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## Editor's Choice

## Development of Structural Color by Niobate Nanosheet Colloids

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Inorganic nanosheets obtained by exfoliation of layered crystals of hexaniobate in water form colloidal liquid crystals. We found that they develop various structural colors by moderating nanosheet concentration and ionic atmosphere.

**Keywords:** Structural color | Nanosheets | Liquid crystal

Inorganic layered materials are composed of nanometer-thick layers of inorganic crystals, which are kept together by electrostatic, van der Waals, or hydrogen-bonding interactions. Inorganic nanosheets prepared by exfoliation of the inorganic layered crystals possess an ultimate thinness of around 1 nm with a lateral length of several tens of nanometers to micrometers.<sup>1,2</sup> The anisotropy of their shape renders stable behavior for the liquid crystalline phase. Various nanosheet liquid crystals (LCs), including clay minerals, metal phosphates, graphene oxide, and transition metal oxides, have been developed in the past few decades.

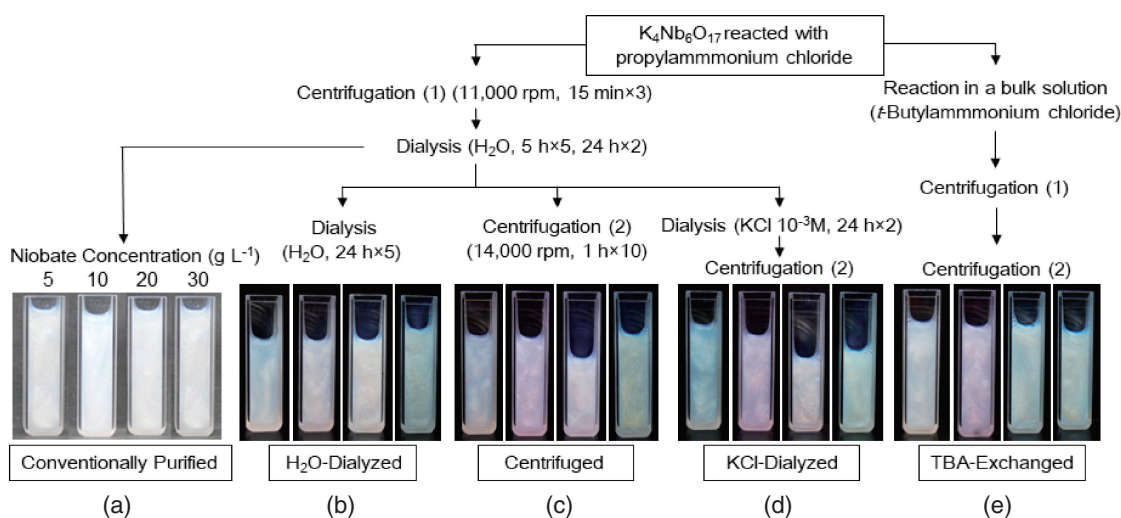
Colloidal assembled structures of inorganic LC nanosheets are characterized by lamellar and nematic ordering of nanosheets with basal spacings up to several hundreds of nanometers.<sup>2</sup> Such a nanosheet ordering is accompanied by the interference of light scattering from ordered nanosheets in the visible-wavelength region. This phenomenon, called structural coloration, has attracted attention because of the lower environmental impact as well as higher stability than those associated with dyeing and stimuli-responsive properties.<sup>3</sup> Several nanosheet LCs have been reported to show structural colors. Gabriel et al. discovered coloration by  $K_3Sb_3PO_{14}$  liquid crystals for the first time in 2001.<sup>4</sup> In more recent years, a variety of structure colorations by inorganic nanosheets have been reported. Sue et al.<sup>5,6</sup> demonstrated that zirconium phosphate nanoplatelets develop structural color with the aid of polymeric surfactants. Aida et al. demonstrated structural coloration originating from the lamellar arrangement of titania nanosheet with the aid of a strong magnetic force.<sup>7</sup>

Structural coloration of nanosheet LCs arises from structures of colloiddally dispersed nanosheets assembled in a lamellar fashion, but not from their chemical nature. Thus, it should essentially be an intrinsic nature of nanosheet LCs. However, there are many nanosheet LCs that appear white and turbid without structural colors, as exemplified by nanosheet LCs of niobate, titanate, and smectite-type clay. Because most of these

non-colored nanosheet LCs are aqueous colloids, we attribute the lack of structural color to the contribution of the ionic atmosphere of these aqueous nanosheet colloids. For aqueous colloidal crystals of spherical particles, optimization of the ionic atmosphere is a common method for adjusting the particle ordering and thus the structural coloration of the colloids.

In this study, we aimed to harness the structural coloration of aqueous nanosheet LCs by adjusting the ionic atmosphere of colloids. Niobate nanosheet LCs in an as-prepared state were used as an example of non-colored nanosheet LCs. Niobate nanosheet LCs are prepared from layered niobate  $K_4Nb_6O_{17}$ , in which negatively charged  $Nb_6O_{17}^{4-}$  layers sandwich inter-layered  $K^+$  ions. Thus, the exfoliated niobate nanosheets bear intrinsic negative charges. Aqueous colloids of niobate nanosheets show stable liquid crystalline phases over a wide range of concentrations. The nanosheets are ordered in a lamellar manner with a basal spacing of several tens of nanometers after a conventional preparation procedure. We fabricated a variety of hierarchical structures composed of niobate nanosheets, utilizing external forces.<sup>8–10</sup> The structures can be modified by adjusting the species and concentrations of electrolytes coexisting in the colloids. However, this phenomenon is related to domain structures of nanosheets at the level of several tens of micrometers; electrolyte effects on structures at smaller length scales have never been examined. Therefore, we have examined structural colors, which reflect the structure at the level of hundreds of nanometers, in niobate nanosheet LCs on the basis of our assumption of optimizing the ionic atmosphere of the colloid.<sup>11</sup>

The electrostatic repulsion between colloidal particles, which maintain constant interparticle distances, is only effective at low salt concentrations because coexisting ions screen the electrostatic interaction between the particles. The same principle can be applied to the aqueous niobate nanosheet colloids since niobate nanosheets have anionic charges at their surfaces. We intended to develop the structural colors by controlling the concentration and species of coexisting ions to alter the ionic atmosphere with further purification or displacement of counter cations of the anionic niobate nanosheets. Most inorganic nanosheets originating from layered materials have intrinsic charges on their surface and this process can give general guidance to other inorganic nanosheet LCs for developing structure colors.



**Figure 1.** Sample preparation process and their appearance with various niobate nanosheet concentrations: (a) Conventionally Purified, (b) H<sub>2</sub>O-Dialyzed, (c) Centrifuged, (d) KCl-Dialyzed, (e) TBA-Exchanged.

The preparation, purification, and adjustment of the ionic atmosphere of niobate nanosheet LCs are summarized in Figure 1. Niobate nanosheet colloids prepared by exfoliation of layered niobate K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> using propylamine chloride as delamination agent were first washed three times with water by centrifugation–redispersion followed by dialysis using the procedure described in our previous paper.<sup>8,9</sup> We labeled this sample as “Conventionally Purified”. This sample Conventionally Purified was then further purified or treated with another electrolyte, as shown in Figure 1. Further purification by additional dialysis against pure water was performed for the Conventionally Purified sample to decrease excess ionic species as much as possible and thus obtain a more purified sample. The sample was called “H<sub>2</sub>O-Dialyzed”. Another purification process was carried out by further repetition of the centrifugation–redispersion process. This sample was named “Centrifuged”. On the other hand, we treated the sample with two electrolyte species: KCl and tetrabutylammonium (TBA) chloride. For KCl, the sample Conventionally Purified was further dialyzed against KCl followed by purification with ten centrifugation–redispersion cycles (denoted as “KCl-Dialyzed”). For the introduction of TBA ions, K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> that had reacted with propylammonium ions was further treated with an aqueous solution of TBA chloride. The product then was subjected to two types of the centrifugation–redispersion processes. This TBA treatment was done to exchange the counter cations of niobate nanosheets for TBA cations; we designate this sample as “TBA-Exchanged”.

Although the Conventionally Purified samples of niobate nanosheet colloids are colorless with a white, turbid appearance, all of the samples after the four types of further treatment show structural colors. The macroscopic appearance of these samples is presented in Figure 1. The further purification and introduction of another electrolyte generates color in the nanosheet LCs. We ascribe this to the structural colors since all of the samples do not contain chromophoric species. The structural colors are dependent on nanosheet concentrations. In Figure 1, sample appearances are compared with the concentrations of niobate nanosheets ranging from 5 to 30 g L<sup>-1</sup>. The color changes from blue to green with increasing niobate nanosheet concentration:

bluish (5 g L<sup>-1</sup>) to pinkish (10 g L<sup>-1</sup>), yellowish (20 g L<sup>-1</sup>), and greenish (30 g L<sup>-1</sup>). This trend is common to all of the four colored sample series, suggesting that the mechanisms for the development of color are the same. We also noted a difference in the vividness of the generated colors, depending on the sample series. The colors observed for the further purified sample (Centrifuged) and the sample with introduced electrolyte (KCl-Dialyzed) are more vivid than the others. The results suggest that the difference in the vividness of color is not ascribed to a simple difference in the treatment, i.e., further purification or electrolyte addition. The vividness of color may thus be related to the appropriate range of electric conductivity.

These results clearly indicate the generation of structural colors from non-colored niobate nanosheet LCs by appropriate treatment related to the ionic atmosphere of the colloids. Modification of the ionic atmosphere with further purification and electrolyte addition is supported by the electroconductivity of the colloids, as summarized in Table 1. Our previous paper has established that nanosheet colloids dialyzed with electrolyte solutions of different electrolyte species and concentrations show similar behavior when the final electric conductivities and pHs are close.<sup>11</sup> Hence, the electric conductivity of niobate nanosheet colloids can be used as a measure of ionic conditions provided by the species and concentration of coexisting electrolytes. All the five samples, including Conventionally Purified, show nearly similar pH values but the electric conductivities

**Table 1.** Characteristics of niobate nanosheet colloids.

Sample Name	pH**	Conductivity* /mS m <sup>-1</sup>	Size /μm
Conventionally Purified	9.3	1.10	ca. 2
H <sub>2</sub> O-Dialyzed	9.1	0.45	4.0
Centrifuged	9.1	0.52	2.7
KCl-Dialyzed	9.2	0.67	2.7
TBA-Exchanged	9.8	0.93	2.6

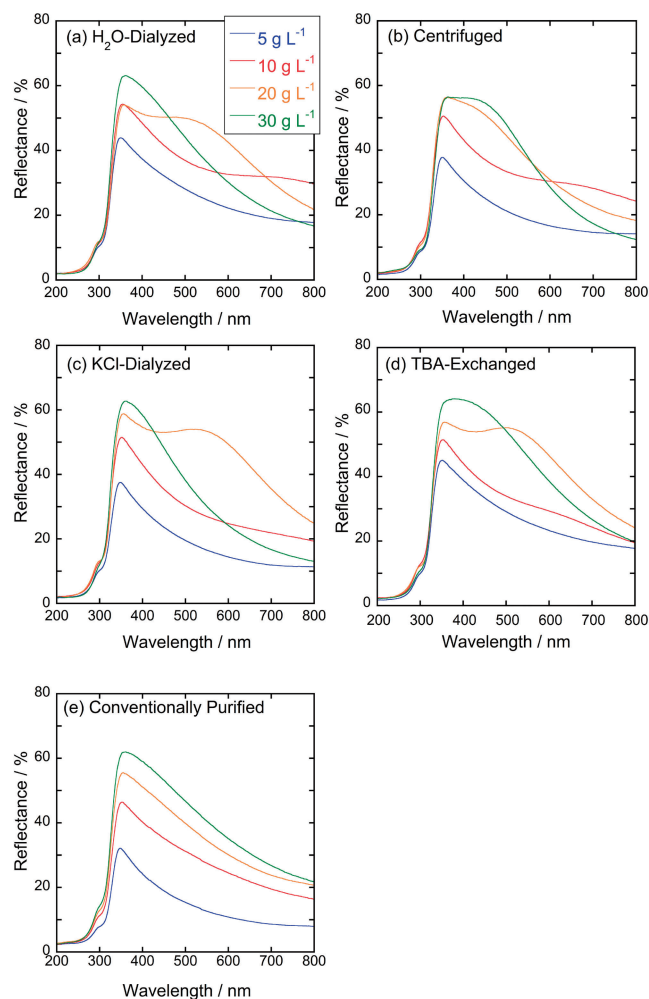
\*Measured with 0.1 g L<sup>-1</sup> nanosheet concentration. \*\*Measured with 5 g L<sup>-1</sup> nanosheet concentration.

decrease for the further treated samples at the same nanosheet concentration. These results indicate that the further treated samples contain lower amounts of ionic species.

The amount of small ions in a colloidal system is a critical parameter for predicting the interaction between the colloidal particles. The iridescence of colloids with spherical particles can only be observed at very low concentrations of co-existing salts,<sup>12</sup> suggesting that the interaction between the colloidal particles is strong enough to create an ordered structure with a very small amount of coexisting ions. Interactions between the colloidal particles are screened and thus weakened by the co-existing ions. The same principle can be applied to niobate nanosheet colloidal systems because niobate nanosheets have anionic charges at their surfaces and the ionic atmosphere is effective for the colloidal behavior.<sup>11</sup> Thus, it is reasonable that the coloration is developed only with niobate colloids with low electric conductivity.

The color variation with nanosheet concentration suggests that the color is developed by the ordered structure of niobate nanosheet colloidal LC and not by the intrinsic nature of niobate because niobate nanosheets themselves do not have any absorption characteristics in the visible-wavelength range corresponding to these varieties of colors. On the other hand, a repeating structure constructed in the niobate nanosheet colloid is reasonably expected to be a lamellar structure of nanosheets with constant spacing between nanosheets on the basis of a previous study of conventionally purified samples.<sup>13</sup> Interlayer spaces for the treated samples can be an order of wavelength of visible light. The spacing of repeating structures decreases with increasing nanosheet concentration because of the geometrical requirements and shows different colors.

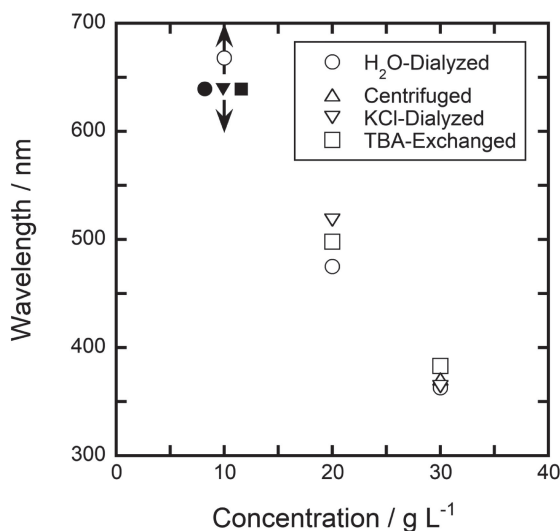
The structural colors of niobate nanosheet LCs depend on the nanosheet concentration and sample treatment procedure, as indicated in the UV-Vis diffuse reflectance spectra measured with an integrating sphere. Figure 2 shows the variation of the spectra with nanosheet concentrations for each treatment process. Although the non-colored samples (Conventionally Purified, see Figure 2e) show a single reflectance maximum at 360 nm, colored samples exhibit an additional reflectance maximum or peak broadening at longer wavelengths. The peak at around 360 nm reflects the summation of the two effects: absorption of niobate by their characteristic band gap and Rayleigh scattering, which depends on  $\lambda^{-4}$ . The additional reflectance or tailing in the wavelength range of visible light (ca. 380–750 nm) indicates the color perceived by human eyes. Positions of the reflectance maxima are summarized in Table S1. Here, positions of the shoulder and unclear peaks contributing to the structure colors are estimated by the following method. For the samples at  $10 \text{ g L}^{-1}$ , their positions are only determined between 600 and 700 nm because peaks are not clearly identified except for the  $\text{H}_2\text{O}$ -Dialyzed sample. The additional peak is particularly pronounced in the samples of  $20 \text{ g L}^{-1}$ , but their positions somewhat vary with the treatment process. The samples at other concentrations also show some differences in their spectral shapes, depending on the treatment procedure. The samples at  $30 \text{ g L}^{-1}$  do not show peaks but have a shoulder at around 400–500 nm overlapping with the intrinsic peak at 360 nm, and the shape of the overlapped peaks is different from those of the samples; the peak positions are defined as the wavelengths that indicate zero in the differentiated spectra. Although the samples



**Figure 2.** Diffused reflective UV-Vis spectra of niobate nanosheet colloids with various niobate nanosheet concentrations: samples with (a) dialysis against pure water, (b) with further centrifugation, (c) dialysis against KCl aq., with (d) ion exchange process with *tetra*-butylammonium ion, and (e) conventionally purified.

at  $5 \text{ g L}^{-1}$  show similar spectra (see Figure 2 and Figure S1), there is still a difference in the intensity of reflected light with the treatment procedure. This suggests that the reflectance value matters as well as peaks in the spectrum contribute to the developing color, which should be further investigated in the future. These variations correspond to a subtle difference in the apparent color observed for the samples with different treatments at the same concentration.

The concentration dependence of the reflection peaks that contribute to the structure colors is explained by the liquid-crystalline ordering of nanosheets in the colloids. In niobate nanosheet LCs, colloidal dispersed nanosheets are ordered in a lamellar fashion even though the macroscopic appearance of the colloids is isotropic, and the basal spacing between the nanosheets ordered in a lamellar fashion decreases with the nanosheet concentration.<sup>13</sup> The structural color is reasonably assigned to the lamellar periodicity of nanosheets in the colloid, and the colloid structure dependent on nanosheet concentration is



**Figure 3.** Peak wavelength variations with niobate nanosheet concentration for four differently treated samples. Closed symbols represent the corresponding samples of open symbol whose peak wavelength is not identified.

consistent with the color variation of the nanosheet LCs. A higher nanosheet concentration leads to a smaller basal spacing and thus a blue shift of the light reflected by the ordered nanosheets. This consideration is supported by plotting peak wavelengths of the reflectance spectra listed in Table S1 against the nanosheet concentration, as shown in Figure 3. The decay is roughly to the  $-1/2$  power of nanosheet concentration for the H<sub>2</sub>O-Dialyzed samples (Figure S2), and other samples show a similar tendency. The power of decay usually falls between  $-1$  (roughly correlated to one dimensional swelling) and  $-1/3$  (three dimensional swelling) as reported in previous studies.<sup>4,14</sup> The decay value is reasonable although data points are not sufficient to discuss quantitatively. As confirmed in the previous study, the lamellar-like structure with constant repeating inter-layer distances is formed by the liquid crystallinity of the nanosheet.<sup>13,14</sup> In general, lamellar spacing decreases with increasing concentration because of the geometrically required condition. Our results match qualitatively with the lamellar assumption and suggest that the development of color is due to the lamellar structure.

In summary, niobate nanosheet LCs show structural colors after adjustment of the ionic atmosphere of the samples with appropriate treatment of colloids such as purification and introduction of electrolytes. The structural color also changes with nanosheet concentration through modification of the periodic

distance between the nanosheets ordered in a lamellar fashion. Our study demonstrates that the facile purification process can produce the coloration of niobate nanosheet colloid and that this process can be applied to other inorganic nanosheet LCs as a common method for generating structure colors.

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Supporting Information is available on <https://doi.org/10.1246/cl.200164>.

## References

- 1 T. Nakato, in *Inorganic Nanosheets and Nanosheet-Based Materials: Fundamentals and Applications of Two-Dimensional Systems*, ed. by T. Nakato, J. Kawamata, S. Takagi, Springer Japan, Tokyo, **2017**, pp. 55–100.
- 2 N. Miyamoto, T. Nakato, *Isr. J. Chem.* **2012**, *52*, 881.
- 3 H. Fudouzi, Y. Xia, *Langmuir* **2003**, *19*, 9653.
- 4 J.-C. P. Gabriel, F. Camerel, B. J. Lemaire, H. Desvaux, P. Davidson, P. Batail, *Nature* **2001**, *413*, 504.
- 5 M. Wong, R. Ishige, T. Hoshino, S. Hawkins, P. Li, A. Takahara, H.-J. Sue, *Chem. Mater.* **2014**, *26*, 1528.
- 6 M. Wong, R. Ishige, K. L. White, P. Li, D. Kim, R. Krishnamoorti, R. Gunther, T. Higuchi, H. Jinnai, A. Takahara, R. Nishimura, H.-J. Sue, *Nat. Commun.* **2014**, *5*, 3589.
- 7 K. Sano, Y. S. Kim, Y. Ishida, Y. Ebina, T. Sasaki, T. Hikima, T. Aida, *Nat. Commun.* **2016**, *7*, 12559.
- 8 T. Nakato, Y. Nono, E. Mouri, M. Nakata, *Phys. Chem. Chem. Phys.* **2014**, *16*, 955.
- 9 T. Nakato, Y. Nono, E. Mouri, *Colloids Surf., A* **2017**, *522*, 373.
- 10 T. Nakato, S. Terada, T. Ishiku, S. Abe, S. Kamimura, E. Mouri, T. Ohno, *Appl. Catal., B* **2019**, *241*, 499.
- 11 J. Zhang, K. Morisaka, T. Kumamoto, E. Mouri, T. Nakato, *Colloids Surf., A* **2018**, *556*, 106.
- 12 S. Hachisu, Y. Kobayashi, A. Kose, *J. Colloid Interface Sci.* **1973**, *42*, 342.
- 13 D. Yamaguchi, N. Miyamoto, S. Koizumi, T. Nakato, T. Hashimoto, *J. Appl. Crystallogr.* **2007**, *40*, s101.
- 14 D. Yamaguchi, N. Miyamoto, T. Fujita, T. Nakato, S. Koizumi, N. Ohta, N. Yagi, T. Hashimoto, *Phys. Rev. E* **2012**, *85*, 011403.