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Stable liquid crystalline phases of colloidally dispersed exfoliated layered niobates†

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Colloidally dispersed niobium oxide nanosheets obtained by exfoliation of layered niobates HNb_3O_8 and $HTiNbO_5$ formed stable liquid crystalline phases; their liquid crystallinity was dependent on the niobate species exfoliated.

Inorganic nanosheets obtained by exfoliation of layered inorganic solids have attracted attention in the last decade as modules of various nanomaterials.[1] The inorganic nanosheets are usually yielded as colloidally dispersed states where the parent layered oxides are infinitely swelled with solvents. Because of the highly anisotropic shape of the nanosheets, they can exhibit peculiar properties in colloidal states. However, only a few investigations have been reported for colloids of inorganic nanosheets except clay suspensions.[2,3]

We have recently found peculiar liquid crystallinity of the nanosheet sols prepared from layered niobate $K_4Nb_6O_{17}$; colloidally dispersed $[Nb_6O_{17}]^{4-}$ nanosheets form a stable liquid crystalline phase with macroscopic alignment.[4] This result has prompted us to investigate the properties of other nanosheet colloids of layered niobates which have rich structural variety. Structural difference of the nanosheets may induce differences in their colloidal behavior, whereas Onsager theory predicts formation of liquid crystalline phases as a general property of the colloids of anisotropic particles.[3,5,6]

We report here liquid crystallinity of nanosheet sols of exfoliated layered niobates HNb_3O_8[7] and $HTiNbO_5$,[8] which are structurally distinguished by their simple interlayer structure from $K_4Nb_6O_{17}$[9] possessing two types of alternating interlayer spaces. Colloids of exfoliated HNb_3O_8 and $HTiNbO_5$ formed stable liquid crystalline phases as well as that of $K_4Nb_6O_{17}$. This fact indicates a general property of colloidally dispersed niobate nanosheets with high aspect ratios. Nevertheless, liquid crystallinity of the colloids differed with the niobates employed, which clarifies that intrinsic properties of each layered niobate largely influence the liquid crystallinity of the nanosheet colloids.

HNb_3O_8 prepared according to the literature[7] was allowed to react with tetrabutylammonium ion (TBA^+), which has often been used as an exfoliating reagent of layered niobates. The product was washed with water, and then re-dispersed in water to form $[Nb_3O_8]^-$ nanosheet sols. Sols of $[TiNbO_5]^-$ nanosheets were prepared from $HTiNbO_5$ by the same procedure. For comparison, $[Nb_6O_{17}]^{4-}$ nanosheet sols were prepared by the method reported previously.[4] Liquid crystallinity of the nanosheet colloids was characterized by naked eye and optical microscope observations under crossed polarizers. We express the concentrations of colloids using volume fraction, ϕ, of the nanosheets.‡

HNb_3O_8 and $HTiNbO_5$ were exfoliated in water after the reactions with TBA^+ to form stable colloidal suspensions. The delaminated nanosheets kept in water as sols were stable for at least a day. X-ray diffraction patterns (Fig. S1 ESI†) of the films prepared by spin-coating the sols indicated intercalation of TBA^+ into the niobates. The basal spacings of TBA–HNb_3O_8 and TBA–$HTiNbO_5$, estimated as 2.4 and 2.2 nm, respectively, give gallery heights of more than 1 nm. Thus, TBA^+ ions should be accommodated in all the interlayer spaces of the niobates as counter cations of the negatively charged niobate layers. Osmotic swelling and subsequent delamination facilitated by TBA^+ can occur in all the interlayer spaces. This is in contrast with the behaviour of $K_4Nb_6O_{17}$, where delamination occurs with every other interlayer space to yield bilayer-type nanosheets because of its peculiar layered structure.[10,11]

Liquid crystallinity of the nanosheet sols is confirmed by birefringence of the samples using optical microscope observations under crossed polarizers. Microscope images of the sols of $[Nb_3O_8]^-$ and $[TiNbO_5]^-$ nanosheets at ϕ = 0.8 vol.% show birefringence accompanied by interference colors due to liquid crystalline domains of the sols (Fig. 1a,b). This result indicates that both the $[Nb_3O_8]^-$ and $[TiNbO_5]^-$ nanosheet sols form liquid crystals as well as the $[Nb_6O_{17}]^{4-}$ nanosheet sol[4] (Fig. 1c); liquid crystalline nature is a general property of the sols of exfoliated niobates. The Schlieren textures observed in the images suggest the existence of nematic phases for all the niobate nanosheet sols. Nematic ordering has been reported by many researchers for clay sols.[3] The niobate nanosheets would be orientationally ordered with retention of the layered nature (see Graphical abstract). We verified that HNb_3O_8 and $HTiNbO_5$ without the TBA^+-treatment were not exfoliated and that they did not form liquid crystalline colloids.

Comparison of the microscope image of the $[TiNbO_5]^-$ sol with those of the $[Nb_3O_8]^-$ and $[Nb_6O_{17}]^{4-}$ sols at the same concentration (ϕ = 0.8 vol.%) shows small birefringence of the $[TiNbO_5]^-$ nanosheet sol evidenced by weak interference colors. In addition, the $[TiNbO_5]^-$ sol loses its birefringence at ϕ = 0.4 vol.% (Fig. 1d), indicating occurrence of the isotropic to liquid crystalline phase

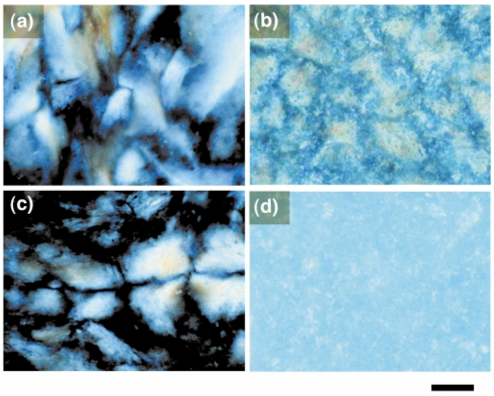

Fig. 1 Optical microscope images of the sols of (a) $[Nb_3O_8]^-$ (ϕ = 0.8 vol.%), (b) $[TiNbO_5]^-$ (ϕ = 0.8 vol.%), (c) $[Nb_6O_{17}]^{4-}$ (ϕ = 0.8 vol.%), and (d) $[TiNbO_5]^-$ (ϕ = 0.4 vol.%) nanosheets under crossed polarizers.

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† Electronic supplementary information (ESI) available: XRD patterns of the samples. See http://www.rsc.org/suppdata/cc/b3/b309628a/

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transition at $\phi = 0.4$–0.8 vol.%. The apparent blue color of the image is ascribed to depolarization due to scattering by the dispersed platelets. These facts clarify that the liquid crystalline phase of the $[TiNbO_5]^-$ sols is less stable than the other niobate sols.

Naked eye observations with crossed polarizers give additional information on the liquid crystalline behavior. Photographs of the colloids in test tubes at $\phi = 0.1$ vol.-% (Fig. 2a–c) show that the $[TiNbO_5]^-$ sol is not birefringent in contrast with the $[Nb_3O_8]^-$ and $[Nb_6O_{17}]^{4-}$ sols, supporting the relatively poor liquid crystallinity of the $[TiNbO_5]^-$ sols. On the other hand, the isotropic to liquid crystalline phase transition concentration of the $[Nb_3O_8]^-$ nanosheet sols is estimated as 0.001–0.003 vol.% by using a 10 cm length glass cell (Figs. 2d,e); the colloid of 0.003 vol.% is liquid crystalline whereas that of 0.001 vol.% is isotropic. These results indicate that the liquid crystalline phases of the $[Nb_3O_8]^-$ and $[TiNbO_5]^-$ sols are somewhat less stable than the $[Nb_6O_{17}]^{4-}$ sols, which show liquid crystallinity at 0.0005 vol.%.[4] However, we note that the liquid crystalline phases of all the niobate nanosheets examined are much more stable than those of previously reported colloidal systems of inorganic plate-like particles such as clay nanosheets and gibbsite disks.[3] In particular, the liquid crystalline niobate sols examined here are highly fluid because of low concentration of the particles, in contrast with the clay systems which show liquid crystallinity only under higher concentrations where the colloids are gelated. This is due to large lateral sizes of the niobate nanosheets as described below. We are also aware that the phase behavior is little affected by the temperature of the sols in the range of room temperature to 353 K.

Transmission electron microscope (TEM) observations of the dried sols show that the shape of niobate nanosheets is related to the difference in their liquid crystalline behavior. The TEM images (Fig. 3) indicate that all the niobate nanosheets possess rectangular shapes.[§] Mean lateral sizes of the nanosheets are estimated from edge lengths as 3.7, 3.4, and 3.6 μm for $[Nb_3O_8]^-$, $[TiNbO_5]^-$, and $[Nb_6O_{17}]^{4-}$, respectively, being similar to each other. Since the thickness of the nanosheets are 0.9, 0.9, and 1.6 nm for $[Nb_3O_8]^-$, $[TiNbO_5]^-$, and $[Nb_6O_{17}]^{4-}$, respectively,[‡] very large aspect ratios (ratio of edge length to thickness) are estimated for these niobate nanosheets. On the other hand, the image of $[TiNbO_5]^-$ nanosheets (Fig. 3c) show many dark platelets indicative of thick nanosheets; hence, the thickness of the $[TiNbO_5]^-$ plates has large polydispersity in contrast with those of the other niobate nanosheets. This fact suggests non-uniform, namely incomplete, exfoliation of $HTiNbO_5$. The polydispersive exfoliation would be due to an intrinsic property of $HTiNbO_5$ related to interactions between the $[TiNbO_5]^-$ layer and TBA^+ ion, since HNb_3O_8 and $HTiNbO_5$ are exfoliated with the same method and stably dispersed.

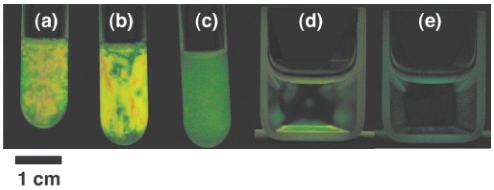

Fig. 2 Photographs of the sols of (a) $[Nb_3O_8]^-$ ($\phi = 0.1$ vol.%), (b) $[Nb_6O_{17}]^{4-}$ ($\phi = 0.1$ vol.%), (c) $[TiNbO_5]^-$ ($\phi = 0.1$ vol.%), (d) $[Nb_3O_8]^-$ ($\phi = 0.003$ vol.%), and (e) $[Nb_3O_8]^-$ ($\phi = 0.001$ vol.%) nanosheets placed between crossed polarizers.

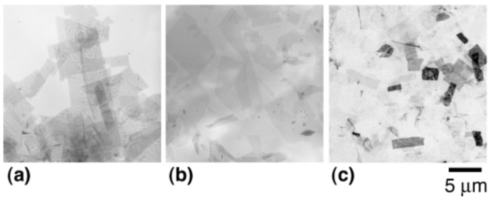

Fig. 3 TEM images of the niobate nanosheets obtained from sols of (a) $[Nb_3O_8]^-$, (b) $[Nb_6O_{17}]^{4-}$, and (c) $[TiNbO_5]^-$.

The above results indicate that liquid crystallinity of the nanosheet sols depends on the niobate exfoliated. Onsager theory explains the liquid crystallinity of hard plate colloids by excluded-volume effects between the platelets; stable liquid crystalline phases are obtained for the plates with larger aspect ratios.[5,12] For the colloids of $[TiNbO_5]^-$ nanosheets, non-uniform exfoliation reduces the effective concentration of nanosheets present in the sols. We suppose that these alterations account for the relatively unstable liquid crystalline phase of the $[TiNbO_5]^-$ colloids. On the other hand, the XRD results show that HNb_3O_8 are exfoliated into monolayer-type nanosheets, in contrast with $K_4Nb_6O_{17}$ which gives bilayer-type nanosheets,[10,11] although the TEM images indicate that both the nanosheets are uniformly thin and have similar lateral sizes. We assume that the somewhat unstable liquid crystalline behavior of the $[Nb_3O_8]^-$ sols compared with the behaviour of the $[Nb_6O_{17}]^{4-}$ colloids is related to nanosheet type, although detailed investigations are currently in progress.

In conclusion, we prepared novel anisotropic colloidal systems consisting of the exfoliated niobates. All the niobate nanosheets examined form liquid crystals because of the extremely high aspect ratio of the oxide plates, indicating that the exfoliated layered niobates generally give liquid crystals in dispersed states. However, the stability of liquid crystalline phases varies with the niobate species exfoliated. The results indicate that differences in the intrinsic properties, such as structure and exfoliative behavior, can alter the conditions of nanosheets exemplified by polydispersity in thickness to influence the liquid crystalline behavior.

Notes and references

[‡] Concentration of colloids is expressed by number density of the dispersed particles, and volume fraction, which can be converted to the number density with known thickness and lateral size of the particle, is often used for representing the concentration. We calculated the volume fraction of the nanosheets from crystallographic parameters of the parent niobates. We adopted the basal spacing of the anhydrous forms of the parent niobates[7–9] as the thickness of each nanosheet.

[§] Since the niobate nanosheets tend to coil or aggregate,[10] we carefully prepared the TEM samples to observe the planar nanosheets. A nanosheet sols was added with methanol (water : methanol = 1 : 9), and loaded on a grid coated with collodion membrane followed by drying under ambient conditions.

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