



Electrolyte-dependence of the macroscopic textures generated in the colloidal liquid crystals of niobate nanosheets

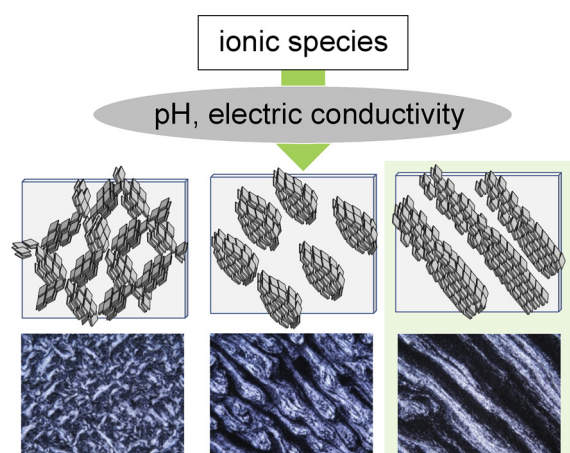


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GRAPHICAL ABSTRACT



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ABSTRACT

Liquid crystalline aqueous colloids of inorganic nanosheets with thickness of 1 nm and lateral size of several micrometers were prepared from exfoliation of layered niobate, and they were hierarchically organized to generate macroscopic textures through the formation of sub-mm nanosheet domains as the secondary building blocks. The nanosheet domains were unidirectionally aligned with orthogonally applied gravity and electric field to generate macroscopic stripes along gravity in ideal cases as we reported previously [Phys Chem Chem Phys (2014) 16: 955–962]. However, other textures such as broken stripes, drops, and nets are also obtained. The generated textures were quantitatively evaluated by image analysis of polarized optical microscope images of the samples. Uniformity and homogeneity of the stripes were evaluated by using contrast of pixels in the longitudinal and transverse directions with respect to gravity. After dialyzing a colloid with electrolytes ($\sim 10^{-3}$ mol L⁻¹), the sample comes to form of stripes more easily and “good stripes” with lengthy and homogeneous nanosheet alignment were generated after dialyzing a nanosheet colloid with KCl. Measurements of pH and conductivity of the dialyzed samples indicated the presence of suitable pH and conductivity regions for the generation of stripes.

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1. Introduction

Hierarchically structured assemblies of colloidal particles prepared by their controlled organization is important for developing novel advanced materials, where functional particles are assembled to macroscopic scales to show integrated functions that are not realized by single particles [1]. Typical examples are colloidal crystals [2] and Pickering emulsions [3]. For the organization of such colloidal structures, spherical particles have been employed in many cases. However, non-spherical particles like 2D plates and 1D rods can be used as important alternatives because their shape anisotropy facilitates low-dimensional and asymmetric hierarchical assemblies, which can be utilized for materials that show gradient functions with their anisotropic structures.

Colloidal liquid crystals (LCs) are one of such higher-order colloidal structures of anisotropic particles [4–7]. The colloidal particles are dispersed with orientational ordering to form LC phases at high concentrations. This phenomenon is entropically explained on the basis of the large excluded volume of anisotropic particles [8,9]. In colloidal LCs, the anisotropic colloidal particles are ordered spontaneously to form the LC domains, and are also aligned under external fields such as electric and magnetic fields. Various hierarchically structured materials are prepared by using colloidal LCs with self-assembly of the anisotropic particles themselves or hybridization with polymers [10,11].

Among anisotropic particles, inorganic nanosheets prepared by exfoliation of layered crystals are characterized by their ultimate thinness of around 1 nm with the lateral length of several tens of nanometers to micrometers. [12,13] Their high shape anisotropy leads to stable liquid crystalline phase behavior [10,14–16]. Various nanosheet LCs have been developed in the past decades, and their alignment under external forces have been achieved with electric and magnetic fields, shear forces, and laser radiation pressures [16–25]. Because of the 2D nature of nanosheets, two orthogonal external forces are necessary for aligning them in a unidirectional manner, being in contrast with 1D particles that can be unidirectionally aligned by a single external force; in other words, the biaxiality enables a wide variation of nanosheet orientations [19].

We have constructed macroscopic hierarchical structures reflecting 2D nature of inorganic nanosheets using hexaniobate ($[\text{Nb}_6\text{O}_{17}]^{4-}$) nanosheet LCs [19,24,26,27] with the strategy of combining LC domain growth based on internal nanosheet–nanosheet interactions and nanosheet alignment under external electric fields. We employed the two-stage process, where the LC domains, which are called tactoids hereafter, grow at the first stage, and application of an AC electric field at the second stage orient the tactoids to yield the final structure [28]. The final structure depends on the relative direction of the applied electric field and gravity; a net-like texture is obtained by the application of the two external forces from the same direction while a stripe texture forms by the orthogonal application, as schematically depicted in Fig. 1. Particularly, the stripe texture is characterized by the unidirectional alignment of nanosheets, and important because of its applicability for various uses that require a specific orientation of nanosheets. Higher nanosheet ordering provides more highly anisotropic optic, electronic, and physicochemical functions, in sharp contrasts

with conventional materials with isotropic structures. Hence, easy and reproducible preparation of highly ordered stripe textures is indispensable for the applications of unidirectionally aligned colloidal nanosheets.

The stripe texture reflects two-dimensionality of nanosheet LCs because it is generated by unidirectional alignment of the nanosheets with the lateral size of 1–2 μm up to the length of more than 1 mm with retention of their colloidal fluidity and without chemical binding between the nanosheets. This is a temporal structure generated by flow-induced alignment of the nanosheets with gravity [29]. The tactoids grown by the incubation of the colloids prior to the application of the AC voltage are stretched and connected to form the stripes. The results demonstrate that nanosheet LCs generate diverse hierarchically organized macroscopic structures on the basis of the 2D particle shape and conditions of the applied external field.

However, because many nanosheet colloids, involving our niobate nanosheet LCs, are aqueous colloids of electrically charged oxide nanosheets, ionic conditions of the colloids should greatly affect the interparticle interactions. This suggests that electrolytes coexisting in aqueous nanosheet LCs are another factor for determining the macroscopic colloidal structures. We report herein the stripe texture of niobate nanosheet LCs characterized by unidirectional nanosheet alignment at a macroscopic scale is greatly influenced by electrolyte coexisting in the colloid. In fact, colloids purified by dialysis with water often exhibit textures other than stripe. Thus, we have investigated the conditions for the nanosheet alignment into stripes, whose length and smoothness have been evaluated by analysis of optical microscope images. Our results show that long and smooth stripes are attained under limited ranges of electrolyte conditions provided by the electric conductivity and pH of the colloid.

2. Materials and methods

2.1. Sample preparation

Milli-Q water was used in all of the experiments. A colloidal LC sample of niobate nanosheets was prepared by the method reported previously. Briefly, tetrapotassium hexaniobate $\text{K}_4\text{Nb}_6\text{O}_{17}$ was treated with a 0.2 mol L^{-1} aqueous propylammonium chloride ($\text{C}_3\text{H}_7\text{NH}_3\text{Cl}$) solution at 120°C for a week in a Teflon-lined stainless steel autoclave. Then, solid product was centrifuged, washed and dialyzed with water to yield the initial stock colloid sample. With these treatments, the layered niobate crystals were exfoliated to form of niobate nanosheet colloidal LCs, where the negatively charged niobate nanosheets were accompanied by $\text{C}_3\text{H}_7\text{NH}_3^+$ cations that were introduced as an exfoliating reagent for the niobate crystal via replacing the interlayer K^+ ions [30]. The average lateral length of the nanosheets estimated by TEM images was $2.0 \mu\text{m}$ with a log-normal size distribution. Then, the colloidal LC was dialyzed with several electrolyte solutions: KCl, K_2CO_3 , propylamine ($\text{C}_3\text{H}_7\text{NH}_2$), and $\text{C}_3\text{H}_7\text{NH}_3\text{Cl}$ at 10^{-4} – $10^{-2} \text{ mol L}^{-1}$. A small portion of the initial stock sample was dialyzed with an electrolyte solution for 24 h and then diluted to 5 g L^{-1} (indicated by the mass of $\text{Nb}_6\text{O}_{17}^{4-}$) with corresponding electrolyte solutions. Values of pH and electric conductivity of the sample were obtained by a Horiba LAQUA act D-71 and LAQUA act D-74 instruments, respectively. Electric conductivity was measured after diluting the sample by water to be 0.1 g L^{-1} nanosheet concentration.

2.2. Formation and observation of the macroscopic textures

A small portion of the colloidal LCs was injected into a LC cell, built up with two ITO-coated glass plates sandwiching a $100 \mu\text{m}$ film spacer. The sample injected into the cell was incubated for 120 min to allow the growth of tactoids by standing the cell with the “flat” cell setting (i.e., at the horizontal position, Fig. 1 left) under ambient conditions. Then, an AC electric field (500 V cm^{-1} , 50 kHz) was applied to the LC sample in

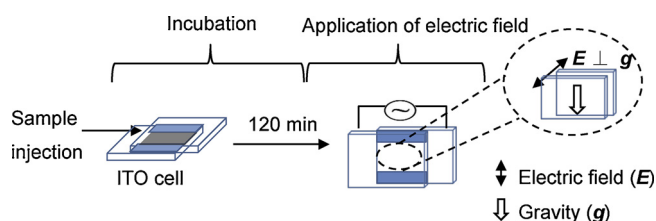


Fig. 1. Schematic representation of the experimental procedure for incubation and the electric field application to niobate nanosheet LCs. The electric field is applied from the direction perpendicular to gravity. The arrows indicate the direction of electric field (E) and gravity (g), respectively.

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