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The Rapid Exfoliation and Subsequent Restacking of Layered Titanates Driven by an Acid–Base Reaction**

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Abstract: *Two-dimensional (2D) (hydro)oxide materials, that is, nanosheets, enable the preparation of advanced 2D materials and devices. The general synthesis route of nanosheets involves exfoliating layered metal (hydro)oxide crystals. This exfoliation process is considered to be time-consuming, hindering their industrial-scale production. Based on in situ exfoliation studies on the protonated layered titanate* $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ *(HTO), it is now shown that ion intercalation-assisted exfoliation driven by chemical reaction provides a viable and fast route to isolated nanosheets. Contrary to the general expectation, data indicate that direct exfoliation of HTO occurs within seconds after mixing of the reactants, instead of proceeding via a swollen state as previously thought. These findings reveal that ion intercalation-assisted exfoliation driven by chemical reaction is a promising exfoliation route for large-scale synthesis.*

Inorganic layered materials, such as graphite,[1] oxides,[2] clays,[3] layered metal dichalcogenides,[4] layered double hydroxides,[5] and MAX phases[6] have been attracting much attention because they can be exfoliated or delaminated into unilamellar sheet units, so-called nanosheets, which exhibit interesting properties owing to their two-dimensional (2D) nature. These nanosheets can be used to build advanced materials and devices.[6,7] For example, $Ti_{0.87}O_2$ nanosheets are attractive candidates for ultrathin high-κ dielectric films with low leakage currents.[8] Nanosheets may also be used to control the orientation of crystalline films.[7f,9] Van der Waals heterostructures, for example, multilayer hybrid films of alternating graphene and $Ti_{0.91}O_2$ layers show ultrafast electron transfer and have potential applications in photocatalysis, capacitors, and sensors.[10] Alternating $Ti_{0.8}Co_{0.2}O_2$-$Ti_{0.6}Fe_{0.4}O_2$ supperlattices show enhanced magneto-optical properties.[11] Developing or discovering an efficient and high-yield exfoliation route to exfoliate the layered parent compounds would certainly be a key step towards the application of nanosheets. To achieve exfoliation, several techniques have been employed, such as manual mechanical exfoliation,[7b] ultrasonication-assisted solvent exfoliation,[12] and ion intercalation-based exfoliation.[13] Among these methods, manual mechanical exfoliation[7b] and ultrasonication-assisted solvent exfoliation[12] are relatively straightforward. However, manual mechanical exfoliation suffers from low yields,[13] and ultrasonication-assisted solvent exfoliation is known to result in mechanical damage to the nanosheets.[14] Ion intercalation-based exfoliation is normally driven by chemical reactions and provides a much milder route. The latter exfoliation method serves for the preparation of 2D metal oxides and other ionic layered compounds, encompassing more than 30 compounds till date.[13] Moreover, this route can yield large quantities of dispersed nanosheets and is potentially the most promising for large-scale production processes among the mentioned exfoliation methods. For example, the chemical exfoliation and intercalation of lepidocrocite-type $Ti_{0.87}O_2$ titanates in water has been reported as an efficient way to prepare two dimensional titania nanosheets and new titania-based hybrid materials with large lateral sizes.[15] However, it is generally thought that the structural evolution of layered oxides upon ion intercalation passes via a swollen state into the exfoliated state.[16] This type of exfoliation via ion intercalation is considered to be time-consuming owing to slow diffusion processes and takes typically 1–2 weeks according to several reports.[16a,17] This slow process is one of the main concerns hampering further development.[13]

Herein, based on in situ studies on exfoliation of the lepidocrocite-type titanate $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ (HTO), one of the best known study model for layered metal oxides, we show that ion intercalation exfoliation driven by an acid–base reaction is in fact a very rapid and time-efficient process. Contrary to previous conclusions from ex situ studies,[16] our in situ experimental data demonstrate that exfoliation occurs directly after mixing of reactants. Isolated nanosheets form that may restack into a hybrid layered structure, as illustrated in Figure 1.

By using the Langmuir–Blodgett technique, a single-layer nanosheet film on a silicon substrate was obtained from an aqueous HTO + TBAOH solution after a reaction time of only 30 s (Figure 2a; see the Supporting Information, Sections S1 and S2 for experimental details). Clearly a substantial concentration of single nanosheets was already present in the solution after this short period of time. The UV/Vis spectra showed that this solution had the same characteristics as an exfoliated nanosheet solution after a reaction time of two weeks (Figure 2b),[15a] even though the TBAOH/HTO ratio of the former solution was so high that it is typically thought

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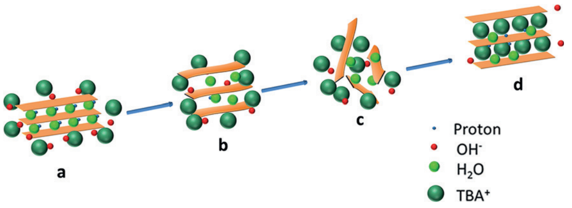

Figure 1. The proposed intercalation mechanism. a) The acid–base reaction starts with diffusion of OH^- ions from tetra-*n*-butylammonium hydroxide (TBAOH) into HTO, followed by their reaction with protons; b) The layered structure of HTO loses its stability because of the acid (HTO)–base (OH^-) reaction; c) isolated nanosheets; d) nanosheets restack into a final hybrid state.

yield a swollen hybrid state rather than isolated nanosheets.[16a] To elucidate the details of this unexpected rapid exfoliation process, we applied time-resolved in situ small-angle X-ray scattering (SAXS)[18] to reveal the dynamics of exfoliation and monitor the structure evolution. SAXS data of the first 27 s of reaction are shown in Figure 2c. The quickly evolving SAXS curves of reacting TBAOH/HTO dispersions indicate fast structure evolution.

The time of injection was 8 s and started at $t=0$. Scattering curves before adding TBAOH ($t<0$) showed a sharp peak at $q=6.792\ \mathrm{nm}^{-1}$, indicating the presence of layered HTO with an interlayer spacing of $d=2\pi/q=0.92\ \mathrm{nm}$.[19] At $t=2$ s (Figure 1c), the same peak was still present. No other peaks were observed, but the background scattering intensity had increased sharply over the entire q range. For example, the scattering intensity at $q=0.622\ \mathrm{nm}^{-1}$ increased from 29.8 (arbitrary units) at $t=-1$ s to 99.9 at $t=2$ s. In a reference experiment without HTO, we verified that the intensity change originated from the reaction (Supporting Information, Figure S1). At $t=2$ s, the net TBAOH/HTO ratio in the solution was 1, a condition where isolated nanosheets are known to form.[17a,20] The high background scattering intensity suggests a contribution from entities that do not have a pronounced SAXS signature, that is, isolated nanosheets. At $t=5$ s a new correlation peak was clearly visible at $q=0.576\ \mathrm{nm}^{-1}$, and the peak at $q=6.792\ \mathrm{nm}^{-1}$ had disappeared completely. This indicates that a new layered structure with clear Bragg-like correlation peaks had just formed, while the original layered structure of HTO had disappeared. The emerging correlation peaks suggest a restacking process of nanosheets into a new layered structure with larger spacings. Swollen hybrid structures have indeed been reported for systems with a TBAOH/HTO ratio of 4, although they were thought to form via another pathway, that is, intercalation of TBA^+, and only after much longer periods of time.[17b]

The experimental SAXS data were fitted to the modified fluctuating gap model (FGM) developed by Connolly et al.[21] for layered systems such as clays and oxides, and modified by Besselink et al.[17b] (see the Supporting Information, Section S3 for further details). Figure 3a shows the stack number m and the interlayer spacing d derived from best fits of the modified FGM to the emerging correlation peak of the newly forming phase. The stack number m describes the average number of layers in a stack of sheets in the colloidal state. Its value increased slowly with time, implying that the new structure grew, most likely by restacking of isolated nanosheets. The interlayer spacing d between these nanosheet platelets in a stack decreased with time, until they reached a more or less constant distance of 10.1 nm after 20 s. The final values are similar to separation distances reported elsewhere for similar HTO+TBAOH mixtures.[17b] The gradually decreasing interlayer spacing, evidenced by the first correlation peak (Figure 2c) as shown in Figure 3a, supports the conclusion that restacking occurs following a very fast exfoliation process. It is noted that in situ SAXS data of a similar system with a TBAOH/HTO ratio of 6:1 showed the same trend as presented in Figure 2c for TBAOH/HTO = 4:1 (Supporting Information, Figure S2a). Direct intercalation of TBA^+ into an existing stack to yield a "swollen" state[2] would lead to an increasing interlayer spacing with time (correlation maximum at decreasing q), rather than a decreasing spacing with time (correlation maximum at increasing q) as the experimental data in Figure 3a show. We ruled out the possibility of TBA^+ intercalation prior to exfoliation by conducting SAXS experiments with a reference solution with

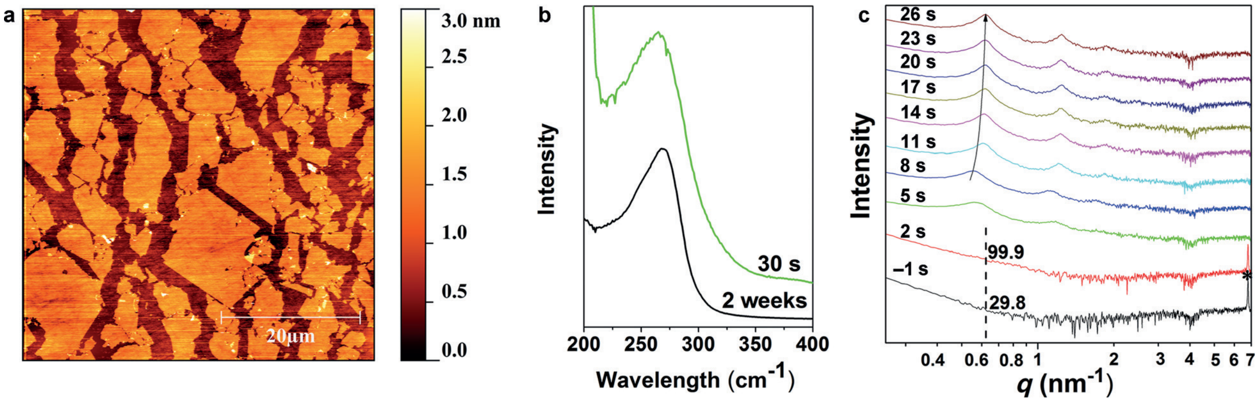

Figure 2. a) AFM image obtained from a Langmuir–Blodgett film obtained from a HTO+TBAOH solution after 30 s reaction time. b) UV/Vis spectra of titanate solutions after 30 s (TBAOH/HTO = 4:1) and after 2 weeks (TBAOH/HTO = 1:1) of reaction time. c) Time-resolved SAXS curves of HTO solution after mixing with TBAOH. The drawn line illustrates the trend of the first correlation maximum in the newly evolving structure.

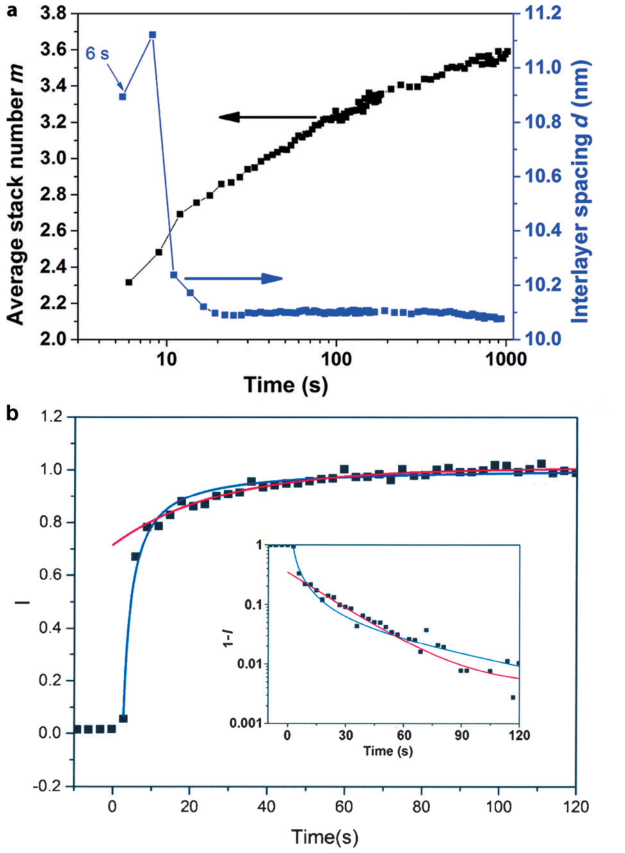

Figure 3. a) Average stack number *m* and interlayer spacing *d* between layers in hybrid stack derived from the modified FGM by fitting to time resolved SAXS profiles of HTO upon reaction with TBAOH. b) The curve depicts the scattering intensity at $q = 0.622\ \mathrm{nm}^{-1}$ (at $t < 5$ s) or at the first peak position (peak height) (at $t > 5$ s). The inset shows normalized intensity data on a logarithmic scale.

a low TBAOH/HTO ratio of 1:1 (Supporting Information, Figure S2b). At this ratio only exfoliation has been reported,[17a,20] and our data showed that intercalation/swelling did not occur. Hence, the data presented above show clearly that exfoliation of HTO occurs upon reaction with TBAOH, yielding isolated nanosheets which then (partially) restack into a new layered hybrid material when the TBAOH/HTO ratio is 4:1. The conclusion is consistent with the results from kinetic modeling as discussed below.

We developed a general kinetic model for the exfoliation and restacking reactions (Supporting Information, Section S4) and used the time-resolved peak intensity of the first correlation maximum to extract kinetic data. In the proposed sequence of reactions, one of two steps will be rate-limiting unless their rates are roughly the same. Fitting the model to the kinetic data in Figure 3b showed that the rate of restacking followed second-order kinetics at $t < 15$ s, while at $t > 15$ s it followed first-order kinetics (Figure 3b). These results indicate that the restacking process is rate-limiting in the early stages of reaction (that is, fast exfoliation rate due to high concentration of HTO, but slow restacking rate due to low concentration of isolated nanosheets), while the exfoliation process becomes rate-determining in the later stages (that is, a slow exfoliation rate is due to depletion of HTO and a fast restacking rate is due to high concentration of 2D nanosheets). This result is in good agreement with the conclusion drawn above that exfoliation of HTO precedes restacking of nanosheets into a new layered hybrid material.

An acid–base reaction between OH^- from TBAOH and protons from HTO was required to initiate the exfoliation of HTO (Supporting Information, Figure S3). Figure 4a–d shows an unexpected temporary rise of pH, especially for low TBAOH/HTO ratios, when TBAOH was added to HTO (black curve). A smaller pH rise was seen when TBAOH was added to a solution in absence of HTO (red curve). The temporary pH rise upon reaction indicates that initially, a net amount of OH^- was formed, probably resulting from the exfoliation process. To investigate the exfoliation chemistry in more detail, XPS and in situ FTIR measurements were carried out. High-resolution XPS measurements were carried out on HTO powders and exfoliated monolayer nanosheets. The Ti $2p_{3/2}$ XPS spectra shown in Figure 4e show peaks at 459.4 eV and 457.6 eV, which can be assigned to Ti^{4+} and Ti^{3+}, respectively.[22] The concentration of Ti^{3+} in monolayer nanosheets was higher than in HTO powder. It increased from 2 at % before to 6 at % after exfoliation, indicating that partial reduction of Ti atoms occurred upon exfoliation of HTO.[23] The same phenomenon was also reported by Sun et al.[22] The in situ FTIR data in Figure 4f (full-range FTIR data are given in the Supporting Information, Figure S4a) show that a new peak appeared at 880 cm^{-1} in the investigated spectral range after reaction times of 16–24 s and longer. The peak at 880 cm^{-1} can be assigned to fully covered OH groups in lepidocrocite-type titanates.[24] The presence of OH groups was verified by O 1s XPS spectra of monolayer $Ti_{0.87}O_2$ nanosheets (Supporting Information, Figure S4b). The data suggest that a large number of protons adsorbed onto nanosheets to form OH groups after the acid–base and exfoliation reactions.

This result is consistent with the high pH of all solutions irrespective of TBAOH/HTO ratio after 30 min of reaction time (Supporting Information, Table S1). It indicates that HTO did not release large numbers of protons. Hence, the reduction of Ti leads to adsorption of more cations to compensate for the loss of positive charge in the sheet. The resulting uptake of protons from solution will lead to an increase of pH in the solution to temporarily higher values than in the reference solution (Figure 4a–d). We propose that the massive uptake of protons is required for exfoliation and surface charge compensation (Supporting Information, Section S5). Combination of partial reduction of Ti ions and uptake of protons from the aqueous solution by exfoliating HTO leads to in situ OH^- formation, serving as reactant for further acid–base reaction. Because of relative long diffusion path for reactants in the layered structure, the in situ generation of OH^- may accelerate the exfoliation process substantially.

In summary, we found that exfoliation of layered titanate driven by an acid–base reaction is much faster than was generally believed. Exfoliation occurs directly instead of proceeding via an intermediate swollen state. We observed reduction of transition-metal titanium atoms and in situ OH^-

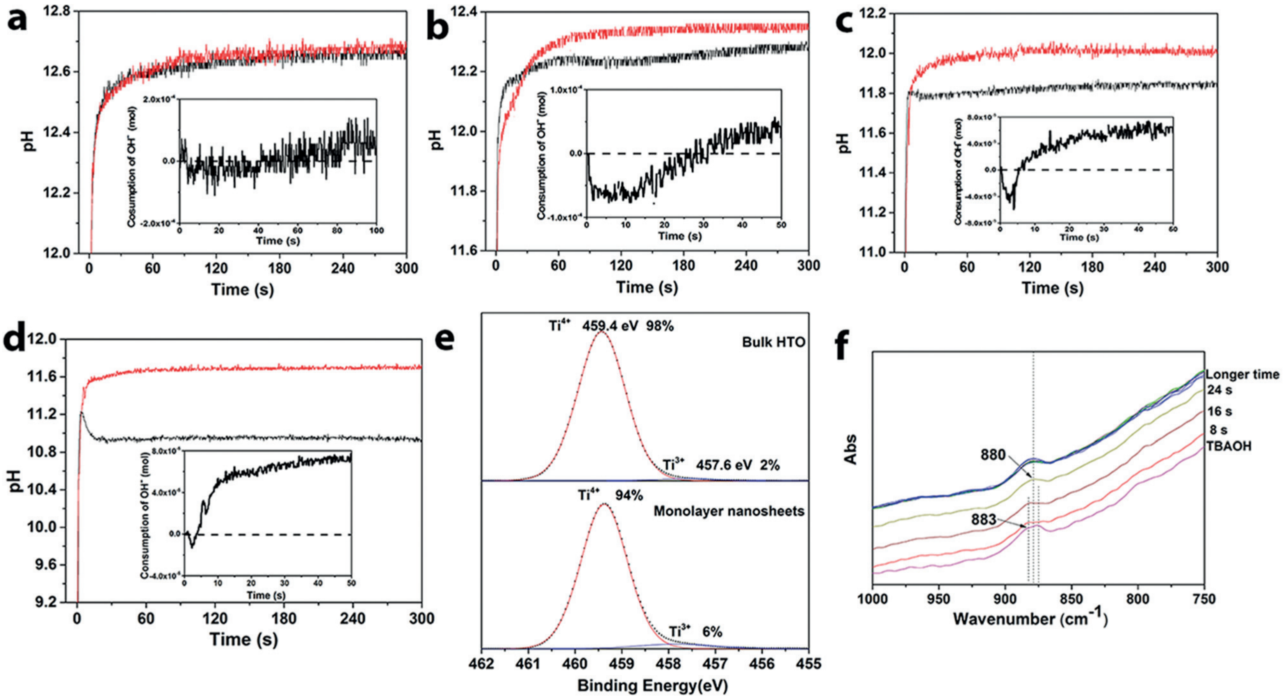

Figure 4. pH change during reaction at varying TBAOH/HTO ratios: a) 2:1, b) 1:1, c) 1:2, and d) 1:4. The black line represents the pH in a HTO-TBAOH solution; the red line represents the reference curve obtained from a water-TBAOH solution. The inset shows the net consumption/release of OH^- in a reacting solution calculated from the difference between the two curves. e) High-resolution XPS spectra of bulk HTO and monolayer $Ti_{0.87}O_2$ nanosheets for Ti $2p_{3/2}$. f) Time-resolved FTIR data at a TBAOH/HTO molar ratio of 4:1.

generation in layered titanate upon exfoliation. Rapid exfoliation was also observed by us in other layered oxides, that is, $HCa_2Nb_3O_{10}\cdot H_2O$, $HTi_2NbO_7\cdot H_2O$, and $H_3Ti_5NbO_{14}\cdot H_2O$ not shown here. Our results highlight that exfoliation driven by chemical reaction is a promising route for efficient large-scale synthesis of 2D materials. Short exfoliation periods are necessary to synthesize isolated nanosheets, as they reorganize into a hybrid stack of sheets after a given period of time when the TBA/HTO ratio is greater than two.[2] We expect that the technique may find more widespread use to exfoliate layered metal oxides and other ionic layered compounds, and may even serve as guidance for exfoliation strategies for non-ionic layered compounds, to achieve rapid and efficient exfoliation via alternative ways such as chemical modification.

Keywords: layered metal hydroxides · layered titanate · nanosheets · rapid exfoliation · two-dimensional materials

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