1. Introduction

Layered inorganic materials have proven to be of great interest for scientific and technological reasons because they can be exfoliated or delaminated into individual metal oxide nanosheets. The 2D structure of nanosheets often exhibits different physicochemical properties than their layered 3D counterparts. The most extensively studied case is the formation of graphene from graphite, in which the layers are held together by weak van der Waals forces.\(^{[5]}\) In a similar fashion, layered inorganic materials can be exfoliated into stable colloidal suspensions of 2D sheets. The layers of layered inorganic compounds are held together by strong electrostatic interactions, and chemical modification is usually necessary to aid the exfoliation process. A wide variety of layered materials have been exfoliated by these means, i.e. clays,\(^{[2]}\) layered metal chalcogenides,\(^{[3]}\) oxides,\(^{[4]}\) hydroxides,\(^{[5]}\) and combinations of these.\(^{[6]}\)

One example is titanium oxide nanosheets, which can be obtained through the exfoliation of protonated layered titanates with lepidocrocite-like structures \((H_{1.07}Ti_{1.73}O_4)\). The parent layered titanates consist of negatively charged metal oxide layers that can be intercalated by a wide range of cations. Following exfoliation, titanium oxide nanosheets have been assembled into thin films with high dielectric constants\(^{[7]}\) and have also been used as seed layers for epitaxial film growth.\(^{[8]}\) Layered titanates, and titanium oxide in general, find applications as photocatalysts,\(^{[9]}\) in photovoltaics\(^{[10]}\) and in batteries.\(^{[11]}\)

Titanium oxide nanosheets in aqueous solution are usually stabilized by surfactants.\(^{[12]}\) A common technique to form titanium oxide nanosheets is through intercalation of bulky ions such as tetrabutylammonium (TBA\(^+\)). This exfoliation process leads to a swollen state and the partial formation of a hybrid restacked system.\(^{[7,13]}\) Surfactants containing amine-derived groups have also been widely used for the delamination of inorganic layered materials.\(^{[14]}\) During intercalation, the amine molecules are concurrently accompanied by a number of solvent molecules (i.e., water); stable colloidal suspensions are formed due to the osmotic swelling that weakens the binding interactions between the nanosheets.\(^{[15]}\) Thus, in this case the

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exfoliation mechanism involves a high degree of swelling, leading to what can be considered as a colloidal system of 2D planar objects.

Amines and amino acids can also participate in acid–base reactions with protons present in the interlayer region. Amino acids are zwitterions with both amine and carboxylic functional groups. When the amine group in a neutral amino acid reacts with the protons in the interlayer, its conjugate acid is formed and the presence of the protonated carboxylic acid groups does not hinder the intercalation. After intercalation, a pH increase in the solution can deprotonate the carboxylic group, thus creating negatively charged amino acid molecules. These anions induce a repulsive electrostatic force on the negatively charged metal oxide nanosheets, triggering the exfoliation process.[16] The use of amino acids contributes to the sustainability of the process in terms of toxicity and waste treatment in comparison to quaternary ammonium ions.[17]

The mechanical properties of materials are determined by the composition and architectural arrangement of atoms and bonds from the nano to the macroscopic.[18] Nanostructured ceramics in the shape of honeycombs are a good example of such deformable ceramics.[19] The regular porous network can absorb strain under tensile force, where traditional dense polycrystalline ceramics would fail. The structural anisotropy leads to an increase in flexibility in specific directions due to the absence of ionic bonds in those directions. Similarly, layered ceramics can undergo plastic deformation when a shear force is applied parallel to the planes, which is at the basis of the application of such ceramics as solid lubricants.[20] Nowadays, graphite is extensively used in industry for lubrication purposes in a wide range of temperatures, due to its relatively high thermal stability, decomposing in air above 700 °C.[21] The layers are held together by weak van der Waals forces, thus the layers can easily slide over each other.[22] Nevertheless, there are some problems related to the use of graphite, for example pitting corrosion on steel surfaces due to its electrical conductivity and the creation of a dirty working environment.[23] Alternatives for graphite are based on salts of polymers such as polytetrafluoroethylene,[24] and 2D inorganic networks like hexagonal boron nitride, or metal dichalcogenides such as molybdenum disulfide (MoS2).[25] The use of these alternatives is limited by their oxidative decomposition in air and at high temperatures. Therefore, there is a need to identify thermally stable alternatives that are not susceptible to catastrophic oxidation within the relatively short time scale of most high-temperature lubrication process, without compromising its lubricious properties. Layered oxide ceramics are most commonly used as additives for oil lubrication,[26] but they have not been used as dry powder solid lubricants for high temperature applications to our knowledge. In order to reduce the electrostatic interactions that hold the layers together, replacement of the original counter ions by the intercalation of bulky ions, typically organic molecules, is usually required. The interlayer distance can be increased by introducing bulky charged organic ions to reduce the Coulombic interactions between the layers, thus facilitating the sliding of sheets relative to one another under influence of shear. Moreover, the use of amino acids as intercalants as described above also offers the possibility of in situ polymerizing polyamide chains between the oxide layers, i.e., a soft and well-connected network that would promote the inorganic layers to slide even more readily than with bulky ionic molecules. The intercalation of polymers in layered ceramics is generally regarded as a challenge.[27] Our approach is to first intercalate amino acid monomers, and then to trigger a polymerization reaction, for example, by means of a catalyst or temperature increase.

We synthesized and characterized a hybrid nanocomposite composed from a layered titanate with lepidocrocite-like structure (H1.67Ti1.73O4, further denoted as HTO) and 11-aminoundecanoic acid (denoted as AUA) zwitterions, and applied this material as solid lubricant in high temperature Pin-on-Disc (PoD) friction experiments. It is generally thought that the intercalation of large species such as AUA is a time-consuming procedure, mainly caused by slow diffusion of the guest molecule into the layered systems.[28] The lack of in situ studies on the exfoliation mechanisms may have contributed to the belief that acid–base exfoliation processes occur over an extended period of time.[29] Recent studies in which tetrabutyl ammonium hydroxide and n-alkylamines were employed, however, support the idea that intercalation–exfoliation occurs within seconds or minutes at room temperature.[29b,30] The AUA molecules are the precursors of nylon-11, which polymer can be formed upon in situ heating of the intercalated hybrid nanocomposite. The enhanced lubricative properties originate from the synergy between the thermally stable oxide layers and the relatively soft polymer.

Here, time-resolved in situ small-angle X-ray scattering (SAXS) was employed to study the structural evolution of the layered titanate crystal (H1.67Ti1.73O4) upon intercalation with the long-chained amino acid AUA at different temperatures. Both the intercalation and subsequent exfoliation mechanisms were studied extensively.

2. Results and Discussion

The K0.8Ti1.71Li0.27O4 (KITO) parent structure consists of a stack of negatively charged layers of (Ti1.71Li0.27O4)0.8– with a lepidocrocite-type structure, where K+ is located in the interlayer region to neutralize the negative charges present in the titanium oxide sheet layers. The substitution of K+ by hydrated protons (H+) in the ion exchange step affects the interlayer distance in the crystals, showing an increase from 0.75 to 0.92 nm after exchange, as seen from the decrease of the (020) peak position in the powder X-ray diffractograms (PXRD) in Figure 1a. The washing process also caused removal of Li+ ions from regular Ti-positions in the crystal lattice, leaving negatively charged Ti vacancies in the nanosheets. The interlayer spacings found with PXRD correspond well with reported d values for both KITO and HTO.[31] The inset shows a visualization of the HTO structure, with the protons present in the space between the titanium oxide layers. The flux synthesis method allowed to obtain large-sized crystals of the layered parent compound KITO with typical sizes of about 50 μm, as shown in Figure 1b.

The formation of the 11-aminoundecanoic acid-titanium oxide (AUATO) nanocomposite was monitored by time-resolved in situ SAXS measurements. The evolution of the
crystallographic reflections of HTO and AUA still present in the suspension as a solid after mixing can be seen in Figure 2. The main diffraction peak of HTO is the (020) reflection, and is located at \( q = 6.8 \text{ nm}^{-1} \) in Figure 2. The layered HTO was completely intercalated with AUA and formed the AUATO nanocomposite phase within 20 min. Its formation rate seems to be conditioned by the dissolution rate of AUA and limited by the diffusion of the molecules into the gallery region of HTO. The nanocomposite gave rise to two new peaks, i.e., the (020) peak at \( q = 2.5 \text{ nm}^{-1} \), and the (040) peak at \( q = 5.0 \text{ nm}^{-1} \). This corresponds to a layered structure with an interlayer spacing of 2.43 nm. The peak at \( q = 3.6 \text{ nm}^{-1} \) is attributed to AUA in suspension, and its intensity decreased as the amino acid dissolved and intercalated into the HTO structure. Two main observations can be noted. Firstly, the well-defined layered structure of HTO was maintained in the nanocomposite phase. The new peaks of AUATO arose from the background, with the full width at half maximum (FWHM) decreasing from 0.09 to 0.03 nm\(^{-1}\) between \( t = 12 \) and 20 min. The formation of sharp peaks indicates that the AUA molecules diffused into the interlayer gallery and quickly rearranged into a well-ordered configuration. The small shoulders of the AUATO (020) and (040) peaks \( (q = 2.57 \text{ nm}^{-1}) \) decreased gradually and were not observed in the final product. They may be attributed to an intermediate state of rearrangement of AUA molecules within the interlayer.

Secondly, the swelling of the crystal can be inferred from the shape and position of the new correlation peaks. The main peaks of AUATO and HTO did not shift during nanocomposite formation, suggesting that the AUA molecules swell the HTO crystals layer-by-layer rather than simultaneously. In the former case the AUA molecules first become intercalated only in the outermost intergallery layers of the crystallites, and then diffuse stepwise into intergalleries closer toward the center of the particle. In contrast, simultaneous partial swelling over the total number of HTO particles would have led to substantial broadening of the (020) peak of HTO, but the latter observation was not made during the actual experiment.

The peak at \( q = 3.85 \text{ nm}^{-1} \) is presumed to be an intermediate form of AUATO (e.g. single paraffinic layer of AUA), but its intensity faded in the course of time and was not present in the final product, see Figure S1 in the Supporting Information.

The driving force for the intercalation process is thought to be the fast acid–base reaction in the interlayer. The amino acid reacts with the protons of the layered host. The \( -\text{NH}_2 \) functional group acts as a base for the protons and becomes positively charged. This reaction facilitates the entrance of the amino acid, helping to keep the charge balance and swell the layers. Syntheses were carried out at very high and low pH to confirm this hypothesis. Suspensions of HTO (20 mL), set to pH 3 or pH 11 by addition of concentrated HCl or NaOH aqueous solutions, were mixed with amino acid solution.
(20 mL) and monitored with SAXS. Figure 3 shows the peak height fit for the (020) peak of HTO at $q = 6.8 \, \text{nm}^{-1}$. The full range SAXS profiles can be found in Figure S2 in the Supporting Information. The intensity decrease of the HTO peak at pH 3 can be attributed entirely to the effect of dilution caused by the mixing of the HTO suspension with the AUA solution. The $\text{-NH}_2$ group was protonated and did not interact with the H$^+$ in the interlayer. As a result, no intercalation was observed.

At pH 11, the $\text{-COOH}$ group was deprotonated and negatively charged. Deprotonated AUA did not enter the interlayer due to charge repulsion. A new peak appeared at $q = 7.05 \, \text{nm}^{-1}$ that can be attributed to the formation of layered $\text{Na}_{x}\text{Ti}_{1.73}\text{O}_4$ following intercalation of Na$^+$ from NaOH present in the suspension. The competing Na intercalation process is facilitated by the high concentration of Na$^+$ and its small hydration sphere, which makes it easier to intercalate than AUA. The (020) peak of $\text{Na}_{x}\text{Ti}_{1.73}\text{O}_4\cdot n\text{H}_2\text{O}$ (denoted as NaTiO) arose from the background at the same time that the HTO peaks faded, and the corresponding interlayer spacing was 0.89 nm, in comparison with 0.92 nm for HTO. These results suggest that the ideal conditions for nanocomposite formation are at a pH equal to or slightly lower than the isoelectric point (IEP) (pH 7.85) of the amino acid, as shown in Figure 2.

2.1. Kinetics of AUATO Formation

The kinetics of the process were assessed by performing amino acid intercalation at temperatures between 25 and 80 °C. The corresponding time-resolved SAXS profiles can be found in Figure S3 in the Supporting Information. The intercalation rate was calculated from the change of the AUATO (020) peak height with time. Figure 4a shows the curve for 25 °C. Assuming Arrhenius-type behavior for the temperature dependency, the conversion rate can be fitted by linear regression, see Figure 4b. The corresponding activation energy was ≈23 ± 1 kJ mol$^{-1}$. The low activation energy may be attributed to the energetically favorable acid–base reactions. As can be seen in Figure 4a, amino acid intercalation occurred after a short time even at 25 °C. Diffusion of the lengthy AUA molecules into the structure was accelerated by temperature increase.

2.2. Exfoliation of the AUATO Nanocomposite into Nanosheets

Upon increasing the pH of the medium to a value well above 7.85, AUA becomes negatively charged. These newly formed charges can induce a strong electrostatic repulsion with the negatively charged layered host and cause fast exfoliation of the layered crystal into separate layers.

This is evidenced by the SAXS data of the exfoliation of an AUATO suspension in Figure 5a,b. The pH was increased by addition of $3 \, \text{m} \text{NaOH (aq)}$ at $t = 84 \, \text{s}$. The pH increased immediately from 6.5 to 11.6. All correlation peaks of AUATO disappeared within 200 s, indicating the disappearance of long-range order in the layered structure. The position of the vanishing peaks of AUATO showed a very small shift over time to lower

Figure 3. Evolution of the peak heights of HTO (020) and NaTiO (020) upon intercalation of AUA in HTO at pH 3 and pH 11. The colored bands serve only as a guide to the eye indicating the general trends.

Figure 4. a) AUATO (020) peak intensity at 25 °C as function of time during synthesis. b) Arrhenius-type representation of the conversion rate at different temperatures. The maximum intercalation rates were used as kinetic parameters to describe the temperature dependence.
q-values, corresponding with an increase of interlayer distance of 0.2 Å in real space. This suggests immediate exfoliation without a significantly swollen or collapsed intermediate state. Peak fits can be found in Figure S4 in the Supporting Information.

The inset in Figure 5a displays the AUATO (020) peak height during exfoliation. The process showed the first order kinetics, in agreement with earlier findings. The concentration of OH$^-$ was high and relatively constant during the process, making the overall reaction seemingly independent of OH concentration. When the main limiting step, the diffusion of the OH$^-$ species into the interlayer and posterior reaction with the amino acid is incorporated into the model, the final equation becomes

$$\text{[AUATO]} = \exp\left(-\sqrt{k(t-t_0)}\right)$$

where $k$, $t$, and $t_0$ are rate constant, time, and starting point of the exfoliation process, respectively. The scattering curves show an intensity increase at low $q$, typical for randomly oriented scattering entities with a finite size, interacting with the light at distances above 30 nm ($q = 0.2$ nm$^{-1}$). Figure 5b shows the full SAXS curves during the exfoliation process. The slope of the SAXS curve in the range $0.2 < q < 0.8$ nm$^{-1}$ increased quickly in the first stages of the process, and then kept increasing more slowly over time. The inset in Figure 5b shows the slope of the linear fit of each scattering curve in the same $q$ range. The slope increased from 1.1 to 1.8, which is attributed to a change of crystal shape toward flatter discs. This observation is in accordance with the expected decrease of stack size of AUATO, ultimately into unilamellar sheets. The absence of pseudo-Bragg peaks after the decay of AUATO peaks indicates the absence of any internal crystallographic order, thus showing that the AUATO crystals were completely exfoliated into individual Ti$_{1.73}$O$_4$ nanosheets, stabilized by AUA acting as dispersant.

When the pH of the colloidal suspensions of isolated nanosheets and AUA was decreased to 4, a partial restacking of the nanocomposite was observed (see Figure S5 in the Supporting Information). In this case the protonation of AUA at low pH allowed the partial recovery of stable mutually attractive electrostatic interactions leading to the reassembly of the layered nanocomposite. The reversibility of the exfoliation process is related to the nature of the acid–base properties of the system. At even lower pH no restacking was observed, which is explained by partial protonation of the surface oxygen atoms of the nanosheets at pH < 3, generating positive surface charges that electrostatically repel protonated AUA.

### 2.3. Structural Changes upon Polymerization

Thermogravimetric analysis combined with differential scanning calorimetry (TGA-DSC) and elemental analysis (EA) experiments were performed to assess the degree of intercalation of AUA in the interlayer region. Both techniques relate the organic content with the interlayer spacing and thus with the arrangement of the AUA molecules. Figure 6 shows the TGA-DSC profiles of the amino acid (AUA) and the nanocomposite.
The partial intercalation of AUA is due to the charge density of the layered HTO host and steric hindrance effects. The 2D unit cell (3.786 × 2.996 = 11.34 Å²) of the titania nanosheets contains two [Ti_{0.37}O_{2}]^{12-} structural units with a combined net charge of −1.04[\ce{e-}]. This corresponds with a gross surface charge density of −4.6[\ce{e-}]-\text{nm}^{-2} on each side of the nanosheet (where [\ce{e-}] is the absolute elementary charge). The d spacing of 2.43 nm in the nanocomposite includes the titania layers (0.73 nm).[38] Thus, with an intergallery spacing of 1.7 nm and a fully stretched AUA chain of 1.85 nm length, a single layer of AUA molecules would be tilted under an angle of 67° with respect to the nanosheet plane. The −NH$_{3}^{+}$ head group of the AUA-H$^{+}$ chain has a diameter of 6.3 Å,[39] which corresponds with a charge density of +3.2[\ce{e-}]-\text{nm}^{-2}. Hence, the difference in charge density between the inorganic host planes and the AUA guest molecules is too large to be compensated in a single paraffinic layer, since the maximum proton substitution would only be 70% in that case. However, it has been reported that alkyl amines tend to form paraffin-like bilayers to overcome the steric and charge restrictions, including the hydrophobic–hydrophilic repulsion between the alkyl chain and the metal oxide surface.[39] An AUA bilayer with a 27° tilt would result in a theoretical degree of proton substitution of 70%, which agrees well with TGA and EA data.

The formation of nylon-11 was confirmed by diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). Figure 7a shows spectra of AUATO up to 250 °C. A comparison between the spectra of AUA and AUATO can be found in Figure S7a in the Supporting Information. The typical antisymmetric stretching vibration (γ$_{1}$) of the C=O bond shifted from 1635 cm$^{-1}$ for free AUA, with predominant deprotonated carboxylic group (COO$^{-}$), to 1704 cm$^{-1}$ in case the protonated form (COOH) was dominant. The shift to lower vibrational energy is attributed to the formation of intermolecular hydrogen bonds with the oxide layer.[146] The symmetric stretching vibration (γ$_{2}$) of C−O was present in both AUA and AUATO at 1390 cm$^{-1}$. The peak at 1492 cm$^{-1}$ could be ascribed to the symmetrical deformation vibration (δ$_{s}$) of the N−H bond in NH$_{3}^{+}$ and indicates that AUA in the interlayer was present in its protonated form. The absorption peaks at 420 cm$^{-1}$ correspond to internal vibrational modes of Ti−O in the TiO$_{2}$ octahedra.[146] An absorption peak emerged at 3300 cm$^{-1}$ upon heating beyond 150 °C, and became more pronounced from 190 °C. It is attributed to N−H stretching of an amide bond. Another indication for the formation of amide bonds was the shift of the N−H symmetrical deformation vibration at 1492 cm$^{-1}$ (amine) to 1543 cm$^{-1}$ (amide) overlapping with the N−H bending in the amide.[40] The typical antisymmetric stretching vibration (γ$_{2}$) of the C=O bond at 1704 cm$^{-1}$ and the symmetric stretching vibration (γ$_{3}$)
of C–O at 1395 cm\(^{-1}\) in protonated carboxylic acid (–COOH) disappeared, indicating the disappearance of free –COOH groups. Moreover, the stretching vibration of the C=O bond became more pronounced in the in situ formed nylon-11. The typical –CH\(_2\)– bending vibration peak at 1465 cm\(^{-1}\) becomes wider upon heating above 180 °C, indicating the formation of a melt.

The structure of AUATO was affected by the temperature. Figure 7b displays the (020) peak of AUATO. It corresponds with the correlation peak in Figure 2 at \(q = 2.5\) nm\(^{-1}\). The peak shifted from 3.7° to 4.5°, indicating that the metal oxide layers collapse upon heating. The overall shift occurring below 125 °C is understood in terms of a partial reorganization of AUA molecules between the layers, and is probably also related to loss of intergallery water. The peak intensity decreased above 125 °C and continued to shift to \(2\theta = 4.5\)°. The latter process was associated with the “melting” of organized AUA molecules and initiation of the polycondensation reaction. The formation of nylon-11 oligomers/polymer from AUA yields a soft plastic intercalation layer. The increasing stacking disorder of titanate layers can be seen by the broadening of the (020) peak.

2.4. Lubricative Properties

High-temperature PoD experiments were performed to relate the structural order and presence of soft layers within the nanocomposite to its mechanical properties. AUATO was applied as a solid lubricant in the form of a suspension onto the surface of a flattened steel bearing ball acting as a pin. The suspension was dried, rendering a film of uncompacted powder particles on the surface of the pin. The solid lubricant films were expected to have negligible cohesive interparticle forces and relatively low adhesion to the steel surface. The pin was then pressed onto the surface of a preheated steel disk at temperatures of 25–580 °C. The recorded friction forces were translated into a coefficient of friction (CoF). The CoF of AUATO was compared with the CoFs for unlubricated metal–metal contact and a film of graphite, which is considered as “state-of-the-art” lubricant. For the sake of clarity and simplicity, the data points of these references are represented in the form of colored bands. The experimentally determined values can be found in Figure S8, in the Supporting Information. The CoF of AUA was >0.3 below its melting point.

Figure 8 shows the CoF of protonated HTO precursor and AUATO films obtained from suspensions at different pH values. HTO exhibits a CoF in the range of the metal–metal contact up to 200 °C and a stable value above 0.55 up to 580 °C. The increase of the CoF between room temperature and 200 °C is attributed to loss of water from the interlayer gallery during heating (see TGA-DSC analysis of HTO in Figure S6 in the Supporting Information). The presence of water at lower temperatures probably acts, to a limited extent, as intraparticle lubricant facilitating the sliding of the sheets relative to one another. The high CoF values above 200 °C indicate strong electrostatic interactions between planes and H\(^+\) counter-ions after dehydration.

Upon suspending AUATO in water and changing the pH, the morphology of the stacked material was changed from strongly ordered at pH < 7.85 to a colloidal suspension of nanosheets and AUA at pH > 7.85. The resulting nanocomposite powder lubricant films are thus composed of a well-defined layered structure when deposited from suspensions at low pH, and a disordered amorphous morphology from suspensions at high pH. In the latter case, the rapid drying of the suspension on top of the bearing ball did not allow the nanosheets to restack in an orderly configuration, as can be seen by the lack of nanocomposite (001) reflections in the XRD patterns presented in Figure S9 in the Supporting Information. However, the behavior of the films as lubricant was comparable in all cases. At room temperature, intercalated AUA did not lead to good lubricative properties in AUATO. The CoF was even higher than for direct metal–metal contact, which indicates a hard material. The densely packed AUA chains, in combination with strong hydrogen bonds between titania planes and counter ions may explain this behavior. A CoF of ≈0.5 was recorded at all pH between 3 and 11. Upon heating, the increase of flexibility of the carbon chains and relative weakening of the hydrogen bonds at temperatures as low as 100 °C yielded values of CoF equal to or slightly lower than metal–metal contact. This hypothesis is supported by the changes in the crystallography and the chemistry of the nanocomposite as shown in Figure 8. A rapid drop in the CoF occurred above 200 °C for all three films irrespective of pH. The change was related to the melting of the freshly formed nylon-11 phase just below 200 °C,\(^{[41]}\) as shown in Figures 6 and 7. The structural order of the layered system at low pH did not influence the CoF of AUATO. The presence of molten nylon-11 between and around the layers lowered the friction, probably by facilitating the sliding of the layers (see Figures S10 and S11 in the Supporting Information). The stability of the oligomeric or polymeric network in and around the titania sheets was sufficient to decrease the overall friction force to CoF values of 0.07–0.10 for all films. Apparently, the degree of disorder between nanosheet planes does not influence the lubricative behavior. Such low CoF values are comparable with the performance of graphite films.
at temperatures of 400 °C and higher. Compared to graphite, the AUATO films were less stable with increasing temperature, with partial nylon-11 oxidation. Nevertheless, the lubricants are adapted to their intended application in fast and short forming processes, such as high temperature metal forging. Although care should be taken to extrapolate these findings to realistic industrial conditions, since the CoF experiments discussed here were performed under much lighter loads, further modification and optimization of this system may lead to an alternative high temperature solid lubricant.

3. Conclusion

A novel hybrid organic–inorganic nanocomposite was synthesized and used as potential solid lubricant at high temperatures. The nanocomposite was obtained by modifying a layered protonated titanium oxide phase via intercalation of 11-aminoundecanoic acid. The intercalation of AUO, driven by an acid–base reaction, was found to be a relatively fast process, in contrast to what is generally thought. Therefore, no time-consuming syntheses are needed for this kind of intercalation. The AUA molecules rapidly intercalated and rearranged into a stable paraffinic layer in between titanate layers. Exfoliation of the layered nanocomposite phase was possible by a pH change. The resulting AUATO nanocomposite structure has an inorganic layered structure reminiscent of well-performing solid lubricants such as graphite and metal dichalcogenides. The intercalated AUA molecules polymerized upon heating, generating oligomeric or polymeric chains of nylon-11, encapsulated in the intergallery spacing of the layered titanate. The presence of the amino acid did not intrinsically improve the lubricating properties of the nanocomposite. However, the softening of the in situ generated polyamide phase at temperatures above 200 °C resulted in low friction forces when applied as lubricant. The in situ formed internal lubricant decreased the CoF by a factor of 5 compared to the unmodified layered protonated titanium oxide ceramic phase. In short term friction experiments resembling fast lubrication processes such as hot metal forging, the performance of the nanocomposite was comparable to that of graphite. Similar modifications can also be applied to other intercalation compounds due to the zwiterionic behavior of the amino acid, thus allowing to develop the concept of soft nanocomposite materials for high temperature lubrication further.

4. Experimental Section

Protonated Layered Titanate (HTO) Synthesis: The layered titanate precursor KLTO was prepared by a flux method reported elsewhere.[8] Typically, a mixture of TiO2, K2CO3, Li2CO3, and MoO3 with a molar ratio of 1.73:1.67:0.13:1.27 was heated in a platinum crucible to 1150 °C at a rate of 3 °C min⁻¹, held at that temperature for 30 min, and cooled down to 950 °C at a rate of 0.1 °C min⁻¹. The mixture was allowed to cool further to room temperature at 5 °C min⁻¹. The KLTO powder was once washed in 500 mL demineralized water to remove the flux material K2MoO4. The crystals were then dispersed in a 2 mol dm⁻³ HNO3 solution (250 mL) at room temperature and stirred in order to protonate the layered titanate by cation exchange. The acid solution was renewed daily by decantation. After treatment for 3 d the crystals were recovered by filtration, washed with abundant demineralized water, and dried in air to obtain HTO powder. HTO powder was used for the in situ SAXS experiments.

AUATO Nanocomposite Synthesis: Typically, 4 g of AUA was dissolved in 500 mL demineralized water and transferred to a round bottom flask. The pH of the solution was adjusted to pH 7, below the IEP of the amino acid at pH 7.85, to avoid the presence of deprotonated carboxyl groups. 1 g of HTO powder was added and the mixture was stirred for 20 min at 80 °C. The product was recovered by filtration and thoroughly washed with demineralized water. The powder was dried in air to obtain the nanocomposite AUATO.

Characterization: SAXS was performed to monitor the kinetics and mechanism of intercalation of AUO in between the layers of the HTO host to form AUATO and the subsequent exfoliation process. The syntheses were performed at controlled temperatures in round bottom flasks placed in an oil bath. For the in situ SAXS experiments involving the formation of AUATO, 100 mg of HTO was suspended in 50 mL demineralized water. The pH of the suspension medium was set slightly below the IEP of AUO. Then, 400 mg of AUO powder was added to the HTO suspension by fast injection. In the exfoliation experiments, the exfoliation of AUATO nanocomposite into colloidal suspensions of nanosheets was achieved by addition of NaOH (aq) (3 mol dm⁻³) to increase the pH to 11.

The suspension was continuously pumped to a homemade reaction chamber closed by Kapton foil walls, to allow the X-ray beam to cross the sample and be recorded by the detector. The characterization was carried out using synchrotron radiation at the Dutch–Belgian beamline, DUBBLE BM-26B, in the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.[38] The X-ray beam was focused at the corner of a 2D Pilatus 1M detector to maximize the range of accessible scattering vector values q. The beam energy was set to 12 keV (λ = 0.103 nm). The samples were placed at a distance of 1.3 m from the detector, and the intensity was measured in the range 0.18 < q < 0.785 nm⁻¹. The interlayer distances in the nanocomposite, d, were calculated from correlation peaks using Bragg’s law, so that d = 2π/q.

The measurement by powder XRD at room temperature was conducted with a Bruker D2 Phaser (Cu Kα radiation λ = 0.15405 nm). The measurement by XRD at different temperatures was conducted with an Empyrean diffractometer (PANalytical) using Cu-Kα irradiation (λ = 1.5418 Å) and recorded with a 1D PIXcel detector. The sample was placed in an Anton Paar TTK 450 chamber and heated from 25 to 250 °C with an increase of 5 °C per step. The patterns were analyzed using the HighScore Plus software package.[38] Scanning electron microscopy (SEM) was performed with a JEOl JSM-6490 operating at 15 kV. TGA-DSC was performed in Pt cups using a Netzsch STA 449 F3 at a constant heating rate of 5 °C min⁻¹ in technical air (N2/O2 = 80/20). EA was performed with a Flash 2000 CHNS-O Elemental Analyzer (Thermo Scientific) to determine the presence and quantity of organic species in the interlayer. Fourier-transformed infrared spectroscopy (FTIR) was carried out with a Bruker Tensor 27 FTIR equipped with a liquid nitrogen cooled detector D315/6 LN. UV–vis spectra of samples were recorded with a Cary 50 UV–vis spectrophotometer in transmission mode. The original suspensions were diluted to obtain an appropriate range of absorbances.

Friction Coefficient Experiments: The lubricative properties of the nanocomposite films were assessed by the use of a high-temperature PoD tribometer of CSM Instruments. The pins consisted of flattened steel bearing balls (10 mm diameter, SKF). The surface of the steel pin was 27 mm², giving a surface concentration of lubricant of 75 µg mm⁻² (or 75 g m⁻³). The applied load was 10 N, resulting in an effective contact pressure of 370 kPa. The rotating disk was made of EN 10278 steel and was polished, as well as the flattened bearing balls, with SiC paper with a maximum mesh of 2000 and diamond paste of 3 µm particle size. The calculated arithmetic roughness of the steel surfaces was Rₐ = 0.90 ± 0.25 µm. The measurements consisted of recording the friction force for a maximum of one rotation of the pin over the disc, at a velocity of 1 mm s⁻¹, to mimic short term lubrication performance such as in high temperature metal forming processes. It is emphasized that the actual loads in industrial forming and forging processes are
typically much higher. Data were collected from the first data points after contact between the pin/lubricant and the disc at a preset temperature varying from 25 to 580 °C. The CoF was averaged after a minimum of five repetitions. The typical time scale of one experiment was up to 30 s since the powder films were susceptible to be worn out due to the limited testing surface. The friction force of a graphite suspension was measured as reference. The graphite powder (Sigma-Aldrich, 99.99%) was milled on a roller bench with zirconium oxide beads (ϕ = 1 mm) for 48 h and applied to the steel pins in an identical way to the AUATO suspensions. The CoF was determined from the experimental data using the equation

\[ F_r = \mu N \]  

(2)

where \( F_r \) is the resistive force of friction, \( \mu \) is the CoF, and \( N \) is the normal force (or applied load).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
friction coefficient, hybrid materials, layered oxide, lubricants, titanium dioxide

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