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Polymer-assisted TEM specimen preparation method for oxidation-sensitive 2D materials

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Abstract

By structural and analytical TEM and scanning electron microscopy experiments we show that atomically-resolved structural characterization of oxidation-sensitive two-dimensional material is strongly hindered when the final step of the preparation process, the transfer to the TEM grid, is performed with a wet etching method involving bases or acids, interacting with the highly reactive sample surface. Here we present an alternative polymer-assisted and mechanicalexfoliation-based sample preparation method and demonstrate it on selected oxidation-sensitive transition metal phosphorus trisulfides and transition metal dichalcogenides. The analysis, obtained from the samples prepared with both of the methods clearly show that oxidation is the origin of discrepancy, the oxidation during the final preparation step is strongly reduced only when the new method is applied, and atomically-resolved structural characterization of the pristine structures is now possible.

Supplementary material for this article is available online

Keywords: 2D material, HRTEM, TMPT, TMD, oxidation-sensitive, specimen preparation

(Some figures may appear in colour only in the online journal)

1. Introduction

Nowadays, the number of two-dimensional (2D) materials is fast-growing and transition metal phosphorous trisulfides (TMPTs) are one of the new-born stars due to their magnetic and electric properties [1–3], allocating them as promising candidates for future heterostructure devices [4–6], for instance, combined with members of the material class of transition metal dichalcogenides (TMDs) [7]. Aberrationcorrected high-resolution transmission electron microscopy (AC-HRTEM) offers a powerful approach to analyse and modify freestanding thin samples at the atomic scale [8–12]. However, surface contamination and oxidation hinder the analysis of the material in its pristine state. Thus, the fabrication of high-quality TEM samples is of fundamental importance. In previous studies, many different sample

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preparation methods were applied for 2D materials: standard transfer with polymer [13], direct transfer for the case of graphene [14], polyimide-assisted transfer for the case of h-BN [15], liquid exfoliation [16], and scotch tape method with potassium hydroxide (KOH). In the following, the scotch tape method with potassium hydroxide will be referred to as the 'KOH method' [17]. The KOH method is an effective method to transfer the flake of interest with predetermined thickness to a certain position on the TEM grid, and therefore commonly used in the TEM community. As the KOH method is conducted in an ambient atmosphere and involves a highly reactive chemical, in this preparation process chemical reactions take place and consequently structural decomposition occurs [18, 19]. Therefore, TEM imaging of the atomic structure of oxidation-sensitive TMPTs and TMDs, when prepared with the KOH method, is very difficult. To prevent the materials from oxidation during TEM preparation, a stamping method conducted in an oxygen-free

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Figure 1. Step by step polymer-assisted preparation of a freestanding TEM sample without base or acid. The substrate is a Si/SiO_2 wafer coated with polyvinyl alcohol (PVA) or poly (methyl methacrylate) (PMMA) (shown in I and II). First, the bulk material is thinned down by mechanical exfoliation with scotch tape. By pressing the scotch tape on the wafer (depiction III), the material flakes are deposited on the polymer layer (depiction IV). Subsequently, thin flakes can be identified with an optical microscope. For calculating the contrast of thin layers on a semi-infinite Si substrate covered with a SiO_2 —PVA/PMMA layer, a theoretical model based on the Fresnel equation was used [22] (see figure S1). In step V, the TEM grid is brought into contact with the wafer by applying water or IPA, depending on the applied polymer layer. Evaporation and adhesion force of the liquid brings the flexible carbon mesh membrane of the TEM grid in contact with the polymer layer. Further, the grid is removed by dissolving the polymer layer (shown in VI). Type 1 (Ultrapure) water is used in the case of a PVA layer and acetone or anisole in the case of PMMA. In VII the TEM grid with deposited material flakes is illustrated.

environment was developed [20, 21]. This method allows to prepare single-layers of oxidation-sensitive 2D materials. However, it faces the challenge of transferring a freestanding material flake to a TEM grid.

Here we propose a new polymer-assisted method for oxidation-sensitive 2D materials performed under ambient conditions, which minimizes oxidation and allows a controlled transfer to the TEM grid (see figure S1, available online at stacks.iop.org/NANO/32/075704/mmedia). This method is exemplarily performed on FePS₃, MnPS₃, 1T-TiSe₂, and 2H-NbSe₂. In addition, the method maintains the possibility to determine the sample thickness (single-layer or few-layer) before the transfer process.

2. Proposed sample preparation method

Figure 1 illustrates the preparation process in detail. Our preparation process starts with thinning down the bulk material by the established mechanical exfoliation technique. The resulting flakes are then deposited on a polymer-coated Si/SiO₂ wafer in which the polymer layer can be either PVA or PMMA. To bring the underlying polymer layer and the sample in contact with the TEM grid, the grid is fixed using a metal or glass tip and wetted from the outside by a drop of isopropyl alcohol (IPA) or water, depending on the polymer layer used. Due to the evaporation of the liquids, the flexible carbon mesh membrane of the TEM grid is directly brought in contact with the material flake. Subsequently, the fixing tool (the metal or glass tip) is removed and the underlying polymer layer is then dissolved by water in the case of PVA, or by acetone if PMMA is used. The most gently way for dissolving the PVA or PMMA layer is to drop the liquids right beside the grid, such that the dissolving process takes place from the edge to the center of the grid. After the underlying polymer layer is dissolved, the grid floats on the liquid drop and can be gently removed by tweezers. This process prevents the material from contacting with acids or bases.

3. Results and analysis

In the following, the performance in the sample quality of the polymer-assisted method is analysed and compared to the KOH method. We start by testing the effect of the KOH solution on the surface morphology and chemistry of KOHtreated and untreated bulk MnPS₃ flakes using scanning electron microscopy (SEM). In figure 2(a), SEM images of pristine MnPS₃ are presented on the left side and after contact with KOH solution on the right side. Dramatic changes in the surface morphology, for example increased roughness, are visible. In figure 2(b), the corresponding energy-dispersive x-ray (EDX) spectra are shown in the energy range of 0-6.6 keV taken from the red-framed and blue-framed areas in figure 2(a). The two spectra show similarities as in both spectra carbon (C-K $\alpha = 0.277$ keV) and oxygen (O- $K\alpha = 0.525$ keV) signals are visible. These peaks may originate from the SEM sample fabrication process, which was performed in air. However, strong differences can be observed in the untreated sample (red curve), the maximum peak ratios of the oxygen peak with respect to the manganese (Mn-K α = 5.900 keV; Mn-L α = 0.637 keV), sulfur (S- $K\alpha = 2.309$ keV), and phosphorous (P-K $\alpha = 2.010$ keV) peaks of MnPS₃ are low, while the ratios in the KOH-treated case (blue curve) are considerably higher. This indicates a stronger oxidation for MnPS₃ after contact with the KOH solution. Additionally, the peak intensities of the P and S peaks in the blue curve are lowered with respect to the former ratios between the metal and the elements P and S (figure S2 provides cross-section SEM images and the corresponding



Figure 2. Structural and chemical characterization of bulk (a)–(b) and few-layer MnPS₃ (c)–(d). (a) shows SEM images of the surfaces of a pristine (left) and KOH treated (right) bulk MnPS₃ crystal. The marked red and blue squares indicate the corresponding areas for EDX analysis, spectra are shown in (b). The strong O peak after contact with KOH is the most obvious difference between both spectra. The peak intensities of the Mn (K α 5.900 keV/L α 0.637 keV), S (K α 2.309 keV), and P (K α 2.010 keV) are clearly visible in both of the spectra. However, the S and P peak intensities are strongly reduced after contact with KOH because of materials decomposition. Moreover, a K peak is only visible in the KOH treated sample. (c) BF-TEM overview image along the [103] zone-axis of few-layer MnPS₃ prepared with the PVA method, the area where the AC-HRTEM image is taken is marked with a red rectangle. The single crystalline nature is clearly visible. (d) BF-TEM overview image of few-layer MnPS₃ prepared with the KOH method, showing heavy damages. From the AC-HRTEM and corresponding FFT images on the right, we see the polycrystalline nature as well as the high degree of amorphisation, right up to the formation of holes in the thin layer (results of FePS₃ are presented in figure S5).

EDX spectra of bulk FePS₃ and MnPS₃ after the treatment with KOH solution). Moreover, a potassium (K) peak (K-K α 3.314 keV) becomes visible for the KOH-treated sample. In the next step, we compared a much thinner MnPS₃ sample (few-layer MnPS₃) prepared with the KOH method and with the polymer-assisted method using AC-HRTEM (the corresponding structure models are given in figure S3). In the latter case, the overview BF-TEM image of few-layer MnPS₃ in figure 2(c) shows an intact flake with sharp edges. The AC-HRTEM image, together with corresponding Fast Fourier Transform (FFT) patterns, clearly demonstrates the crystalline nature of the material. On the contrary, the BF-TEM image of the flake prepared with the KOH method in figure 2(d) shows the deterioration of the flake. The corresponding AC-HRTEM image (taken from the red rectangular in the BF-TEM image) demonstrates the presence of holes and a polycrystalline nature of the material, underlined by the corresponding FFT patterns in the upper right. Results on FePS3 showed amorphisation after the material was treated by the KOH solution as well (see figure S4 and the more detailed description of the decomposition process).

To prove the adaptability of the proposed polymerassisted preparation method to highly oxidation-sensitive TMDs, we now study 1T-TiSe₂. Two samples of few-layer 1T-TiSe₂ are prepared for TEM investigation using the polymers PVA and PMMA as substrate, respectively. The intension of applying two polymers is to find out whether the success of the proposed method is sensitive to the type of the polymer and the different related solvents, water or acetone. The results of BF-TEM, AC-HRTEM, and EELS analysis are presented in figure 3 (additional SEM and EDX results are provided in figure S6). By comparing the overview BF-TEM images, it is clearly seen that the edge of the flake is not sharp and shows a deterioration in the KOH-treated sample, as highlighted by the two red arrows in figure 3(a). The other two samples show sharp edges, see figures 3(b) and (c). Comparing the AC-HRTEM images and their FFTs placed as insets obtained from the red rectangles marked in the corresponding BF-TEM images in figures 3(a)-(c), the differences in the atomic structures are obvious. The crystalline 1T-TiSe₂ atomic structure is shown in the AC-HRTEM images in figures 3(b) and (c), highlighted by the FFTs (the corresponding structure models are given in figure S3). In contrast, the AC-HRTEM image of the KOH treated sample in figure 3(a) shows a predominant amorphous structure, as also seen in the FFT at low spatial frequencies. Furthermore, the chemical information of each sample are revealed in the EELS data showing the Ti-L and O-K energy loss edges, see figure 3(d). An oxygen peak starting at 530 eV is only present in the KOH treated sample [23]. Slight oxidation after PVA

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Figure 3. Comparison of the degree of oxidation in few-layer 1T-TiSe₂ prepared by KOH- and polymer-assisted (PVA and PMMA) methods. Images (a)–(c) show 80 kV overview BF-TEM images on the left (the arrow in (a) marks the edge-contamination) and Cs-corrected HRTEM images on the right along the [001] zone-axis (with their FFTs as insets), obtained from the red-squared areas in the BF-TEM images. By comparing the Cs-corrected HRTEM images in (a)–(c), the oxidation of TiSe₂ in (a) can be clearly seen. Accordingly, the corresponding EELS spectra in (d) show that in the case of the KOH method prepared sample, an O peak at 530 eV occurs and a splitting of the Ti-L₃ edge (see the black arrows) originating from oxidation (TiO₂ formation) is visible. In the PVA and PMMA method cases, the positions and shapes of the Ti-L₂, a peaks at 462 and 456 eV show just the edge structure for Ti in 1T-TiSe₂ (the raw data of the spectra is given in figure S7).

and PMMA treatment might be expected as well, as they are prepared under ambient conditions. As no O-K peak was measured in EELS, the amount of oxidation must at least be below the signal to noise ratio for O detection for the settings used to acquire the spectra.

Moreover, the changes in the chemical bonding due to the oxidation are also visible in the Ti-L₃ edges. The Ti spectra contain bands attributed to the $3d \leftarrow 2p_{3/2}$ and $3d \leftarrow 2p_{1/2}$ transitions showing up as two main peaks at around 455–463 eV (L_3 peak) and 463 eV–470 eV (L_2 peak), respectively. The fine structure of the Ti-L_{2,3} edge is determined by the chemical composition and structure of the material. Crystal field splitting leads in the case of pristine TiSe₂ to a splitting of the 3d orbitals to the lower energy t_{2g} and higher energy eg levels [24, 25]. Red and green dotted boxes in figure 3(d) highlight the L₃ and L₂ edges for the different TiSe₂ samples, respectively. The corresponding peaks expected for the transition into the empty t_{2g} and e_g levels merge due to the limited EELS energy resolution of 0.6 eV and acquisition at room temperature [24, 26]. As a result, the weaker t_{2g} transition appears as a broad shoulder. In figure 3(d), in the case of the KOH prepared sample, the Ti-L₃ peak splits (see black arrows) and an O peak appears thus Ti-O bonds formed. The process of oxidization can be described by the formation of $TiO_x Se_{2-x}$ and a gradual replacement of Se by O atoms in the crystal [27]. The split in the L_3 peak at the higher energy site might be described as a superposition of the spectra of the oxide with the pristine 1T-TiSe₂ layer. Crystalline TiO₂ (e.g. anatase and rutile) [27-29] shows a similar core loss Ti (L_{2.3}) edge fine structure as 1T-TiSe₂ but shifted by several eV to higher energies [25]. When the outer layers oxidize and the inner layers of TiSe₂ stay intact, a superposition of the titanium oxides L3-edge with the 1T-TiSe₂ L₃-edge would result in the observed spectra [27], supplementary information (SI) figures S3 and S5. However, due to the limited energy resolution, unambiguous identification of the titanium oxide structure is not possible. Overall, the shown $L_{2,3}$ edges for the PVA and PMMA samples coincide with previous reported Ti-L_{2.3} edges in pristine 1T-TiSe₂ [24, 26, 30]. Moreover, it should be noticed that there is no significant difference between samples prepared via PVA or PMMA.

We verified the applicability of the polymer-assisted sample preparation method to single-layers using another oxidation-sensitive TMD. 2H-NbSe₂ was chosen as it exhibits superconducting properties and thus excellent TEM sample preparation may be crucial for understanding the property's structural origin [31]. The structural model of 2H-NbSe₂ is shown in figure 4(a). AC-HRTEM experiments were performed for single-layer and few-layer 2H-NbSe₂ using the Cc/Cs (chromatic and spherical aberration)—corrected *SALVE* instrument operated at 80 kV (SEM image and EDX



Figure 4. Results of a PVA prepared few-layer and single-layer 2H-NbSe₂ samples. In (a) the structural model of single-layer 2H-NbSe₂ is shown in top and side view in which selenium atoms are green and niobium atoms are blue colored. (b) and (c) show 80 kV Cc/Cs-corrected HRTEM images along the [001] zone-axis demonstrating successful sample preparation without deterioration due to oxidation. FFTs are inserted in the top right corner. A depiction of a selected enlarged region is highlighted by green circles in (c), showing a double Se vacancy (marked by a red dotted circle).

results see figure S6). As figures 4(b) and (c) show, atomically-resolved crystalline structures are visible both for fewlayer and single-layer 2H-NbSe₂, respectively (see figure S1 for optical images of the single-layer). Atomic defects are also present, which may originate from oxidation during sample preparation and subsequent interaction between the electron beam and the specimen during the imaging process. One defect is enlarged in figure 4(c), representing a double Se vacancy marked by a red dotted circle in the enlarged depiction [31]. Thus it is shown that there is no underlying second layer.

Recent studies showed the sensitivity of 2H-NbSe₂ nanosheets to oxygen [32–34], significantly altering the electronic properties [32]. Therefore, atomically-resolved (S) TEM studies of single-layer 2H-NbSe₂ were only conducted in a graphene-encapsulated 3-layer geometry, as the free-standing single-layer oxidized too fast [33, 34]. Here, atomically-resolved AC-HRTEM characterization of freestanding single-layer 2H-NbSe₂ is reported for the first time.

4. Summary

We presented a new, polymer-assisted TEM sample preparation method, which was based on the conventional scotchtape method. Due to the use of polymers, any contact with bases or acids was avoided during transfer of the 2D sample to the TEM grid. The performance of the proposed method was examined on different oxidation-sensitive TMPTs (MnPS₃ and FePS₃) and TMDs (1T-TiSe₂ and 2H-NbSe₂). By applying SEM, AC-HRTEM and EELS analysis, a significant increase of the TEM sample quality compared to the KOH method was demonstrated, which we attributed to strongly reduced oxidation.

We demonstrated that atomically-resolved HRTEM images of the almost pristine crystalline structures can be obtained even of very thin samples such as few-layer 1T-TiSe₂ and few-layer 2H-NbSe₂, as well as single-layer

2H-NbSe₂. Moreover, on the example of 1T-TiSe₂, we showed that the effect of the actual used polymer (PVA and PMMA) and associated solvent (water or acetone) does not influence the TEM sample quality.

In conclusion, our new polymer-assisted TEM sample preparation method provides an enhanced sample quality, enabling atomically precise analysis of structural and chemical properties of oxidation-sensitive freestanding 2D layers.

5. Method

5.1. Materials and Instrumentations

In the preparation experiments, the concentration of the KOH solution was c (KOH) = 0.317 mol 1⁻¹. The PMMA and PVA solutions were produced by dissolving the powder in Type 1 (Ultrapure) anisole and water, respectively. The used concentration was 3% weight ratio, and the liquids were baked for 24 h on a hot plate at 60 °C-70 °C with a magnetic stirrer at medium speed in the solution. The thickness of the SiO_2 layer on the Si/SiO₂ wafer was 90 nm \pm 5%. The SEM measurements were performed with an SEM/FIB Zeiss NVision 40. TEM experiments were conducted with a Cscorrected TEM FEI Titan 80-300 and the Cc/Cs-corrected SALVE (Sub-Ångström Low-Voltage Electron microscopy) instrument operated at 80 kV [35]. For acquiring the spectra, a 50 μ m selected area aperture was used and the energy resolution during the experiment was determined to be 0.6 eV. Furthermore, all experiments were conducted at room temperature. In the SI, an alternative way of conducting our polymer method is illustrated and explained in figure S8.

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