Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information

Multiphase coexistence and destabilization of liquid crystalline binary nanosheet colloids of titanate and clay

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Experimental details

Sample preparation

Single crystalline lepidocrocite-type layered titanate $K_{0.8}Ti_{1.73}Li_{0.24}O_4$ was prepared and exfoliated by using the method of Sasaki et al.[1, 2] A stoichiometric mixture of TiO_2, K_2CO_3, and Li_2CO_3 was heated with a MoO_3 flux at 1200 °C for 10 h. The obtained solid was treated with a 0.5 mol L^{-1} HCl for 5 d at room temperature with replacing the acid solution everyday. The acid-treated product $H_{0.7}Ti_{1.73}O_4$ was thoroughly washed with water and dried under ambient conditions. Formation of $K_{0.8}Ti_{1.73}Li_{0.24}O_4$ and $H_{0.7}Ti_{1.73}O_4$ was confirmed with XRD.

The obtained layered titanic acid was treated with tetrabutylammonium hydroxide (TBAOH) to delaminate into nanosheets. The solid (0.4 g) was allowed to react with a 0.1 mol L^{-1} aqueous TBAOH solution (100 mL) at room temperature for 2 weeks. The reaction mixture was shaken once a day during the reaction. The reaction product was centrifuged and the deposit was washed three times with water. The wet deposit after washing was redispersed in water (100 mL) to yield a stable colloidal dispersion of the titanate nanosheets. This sample was diluted with water to prepare the colloids with various concentrations.

A binary colloid of the titanate and clay nanosheets (titanate–clay colloids) was prepared by adding a clay colloid to a titanate colloid. The clay colloid was obtained by dispersing synthetic hectorite (Laponite RD, ideal formula $Na_{0.7}Si_8Mg_{5.4}Li_{0.4}H_4O_{24}$, supplied by Rockwood Additives Ltd.) in water. The mixed sample was gently agitated, and then kept static under ambient conditions.

A macroscopically separated binary colloid was prepared by contacting a titanate colloid (3.4 g L^{-1}, 10 mL) and a clay colloid (10 g L^{-1}, 40 mL) through a cellulose membrane. The sample was stood for 48 h, and the organic content in the titanate phase was determined with thermogravimetry after evaporation of water.

Characterization of the colloids

TEM images were recorded on a Hitachi H-700 microscope operating at 100 kV. Prior to the observation, methanol was added to a small portion of colloid, and the sample was loaded on a grid coated with collodion membrane, and dried under ambient conditions. SEM images were obtained with JEOL JSM–5500LV microscope. For the observation, a colloid sample was dried and coated by gold through ion-sputtering. Optical microscope observations were carried out with an Olympus BX-51 microscope.

References

1. T. Tanaka, Y. Ebina, K. Takada, K. Kurashima and T. Sasaki, *Chem. Mater.*, 2003, **15**, 3564-3568.
2. T. Nakato, Y. Yamashita and K. Kuroda, *Thin Solid Films*, 2006, **495**, 24-28.

Fig. S1

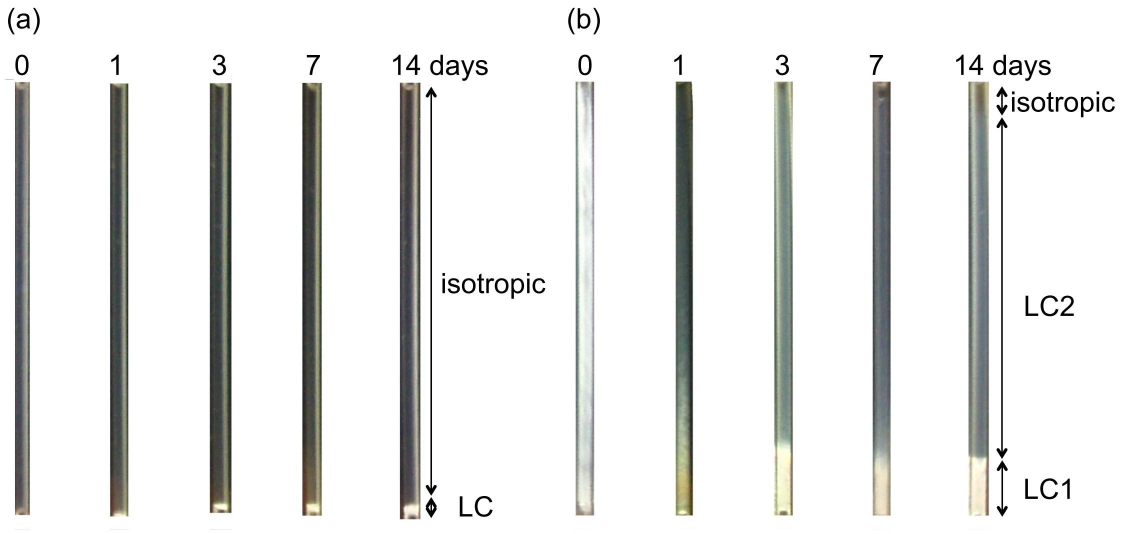


Fig. S1. Time courses of the (a) biphasic ([titanate] = 0.3 g L^{-1}, [clay] = 0.005 g L^{-1}) and (b) triphasic ([titanate] = 3 g L^{-1}, [clay] = 0.005 g L^{-1}) colloids in cylindrical capillaries observed between crossed polarizers.

Fig. S2

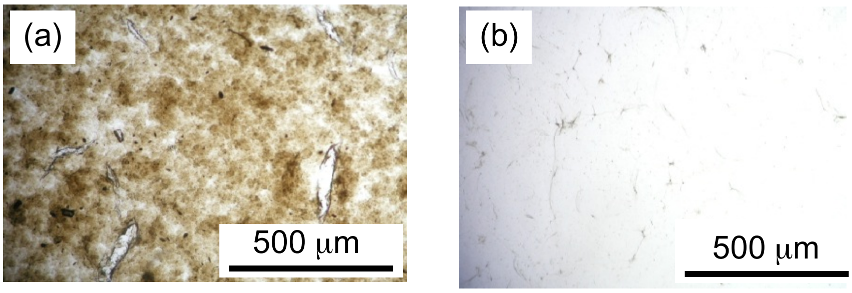


Fig. S2. Optical microscope images (without crossed polarizers) of the (a) flocculated ([titanate] = 0.15 g L^{-1}, [clay] = 1 g L^{-1}) and (b) biphasic ([titanate] = 0.15 g L^{-1}, [clay] = 0.01 g L^{-1}) samples of the titanate-clay binary colloids.

Fig.S3

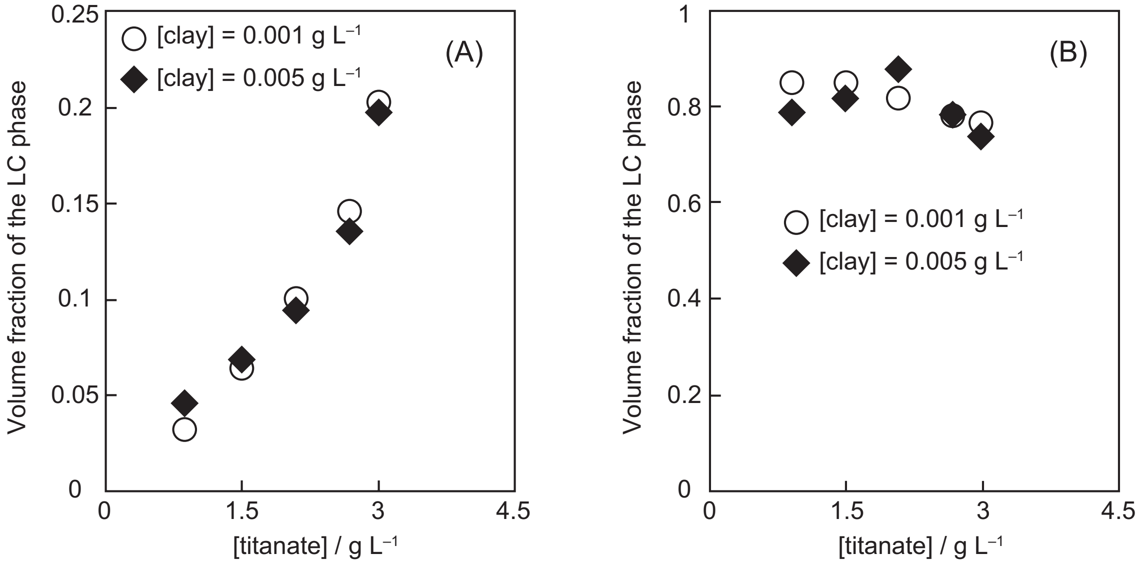


Figure S3. Volume fraction of the (A) lower and (B) middle LC phases in the triphasic titanate–clay binary colloids as a function of the titanate concentrations at the constant clay concentration of 0.001 or 0.005 g L^{-1}.

Fig. S4

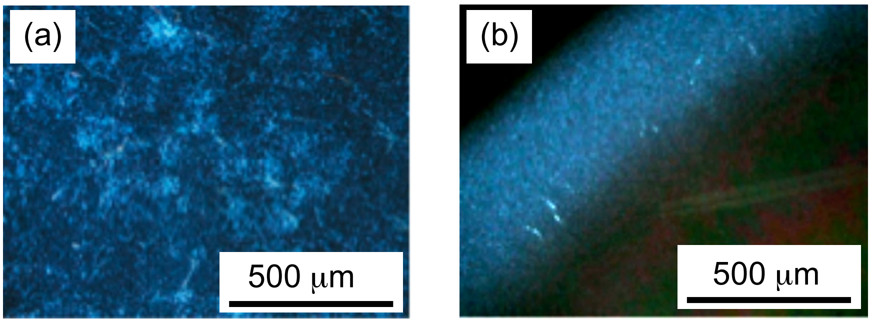
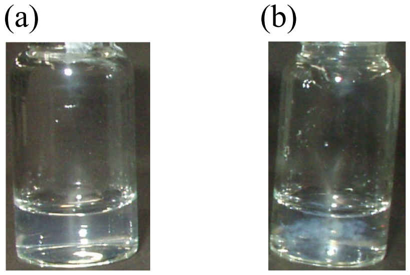
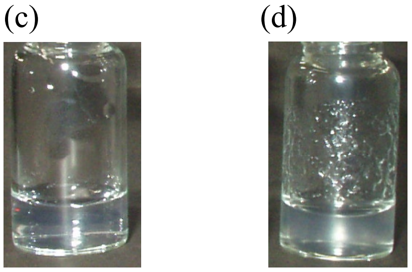


Fig. S4. Polarized optical microscope images of the (a) middle and (b) lower LC phases of a triphasic sample of the titanate-clay binary colloid ([titanate] = 1.7 g L^{-1}, [clay] = 0.005 g L^{-1}).

Fig. S5



Photographs of the titanate colloid ([titanate] = 0.0073 g L^{-1}) in the presence of (c) 0.001 mol L^{-1} and (d) 0.05 mol L^{-1} KCl was added.



Photographs of the clay colloid ([clay] = 1.0 g L^{-1}) in the presence of (c) 0.001 mol L^{-1} and (d) 0.05 mol L^{-1} KCl was added.