Imaging and diffraction characterisation of 2D inorganic nanostructures

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Abstract. 2D nanomaterials are a novel class of materials, noted for their potential in a range of high impact applications, such as sensing, catalysis, and composite reinforcement. However, their structural features have not yet been fully characterised. In this work we have shown that 2D nanostructures of hBN, MoS\textsubscript{2}, and WS\textsubscript{2}, prepared by liquid exfoliation, can stack in sequences different from the bulk stacking. In 2D hBN non-sequential stacking was observed. 2D MoS\textsubscript{2} and WS\textsubscript{2} appear to have stacking where Mo/W atoms are located on the top of each other which differs from naturally occurring 2H and 3R polytypes. The majority of the hBN and MoS\textsubscript{2} 2D nanostructures retain the stacking of their bulk counterparts, while in 2D WS\textsubscript{2} non-bulk stacking dominates. The conclusions are based primarily on the atomically resolved ADF STEM images with supporting evidence from electron diffraction.

1. Introduction

Initially, two-dimensional (2D) nanostructures were considered as the fundamental building blocks for layered materials [1] and later for nanotubes [2]. Following the discovery of graphene [3], 2D nanostructures became a separate class of materials, and were noted for their potential in a range of high-impact applications, such as sensing [4], catalysis [5], and composite reinforcement [6]. Liquid exfoliation [6] and chemical vapour deposition [7] demonstrated the feasibility of mass-scale production. With the advent of mass-produced 2D nanostructures a new focus of the research is to characterise these materials.

Structural properties of any material play a particularly important role as they determine its intrinsic properties and performance in applications. Furthermore, for the case of 2D nanomaterials knowledge of the topological defects and edge structure might offer insight towards functionalisation approaches.

The primary focus of this work is stacking variations in 2D nanostructures of hexagonal boron nitride - hBN, molybdenum disulfide - MoS\textsubscript{2}, and tungsten disulfide - WS\textsubscript{2}, investigated using aberration corrected annular dark field (ADF) scanning transmission electron microscopy (STEM) with supporting evidence from electron diffraction. The particular advantage of this study is the choice of ADF STEM imaging as the main characterisation technique. The acquired images show intensities that are strongly dependent on the atomic number of the species present in the sample. All of the samples were produced by liquid exfoliation of the bulk material in either N-methyl-2-pyrrolidone or isopropanol (more details on the sample preparation and analysis of the exfoliated material can be found here [6]). Suitability of this production method for inorganic layered materials has been...
demonstrated only recently. Out of 2D nanostructures of hBN, MoS$_2$, and WS$_2$ produced by liquid exfoliation, only hBN has been studied before [8][9].

2. Results and Discussion
2.1 2D Hexagonal Boron Nitride
In this work, initial experimental evidence of the stacking variation came from electron diffraction patterns. The ratio of the spot intensities in the electron diffraction pattern can be related to the corresponding squared modulus ratio of the structure. Depending on the stacking this ratio will change. Here we consider 4 different stacking sequences of hBN (Fig. 1). Experimentally, two different ratios of the (100) and (110) spot intensities, $I_{100}/I_{110}$, were observed (Fig. 2). In Figs. 2b and 2e ratios are 9.3±2.5 and 0.29±0.09, correspondingly. While the first ratio doesn’t agree with any of the calculated values (Table 1), the second corresponds to AB. Tilt of the sample combined with stacking faults may be the reason for the discrepancy between theoretical prediction and experimental values. Furthermore, the observed differences cannot be explained by considering fractional unit cells. Overall, for this case electron diffraction doesn’t enable reliable determination of the stacking sequence. However, it suggests that stacking variations can exist in 2D hBN nanostructures.

![Figure 1: hBN structural models. View along [001] shows pattern expected for atomically resolved ADF image. View along [110] unambiguously shows stacking sequence. The interlayer distance is shown to scale.](image1)

![Figure 2: (a), (d) Low resolution TEM images with corresponding (b), (e) diffraction patterns and (c), (f) intensity profiles. Additional spots marked with arrows in (e) are likely to correspond to the presence of in-plane rotated layers.](image2)
Table 1: Calculated ratios of intensities, $I_{100}/I_{110}$, for the different stacking sequences described in Fig. 1. Ratios were calculated using atomic scattering amplitudes for neutral atoms. The electron beam direction is considered perpendicular to the hBN basal plane.

| No. of layers: | 1   | 2   | 3   | 5   | 11  | bulk |
|---------------|-----|-----|-----|-----|-----|------|
| AA’, AA       | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1  |
| AB            | 1.1 | 0.28| 0.37| 0.31| 0.28| 0.28 |
| ABC           | 1.1 | 0.28| 0   | 0.04| 0.01| 0    |

Fig. 3a shows characteristic atomic resolution ADF STEM image of a typical hBN nanosheet. An accurate comparison between the ADF STEM projected pattern in Fig. 3a with the models in Fig. 1 shows that the stacking sequence corresponds either to AA’ or AA. Theoretical calculations [10] indicate that AA stacking is the least energetically favourable; therefore one can assume that the structure in Fig. 3a should correspond to bulk.

Two out of approximately 20 high resolution ADF images did not show the honeycomb pattern observed in Fig. 3a (Fig. 3b). Fig. 3c shows region where the transition between the honeycomb and the new pattern can be seen. This non-honeycomb pattern is similar to patterns formed by AB and ABC structures. Another feature of Figs. 3b,c, which is not present in Fig. 3a, is the large number of bright spots, corresponding to the presence of impurity atoms. One possibility is that high concentration of impurities can stabilise stacking disorder.

2.2 2D Molybdenum Disulfide and Tungsten Disulfide

The structure of the 2H polytype, which is dominant for MoS$_2$ and WS$_2$, is shown in Fig. 4a. Since the atomic number of Mo/W is much higher than S, in MoS$_2$/WS$_2$ ADF images the signal from S atom is swamped by the neighbouring W/Mo signal. Indeed, experimental images of MoS$_2$ in Fig. 5 do not show S signal. As a result, the pattern created by the Mo/W atoms for the 2H polytype is different for the mono- and the multi-layer regions (Fig. 4b). Therefore, it follows that in Fig. 5a the 2D nanostructure has stacking similar to 2H polytype. In Fig. 5b the pattern is the same for the entire field of view of the image and the presence of a step can be clearly seen. It means that Mo atoms must be stacked on the top of each other. Such stacking sequence exists in neither 2H nor 3R polytypes. Statistical analysis on the intensities of the possible S sites might allow determination of the complete crystallographic structure. Out of approximately 20 MoS$_2$ nanostructures, only one of them had the structure with Mo atoms stacking on the top of each other, while the rest of them were consistent with 2H polytype. For WS$_2$ nanostructures, similar results were observed. However, unlike the case of 2D MoS$_2$, stacking of W on top of each other is dominant.
3. Conclusions

In this work imaging and structural characterisation of 2D inorganic nanostructures, produced by liquid exfoliation, was carried out. The primary focus of the structural analysis was stacking. On the basis of electron diffraction and ADF STEM non-bulk stacking was reliably determined in 2D nanostructures of hBN, MoS$_2$, and WS$_2$. However, based on the set of acquired images, with the exception of WS$_2$, the majority of the 2D nanostructures retain the stacking of their bulk counterparts. Observed variations in stacking sequences are expected to affect the electronic properties of 2D nanostructures, having considerable impact for their potential applications.

References

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