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

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Abstract—Because inorganic nanosheets, such as clay minerals, are anisotropic, the manipulation of nanosheet orientation is an important challenge in order to realize future functional materials. In the present study, a novel methodology for nanosheet manipulation using laser radiation pressure is proposed. When a linearly polarized laser beam was used to irradiate a niobate ($Nb_6O_{17}^{4-}$) nanosheet colloid, the nanosheet was trapped at the focal point so that the in-plane direction of the nanosheet 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, unidirectional alignment of a nanosheet can be achieved simply by irradiation using 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 photon momentum change when the photon is reflected or refracted by a particle. The size of the target particles is generally on the scale of <1 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, which is 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 can be used to realize on-demand particle trapping and release by switching the incident laser beam on and off.

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, as well as the spherical particles, are trapped at the focal point, the radiation pressure also contributes to the manipulation of 1D particle orientations, meaning that the particles orient with their long axis parallel to the propagation direction of the incident laser beam. The result has been to establish optical manipulation as an alignment technique for anisotropic particles.

Recent developments using various nanoparticles have evoked interest in two-dimensional (2D) plate-like particles in addition to 1D particles. In particular, inorganic nanosheets prepared by the exfoliation of layered crystals, such as clay minerals, have attracted great attention owing to the large shape anisotropy (Nakato *et al.*, 2017). A variety of nanosheets have been prepared and examined as the building blocks of functional nanoassemblies. Oxide nanosheets of smectite-type clay minerals and other layered oxides have been used to produce 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 colloids in many cases, the 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 the biaxial shape, which requires an orthogonal application of two external forces for uniform or unidirectional alignment. This was achieved for colloidal nanosheets of an exfoliated, layered Nb oxide, and unidirectional nanosheet alignment was attained after orthogonal application of an electric field and gravity (Nakato *et al.*, 2014). Optical manipulation of

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2D plate-like materials, however, has not been attempted to date.

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

EXPERIMENTAL SECTION

Sample preparation

A niobate nanosheet colloid, which has negatively charged oxide nanosheets with propylammonium cations as counterions, was prepared by the exfoliation of layered $K_4Nb_6O_{17}$ according to a 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 using transmission electron microscopy (TEM) observations exhibited a size distribution that obeyed a log-normal distribution with 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 Olympus IX70 inverted microscope (Olympus, Tokyo, Japan) using the experimental setup shown in Figure 1. A linearly polarized continuous-wave laser beam emitted at 532 nm (Millennia Pro, Spectra Physics, Santa Clara, California, USA) was focused at the center of the cell (50 μm from the cell-sample interface) using a 40× apochromatic objective lens with a numerical aperture of 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 after the objective lens was set at 20 mW. The beam diameter was adjusted to the pupil diameter of the objective lens using a beam expander. The resulting beam width at the focal point was calculated to be 0.4 μm.

For optical microscopy observations during irradiation with a laser beam, the sample was illuminated using a halogen lamp and the image was monitored using an Orca-Flash 4.0 V3 digital camera (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 resolution and 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 cell thickness.

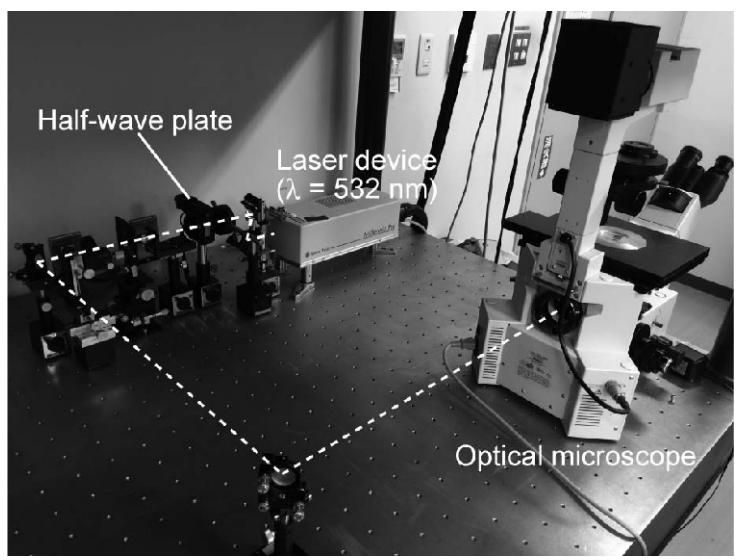

Figure 1. Photograph of the experimental setup. The broken line indicates the beam path of the laser.

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RESULTS

An object that looked like a line or a rod with a length of 1−10 μm was found to be trapped at the focal point when the sample was irradiated with the laser beam. Hereafter, these objects will be referred to as "line-shaped objects." The optical microscope images of the nanosheet colloid before and after irradiation with a linearly polarized laser beam (Figure 2) revealed that, before laser irradiation, many line-shaped objects were observed within the microscope field (Figure 2a). The line-shaped objects moved and/or appeared and disappeared due to the focusing and de-focusing caused by three-dimensional Brownian motion. The line-shaped objects were believed 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) indicated no apparent change at the focal point, whereas Brownian motion was continuously observed over the entire microscope field. After 30 s of continuous laser irradiation, a line-shaped object appeared near the focal point (Figure 2c). This line-shaped object moved toward the focal point and then was completely trapped at the focal point after 34 s of continuous laser irradiation (Figure 2d) and remained

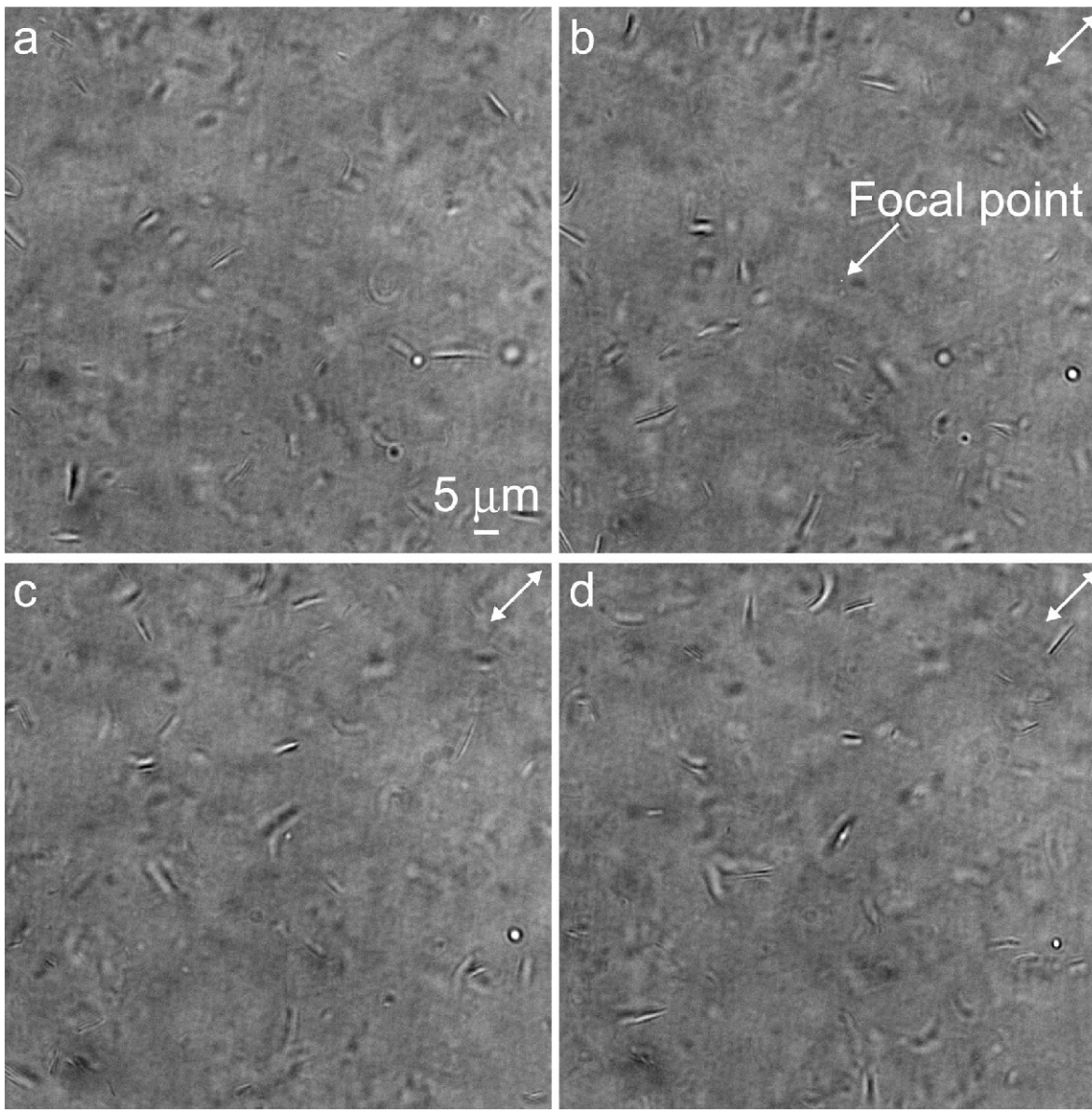

Figure 2. Optical microscope images of a niobate nanosheet colloid (a) before laser irradiation and after (b) 15 s, (c) 30 s, and (d) 34 s of continuous irradiation using a linearly polarized laser beam. The very small white point shown in (b) represents the focal spot with a 0.4 μm diameter. The white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

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visible during laser irradiation. The orientation of the object was parallel to the polarization direction of the incident laser beam. The time required to trap the line-shaped object ranged from 20 s to 34 s.

The line-shaped object was gradually released when laser irradiation was stopped. Brownian motion of the object trapped at the focal point began again just after the laser irradiation was stopped (Figure 3a). The object image then gradually became more diffuse and blurred (Figure 3b and 3c). At 15 s after 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 switching the laser irradiation on and off. After laser-beam irradiation ceased for 15 s, then switched back on, the object was trapped again at the focal point after approximately 30 s (Figure 4a). After the laser irradiation was turned off a second time, the image of the trapped object became diffuse and was no longer observed (Figure 4b). Trap and release of the line-shaped object was further repeated by on-off switching cycles of the laser irradiation and revealed that the orientation phenomenon can be reversibly controlled by on-off switching cycles of the laser irradiation. (Figures 4c and 4d).

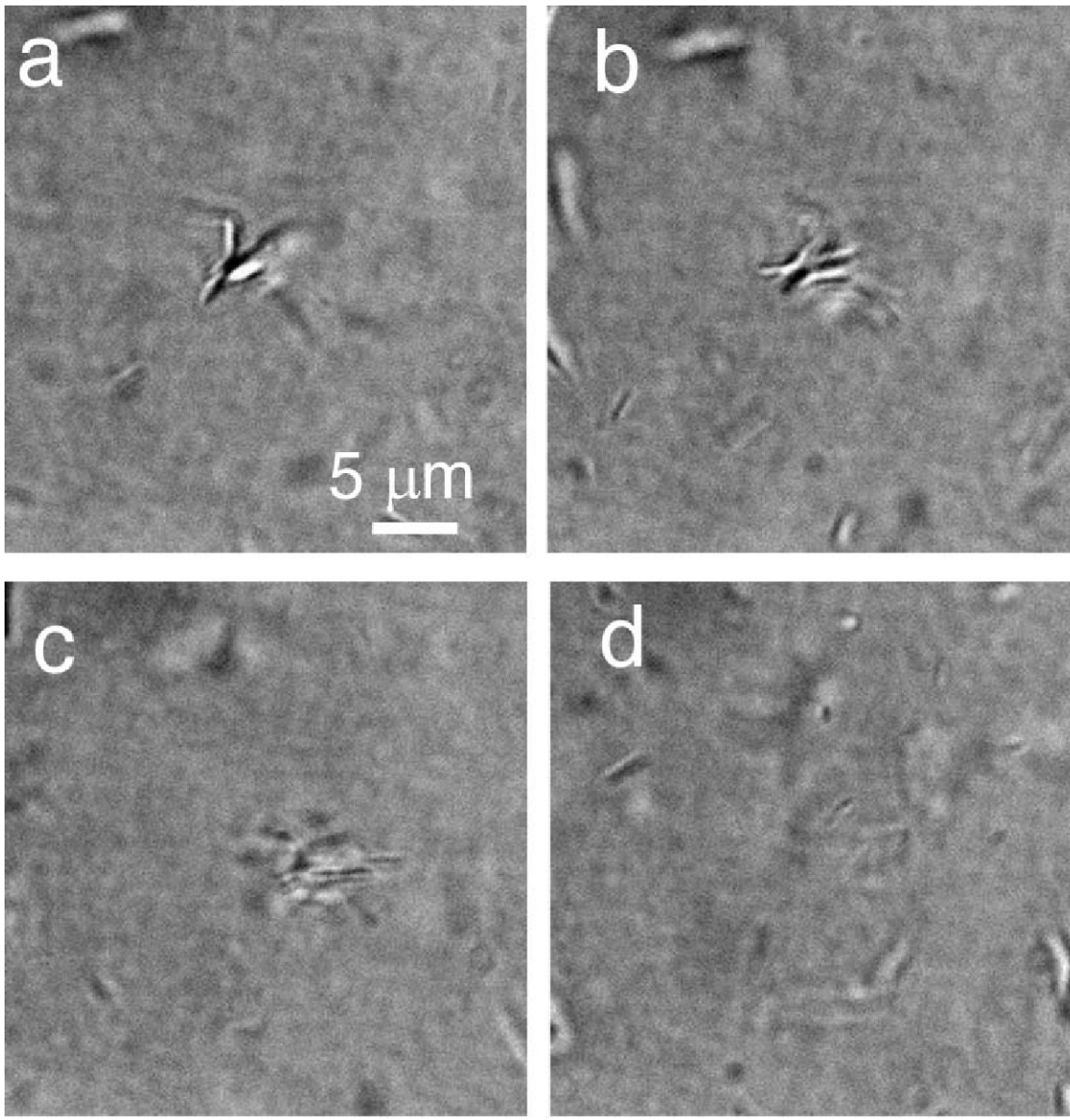

Figure 3. Optical microscope images of a niobate nanosheet colloid at (a) 0 s, (b) 2 s, (c) 10 s, and (d) 15 s after laser irradiation was stopped.

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Rotation of the polarization direction of the incident laser beam further revealed that the trapped line-shaped object also rotated (Figure 5). A nanosheet (Figure 5a) was trapped with a 45º polarization direction with respect to the field of view. When the polarization direction was rotated clockwise by 45º, the object also rotated 45º clockwise (Figure 5b). When the laser polarization direction was sequentially rotated another 45º, the object again rotated with the polarization direction (Figures 5c and Figure 5d). The rotation of the object followed the laser beam polarization direction in real-time up until the upper limit of the rotation speed of the experimental setup of 0.4 π rad/s was reached.

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 laser beam propagation direction. When the in-plane direction of a nanosheet orients parallel to the propagation direction of an incident laser beam, the nanosheet should be observed as a line. In fact, the nanosheet orientation was also confirmed using polarized-light optical microscope observations (data not shown) and the image before laser irradiation was dark (isotropic). After approximately 30 s of continuous laser irradiation, which was the time needed to trap the nanosheet at the focal point, a

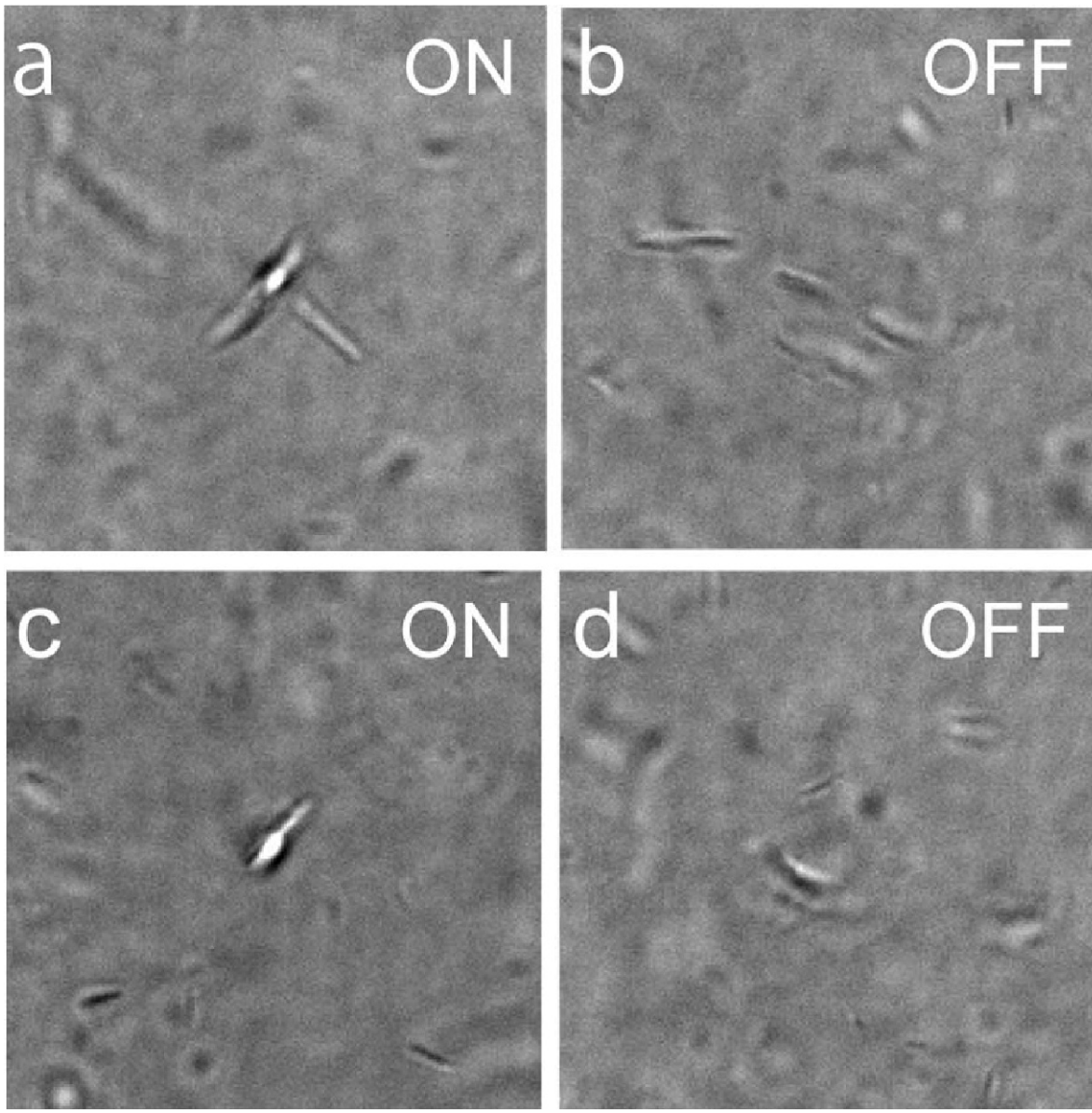

Figure 4. Optical microscope images of re-trapped objects and released line-shaped objects produced by switching the laser irradiation on and off.

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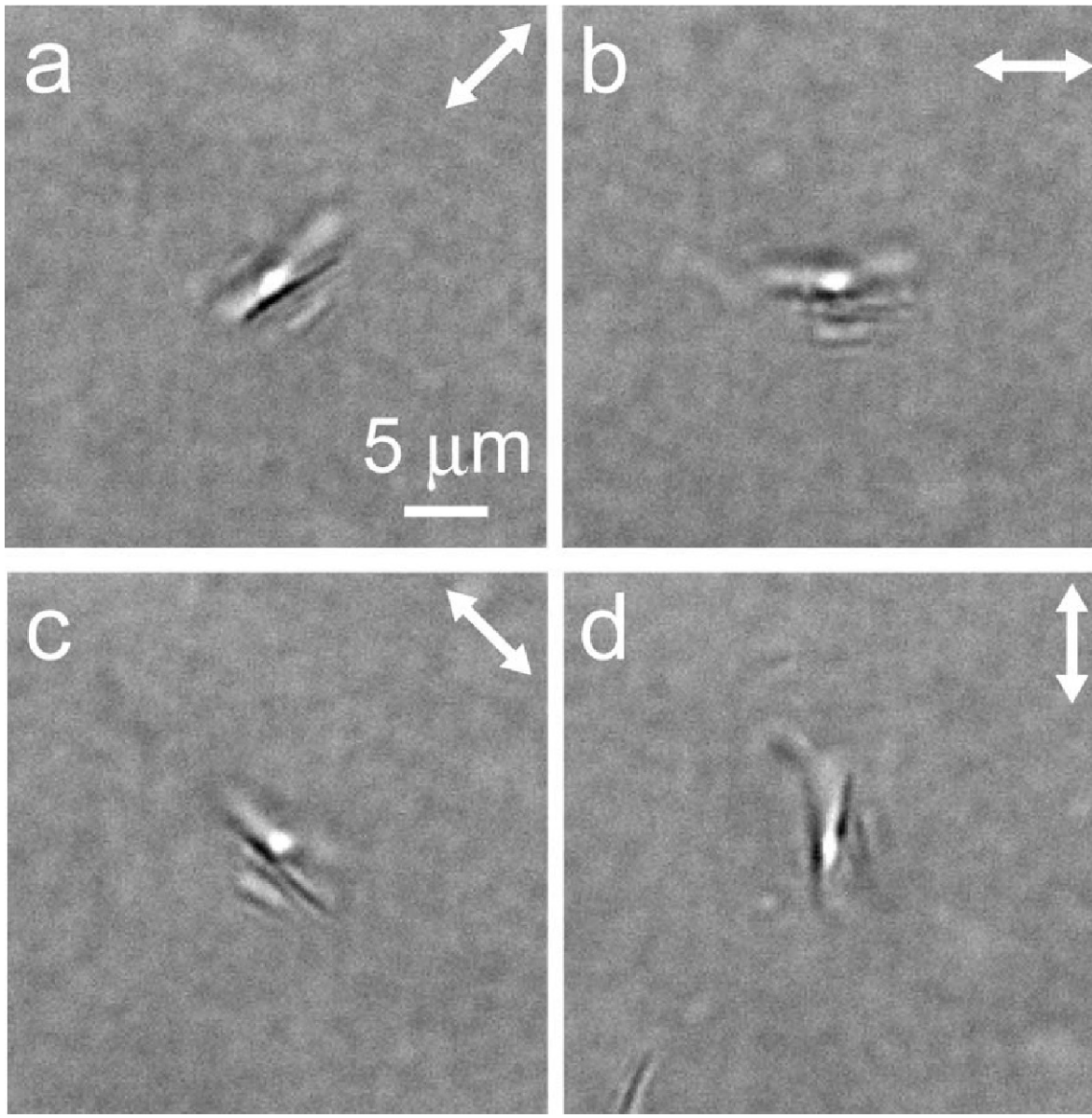

Figure 5. Optical microscope images of a niobate nanosheet colloid after the polarization direction of the incident laser beam was rotated to different positions. The white arrows indicate the polarization direction.

birefringent line appeared. The birefringence was ascribed to a nanosheet oriented with the in-plane direction perpendicular to the cell surface (Nakato *et al.*, 2011).

The orientation behavior of nanosheets produced by laser irradiation can be considered to be analogous to the manipulation of 1D particle orientations. In general, a focused laser beam provides two types of forces as radiation pressure on a particle (Ashkin, 1992; Harada and Asakura, 1996). One of the forces is a scattering force applied to the object along the propagation direction of the incident laser beam. In other words, when the scattering force is applied to an object, the object moves along the propagation direction of the incident laser beam. The other force is a gradient force applied perpendicular to the propagation direction of the incident laser beam. Because of the gradient force, an object located within the focal plane is attracted to the focal point. 1D particles have been reported to orient their long-axis parallel to the propagation direction of an incident laser beam to minimize the scattering force and are then trapped by the gradient force when irradiated by a focused laser beam (Tong *et al.*, 2010). In the case of a nanosheet, the lateral length to thickness aspect ratio is approximately 1:1000. Therefore, the forces applied in the direction perpendicular to the nanosheet surface are

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dominant and the force applied parallel to the nanosheet surface is negligible. As is the case for 1D materials, a nanosheet was thought to orient 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 100 μm sample cell thickness was approximately 250 times larger than the depth of field. As described above, nanosheets in the colloids randomly move by three-dimensional Brownian motion. A nanosheet that moves into the optical path, which includes the defocus field, should be attracted to the focal point by a scattering and/or a gradient force and the object will then appear in the microscope image. Continuous laser irradiation for approximately 30 s was required before the line-shaped object appeared in Figure 2c. The reason why such a long time was required is considered to be due to the low nanosheet colloid concentration used in this study. Hence, approximately 30 s was required for a nanosheet to move into the optical path. Actually, the time required to trap a line-shaped object became longer as the colloid concentration became more dilute (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 to each other, are required due to the biaxial shape of nanosheets. So far, unidirectional alignment of a nanosheet has been realized using an orthogonal application of the electric field and gravity (Nakato *et al.*, 2011, 2014). In this study, a unidirectional alignment of 2D particles was realized by using one external stimulus that consisted 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 the present study, on-demand manipulation of the orientation of a nanosheet was conducted by irradiating samples with a linearly polarized laser beam. The nanosheet was trapped at the focal point to orient the nanosheet in-plane direction parallel to the propagation direction of the incident laser beam. In addition, the nanosheet trapped at the focal point was aligned along the laser polarization direction and was rotated by rotation of the polarization direction of the incident laser beam. After laser irradiation was stopped, Brownian motion of the trapped nanosheet caused the alignment to be lost and the sample to return to an isotropic state. This appears to be the first report of an optically controlled time and space orientation of 2D particles.

In order to maximize the functionality of 2D particles, a methodology that enables the local and on-demand manipulation of 2D particle orientations has been needed. Optical manipulation established in the present study should provide a powerful methodology to achieve the required orientation of 2D particles and, therefore, should expand the number of applications into areas such as optical switching and light modulation using 2D particles which can include clay nanosheets.

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