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OPTICAL TRAPPING AND ORIENTATION MANIPULATION OF 2D INORGANIC MATERIALS USING A LINEARLY POLARIZED LASER BEAM

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Abstract—Owing to the large anisotropy of inorganic nanosheets, such as clay minerals, the orientation manipulation of nanosheets is an important challenge for realizing future functional materials. In this study, the methodology for a novel nanosheet manipulation by using laser radiation pressure is proposed. When a linearly polarized laser beam was used to irradiate a niobate nanosheet colloid, the nanosheet was trapped at the focal point so that its in-plane direction was oriented parallel to the propagation direction of the incident laser beam so as to minimize the scattering force. In addition, the trapped nanosheet was aligned along the polarization direction of the linearly polarized laser beam. Thus, a unidirectional alignment of nanosheet can be realized simply by irradiation with a laser beam.

Key Words—Laser Radiation Pressure, Optical Trapping, Polarized Laser Beam, Two-dimensional Inorganic Material.

INTRODUCTION

Optical manipulation is a technique for non-contact and non-invasive trapping, and for the transport of colloidal particles by the radiation pressure of a tightly focused laser beam (Ashkin, 1992; Dholakia *et al.*, 2008). The pressure arises from a momentum change of a photon when the photon is reflected or refracted by a particle. The size of the target particles is generally on the scale of sub-μm to several tens of μm. Typically, spherical shaped particles, such as latex particles (Wright *et al.*, 1994; Won *et al.*, 1999), glass beads (Ashkin *et al.*, 1986), and metal nanoparticles (Ohlinger *et al.*, 2011; Lehmuskero *et al.*, 2015), have been manipulated. The target particles are trapped at the focal point of an incident laser beam, the point at which the strongest trapping field is produced by the radiation pressure. The trapping is relaxed when the laser irradiation ceases. The optical manipulation realizes on-demand particle trapping and release by the on-off switching of the incident laser beam.

Recently, optical manipulation has been extended from spherical particles to one-dimensional (1D) rod-like particles such as carbon nanotubes (Wu *et al.*, 2017), nanowires (Tong *et al.*, 2010; Yan *et al.*, 2012), and nanofibers (Neves *et al.*, 2010). Although the 1D particles are trapped at the focal point as well as the spherical particles, the radiation pressure contributes to the orientation manipulation of the 1D particles. Namely, the particles are oriented with their long-axis parallel to the propagation direction of the incident laser beam. The results have establish optical manipulation as an alignment technique for anisotropic particles.

Recent developments of various nanoparticles have evoked interests in two-dimensional (2D) plate-like particles in addition to 1D particles. In particular, inorganic nanosheets prepared by exfoliation of layered crystals, such as clay minerals, have attracted great attention owing to their high shape anisotropy (Nakato *et al.*, 2017). A variety of nanosheets have been prepared and examined as building blocks of functional nanoassemblies. Oxide nanosheets of smectite-type clay minerals and other layered oxides have been applied for layer-by-layer assemblies, thin films, porous solids, inorganic-polymer hybrids, and so forth (Suzuki *et al.*, 2012; Schoonheydt, 2014; Okada *et al.*, 2015; Tominaga *et al.*, 2016). Because the nanosheets are provided as their colloids in many cases, manipulation of colloidal nanosheets provides a novel fundamental technique for assembling the nanosheets.

In contrast to spherical and 1D particles, 2D particles are characterized by their biaxial shape, which requires an orthogonal application of two external forces for uniform, or unidirectional alignment. This has been realized for colloidal nanosheets of an exfoliated layered niobium oxide; unidirectional nanosheet alignment was realized under orthogonal application of an electric field and gravity (Nakato *et al.*, 2014). However, optical manipulation of 2D plate-like materials has not been attempted to date.

In this study, optical manipulation of colloidal nanosheets dispersed in water was conducted by irradiation with a linearly polarized laser beam. As a model of a nanosheet, negatively charged niobate ($Nb_6O_{17}^{4-}$) was employed because its orientation behavior by an external field has extensively been studied in recent years (Nakato et al., 2011; Nakato et al., 2014; Nakato et al., 2017). When a laser beam, as an external field, is applied to colloidal nanosheets, the 2D particles should be trapped at the focal point due to the strongest trapping field and oriented with one of their axes parallel to the propagation direction of the incident laser beam as is the case of optical manipulation of 1D particles. In addition, the other axis of trapped 2D particles should be aligned parallel to the optical electric field of the linearly polarized laser beam because nanosheets are aligned along to an alternating electric field due to their high shape anisotropy. As a result, a unidirectional alignment of a nanosheet is expected to be realized by one external force of a linearly polarized laser beam.

EXPERIMENTAL SECTION

Sample preparation

A niobate nanosheet colloid, where negatively charged oxide nanosheets are accompanied by propylammonium ions as their countercations, was prepared by exfoliation of layered $K_4Nb_6O_{17}$ according to the previously reported method (Miyamoto and Nakato, 2004; Nakato *et al.*, 2014). The nanosheet concentration was 0.05 g L^{-1} and the colloid sample exhibited an isotropic phase at room temperature. The lateral lengths of the nanosheets obtained from transmission electron microscopy (TEM) observations exhibited a size distribution that obeyed a log-normal distribution to give an average size of 1.6 μm.

Optical microscopy

The colloid sample was injected into a thin-layer glass cell with a 100 μm thickness. The cell was set on the stage of an inverted microscope (IX70, Olympus, Tokyo, Japan). Figure 1 shows a photograph of the experimental setup. A linearly polarized continuous-wave laser beam emitting at 532 nm (Millennia Pro, Spectra Physics, Santa Clara, California, United States) was focused at the center of the cell (50 μm from the cell-sample interface) using an objective lens (Apo, 40×, numerical aperture = 0.90, Olympus, Tokyo, Japan) at room temperature. The polarization direction of the linearly polarized laser beam with respect to the sample was varied by rotating a half-wave plate mounted on a stepper motor. The laser power was set at 20 mW after the objective lens. The beam diameter was adjusted to the pupil diameter of the objective lens using a beam expander. The resulting beam waist at the focal point was calculated to be 0.4 μm.

For optical microscopy observation upon irradiation with a laser beam, the sample was illuminated by a halogen lamp and the image was monitored with a digital camera (ORCA-Flash 4.0 V3, Hamamatsu Photonics, Hamamatsu, Japan). The incident laser beam was completely blocked by a dichroic mirror and a band pass filter inserted before the camera. Spatial resolutions and the depth of field in the experimental setup were approximately 440 and 420 nm, respectively, which were almost the same sizes as the diffraction limits. The depth of field was 0.42% of the thickness of the cell.

RESULTS

An object looks like a line or rod shape with a length of 1–10 μm was found to be trapped at the focal point when the laser beam was irradiated. Hereafter, these objects are referred as “line-shaped object”. The optical microscope images of a nanosheet colloid before and after irradiation with a linearly polarized laser beam are shown in Figure 2. Before laser irradiation, many line-shaped objects were observed within the microscope field (Figure 2a). The line-shaped objects were moved and/or appeared and disappeared owing to the focusing and de-focusing by three-dimensional Brownian motion. As described in the discussion, the line-shaped objects were attributed to be nanosheets oriented with their in-plane direction perpendicular to the cell surface. The image after 15 s of continuous laser irradiation (Figure 2b) indicates no apparent change at the focal point, whereas the Brownian motion seen over the entire microscope field was continuously observed. After 30 s of continuous laser irradiation, a line-shaped object appeared near the focal point (Figure 2c). This line-shaped object was moved toward the focal point and then was completely trapped at the focal point after 34 s of continuous laser irradiation (Figure 2d) and no longer disappeared during laser irradiation. The orientation of the object was parallel to the polarization direction of the incident laser beam. The time required for trapping of the line-shaped object was from 20 s to 34 s.

The line-shaped object was gradually released when the laser irradiation was ceased. The line-shaped object trapped at the focal point began the Brownian motion again just after the laser irradiation was ceased (Figure 3a). The object was then gradually diffused and became blurred (Figure 3b and 3c). At 15 s after the laser irradiation ceased (Figure 3d), the image was essentially the same as that before laser irradiation (see Figure 2a).

The line-shaped object was repeatedly trapped at the focal point by on-off switching of the laser irradiation. Upon irradiation with the laser beam 15 s after the laser irradiation ceased, the line-shaped object was re-trapped at the focal point after approximately 30 s of continuous laser irradiation (Figure 4a). After the laser irradiation was ceased again, the re-trapped line-shaped object diffused and was no longer observed (Figure 4b). The re-trapping and releasing was repeated by further on-off switching cycles of the laser irradiation (Figure 4c and Figure 4d).

Figure 5 shows that the trapped line-shaped object was rotated following rotation of the polarization direction of the incident laser beam. A trapped nanosheet (Figure 5a) by irradiation of a laser beam with a polarization direction of 45° with respect to the viewing direction can be seen. When the polarization direction was rotated clockwise by 45°, the line-shaped object was also rotated clockwise by 45° (Figure 5b). When the polarization direction was sequentially rotated by a further 45°, the line-shaped object was rotated following the rotation of the polarization direction (Figure 5c and Figure 5d). The rotation of the trapped line-shaped object followed that of the polarization direction in real-time until the upper limit of the rotation speed of the employed experimental setup, which was 0.4 π rad/s.

DISCUSSION

The line-shaped object observed in Figures 2, 4 and 5 was proposed to be a nanosheet oriented with the in-plane direction parallel to the propagation direction of the laser beam. When a nanosheet orients its in-plane direction parallel to the propagation direction of an incident laser beam, the nanosheet should be observed as a line. In fact, the orientation of the nanosheet was also confirmed by polarized optical microscopy observation (data not shown). The image before laser irradiation was dark. After approximately 30 s of continuous laser irradiation, which was the time when the nanosheet was trapped at the focal point, a birefringent line appeared. The birefringence was ascribed to the orientation of the nanosheet with its in-plane direction perpendicular to the cell surface (Nakato *et al.*, 2011).

The orientation behavior of a nanosheet by laser irradiation can be considered as an analogy of the orientation manipulation of 1D particles. In general, a focused laser beam provides two types of forces as a radiation pressure on a particle (Ashkin, 1992; Harada and Asakura, 1996). One is a scattering force which is applied toward the propagation direction of the incident laser beam to the object. Namely, when the scattering force is applied to an object, the object moves along the propagation direction of the incident laser beam. The other is a gradient force which is applied perpendicular to the propagation direction of the incident laser beam. Owing to the gradient force, an object located within a focal plane is attracted to the focal point. It has been reported that 1D particles orient their long-axis parallel to the propagation direction of an incident laser beam to minimize the scattering force and then they are trapped by the gradient force when a focused laser beam is used to irradiate them (Tong *et al.*, 2010). In the case of a nanosheet, the aspect ratio of the lateral length to its thickness is approximately 1:1000. Therefore, the forces being applied in the direction perpendicular to the surface of the nanosheet are dominant and the force being applied in the direction parallel to the surface of the nanosheet is negligible. As is the case for 1D materials, a nanosheet was thought to be oriented with its in-plane direction parallel to the propagation direction of an incident laser beam so as to minimize the scattering force.

The appearance of a line-shaped object at the focal point can be explained by the following mechanism. The thickness of the sample cell, 100 μm, was approximately 250 times larger than the depth of field. As described above, the nanosheets in the colloids randomly move by three-dimensional Brownian motion. A nanosheet coming into the optical path, including the defocus field, should be attracted to the focal point by a scattering and/or a gradient force and then the object will appear in the obtained microscope image. Continuous laser irradiation of approximately 30 s was required until the line-shaped object appeared in Figure 2c. The reason why such a long time was required is considered to arise from the low concentration of the nanosheet colloid used in this study. Hence, approximately 30 s was required for a nanosheet to come into the optical path. Actually, it was confirmed that the time required for trapping a line-shaped object became longer when the concentration was further diluted (data not shown).

The nanosheet trapped at the focal point was aligned with its edge parallel to the polarization direction of the incident laser beam as shown in Figure 5. This fact indicates that the alignment was determined by the optical electric field of the linearly polarized incident laser beam. For unidirectional alignment of a nanosheet, two external forces, which are orthogonal with each other, are required owing to the biaxial shape of nanosheets. This has been realized by an orthogonal application of the electric field and gravity (Nakato *et al.*, 2014; Nakato *et al.*, 2011). In this study, a unidirectional alignment of 2D particles was realized by using one external stimuli consisting of two forces, which were the scattering force and the polarization direction of the laser beam. In addition, the induced alignment of the nanosheet was on-demand, as shown in Figure 4.

CONCLUSIONS

In this study, on-demand orientation manipulation of a nanosheet was conducted by irradiation with a linearly polarized laser beam. The nanosheet was trapped at the focal point to orient its in-plane direction parallel to the propagation direction of the incident laser beam. In addition, the alignment of the nanosheet trapped at the focal point was along the polarization direction and rotated following the rotation of the polarization direction of the incident laser beam. After laser irradiation was ceased, the trapped nanosheet diffused by Brownian motion and returned to be isotropic. This optical control of time, space and orientation of 2D particles was realized for the first time.

In order to maximize the functionality of 2D particles, a methodology that enables the local and on-demand orientation manipulation of 2D particles has needed. Optical manipulation established in this study should provide a powerful methodology for realizing required orientation of 2D particles and therefore should expand the application, such as optical switching and light modulation, using 2D particles including clay nanosheets

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REFERENCES

Ashkin, A. (1992) Forces of a single-beam gradient laser trap on a dielectric sphere in the ray optics regime. *Biophysical Journal*, **61**, 569-582.

Ashkin, A., Dziedzic, J. M., Bjorkholm, J. E., and Chu, S. (1986) Observation of a single-beam gradient force optical trap for dielectric particles. *Optics Letters*, **11**, 288-290.

Dholakia, K., Reece, P., and Gu, M. (2008) Optical micromanipulation. *Chemical Society Reviews*, **37**, 42-55.

Harada, Y. and Asakura, T. (1996) Radiation forces on a dielectric sphere in the Rayleigh scattering regime. *Optics Communications*, **124**, 529-541.

Lehmuskero, A., Johansson, P., Rubinsztein-Dunlop, H., Tong, L., and Käll, M. (2015) Laser trapping of colloidal metal nanoparticles. *ACS Nano*, **9**, 3453-3469.

Miyamoto, N. and Nakato, T. (2004) Liquid Crystalline Nanosheet Colloids with

Controlled Particle Size Obtained by Exfoliating Single Crystal of Layered Niobate $K_4Nb_6O_{17}$. *The Journal of Physical Chemistry B*, **108**, 6152-6159.

Nakato, T., Kawamata, J., and Takagi, S. (2017) *Inorganic nanosheets and nanosheet-based materials*. Springer, Japan.

Nakato, T., Nakamura, K., Shimada, Y., Shido, Y., Houryu, T., Iimura, Y., and Miyata, H. (2011) Electrooptic response of colloidal liquid crystals of inorganic oxide nanosheets prepared by exfoliation of a layered niobate. *Journal of Physical Chemistry C*, **115**, 8934-8939.

Nakato, T., Nono, Y., and Mouri, E. (2017) Textural diversity of hierarchical macroscopic structures of colloidal liquid crystalline nanosheets organized under electric fields. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **522**, 373-381.

Nakato, T., Nono, Y., Mouri, E., and Nakata, M. (2014) Panoscopic organization of anisotropic colloidal structures from photofunctional inorganic nanosheet liquid crystals. *Physical Chemistry Chemical physics*, **16**, 955-962.

Neves, A. A. R., Camposeo, A., Pagliara, S., Saija, R., Borghese, F., Denti, P., Iatì, M. A., Cingolani, R., Maragò, O. M., and Pisignano, D. (2010) Rotational dynamics of optically trapped nanofibers. *Optics Express*, **18**, 822-830.

Ohlinger, A., Nedev, S., Lutich, A. A., and Feldmann, J. (2011) Optothermal escape of plasmonically coupled silver nanoparticles from a three-dimensional optical trap. *Nano Letters*, **11**, 1770-1774.

Okada, T., Oguchi, J., Yamamoto, K., Shiono, T., Fujita, M., and Iiyama, T. (2015) Organoclays in water cause expansion that facilitates caffeine adsorption. *Langmuir*, **31**, 180-187.

Schoonheydt, R. A. (2014) Functional hybrid clay mineral films. *Applied Clay Science*, **96**, 9-21.

Suzuki, Y., Tenma, Y., Nishioka, Y., and Kawamata, J. (2012) Efficient nonlinear optical properties of dyes confined in interlayer nanospaces of clay minerals. *Chemistry-An Asian Journal*, **7**, 1170-1179.

Tominaga, M., Oniki, Y., Mochida, S., Kasatani, K., Tani, S., Suzuki, Y., and Kawamata, J. (2016) Clay–organic hybrid films exhibiting reversible fluorescent color switching induced by swelling and drying of a clay mineral. *The Journal of Physical Chemistry C*, **120**, 23813-23822.

Tong, L., Miljković, V. D., and Käll, M. (2010) Alignment, rotation, and spinning of single plasmonic nanoparticles and nanowires using polarization dependent optical forces. *Nano Letters*, **10**, 268-273.

Won, J., Inaba, T., Masuhara, H., Fujiwara, H., Sasaki, K., Miyawaki, S., and Sato, S.

(1999) Photothermal fixation of laser-trapped polymer microparticles on polymer substrates. *Applied Physics Letters*, **75**, 1506-1508.

Wright, W. H., Sonek, G. J., and Berns, M. W. (1994) Parametric study of the forces on microspheres held by optical tweezers. *Applied Optics*, **33**, 1735-1748.

Wu, M., Ling, D., Ling, L., Li, W., and Li, Y. (2017) Stable optical trapping and sensitive characterization of nanostructures using standing-wave raman tweezers. *Scientific Reports*, **7**, 42930.

Yan, Z., Jureller, J. E., Sweet, J., Guffey, M. J., Pelton, M., and Scherer, N. F. (2012) Three-dimensional optical trapping and manipulation of single silver nanowires. *Nano Letters*, **12**, 5155-5161.

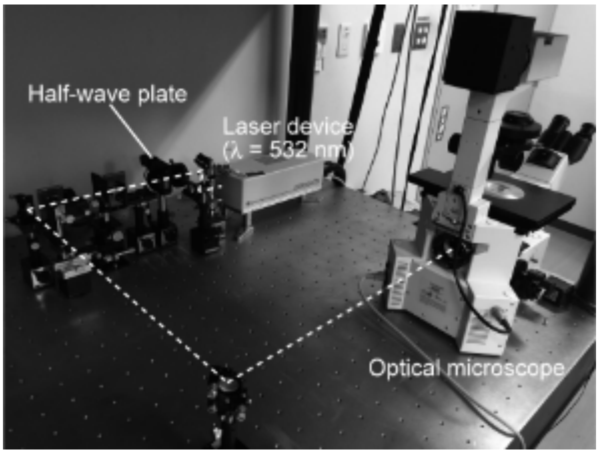

Figure 1. Photograph of the experimental setup. The broken line indicates the beam path of the laser.

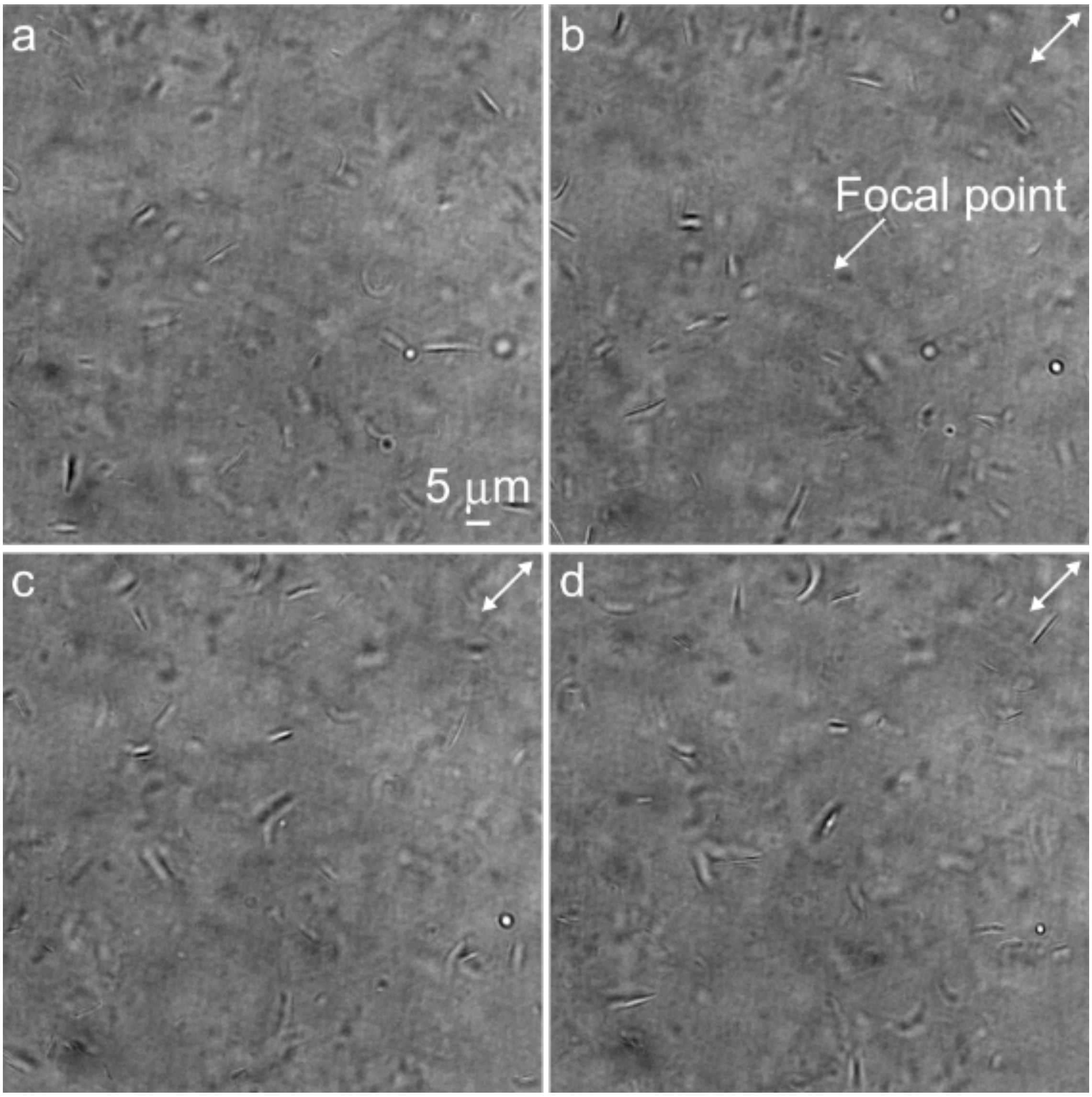

Figure 2. Optical microscopy images of a niobate nanosheet colloid (a) before laser irradiation and after (b) 15 s, (c) 30 s, (d) 34 s of continuous laser irradiation with a linearly polarized laser beam. The very small white point shown in (b) represents the focal spot with a diameter of 0.4 μm. The white arrow indicates the polarization direction.

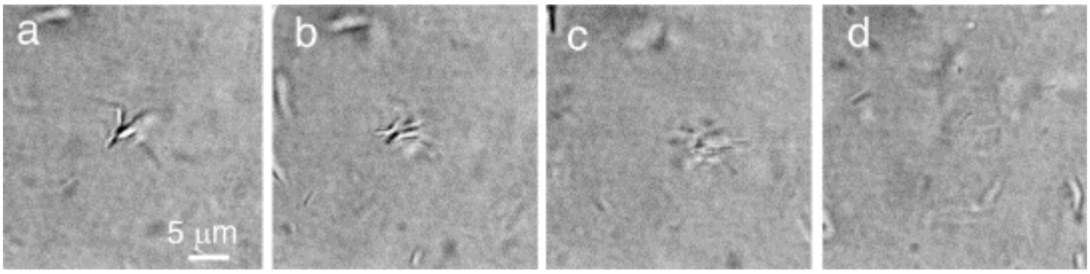

Figure 3. Optical microscopy images of a niobate nanosheet colloid (a) 0 s, (b) 2 s, (c) 10 s, (d) 15 s after laser irradiation ceased.

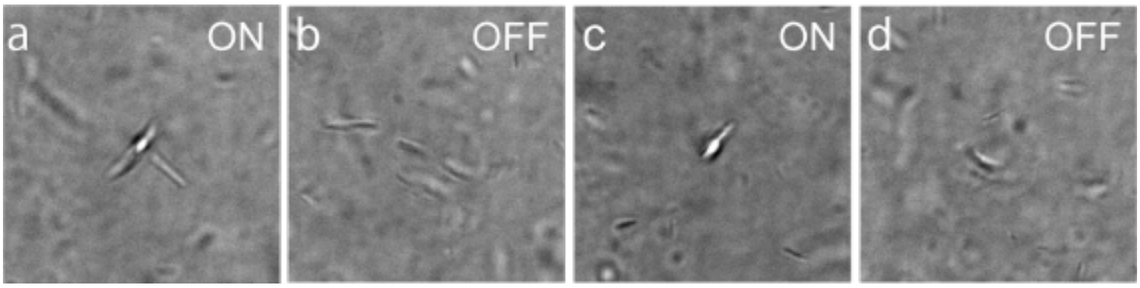

Figure 4. Optical microscopy images of re-trapped and released line-shaped objects by on-off switching of the laser irradiation.

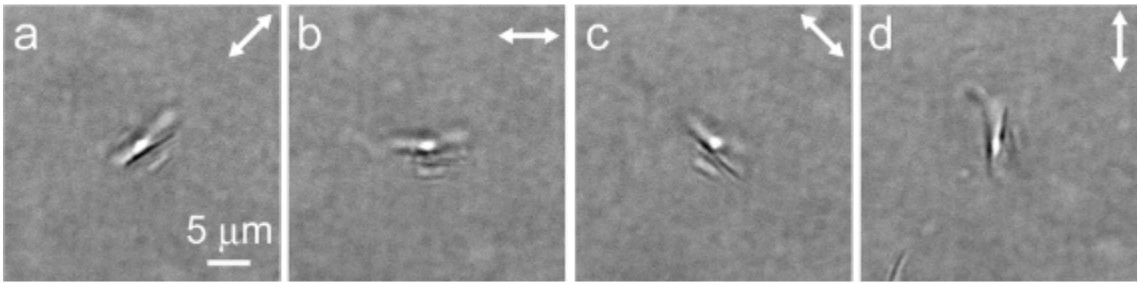

Figure 5. Optical microscopy images of a niobate nanosheet colloid under rotation of the polarization direction of the incident laser beam. The white arrows indicate the polarization direction.