Chemically exfoliated nanosheets of $\beta$-Bi$_2$O$_3$

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Abstract
Exploring two dimensional (2D) materials is important for further developing the field of quantum materials. However, progress in 2D material development is limited by difficulties with their production. Specifically, freestanding 2D materials with bulk non-layered structures remain particularly challenging to prepare. Traditionally, chemical or mechanical exfoliation is employed for obtaining freestanding 2D materials, but these methods typically require layered starting materials. Here we put forth a method for obtaining thin layers of $\beta$-Bi$_2$O$_3$, which has a three-dimensional covalent structure, by using chemical exfoliation. In this research, Na$_3$Ni$_2$BiO$_6$ was exfoliated with acid and water to obtain $\beta$-Bi$_2$O$_3$ nanosheets less than 10 nm in height and over 1 $\mu$m in lateral size. Our results open the possibility for further exploring $\beta$-Bi$_2$O$_3$ nanosheets to determine whether their properties change from the bulk to the nanoscale. Furthermore, this research may facilitate further progress in obtaining nanosheets of non-layered bulk materials using chemical exfoliation.

1. Introduction
Delving into the world of quantum materials opens up the possibility for exploring novel properties that cannot be predicted by the laws of classical mechanics. Because quantum confinement dictates behavior, the advent of two dimensional (2D) materials introduced a subclass of quantum materials, which can lead to distinct electronic properties not seen in the bulk counterpart [1]. Such is the case with MoS$_2$, which famously transitions from an indirect to direct bandgap semiconductor between its bulk and monolayer form, respectively [2]. Thus, there is much interest in exploring other 2D materials to add to this remarkable field.

Currently, 2D materials are limited by the challenge of preparing them, as evidenced by far fewer materials having been exfoliated down to the 2D limit than are predicted to be exfoliable [3]. Top-down methods, including scotch tape and chemical exfoliation, remain common for obtaining free-standing 2D sheets; however, these methods require layered materials for proper exfoliation. To prepare non-layered 2D materials, bottom-up methods—such as chemical vapour deposition or molecular beam epitaxy—may be employed, though substrate interactions with the non-freestanding sheets may introduce strain and alter the electronic properties of the material [4].

Due to these limitations, there is an interest in using top-down exfoliation for preparing 2D materials that do not have a bulk layered structure. A few methods have been employed for exfoliating non-layered materials, including electrostatic-driven exfoliation, amphiphile-assisted exfoliation, and liquid-phase exfoliation from a lamellar hybrid intermediate [5–7]. One example of the latter method is the liquid-exfoliation of a layered structure consisting of alternating slabs of CoSe$_2$ and protonated amine, to form CoSe$_2$ nanosheets within its 3D pyrite structure [8–10]. Another approach is to start with a layered structure consisting of the desired final elements and use exfoliation to not only form thin sheets but also remove the undesired elements. For example, NaCrS$_2$, which consists of alternating layers of [CrS$_2$]$^-$ and Na$^+$, can be exfoliated to form CrS$_2$$_{2-x}$ sheets. During exfoliation, the Na is leached out of the structure,
leaving behind only the desired Cr and S. Such a method can distort the perfect layered structure. Upon deintercalating Na from NaCrS$_2$, Song et al reported partial Cr migration out-of-plane to fill the Na$^+$ vacancies [11]. The resulting nanosheets consequently adopt the 3D structure of defective CrS rather than [CrS$_2$]$^-$ layers.

One interesting material to study thin sheets of is Bi$_2$O$_3$, which has four main polymorphs (figure 1): monoclinic $\alpha$-Bi$_2$O$_3$ [12], tetragonal $\beta$-Bi$_2$O$_3$ [13], body-centered cubic $\gamma$-Bi$_2$O$_3$ [14] and face-centered cubic $\delta$-Bi$_2$O$_3$ [15]. On the macroscale, the $\alpha$ structure is the most stable phase at standard temperature and pressure (STP), whereas the $\delta$ phase is a high-temperature stable phase and the $\beta$ and $\gamma$ phases are metastable [16]. This does not remain true at the nanoscale, where the $\beta$-phase becomes the most stable phase at STP [17, 18]. Each of the different polymorphs displays unique properties, diversifying the fields to which Bi$_2$O$_3$ contributes. Such areas include biomedical, environmental, and electrochemical, where they have influenced research in medical imaging, gas sensors, and fuel cells, to name a few [19–21]. $\beta$-Bi$_2$O$_3$ is particularly established as a photocatalyst, in which it has proven effective for decomposing waste-water toxins, such as dyes and medicine [22–25]. Much of this may be attributed to its direct bandgap of 2.55 eV, which enables visible light absorption [26]. The increased surface-area-to-volume ratio inherent in 2D materials typically improves their catalytic activity compared to that of their bulk counterparts [27, 28]. Previous studies on the photocatalytic activity of $\beta$-Bi$_2$O$_3$ nanosheets yielded promising results [29–31]. Nevertheless, the number of studies conducted on $\beta$-Bi$_2$O$_3$ nanosheets remains limited, possibly because $\beta$-Bi$_2$O$_3$—as well as all other known polymorphs of Bi$_2$O$_3$—is non-layered, impeding the preparation of these nanosheets. Previous methods for obtaining $\beta$-Bi$_2$O$_3$ nanosheets were bottom-down, consisting of an initial preparation of Bi$_2$O$_3$CO$_3$, followed by calcination at $T > 300$ °C [29, 31]. Not only does this complicate the procedure, but such high temperatures can be damaging to the sheets, inducing the formation of holes. Furthermore, at temperatures slightly higher than that required for sufficient $\beta$-Bi$_2$O$_3$ formation, the $\alpha$-phase begins to form [29].

In this paper, we propose a method for obtaining $\beta$-Bi$_2$O$_3$ nanosheets from the metastable layered structure, NaNi$_2$BiO$_6$, which consists of layers of nickel(II)-bismuth(V) honeycomb lattice, separated by layers of Na-ions [32]. Seibel et al showed that by stirring the bulk material in a 6 M solution of Br$_2$/acetonitrile (ACN), they could remove about 2/3 of the Na-ions, to form NaNi$_2$BiO$_6$·$\delta$, where $\delta$ is 0.34 [33]. Furthermore, after leaving the partially deintercalated material in the laboratory air, moisture from the environment hydrated the material to form NaNi$_2$BiO$_6$·$\delta$·1.7 H$_2$O, increasing the interlayer spacing to 7.1 Å. They modelled the deintercalated material to have a slight defect structure, wherein 8% of the Bi migrates out-of-plane. Thus, NaNi$_2$BiO$_6$ is a promising material to chemically exfoliate since, upon Na$^+$ deintercalation, the bismuth ions can migrate to the newly vacant intralayer sites. This is similar to what Song et al observed while exfoliating NaCrS$_2$, as mentioned above [11]. As the exfoliation of NaNi$_2$BiO$_6$·$\delta$·1.7 H$_2$O proceeds, the bismuth ions should fully leave the honeycomb lattice. Furthermore, through chemical treatment in ambient air, the high oxidation state should become unstable, and the bismuth will be reduced to Bi$^{3+}$, causing Bi$_2$O$_3$ formation. Meanwhile, the nickel should leave the structure as Ni$^{2+}$ and remain in solution [17, 18].

2. Experimental

2.1. Preparation of Na$_3$Ni$_2$BiO$_6$ and Na$_3$Ni$_2$BiO$_6$·$\delta$·1.7 H$_2$O

Both polycrystalline Na$_3$Ni$_2$BiO$_6$ and Na$_3$Ni$_2$BiO$_6$·$\delta$·1.7 H$_2$O were prepared via the synthesis reported by Seibel et al. To synthesize the former, NiO (BeanTown Chemical, 99% trace metal basis), Na$_2$CO$_3$ (Sigma-Aldrich, ≥99.5%), and NaBiO$_3$ (Acros Organic$^{\text{TM}}$, ACS reagent) were pressed into a pellet and heated under O$_2$ in a flow furnace at 700 °C for 8 h. After cooling, the pellet was ground and reheated to
Figure 2. Schematic of exfoliation procedure from Na$_3$Ni$_2$BiO$_6$ to β-Bi$_2$O$_3$. The first structure shows the structure of Na$_3$Ni$_2$BiO$_6$ with alternating layers of sodium ions and the Ni$_2$BiO$_6$ honeycomb lattice. The middle structure, NaNi$_2$BiO$_6$−δ, models the partial migration of Bi in the c-direction, which occurs with the partial removal of Na. The white atoms represent vacancies. The final structures are Bi$_2$O$_3$ sheets, formed by treating the NaNi$_2$BiO$_6$−δ hydrate with acetic acid and exfoliating the resulting product in water.

750 °C for 12 h. The latter was prepared by stirring the obtained powder in 6 M Br$_2$ (Sigma-Aldrich®, reagent grade) in acetonitrile [32, 33].

2.2. Preparation of β-Bi$_2$O$_3$

The NaNi$_2$BiO$_6$−δ · 1.7 H$_2$O powder was shaken at 300 rpm in a solution of 0.1 M acetic acid for 24 h. The ratio of powder to liquid was 1 mg: 2 ml. The powder was washed three times with water by centrifuging at 10 000 rpm and replacing the supernatant. The resulting powder was then stored in water on a shaker at 300 rpm. After at least three days, the suspension was sonicated for 5 min with 70% power and centrifuged at 1000 rpm to obtain thin Bi$_2$O$_3$ sheets in the supernatant.

2.3. Materials characterization

The bulk powder was analyzed with powder x-ray diffraction (PXRD) using a STOE STADI P x-ray diffractometer (Mo K$_\alpha_1$ radiation, Ge monochromator, Single-Mythen detector, Debye-Scherrer geometry). The bulk powder was also analyzed with energy dispersive x-ray diffraction (EDX) using a Quanta 200 FEG Environmental-SEM. The resulting nanosheets were characterized with transmission electron microscopy (TEM) with EDX attachment, using a Talos™ F200X Scanning/Transmission Electron Microscope (S/TEM), as well as atomic resolution scanning transmission microscopy (ARSTEM) using a Titan Cubed Themis 300 double Cs-corrected S/TEM. EDX was used for elemental analysis, since it is capable of analyzing small quantities of material. Furthermore, because EDX works in conjunction with the TEM, sheets can be easily located prior to analysis. Other techniques, (i.e. Raman, XPS, XRD, etc) that are often used to characterize crystals, could not be feasibly employed for this project, since we did not obtain enough material. ImageJ was used to calculate distances in the acquired selected area electron diffraction (SAED) and ARSTEM images [34]. Simulated (hkl) d-spacings were found using the CrystalMaker® software Ltd SingleCrystal™ (www.crystalmaker.com), while VESTA was used to determine distances between atom planes in the structure files [35]. All crystal structures were obtained from the Inorganic Crystal Structure Database (ICSD) [36]. Fast Fourier Transform (FFT) images were created with DigitalMicrograph®, and distances in both the FFT and ARSTEM images were measured using the DigitalMicrograph® software. The nanosheets’ thicknesses were determined using a Bruker NanoMan atomic force microscope (AFM). Sheet height was measured from AFM images using Gwyddion [37].

3. Results and discussion

The layered Na$_3$Ni$_2$BiO$_6$ was stirred in 6 M Br$_2$ in ACN to partially remove the sodium atoms as first reported by Seibel et al [33] The ensuing hydrate was then treated with 0.1 M acetic acid in a ratio of 1 mg: 2 ml sample to solution. A more detailed procedure can be found in the Experimental section. Figure 2 shows a schematic of the overall experimental process, including the partial migration of Bi in the c-direction (middle structure). The process did not yield a significant structure change (as noted by figure 3), though. EDX results, in figure S1, show a significant increase in oxygen content. Placing the charged species in a polar environment, i.e. water, facilitates exfoliation.

Figure 4 shows an STEM image of a thin sheet as well as EDX mapping that shows the homogeneous presence of bismuth and oxygen. Quantification analysis indicate that the sheets contain trace amounts of Na
and Ni; between 0–5 at% Na and 1–3 at% Ni remain in each sample. After confirming with EDX that we had prepared bismuth oxide sheets, we used a combination of SAED and ARSTEM to ascertain the crystal structure. The SAED for a sheet was matched to the (001) plane of $\beta$-Bi$_2$O$_3$ (figures 4(D) and (E)). Of the four polymorphs noted in figure 1, the $\beta$, $\gamma$, and $\delta$ phases have a square diffraction pattern in that zone. Although the d-spacings for each of the remaining polymorphs are similar, the SAED contains extra, less intense peaks that can only be found in the simulated pattern of the $\beta$ phase. Figure 4(F) shows the comparisons for (hkl) = (260), (040), (310), (220), wherein error differences are less than 5% for all indexed values.

Figure 5 shows TEM images of the sheets, which the high transparency indicates are several nm thin. The insets are SAED patterns showing high crystallinity with a square diffraction pattern. The d-spacing of selected reflections for each pattern are cited in table 1 showing the specific values for (hkl) = (260), (040),
Figure 5. (A)–(D) TEM images showing thin sheets. Insets are electron diffraction images showing a square lattice that best matches $\beta$-Bi$_2$O$_3$. The circle marks the (040) reflection.

Table 1. Table of d-spacing for (hkl) = (260), (040), (310), (220). Letters correspond to the images in figure 5.

| (hkl) | A    | B    | C    | D    |
|------|------|------|------|------|
| (260) | 1.24 | 1.22 | 1.16 | 1.17 |
| (040) | 1.94 | 1.93 | 1.84 | 1.85 |
| (310) | 2.45 | 2.42 | 2.31 | 2.34 |
| (220) | 2.73 | 2.72 | 2.60 | 2.62 |

(310), (220). As can be concluded from both figure 5 and table 1, the nanosheets can be consistently indexed with the $\beta$-phase. While all the samples in figure 5 were prepared at room temperature, sheets heated to 200 °C in an Argon glovebox also showed this diffraction pattern, suggesting that this phase is stable well above room temperature. To further confirm the $\beta$-phase, ARSTEM images were taken of some of the Bi$_2$O$_3$ samples, including the sheet shown in figure 6(A). The ARSTEM image, presented in figure 6(B), shows high-quality sheets with a distinct repeating square lattice of Bi atoms. The oxygen atoms are absent from the image because of the element’s small atomic number. Additionally, EDX results found up to 5 at% Ni remained in the sheets, also not visible in the ARSTEM images. The distances between atoms, labeled as a and b, were compared with those of the structure file from ICSD collection code 189995 (figure 6(C)) [13], and can be found in figure 6(E). The actual atomic distances are ~0.1 Å off from the expected values, well within a 5% error, further indicating the $\beta$-phase. Figure 6(D) shows the calculated FFT pattern from the
Figure 6. (A) TEM image of a sheet and its corresponding (B) ARSTEM image. Inset shows a zoomed-in image of the ARSTEM which is compared to the (C) Bi atoms of the (001) plane of $\beta$-Bi$_2$O$_3$. (D) FFT of the ARSTEM. (E) Shows the calculated measured distances between nearest neighbor ($d_1$) and next-nearest neighbor ($d_2$) from the data in (B) and structure file (C).

Figure 7. (A) AFM image of a sheet and its corresponding (B) height profile showing a thickness less than 10 nm.

ARSTEM image, which has the characteristic square pattern seen by the SAED in figures 4(E) and 5. Furthermore, the d-spacings for (hkl) = (040) and (220), calculated from the FFT, were 1.97 Å and 2.72 Å, respectively. These are in excellent agreement with the expected values for $\beta$-Bi$_2$O$_3$. Interestingly, in rare cases, one additional Bi$_2$O$_3$-type phase was found in the ARSTEM, which matched no previously reported phases. More experimental work is required for a better understanding of the phase and additional information can be found in the supporting information.

Using AFM, the thickness of the sheets was determined to be consistently <10 nm, as exemplified in figures 7 and S3. Although the sheet shown in figure 7 is relatively flat and uniform, bright-colored spots representing thicker areas may indicate rippling. Alternatively, they may be due to environmental contamination. AFM data collected on nine sheets all showed average thicknesses of 10 nm or less, with relative uniformity in sample thickness over each sheet.

4. Conclusion

We demonstrated a method for obtaining nanosheets of Bi$_2$O$_3$ from a non-layered bulk material via chemical exfoliation. Typical sheets are less than 10 nm thick, with lateral size on the microscale. Electron diffraction and ARSTEM both show evidence of the tetragonal $\beta$ structure, with nano-thickness in the [001] direction.
Moreover, a plethora of trials proved this method to be highly reproducible, albeit the yield was too low to be quantifiable. We thus provide a novel method for obtaining nanosheets of $\beta$-Bi$_2$O$_3$, enhancing the possibility of studying how their properties change between the bulk and nanoscale. Furthermore, these results broaden the scope of chemical exfoliation by describing a route for obtaining nanosheets of a material with a bulk covalent 3D structure through a metastable intermediate. We propose that this method may further be applied to exfoliate other Na$_2$M$_2$M'O$_6$ in the $\alpha$-NaFeO$_2$ crystal family. Such crystals, in which M and M' have 2$^+$ and 5$^+$ oxidation states, respectively, could also support a structural shift upon exfoliation, enabling the highly oxidized M' species to adopt a more reduced state.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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