

Synopsis

Unique ranges of properties of two dimensional (2D) materials foster new opportunities in many scientific and technological fields. Beyond pristine 2D materials, their heterostructures provide more possibilities in real application as the stack can be tailored according to desired properties. Besides, exotic combination can give rise to new functionalities. Despite experimental success in many lab-grade devices, large scale commercialization of 2D technology is still being actively worked on. This requires easy and cost effective synthesis technique which can give high quality sample in large scale. In this thesis, we discuss the scalable, application specific growth of 2D materials and their heterostructures.

The easiest preparation method (micromechanical cleavage) does not offer a very good route for commercial use and alternative approaches can offer large scale production. A brief survey on the various production methods have been carried out in Chapter 2. It is shown that through bottom up approach a balance between growing large scale and high quality can be achievable and CVD is one such controllable growth platform. However to control materials at such atomic level require detail understanding of nucleation, surface science and defect control.

Next in Chapter 3, taking graphene growth as an example, a CVD based growth method is first established which can also be applied for other 2D materials.

The grain size of a CVD grown monolayer large area graphene film is key to its performance. Microstructural design for the desired grain size requires a fundamental understanding of graphene nucleation and growth. Hence, first the CVD growth phenomenon of graphene has been exploited. In this course,

two ultimate levers for controlling the nucleation density are identified and they are substrate defect density, which are the active nucleation sites and “gas-phase supersaturation”. It is observed that defects on copper surface, namely dislocations, grain boundaries, triple points and rolling marks, initiate the nucleation of graphene. It has been shown that among these defects, dislocations are the most potent nucleation sites, as they get activated at lowest supersaturation.

Defects in graphene can be made useful in functionalization or making heterostructures which can be useful in chemical sensing or energy generating fields. Specifically, combination of graphene with plasmonic nanostructures would allow for making surface enhanced Raman spectroscopy (SERS) based sensing platform. Graphene being atomically thin can ideally be placed between plasmonic metal dimers to create precise sub-nm gap. Such hybrid structure of metal dimers with graphene spacer increases the Raman signal by several orders by near-field enhancement resulting from strong electromagnetic coupling between the particles. Besides these hybrids have applications in other different areas such as optical switch, displays, and photodetectors.

In Chapter 4, wet-chemistry-based method is applied to fabricate a SERS substrate with $7 \times 10^6 \text{ cm}^{-2}$ Au nanoparticle dimers, separated by a single graphene layer in which each dimer can act as a plasmonic enhancer. The method involves selective growing of Au particle on top of a graphene covered another Au particle. It is shown that desired density of graphene separated dimers can be obtained effortlessly by controlling the nucleation and growth of the Au particles. A 35x enhancement in graphene spectra, seen from a single such dimer indicates that this could find applications in identifying ppb concentration of Raman active substances. Furthermore, using R6G as a probe molecule, it is shown that these substrates can be

efficient reliable SERS substrates in low cost SERS based sensing application.

In Chapter 5 heterostructure of graphene and Sb_2Te_3 has been demonstrated. A very simple wet chemical transfer method is applied to make this heterostructure. Structural properties of the individual in the heterostructure have been investigated throughly by microscopic and spectroscopic analysis to verify the preservation of the properties. Further, graphene has been found to increase the stability of Sb_2Te_3 in ambient condition.

In Chapter 6 a new facile method to grow Bi_2Te_3 – Sb_2Te_3 heterostructure in large scale is described. This method is based on an extended liquid phase exfoliation methodology, which has been applied to many oxide layered materials such as GO, $\text{Ti}_{0.87}\text{O}_2^{0.52-}$, and $\text{Ca}_2\text{Nb}_3\text{O}_{10}^-$ nanosheets. Analysis of optimized dispersion of heterostructure was conducted using SEM, Raman and TEM-EDS, where the presence of both the materials- Bi_2Te_3 and Sb_2Te_3 were discovered. Current thermoelectric application requires mass production of such superlattice and this method can provide that in cost-effective way.

In summary, starting with controllable growth of 2D materials, we have discussed formation of hybrid structures of 2D materials and explored some of the applications thereof.