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Exfoliation of layered rutile and perovskite tungstates

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Received (in Columbia, MO, USA) 7th November 2001, Accepted 21st December 2001
First published as an Advance Article on the web 4th March 2002

The layered trirutile phases $HMWO_6$ (M = Nb, Ta) and the layered perovskite $H_2W_2O_7$ (synthesized by acid leaching of $Bi_2W_2O_9$) were exfoliated into nanoscale colloids by reaction with quaternary ammonium hydroxides.

Layered solid acids, including α-$Zr(HPO_4)_2\cdot H_2O$,[1] $HTiNbO_5$,[2] and layered perovskites such as the Dion–Jacobson phases $HCa_2Nb_3O_{10}$ and $HLaNb_2O_7$,[3] are well known to exfoliate into nanoscale colloidal sheets when reacted with a bulky organic base. These sheets can often be used as building blocks for self-assembled thin films[1–4] and nanostructured organic/inorganic hybrid materials.[5] In order to exfoliate a layered solid acid, the interlayer protons must be amenable to acid–base chemistry. Among layered transition metal oxides, titanates are less acidic than niobates and tantalates based on periodic electronegativity trends.[6,7] This suggests that Group 6 cations such as W^{6+}, which are more acidic than those of Group 4 and Group 5, should make layered solid acids even more amenable to acid/base exfoliation.

We report here the first examples of tungsten-based colloidal sheets derived from layered solid acids, including the layered trirutile phases $HMWO_6$ (M = Nb, Ta)[8] and the new layered perovskite $H_2W_2O_7$, prepared by acid leaching the interlayer bismuth oxide from $Bi_2W_2O_9$,[9] which is related to the Aurivillius family of layered perovskites.[10] As bulk solids, the trirutile tungstates possess interesting luminescence and non-linear optical behavior,[11] and layered perovskite and distorted ReO_3-type tungstates are well known as ferroelectrics and photochromic materials.[12]

$LiMWO_6$ (M = Nb, Ta) are layered rutile phases that contain lithium cations between the trirutile layers,[13] and the proton forms are strong acids that intercalate a wide range of organic bases, including pyridine (pK_a = 5.25) and quinoxaline (pK_a = 0.56).[8] $LiMWO_6$ and $HMWO_6$ were synthesized as previously reported,[8,13] and the X-ray diffraction (XRD) patterns for all of the phases matched those reported in the literature. $HMWO_6$ was reacted with a 25-fold molar excess of tetra(*n*-butyl)ammonium hydroxide (TBA^+OH^-) to form $TBA_xH_{1-x}MWO_6$, and TEM analysis confirms that colloidal sheets were formed (Fig. 1(a)).[14] The low and uniform contrast in the TEM micrograph in Fig. 1(a), in conjunction with AFM height scans, suggests that the colloidal sheets are unilamellar.

When electrostatically adsorbed to a Si/SiO_2/PDDA [PDDA = poly(diallyldimethylammonium chloride)] surface (see refs. [1–4]), surfaces similar to those shown in Fig. 1(b) are obtained. Fig. 1(b) shows an AFM image of a monolayer of $TBA_xH_{1-x}TaWO_6$ sheets. Surface coverage is relatively high, and little overlap of sheets is observed. Thus, this well-established exfoliation and layer-by-layer assembly technique can also be applied to the trirutile phases, although the monolayers are not as uniformly tiled as those obtained from some layered perovskite precursors.

Interestingly, when adsorbed to a polycationic surface, the $TBA_xH_{1-x}TaWO_6$ sheets showed some tendency toward curling. (Interestingly, no curling was observed in the TEM analysis.) This behavior has previously been observed for the $H_xK_{4-x}Nb_6O_{17}$ system,[15] as well as for the some members of the Ruddlesden–Popper family of layered perovskites.[7] The curled sheets in Fig. 1(b) do not appear to form tight scrolls, but their curling suggests that it may be possible to more carefully control the morphology of the colloids by optimizing the exfoliation and layer-by-layer assembly conditions.

In addition to the trirutile phases, we were also able to prepare tungsten-based lamellar colloids by using a novel new layered perovskite. Ion-exchangeable layered perovskites predominantly contain metal–oxygen octahedra that are limited to Group 4 and Group 5 cations. An alternate approach is to begin with an Aurivillius phase (an intergrowth of perovskite and bismuth oxide),[10] which is more covalent and can stabilize highly charged cations. Recently, Sugahara and coworkers reported a reaction that converts an Aurivillius phase into the proton form of a Ruddlesden–Popper phase by leaching the interlayer bismuth oxide with acid.[16] By starting with the double-layer Aurivillius-related phase $Bi_2W_2O_9$ (which contains vacant A-sites in the perovskite block),[9] we were able to prepare a new A-site defective Ruddlesden–Popper solid acid, $H_2W_2O_7$, by a similar acid leaching reaction.

$Bi_2W_2O_9$ (a = 5.440, b = 5.413, c = 23.740, from ref. 9) was synthesized by heating stoichiometric amounts of Bi_2O_3 and WO_3 to 800 °C for 16 h, similar to literature methods,[9] and the XRD pattern[17] (Fig. 2(a)) matches previously published data. $Bi_2W_2O_9$ was reacted with 6 M HCl for 3 days to replace $Bi_2O_2^{2+}$ with $2H^+$ according to the reaction shown in the inset of Fig. 2. (Energy-dispersive X-ray analysis (EDS) indicates that *ca.* 10% of the Bi remains after the acid leaching reaction, which may be a result of either incomplete exchange or some disorder of the Bi among the interlayer and vacant A-sites in the parent $Bi_2W_2O_9$ phase.) The XRD pattern for $H_2W_2O_7$, shown in Fig. 2(b), indexes to an orthorhombic unit cell with a = 5.441(2), b = 5.415(2) and c = 18.81(1). A simulated powder pattern showed reasonable agreement in peak intensities with the pattern shown in Fig. 2, but the quality of the data did not permit refinement of the structure. The peaks are broad, which is consistent with the structural disorder that is introduced upon

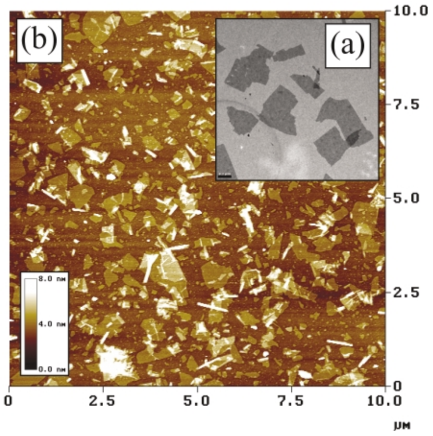

Fig. 1 A TEM micrograph of $TBA_xH_{1-x}NbWO_6$ sheets is shown in (a) and an AFM image of $TBA_xH_{1-x}TaWO_6$ sheets on a Si/SiO_2/PDDA surface is shown in (b); the scalebar in (a) is 200 nm.

DOI: 10.1039/b110220f

replacing the large interlayer $Bi_2O_2^{2+}$ with H^+. A few sharp peaks are also present in the XRD pattern, and these can be indexed to WO_3. Thus, it is possible that some decomposition occurred. However, the XRD pattern in Fig. 2(b) clearly resembles that of a lamellar solid with a layer spacing of 18.81 Å, which is consistent with the expected thickness of a double-layer perovskite with protons between the layers. Upon replacing the interlayer $Bi_2O_2^{2+}$ with H^+, the *c* axis contracted by 4.93 Å, which is consistent with both the expected decrease as well as the observed decrease for acid leaching $Bi_2O_2^{2+}$ from analogous Aurivillius niobates,[16a] tantalates,[16b] and manganates.[18] Interestingly, attempts to form the single-layer Ruddlesden–Popper phase H_2WO_4 from the Aurivillius phase Bi_2WO_6 yielded a product having the predicted XRD pattern, but the similarity in structure to a naturally occurring polymorph, $WO_3{\cdot}H_2O$ (tungstite), precluded unambiguous indexing. (Another form of $H_2W_2O_7$, $WO_3{\cdot}0.5H_2O$, has also been reported previously,[19] although there is no evidence for this polymorph in the XRD data.)

Upon reaction with a 25-fold molar excess of tetramethylammonium hydroxide (TMA^+OH^-), unilamellar colloids of $TMA_xH_{2-x}W_2O_7$ are formed. (We were unable to exfoliate $H_2W_2O_7$ using the larger TBA^+ cation.) The TEM micrograph in Fig. 3 shows that the $TMA_xH_{2-x}W_2O_7$ sheets appear similar to the sheets of $TBA_xH_{1-x}TaWO_6$ shown in Fig. 1(a). Most of the sheets in Fig. 3 are of uniform contrast and likely unilamellar, although some sheets may exist as bilayers or trilayers. In contrast to the $TBA_xH_{1-x}TaWO_6$ sheets, which have well-defined edges that result from cleavage along particular crystallographic planes of the parent crystallites, the sheets of $TMA_xH_{2-x}W_2O_7$ are less uniform and not as crystalline, which likely results from the acid leaching step. (TEM analysis indicates that some of the $H_2W_2O_7$ crystallites also exist as thin sheets, but most of the sample prior to exfoliation consisted of significantly thicker particles.) Unfortunately, attempts to adsorb $TMA_xH_{2-x}W_2O_7$ sheets to a polycationic surface failed, presumably because of the difficulty of displacing the TMA^+ cation for a surface-bound ammonium group. (Note that TMA^+ has a higher charge density than TBA^+.) Spin-casting these lamellar colloids could lead to oriented films of $H_2W_2O_7$, which could provide a convenient route to photochromic WO_3 thin films, since $H_2W_2O_7$ converts cleanly to WO_3 at 300 °C.

We have demonstrated that the simple acid/base exfoliation strategy can be extended to the layered rutile tungstates $HMWO_6$ (M = Nb, Ta) and the novel new A-site defective layered perovskite $H_2W_2O_7$, synthesized by acid leaching the interlayer $Bi_2O_2^{2+}$ from the Aurivillius phase $Bi_2W_2O_9$. The resulting lamellar colloids could provide a convenient route to thin films and nanostructured materials based on tungsten oxides, which are known to possess a variety of interesting properties.

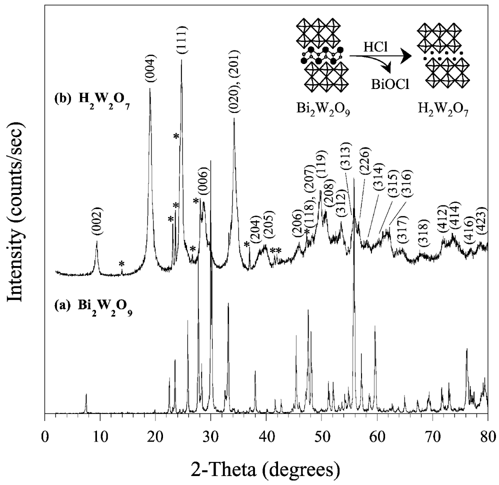

Fig. 2 Powder X-ray diffraction patterns for (a) $Bi_2W_2O_9$ and (b) $H_2W_2O_7$. Reflections from WO_3 impurities in (b) are highlighted with an asterisk (*). The acid-leaching reaction is shown schematically in the inset.

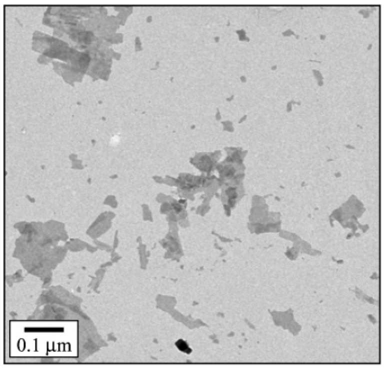

Fig. 3 TEM micrograph of $TBA_xH_{2-x}W_2O_7$ sheets.

This work was supported by National Science Foundation grant CHE-0095394. This material is based upon work supported under a National Science Foundation Graduate Fellowship.

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