Exfoliation of layered rutile and perovskite tungstates

Raymond E. Schaak and Thomas E. Mallouk*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA.
E-mail: tom@chem.psu.edu

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 HMWO₆ (M = Nb, Ta) and the layered perovskite H₂W₂O₇ (synthesized by acid leaching of Bi₂W₂O₉) were exfoliated into nanoscale colloids by reaction with quaternary ammonium hydroxides.

Layered solid acids, including α-Zr(HPO₄)₂·H₂O, HTiNbO₅ and layered perovskites such as the Dion-Jacobson phases H₂Ca₂NbO₄ and HLaNb₂O₆, 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 and nanostructured organic/inorganic hybrid materials. 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. This suggests that Group 6 cations such as W⁶⁺, which interlayer protons must be amenable to acid-base chemistry. These sheets can often be used as building blocks for self-assembled thin films and nanostructured organic/inorganic hybrid materials.

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 W⁶⁺, which contains vacant A-sites in the parent 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 coherent 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.15 By starting with the double-layer Aurivillius-related phase Bi₂W₂O₉ (which contains vacant A-sites in the perovskite block),9 we were able to prepare a new A-site defective Ruddlesden–Popper solid acid, H₂W₂O₇, by a similar acid leaching reaction.

Bi₂W₂O₉ (a = 5.440, b = 5.413, c = 23.740, from ref. 9) was synthesized by heating stoichiometric amounts of Bi₂O₃ and WO₃ to 800 °C for 16 h, similar to literature methods,15 and the XRD pattern 17 (Fig. 2(a)) matches previously published data. Bi₂W₂O₉ was reacted with 6 M HCl for 3 days to replace Bi⁶⁺ 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 Bi₂W₂O₉ phase.) The XRD pattern for H₂W₂O₇, shown in Fig. 2(b), indexes to an orthorhombic unit cell with a = 5.441(2), b = 5.415(2) and c = 18.811(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 the Ruddlesden–Popper family of layered perovskites.7 The curved 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 coherent 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.15 By starting with the double-layer Aurivillius-related phase Bi₂W₂O₉ (which contains vacant A-sites in the perovskite block),9 we were able to prepare a new A-site defective Ruddlesden–Popper solid acid, H₂W₂O₇, by a similar acid leaching reaction.

Bi₂W₂O₉ (a = 5.440, b = 5.413, c = 23.740, from ref. 9) was synthesized by heating stoichiometric amounts of Bi₂O₃ and WO₃ to 800 °C for 16 h, similar to literature methods,15 and the XRD pattern 17 (Fig. 2(a)) matches previously published data. Bi₂W₂O₉ was reacted with 6 M HCl for 3 days to replace Bi⁶⁺ 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 Bi₂W₂O₉ phase.) The XRD pattern for H₂W₂O₇, shown in Fig. 2(b), indexes to an orthorhombic unit cell with a = 5.441(2), b = 5.415(2) and c = 18.811(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](image-url) A TEM micrograph of TBA₄H₁₋ₓNbWO₆ sheets is shown in (a) and an AFM image of TBA₄H₁₋ₓTaWO₆ sheets on a Si/SiO₂/PDDA surface is shown in (b); the scalebar in (a) is 200 nm.
replacing the large interlayer Bi$_2$O$_2$$_2$ with H$^+$. A few sharp peaks are also present in the XRD pattern, and these can be indexed to WO$_3$. Thus, it is possible that some decomposition occurred. However, the XRD pattern in Fig. 2(b) clearly resembles that of a lamellar solid with a layer spacing of 18.81 Å, which is consistent with the expected thickness of a double-layer perovskite with protons between the layers. Upon replacing the interlayer Bi$_2$O$_2$$_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$_2$O$_2$$_2$ from analogous Aurivillius niobates, tantalates, and manganates. Interestingly, attempts to form the single-layer Ruddlesden–Popper phase H$_2$WO$_7$ from the Aurivillius phase Bi$_2$WO$_7$ yielded a product having the predicted XRD pattern, but the similarity in structure to a naturally occurring polymorph, WO$_3$H$_2$O (tungstite), precluded unambiguous indexing. (Another form of H$_2$WO$_7$, WO$_3$H, has also been reported previously, 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 polycationic surface failed, presumably because of the difficulty in adsorbing TMA$^+$ cations.) The TEM micrograph in Fig. 3 shows that the TMA$^+$ sheets in Fig. 3 are of uniform contrast and likely unilamellar, although some sheets may exist as bilayers or triple layers. In contrast to the TBA$^+$ sheets, which have well-defined edges that result from cleavage along particular crystallographic planes of the parent crystallites, the sheets of TMA$^+$-W$_2$O$_7$ are less uniform and not as crystalline, which likely results from the acid leaching step. (TEM analysis indicates that some of the H$_2$WO$_7$ crystallites also exist as thin sheets, but most of the sample prior to exfoliation consisted of significantly thicker particles.) Unfortunately, attempts to adsorb TMA$^+$-W$_2$O$_7$ sheets to a polycrystalline 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$_2$WO$_7$, which could provide a convenient route to photochromic WO$_3$ thin films, since H$_2$WO$_7$ 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 lanthanum manganates.18 Interestingly, attempts to adsorb TMA$^+$ onto H$_2$WO$_7$ using the larger TBA$^+$ cation.) The TEM micrograph of TBA$^+$ shown in Fig. 3(a). Most of the sheets in Fig. 3 are of uniform contrast and likely unilamellar, although some sheets may exist as bilayers or triayers. In contrast to the TBA$^+$ sheets, which have well-defined edges that result from cleavage along particular crystallographic planes of the parent crystallites, the sheets of TMA$^+$-W$_2$O$_7$ are less uniform and not as crystalline, which likely results from the acid leaching step. (TEM analysis indicates that some of the H$_2$WO$_7$ crystallites also exist as thin sheets, but most of the sample prior to exfoliation consisted of significantly thicker particles.) Unfortunately, attempts to adsorb TMA$^+$ sheets to a polycrystalline 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$_2$WO$_7$, which could provide a convenient route to photochromic WO$_3$ thin films, since H$_2$WO$_7$ 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$_2$WO$_7$, synthesized by acid leaching the interlayer Bi$_2$O$_2$$_2$ from the Aurivillius phase Bi$_2$WO$_7$. 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.

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.

Notes and references


10 (a) B. Aurivillius, Ark. Kemi, 1949, 1, 463; (b) B. Aurivillius, Ark. Kemi, 1949, 1, 499.


14 Electron micrographs were obtained at the Electron Microscope Facility for the Life Sciences in the Biotechnology Institute at the Pennsylvania State University.


17 X-Ray diffraction patterns were obtained on a Philips X-Pert MPD diffractometer using monochromatized Cu-Kα (λ = 1.5418 Å) radiation.
