Reassembling process of colloidal single-layers of an exfoliated titanate

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Colloidal nanosheets of an exfoliated titanate start to be reassembled from a novel associated pair, accommodating an interlayer water cluster of > 100 Å thickness, to produce a restacked layer structure.

Recently it has been reported that several classes of layered materials can be exfoliated to single-layers by some chemical treatments.[1] The resulting colloidal nanosheet suspensions are of great interest because of their expected molecule-like behaviour. However, the physical and chemical nature of such suspensions has not been fully appreciated. In this report, we present an *in situ* XRD study on a colloidal suspension of a delaminated titanate by which the dynamic reassembling process of the nanosheets was followed.

The material which we examined for exfoliation is a protonic titanate, $H_xTi_{2-x/4}\square_{x/4}O_4{\cdot}H_2O$ (x = 0.7, □: vacancy), with a lepidocrocite-related layer structure.[2] A conventional solid-state reaction of a stoichiometric mixture of Cs_2CO_3 and TiO_2 at 800 °C produced the Cs-titanate, $Cs_xTi_{2-x/4}\square_{x/4}O_4$, which was subsequently converted into a protonated form by acid exchange.[2,3]

The delamination experiments were carried out by interacting a powder of $H_xTi_{2-x/4}\square_{x/4}O_4{\cdot}H_2O$ with an aqueous solution of tetrabutylammonium hydroxide (TBAOH). The TBA concentration was 0.1 mol dm^{-3} and the solid-to-solution ratio was 0.004 g cm^{-3}. Vigorous shaking of the mixture gave an opalescent dispersion which was stable without noticeable sedimentation even after several days. Colloidal nanosheets were collected by centrifugation (15000 rpm, 30 min) and were subjected to X-ray measurements, which were carried out using a powder diffractometer equipped with a horizontal sample stage in a humidity/temperature controllable chamber (Rigaku Rint 2000S).

The XRD pattern immediately after centrifugation was principally of amorphous character suggesting that the layer structure was collapsed to individual nanosheets. Besides this broad feature, a series of diffraction lines were detected at a very low angular range [Fig. 1(*a*)], indicating that a small portion of the sheets were stacked. The spacings of the three reflections observed were 55, 38 and 28 Å which were indexed as 020, 030 and 040, respectively and the intersheet separation was ≈ 110 Å. By drying the sample slowly at a relative humidity of 95%, the amorphous component disappeared almost completely and the amount of crystalline phase increased. The interlayer spacing diminished gradually during this process as exemplified for a sample aged for 7 h [Fig. 1(*b*)]. The final air-dried product can be identified as the TBA intercalated compound having an interlayer spacing of 17.5 Å [Fig. 1(*c*)].

It is noteworthy that the profile in Fig. 1(*a*) is characterized by a wavy variation of intensity without a flat region between the peaks, which implies a very small number of sheets participating in diffraction. To make a more accurate estimation, the diffraction patterns for the 0*k*0 series were simulated numerically using eqn. (1) where the first, second and third

$$I(\theta) = \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta} \cdot F^2(\theta) \cdot \frac{\sin^2(2\pi N d_{010}\sin\theta/\lambda)}{\sin^2(2\pi d_{010}\sin\theta/\lambda)} \qquad (1)$$

terms are the Lorentz-polarization factor, structure factor and interference function, respectively. The structure factor was calculated as below on the basis of the model (Fig. 2) which comprises two parallel lepidocrocite-type layers with liquid water between them [eqn. (2)].

$$\begin{aligned} F(\theta) = {} & 2\textstyle\int_0^{d_w/2}(f_o/2.5)\cdot\cos 2\pi(2y\cdot\sin\theta/\lambda)\mathrm{d}y \\ & + 2\cdot 0.9125 f_{Ti}\cos 2\pi(2y_{Ti}\cdot\sin\theta/\lambda) \\ & + 2f_o\cos 2\pi(2y_{O(1)}\cdot\sin\theta/\lambda) \\ & + 2f_o\cos 2\pi(2y_{O(2)}\cdot\sin\theta/\lambda) \end{aligned} \qquad (2)$$

The first term is the contribution from interlayer water of thickness d_w and the others are from the titanate sheet. The scattering power of the interlayer water cluster was modelled as liquid water, being constant throughout the gallery. Detailed calculation procedures will be described elsewhere.

The observed diffraction pattern [Fig. 1(*a*)] showed a close match to the calculated pattern for N = 1 in terms of oscillating

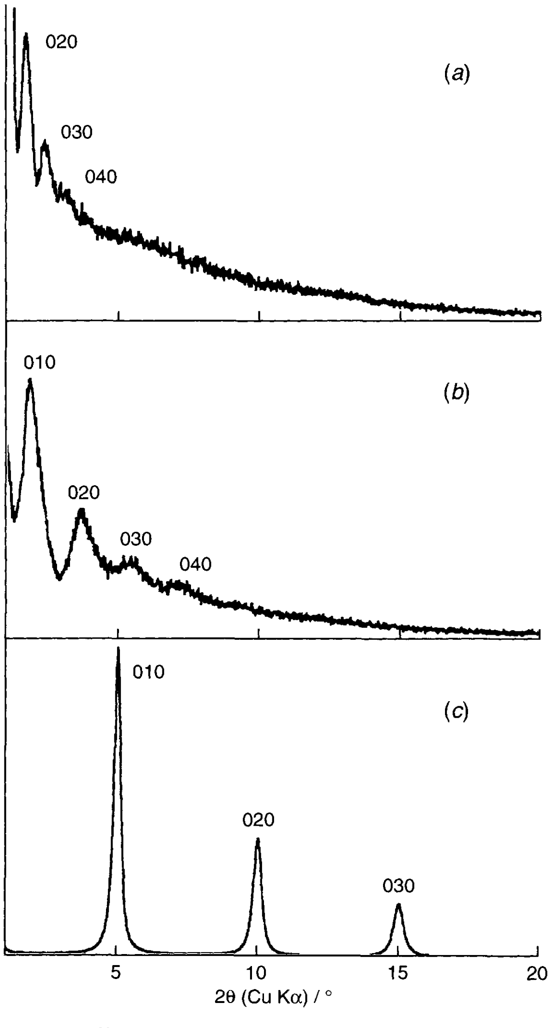
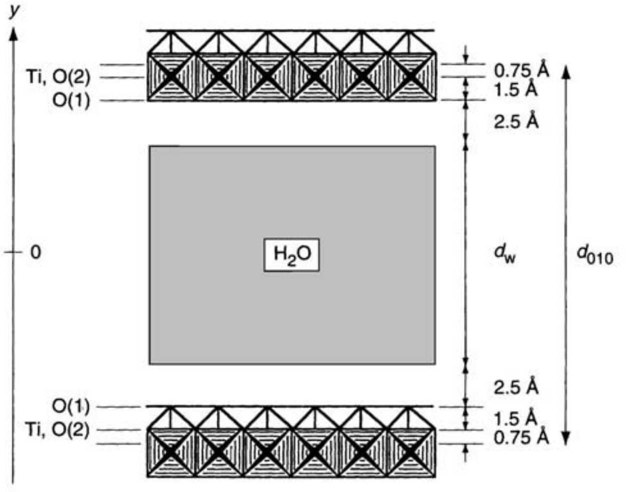


Fig. 1 X-Ray diffraction patterns for an aggregate centrifuged from the colloidal single-layer suspension. (*a*) Immediately after separation from the liquid phase, (*b*) conditioned at a relative humidity of 95% for 7 h and (*c*) air-dried. Intensity scale in (*c*) is 1/20th of that in (*a*).

line profile as well as intensity ratio for 0*k*0 reflections. The full width at half maximum for the 020 line is calculated to be 0.37, 0.24 and 0.18° for N = 1,2 and 3 respectively, while the corresponding observed value was 0.36°. This definitely indicates that the diffraction is derived from a pair of the titanate sheets, incorporating water, of thickness 110 Å. Similar estimations revealed that the number of restacked sheets increased during the drying process. The final TBA intercalated material was accounted for by a sequence of fourteen to fifteen sheets. Furthermore, theoretical evaluations on the diffraction intensity based on the equations above suggests that only a few of the delaminated sheets were stacked at a very early stage [Fig. 1(*a*)].



Atom	n	y
Ti	0.9125	$(\pm d_{010}/2)-0.75$
O(1)	1	$(\pm d_{010}/2)-2.25$
O(2)	1	$(\pm d_{010}/2)-0.75$
H_2O	$d_w/2.5$	$-d_w/2\sim+d_w/2$ (continuous)

Fig. 2 Structural model for the XRD data simulation

In conclusion, the observed phenomena can be interpreted as follows: the reassembling of the nanosheets was initiated by pairwise assembly and resulted in a well restacked layer structure. The process involved an increase in population of crystallites consisting of a number of sheets but with reduced intersheet distance.

The initial associated pair is novel in terms of its exceptionally large intersheet spacing (> 100 Å) as well as its very limited number (*i.e.* 2) of constituent nanosheets. This species may be regarded as a nucleus for reassembling. Such a high degree of hydration observed here with the gallery height exceeding 100 Å has seldom been observed for inorganic layered materials except for smectite clay minerals which undergo osmotic swelling.[4,5]

Note that the reassembling process reveals some similarities to crystallization of organic macromolecules and polymer blends. The features observed here may be common for other colloidal single-layers, including those from clay minerals, and may provide some insight into their inherent nature.

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