Understanding the exfoliation of 2D materials through nanoindentation

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1. Introduction

Graphene is typically produced by the ultrasonication of graphite in a suitable solvent to exfoliate individual sp^2 sheets. However, the relationship between the graphite's microstructure, processing conditions and resultant graphene is still poorly understood.

Graphite is considered as a kinking, nonlinear, elastic solid material. For example, kink boundaries are created were a normal stress is applied to the basal plane of the graphite during nanoidentation tests (Figure 1) [1,2]. Incipient kink bands (IKBS) result from two parallel dislocation walls which are stable as long as the stress is applied. The dislocation walls then collapse when the stress is removed, leading to delamination in the basal plane [3]. Thus, we propose that through understanding the delamination of graphite during nanoindentation in the presence of solvents that we can understand the exfoliation of graphene.

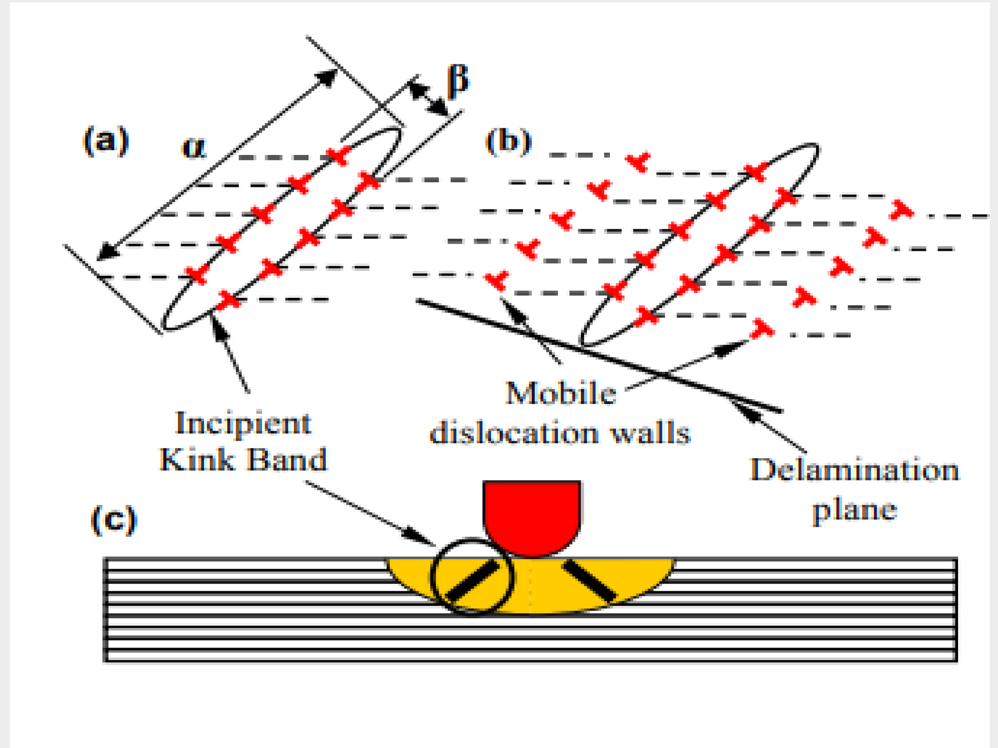

Figure 1: Schematic diagram of a) incipient kink band with dislocation of the wall due to opposite polarity .b) the IKB after delamination occur, c) the formation of two IKB under indentation.

2. Results and discussion

Nanoindention of HOPG in the presence of NMP

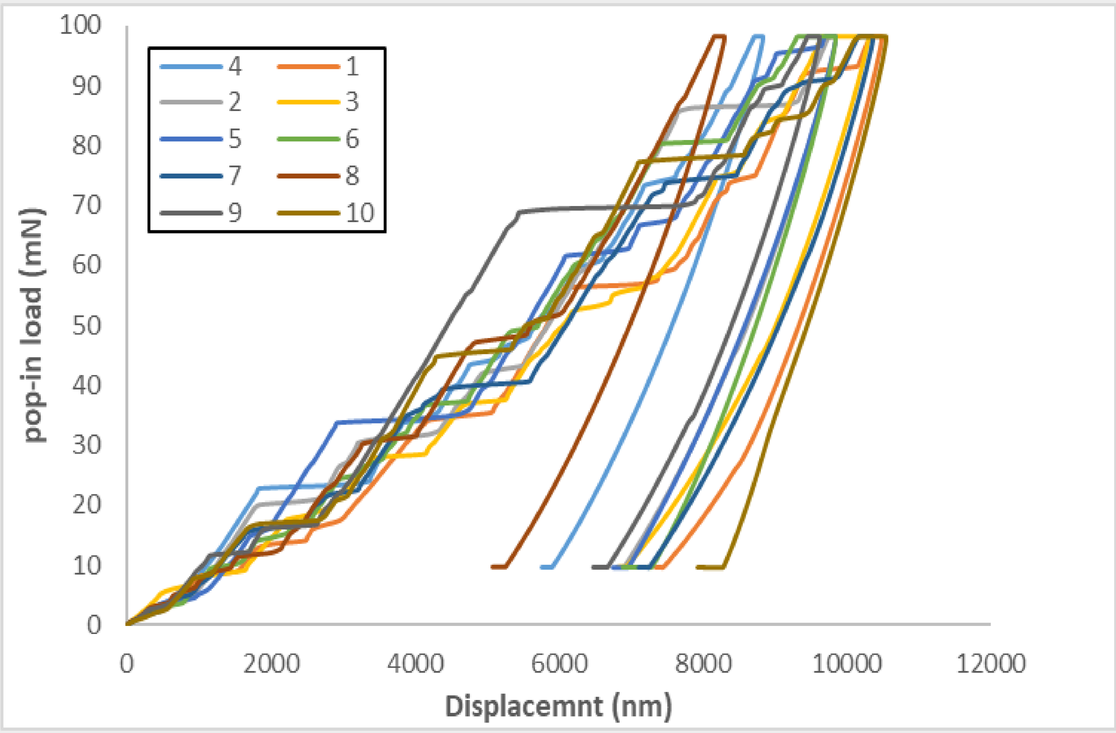

Figure 2: Load-displacement curve of 10 indentation for HOPG immersed with NMP.

Highly ordered pyrolytic graphite (HOPG) or MoS_2 was indented under the immersed in different solvents. For example Figure 2 shows the data for HOPG immersed in NMP, a common solvent for graphene production.

The average first pop-in load was extracted from the loading curves as a function of solvent composition (ie 4.58 ± 0.81 mN in Figure 1). This pop-in load was then compared to the ability of the solvent to exfoliate graphite to graphene, as denoted by the concentration graphene produced when the graphite was ultrasonicated in that solvent.

HOPG in water-ethanol mixtures

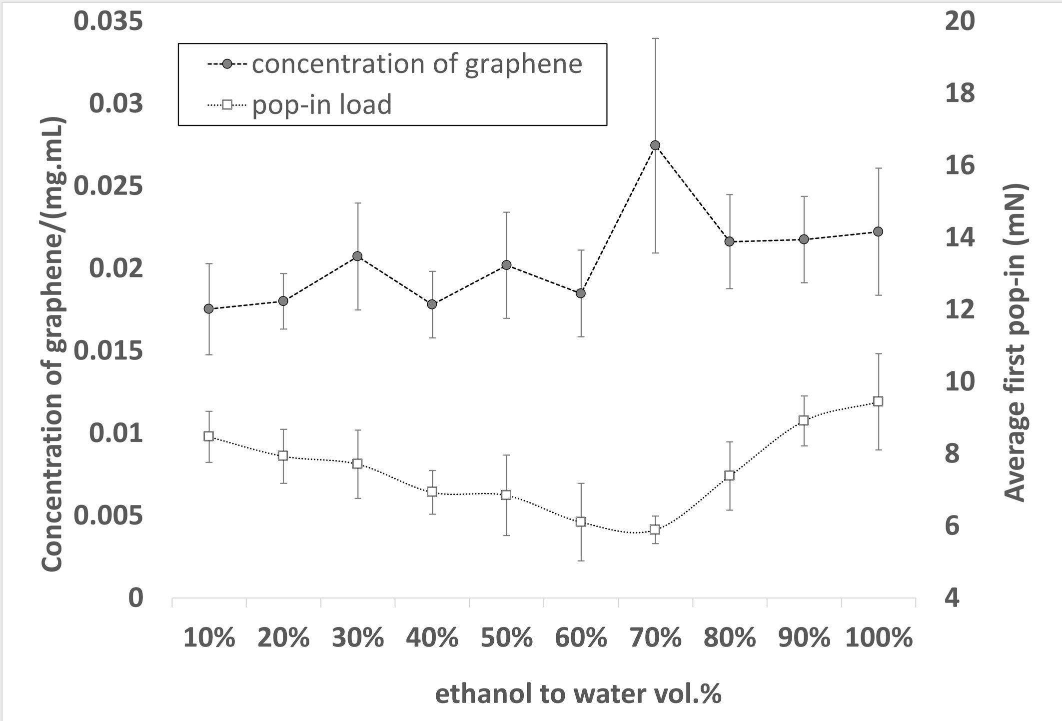

Figure 3: The average load pop-in to occur for HOPG mix with ethanol and the UV-vis absorbance of the dispersion exfoliated in different ethanol-water mixtures.

The minimal load for the first pop-in in the nanoindentation and maximum concentration of the graphene in the exfoliation process were found to both by for 70% ethanol in water, suggesting a correlation of the two parameters (Figure 3).

MoS_2 in IPA-water mixtures

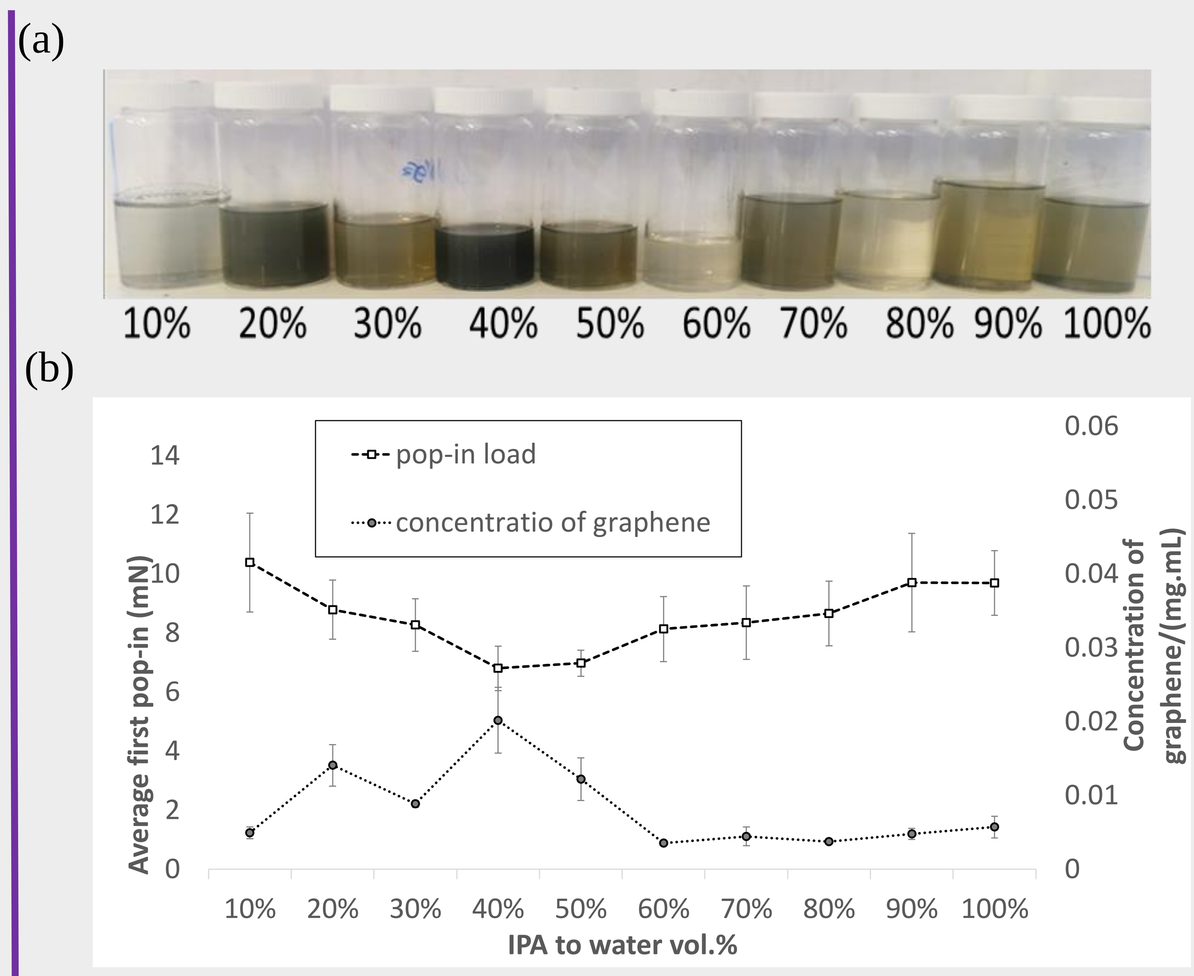

Figure 4: (a) Photograph of dispersions formed by exfoliating MoS_2 in IPA-water mixtures. (b) The average pop-in load for MoS_2 and the UV-Vis absorbance (proportional to concentration) of the MoS_2 dispersions as a function of IPA-water mixture.

A similar correlation between minimum pop-in load and concentration of exfoliated flakes was also found for MoS_2 immersed in IPA-water mixtures.

3. Raman spectroscopy from an indent

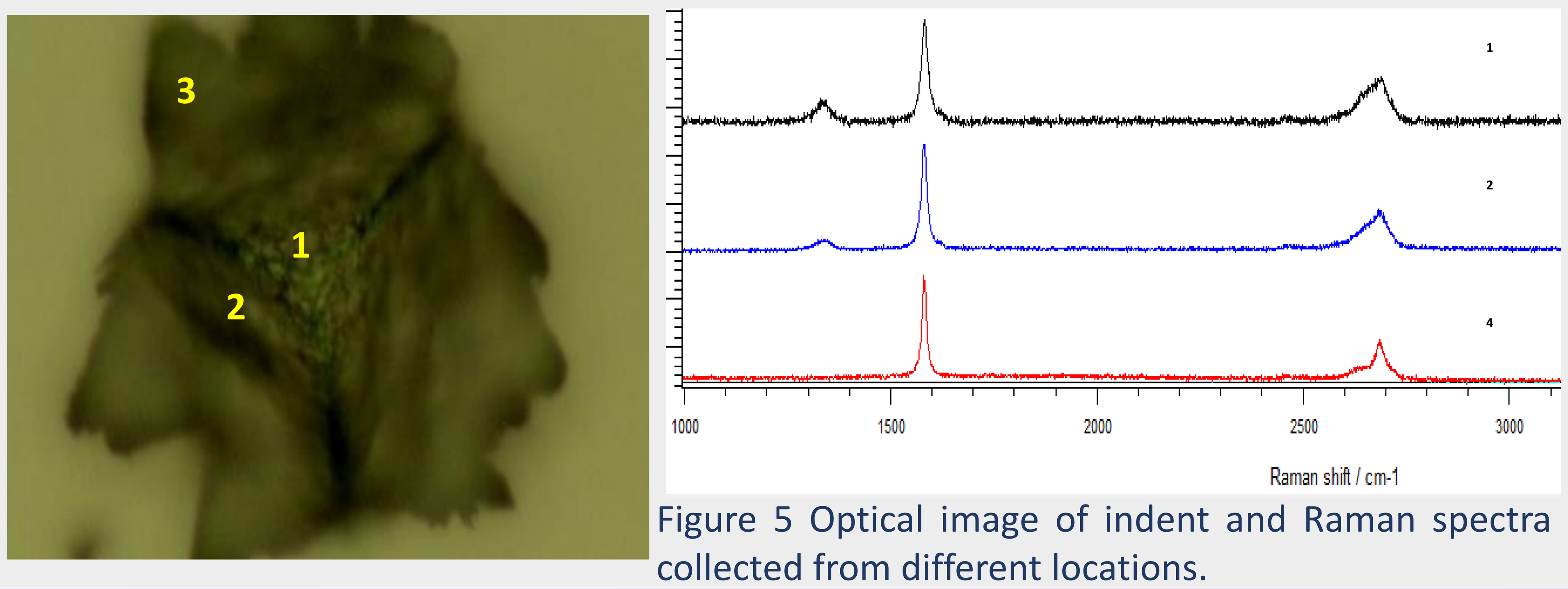

Figure 5 Optical image of indent and Raman spectra collected from different locations.

Raman spectra were collected from an indent in HOPG immersed in SOLVENT. The characteristic D, G and 2D peaks can be seen in the spectra at approximately 1350 cm^{-1}, 1600 cm^{-1} and 2700 cm^{-1} respectively. The area away from the indent (1) showed no D peak, which is related to the creation of defects and edges in the sp^2 lattice. However, the areas closer (2 and 3) to the indent, did have a D peak, showing the disruption to the lattice. Furthermore, the change in the shape in the 2D peak for these areas implies delamination and stacking faults. More detailed studies on the Raman spectra are underway.

6. Conclusions

Nanoindentation of HOPG and MoS2 in the presence of solvents showed that there was a strong correlation between the load that the first pop-in occurred at and the efficiency of the selected solvents to be used for exfoliation process. Further studies are underway to elucidate the how the solvents change the kink-band formation.

References:

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