

Growth of 2D transition metal dichalcogenides in the 1H and 1T' phase and their applications

Carl H. Naylor A.T. Charlie Johnson

University of Pennsylvania, 209 south 33rd street,
Philadelphia PA, United States
naylorc@sas.upenn.edu

"Beyond graphene" is a field of science that has attracted tremendous attention in recent years. From phosphorene to transition metal dichalcogenides (TMDs), these novel materials possess fascinating electrical, mechanical and tribological properties. To study these materials in the monolayer form, scientists most commonly rely upon mechanical exfoliation for sample production, a low yield and repetitive method that slows the pace of experiments. There is a genuine need for reproducible growth methods for high quality monolayer materials that could enable comprehensive studies of their unexplored properties and potentially scalable fabrication of novel devices and circuits. In my presentation I will discuss our recent progress in the field "beyond graphene" and more specifically the growth by chemical vapor deposition (CVD) of monolayer TMDs in different atomic configurations (1H and 1T' phase) and their application as biosensors.

We have developed a reproducible CVD growth method for monolayer single crystal MoS₂ and WS₂ flakes in the 1H phase. The flakes are n-type semiconductors with reasonable values of mobility, high on/off ratio and a tunable band gap dependent on the layer number. Using a patterned growth technique,¹ we can predetermine the growth location of MoS₂ flakes (figure 1a) in desired structures, for example "NBIC @ UPENN" consisting solely of monolayer MoS₂ flakes (figure 1b). Patterned growth of MoS₂ provides a feasible pathway towards growth of arrays of MoS₂ flakes at precise locations suitable for fabrication of scalable arrays of compact MoS₂ FETs (figure 1c).

We extended this growth process for high quality monolayer MoS₂ to high-yield production of MoS₂-based nano-biosensor devices. We have incorporated monolayer MoS₂ into scalable arrays of highly sensitive sensors for enkephalin (figure 2ab).² Natural enkephalins are endogenous opioid pentapeptides involved in pain perception, cognitive functions, affective behaviors and locomotion. We have also studied the remarkably large responses of MoS₂ based sensors to various vapor analytes. Using the Transmission Line Measurement (TLM) approach, we quantified the intrinsic MoS₂ contribution to the sensor response and that due to the contact resistance.³ These sensors are currently being incorporated into wearable/flexible formats on plastic substrates (figure 2c).

Chemical functionalization procedures for graphene and TMDs (e.g., MoS₂) reported to date differ dramatically due to their divergent surface chemistries. A universal chemical functionalization scheme for any given 2D material is highly desirable but fundamentally challenging. We have resolved this issue by developing a universal functionalization scheme based upon a heterostructure of two-dimensional materials. This heterostructure performs admirably as a biosensor, with high yield, excellent reproducibility, and low concentration detection limits.

Monolayer MX₂ materials manifest in 3 different atomic configurations referred to as 1H, 1T and 1T' (figure 3a). The 1H phase is highly symmetric, typically air stable, and the most commonly studied phase to this point. The 1T phase differs from the 1H phase by a rotation of the top layer of chalcogenide atoms with respect to the bottom layer so that as viewed along the c-axis, the chalcogenide atoms form a hexagon around the metal atom. The 1T' phase is created by a distortion of the 1T phase and has attracted high interest due

to theoretical predictions that it supports non-trivial topological electronic states. It has been proposed that monolayer $1T'$ - MX_2 compounds are large-gap quantum spin Hall insulators, making them promising for applications in novel switching devices, spintronics, and quantum computation. Experimentally the $1T'$ phase is extremely challenging to achieve and difficult to isolate by exfoliation in the monolayer form due to its high instability in air. We recently reported successful growth and study of CVD grown monolayer $1T'$ - $MoTe_2$.⁴ Aberration-corrected scanning TEM (ACSTEM) images confirm the atomic distortion that differentiates the $1T$ from the $1T'$ phase (figure 3b), and initial electrical data suggest a weak antilocalization effect in the material. We applied a related growth process to produce monolayer $1T'$ - WTe_2 which enabled experiments probing its degradation process in air.⁵ We also developed novel encapsulation methods to stabilize the $1T'$ materials and enable multiple characterization measurements of this phase.

Through reproducible growth methods we are able to grow a variety of monolayer MX_2 materials by CVD. We incorporated the $1H$ - MX_2 materials into scalable bio and vapor sensors and onto flexible substrates. We were able to grow materials in the $1T'$ phase and perform initial studies on monolayer $1T'$ - MX_2 materials with compelling ACSTEM images revealing the distorted phase.

References

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- [2] Carl H. Naylor* et al., ACS Nano, 10 (2016) 6173-6179.
- [3] Carl H. Naylor et al., In prep.
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Figures

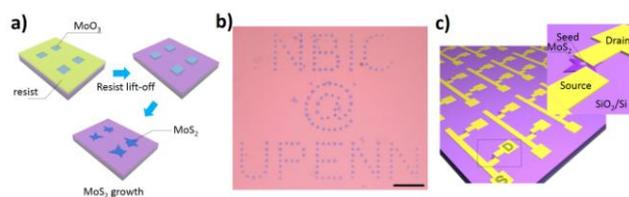


Figure 1: MoS₂ pattern growth. a) Schematic of the growth process for MoS₂ using patterned molybdenum source. b) Optical micrograph of MoS₂ flakes grown at locations that form NBIC @ UPENN. Scale bar, 100 μm . c) Schematic of scalable MoS₂ FETs by pattern growth technique

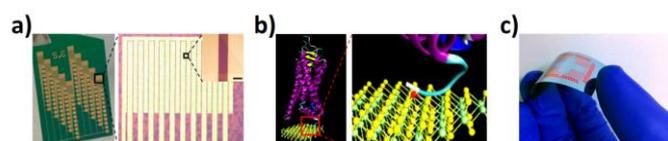


Figure 2: MoS₂ biosensor. a) Photograph of the electrode array chip. Optical micrograph showing interdigitated electrodes corresponding to a set of 10 sensors, scale bar 500 μm and 10 μm respectively. b) MoS₂ structure and functionalization schematic. c) Photograph of scalable flexible MoS₂ biosensor.

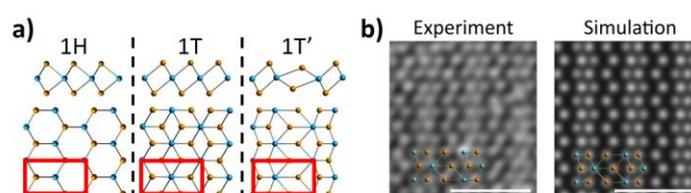


Figure 3: $1T'$ - $MoTe_2$. a) Ball and stick model displaying all three phases of TMDs. b) ACSTEM image of as grown $1T'$ - $MoTe_2$ and the simulation are in good agreement, scale bar is 1 nm.
