blue analogues were prepared by a solution reaction of $K_3[Fe(CN)_6]$ (Wako Pure Chemical Industries Ltd., Osaka, Japan) and $CoCl_2$ (Nakarai Tesque Inc., Kyoto, Japan), controlling the NaCl concentration and adjusting the reaction temperature by a water bath. Three kinds of Co–Fe polycyanide compounds were synthesized under different conditions: compound **1**, [NaCl] = 0 M, 25 °C, compound **2**, [NaCl] = 5 M, 50 °C, and compound **3**, [NaCl] = 5 M, 75 °C. A Co–Fe polycyanide precipitate was produced soon after the addition of an aqueous solution of $K_3[Fe(CN)_6]$ (2 mM) and NaCl (0 or 5 M) to an aqueous solution of $CoCl_2$ (2 mM) and NaCl (0 or 5 mM). The precipitate was filtrated, washed with milli-Q water and dried, yielding 1–2 µm sized fine crystalline powder sample. One mg of the powder was dispersed in 3 mL milli-Q water by sonication, and this was used as a sample solution.

Fig. 1 illustrates the laser-induced magnetophoresis apparatus used in this study. The square fused-silica capillary with 100 × 100 µm inner section was used as a flow cell for the magnetophoresis. An inhomogeneous magnetic field was generated by a pair of iron pole pieces and Nd–Fe–B permanent magnets (0.4 T).[13] The optical components were assembled by New Wave Research Inc, Tokyo, Japan. The second harmonic light (532 nm) of a pulsed Nd:YAG Laser (New Wave Research, MiniLaseII 20, CA, USA) was irradiated into the focal plane of the microscopic system *via* a slit, a tube lens (Mitsutoyo, VMU-L, Kanagawa, Japan), and the objective (Mitsutoyo, MPlan NUV 50×, Kanagawa, Japan). The pulse width and energy density of the laser were 5–7 ns and 100 mJ cm^{-2} per pulse. The irradiation area was set to 60 × 60 µm by adjusting the slit. The magnetophoretic behavior near the edge of the pole pieces was observed by CCD camera (ELMO, CN42H, Nagoya, Japan), and the magnetophoretic velocities were obtained from the captured images. All measurements were carried out in a thermostated room at 25 ± 1 °C.

Typical magnetophoretic behaviors of the single crystalline particles of compounds **1**, **2** and **3** are shown in Fig. 2 (b), (a) and (c), respectively. These images were made by superimposing
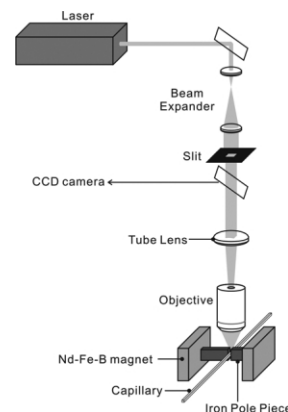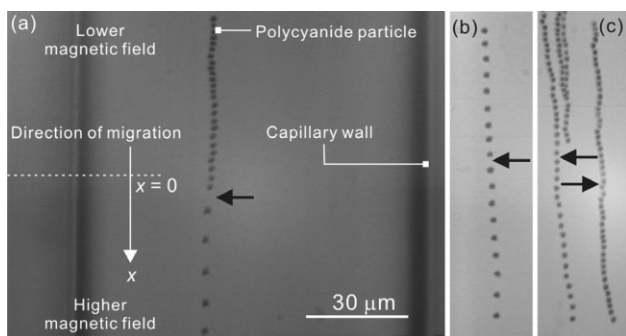

Fig. 1 Experimental setup for the measurement of the photo-induced spin transition during the magnetophoretic migration of a single particle.

† Electronic supplementary information (ESI) available: movie files showing the magnetophoretic behaviours of compounds **1**, **2** and **3**. See http://www.rsc.org/suppdata/cc/b4/b403386h/

Fig. 2 Typical magnetophoretic behavior of Co–Fe Prussian blue analogues of **2** (a), **1** (b) and **3** (c). These microphotographs were made by superimposing images observed at 0.1 s intervals. The dashed line in (a) illustrates the edge of the pole pieces, and the black arrows indicate the position where the micro-particles were irradiated by the pulse laser.

microphotographs observed at 0.1 s intervals. All particles were attracted into the gap of the pole pieces by the magnetic force, but only with particles of compound **2** did the magnetophoretic velocity suddenly increase after the irradiation of a single shot of pulse laser, as shown in Fig. 2(a). This phenomenon could not be observed in the cases of compounds **1** and **3** (Fig. 2(b) and 2(c)). The comparison of magnetophoretic velocities between **1**, **2** and **3** is shown in Fig. 3. The position of the particles is plotted against time. The x-direction is defined as that directed into the gap of the pole pieces along the capillary and $x = 0$ is set at the edge of the pole pieces as indicated in Fig. 2(a). The slope of each plot in Fig. 3 indicates the magnetophoretic velocity. As mentioned above, for compounds **1** and **3**, no photochemical charge transfer that induced spin transition was observed. These experimental results of the acceleration of the velocity of **2** is not attributable to the radiation pressure of the laser beam, but ascribable to the increase of the magnetic susceptibility of the single crystal, associated with the photo-induced spin transition. Hashimoto *et al.* reported that in the temperature region from 50 K to 350 K, compounds **1** and **3** belonged to HT and LT phases, respectively, and did not show any photochemical charge-transfer induced spin transition.[11] On the other hand, compound **2** had a bistability and exhibited photo-induced spin transition at room temperature.[12]

In order to analyze the photo-induced acceleration in the magnetophoretic velocity of the crystalline micro-particle of the compound **2** by the change of its magnetic susceptibility, we should apply the general principle of magnetophoresis.[8,14] The x-component of magnetophoretic velocity, v_m, in a liquid medium can be expressed as follows:

$$v_m = \frac{(\chi_p - \chi_m)}{\mu_0}\frac{V}{f}B\frac{dB}{dx} \qquad (1)$$
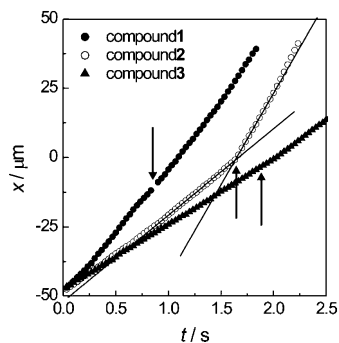
Fig. 3 Positions of micro-particles of **1** (●), **2** (○) and **3** (▲) plotted as a function of time. The black arrows indicate the point of irradiation. The magnetophoretic velocity is obtained from the slope of these plots.

where χ_p and χ_m are the volume magnetic susceptibility of the particle and the medium, respectively, μ_0 the vacuum magnetic permeability, V the volume of the particle, f a friction factor and B the magnetic flux density. The magnetophoretic velocity of compound **1** (HT phase) was larger than that of compound **3** (LT phase), because the magnetophoretic velocity is proportional to the difference of magnetic susceptibilities between a particle and medium as indicated in eqn. (1). $B(dB/dx)$ is the function of a position, however, $B(dB/dx)$ was found to be actually constant in the observation region, because the magnetophoretic velocity of **1** and **3** were constant in the region. Therefore, the increase in the ratio of the magnetophoretic velocity after the irradiation of pulse laser can be evaluated by the equation:

$$\left.v_{m,a}\middle/v_{m,b}\right. = \left.(\chi_{p,a} - \chi_m)\middle/(\chi_{p,b} - \chi_m)\right. \qquad (2)$$

where the subscripts a and b represent after and before the irradiation, respectively. The observed velocities were obtained from the slopes of Fig. 3. The regions used for the determination of the velocities, $v_{m,b}$ and $v_{m,a}$, were from the irradiated point to the 15 μm forward point and from the irradiated point to the 15 μm backward point, respectively. The mean of the velocity ratio for compound **2** was 2.46 ± 0.90 for 67 particles. This was in good agreement with the value of 2.5, which was measured by SQUID magnetometer.[12] Therefore, it was confirmed that photo-induced spin transition of the "single" crystalline micro-particle was detected by magnetophoretic velocimetry. The observed velocity ratios seem to be somewhat dispersed. Since this dispersion is larger than the expected measurement error, it may reflect the difference in the magnetic properties of individual particles. Therefore, laser-induced magnetophoretic acceleration will provide a new technique for the characterization of magnetic properties of single micro-particles, and the reason of this dispersion will become a subject of future investigation. Furthermore, if these materials are used as magnetic labels of bio-particles in cell sorting techniques, a novel photo-induced magnetic separation mode will be invented.

Notes and references

1 S. R. Springston, M. N. Myers and J. C. Giddings, *Anal. Chem.*, 1987, **59**, 344.
2 M. Mesaros, P. F. Gavin and A. G. Ewing, *Anal. Chem.*, 1996, **68**, 3441.
3 M. Tamagawa, H. Monjushiro and H. Watarai, *Colloids Surf., A*, 2003, **220**, 279.
4 I. Ikeda, S. Tsukahara and H. Watarai, *Anal. Sci.*, 2003, **19**, 27.
5 Y. Iiguni, M. Suwa and H. Watarai, *J. Chromatogr., A*, 2004, **1032**, 165.
6 M. Schimpf, K. Caldwell and J. C. Giddings, *Field Flow Fractionation Handbook*, Wiley, New York, 2000.
7 C. B. Fuh, *Anal. Chem.*, 2000, **72**, 266A.
8 L. R. Moore, A. R. Rodriguez, P. S. Williams, K. McCloskey, B. J. Bolwell, M. Nakamura, J. J. Chalmers and M. Zborowski, *J. Magn. Magn. Mater.*, 2001, **225**, 227.
9 M. Suwa and H. Watarai, *Anal. Chem.*, 2001, **73**, 5214.
10 M. Suwa and H. Watarai, *J. Chromatogr., A*, 2003, **1013**, 3.
11 N. Shimamoto, S. Ohkoshi, O. Sato and K. Hashimoto, *Inorg. Chem.*, 2002, **41**, 678.
12 N. Shimamoto, S. Ohkoshi, O. Sato and K. Hashimoto, *Chem. Lett.*, 2002, **31**, 486.
13 H. Watarai and M. Namba, *J. Chromatogr., A*, 2002, **961**, 3.
14 H. Watarai and M. Namba, *Anal. Sci.*, 2001, **17**, 1233.