

INTERFACIAL CONTROL IN GRAPHENE- AND TRANSITION METAL DICHALCOGENIDE-POLYMER NANOCOMPOSITES

Fang Wang¹, Mark Bissett², Andinet Aynalem³, Robert A.W. Dryfe³, Daniel Wolverson⁴, Reshef Tenne⁵, Robert J. Young⁶ and Ian A. Kinloch⁷

¹ National Graphene Institute & School of Materials, University of Manchester, UK
Email: fang.wang-2@postgrad.manchester.ac.uk

² National Graphene Institute & School of Materials, University of Manchester, UK
Email: mark.bissett@manchester.ac.uk

³ National Graphene Institute & School of Chemistry, University of Manchester, UK

⁴ Department of Physics, University of Bath, UK

⁵ Department of Materials and Interfaces, Weizmann Institute, Israel

⁶ National Graphene Institute & School of Materials, University of Manchester, UK
Email: robert.young@manchester.ac.uk

⁷ National Graphene Institute & School of Materials, University of Manchester, UK
Email: ian.kinloch@manchester.ac.uk

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ABSTRACT

The nature of the interface between a reinforcement and the matrix is crucial in determining the degree of dispersion and mechanical properties. Controlling the interface is particularly important when 2D materials are used as reinforcements, as their flat nature eliminates bonding mechanisms such as mechanical lock-in. For example, we have previously shown that unfunctionalised graphene in an epoxy matrix has just a tenth of the interfacial strength of a carbon fibre.

Herein, we have developed chemical functionalization of two-dimensional (2D) materials as a route to control their interface with thermosets, thermoplastics and elastomers. One well-established method for functionalizing graphene is the use of aryl diazonium chemistry. This functional step is typically applied on as-made powder, however we have found that graphene can be simultaneously functionalized and exfoliated from graphite by electroreduction. This one-step process prevents aggregation, increases thin-flake yield and leads to high quality dispersions. However, similarly structured inorganic 2D materials such as transition metal dichalcogenides (TMDs) have generally been considered to be chemically inert, with few studies into the covalent modification and functionalization of them. Previously, it was believed that only the 1T phase of TMDs could be functionalised by aryl diazonium due to the difference in electronic structure. However, in this work we demonstrate that the more stable and naturally occurring 2H-phase can be successfully functionalised *via* aryl diazonium chemistry.

We have measured the interfacial strength of these functionalized materials within different matrices using Raman mapping of *in-situ* mechanical tests of single flakes and applying a simple shear lag model. Bulk composites were then produced with flakes processing different aspect ratios to prove that these micromechanics approaches can be translated to the macroscale.

1. INTRODUCTION

The isolation of graphene in 2004 launched interest worldwide in the material due to its intriguing combination of mechanical, electrical and thermal properties. The use of graphene as a reinforcement in composites is a particularly promising approach to realize these properties on the bulk scale [1,2,3]. In particular, the high intrinsic modulus (1 TPa) and strength of graphene (130 GPa) makes an ideal structural reinforcement, particular in applications where conventional macroscale carbon fibres cannot be used. Such applications include (i) matrix additive in conventional fibre reinforced polymers, (ii) additive manufacture, and (iii) coatings [4,5]. However, it was initially uncertain

whether reinforcement could be achieved by using a filler that is just one atom thick and if so, whether the micromechanics of such a system could be explained by the continuum micromechanics developed for conventional composites. To address this question, the present authors produced model experimental systems, where single graphene flakes were placed on substrates or embedded into polymer matrices. These flakes were then deformed *in-situ* under a Raman spectrometer, with the change of the position of the Raman bands being proportional to the stress within the flakes. Furthermore, the high spatial resolution of the Raman spectrometer (~ 1 micron) allowed the stress within a given flake to be mapped. These experiments found that the behavior of graphene could be described by shear-lag theory with a critical length of ~ 3 microns and a modulus of 1 TPa. This relatively long critical length (corresponding to an aspect ratio of 10,000) was related to the poor graphene-interface which relied on only van der Waal forces [6]. Further micromechanical studies and modeling have enabled the design rule for graphene composites to be understood further; in addition to the critical length of 3 microns, an optimal flake thickness of 6-8 layers exists and the 2-dimensional nature of the flakes mean that the Krenchel orientation factor of graphene is $8/15^{\text{th}}$ compared to $1/5^{\text{th}}$ for fibres [7,8].

Graphene has triggered interested in a broad range of other 2-dimensional materials, in particular the transition metal transition metal dichalcogenide (TMDCs). The TMDC class of materials is usually expressed as MX_2 , where M is a transition metal atom, such as Mo, W, Nb, etc. and X represents a chalcogen atom, for instance S, Se, etc. Although the number of known combinations of MX_2 has exceeded 40 species, not all of them are of particular interest. Some tend to be instable under ambient conditions, react rapidly with the atmosphere and so lose their special properties [9]. Hence, most research has focused upon the limited number of stable materials that includes WS_2 , MoS_2 , WSe_2 and MoSe_2 . Several groups have undertaken research into the effects of strain, on the electronic structure, phonon vibrational modes and interaction of phonons and electrons in TMDs using Raman spectroscopy. The majority of the studies have been undertaken on MoS_2 that gives well-defined band shifts under strain. Rice *et al.* [10] reported uniaxial strain induced phonon softening in monolayer and few-layer MoS_2 which gives shift rates of $-0.4 \text{ cm}^{-1}/\%$ strain for A_{1g} mode in both mono- and few-layer structures, and $-2.1 \text{ cm}^{-1}/\%$ strain, $-1.7 \text{ cm}^{-1}/\%$ strain for the E_{2g1} mode in monolayer and few-layer crystals respectively. The E_{2g1} mode is believed to be more sensitive to uniaxial strain since its corresponding vibration moves in-plane along with the strain plane where the A_{1g} mode is perpendicular to it. Moreover, a splitting of the E_{2g1} mode was observed in a similar experiment when strained up to 0.8%, indicating the removal of degeneracy arising from the breaking of symmetry by strain (11, 12). In addition, Nayak *et al.* demonstrated a pressure-induced semiconducting-to-metallic transition in few-layer MoS_2 using ultra-high hydrostatic pressure (35 GPa) indicating the successful modulation of electronic structure with strain [13]. A similar transition was later achieved in few-layer WS_2 , showing similar behaviour to MoS_2 [14].

We have previously reported on the micromechanics on MoS_2 composites [10] and thus focus herein on WS_2 composite systems. Recently, we have showed that Raman band shifts under deformation can be used to investigate the stress transfer from a polymer to WS_2 nanomaterials, including nanotubes and flakes. Good stress transfer was achieved with the flakes whether one or both surfaces of the flake were in contact with the polymer (ie if the flake was a coating or embedded within a polymer), whereas the nanotubes had to be fully embedded within the polymer to achieve good transfer [15]. Herein, we show that WS_2 flakes can be described by conventional, continuum micromechanics despite their atomic thickness, as we found earlier with graphene. Model experimental systems were produced through micromechanical exfoliation and the behavior of the system studied by mechanical testing *in-situ* under a Raman spectrometer. Mapping of the band positions as a function of strain allows us to measure the critical length of the WS_2 and calculate its interfacial strength. Composites were then produced with diameter-selected flakes to establish if this critical length is transferred to bulk systems. Finally, data will be presented at the conference to show that by functionalizing the flakes, the interface can be improved, reducing the critical length and allowing the small diameter flakes to be used in composites.

2. EXPERIMENTAL METHODS

Model composite systems: 2D material flakes (graphene and WS₂) were prepared by the mechanical exfoliation method where sellotape was used to repeatedly cleave a bulk crystal until suitably thin crystals were obtained. The morphology of these flakes was then investigated using atomic force microscopy (AFM), scanning electron microscopy (SEM), photoluminescence (PL) and Raman spectroscopy. The flakes were transferred to a PMMA substrate in order to assess the interface of the nanomaterials with a polymer (Fig. 1). The substrates were then deformed *in-situ* under a Raman spectrometer using a small 4-point bending rig. The strain was increased stepwise with Raman spectra collected at each step. A piezoresistive strain gauge being used to measure the strain in the composite. Renishaw inVIVA and Horiba LabRAM spectrometers were used with an excitation wavelength of 514 nm.

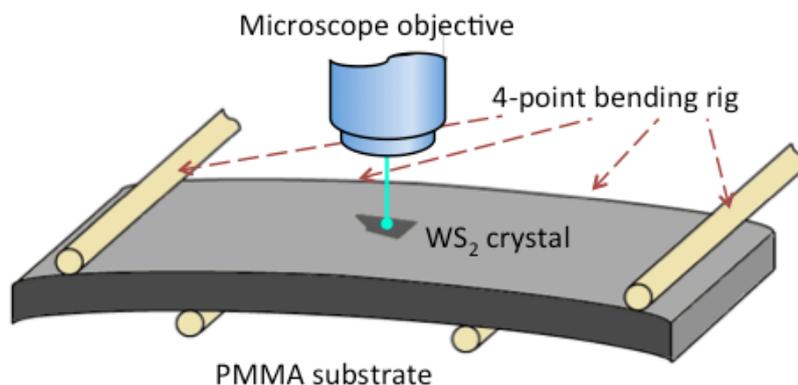


Figure 1. A schematic of the *in-situ* Raman spectroscopy deformation set up. The WS₂ flakes are deposited on the PMMA substrate in the 4-point bending rig under a micro-Raman spectrometer.

Bulk composites: Functionalised graphene was produced by simultaneous reductive electrochemical exfoliation and functionalization as described in Ejigu *et al.* [16] In brief, a three-electrode setup consisting of an isomolded graphite rod working electrode, a silver wire reference electrode, and an isomolded graphite rod counter electrode was used. The electrolyte comprised 0.3 M CsClO₄ and up to 100 mM of either nitrobenzenediazonium (NBD) or bromobenzenediazonium (BBD) in anhydrous DMSO. The reaction was performed using chronoamperometry at a potential of -4.0 V vs Ag wire for 2 h under constant stirring.

WS₂ flakes were produced by exfoliating bulk crystals in a isopropanol-water (1:1) solvent using an ultrasonic bath. The exfoliated flakes were then fractionated into three groups based upon size by centrifuging at different accelerations. Some of the flakes were subsequently functionalized with strong electrophilic aryl diazonium salts such as NBD and BBD.

Polyvinyl alcohol (PVA)-2D material composites were then produced by solvent (dionised water) casting at loadings of ~ 0.5wt%.

3. RESULTS

3.1 Model Experimental System of WS₂

Raman spectroscopy revealed the E_{2g}¹ (~351 cm⁻¹) and A_{1g} bands (~420 cm⁻¹) for the WS₂ materials. In addition, the longitudinal acoustic phonon mode (2LA) was observed very close to the E_{2g}¹ band (within ~ 5cm⁻¹), which caused some ambiguity the peak fitting of the E_{2g}¹ mode (Fig. 2). As the bulk WS₂ is exfoliated down to monolayer, the A_{1g} mode is known to red shift by ~3 cm⁻¹ whereas there is a minor blue-shift of the E_{2g}¹ mode by ~0.5 cm⁻¹ [17]. This thickness dependence of the Raman spectra allowed monolayer and few layer flakes to be identified on the PMMA beam (Fig. 2), with the identification of monolayer being further confirmed by its photoluminescence peak (Fig. 2 insert).

The strain was increased stepwise on the beam upto a maximum strain of 0.55 % at which point Raman spectroscopy maps were taken of the monolayer and few layers flakes (Fig. 3). Line scans of

the strain in the flake parallel to the direction of applied load were then extracted from these maps. For the monolayer flake, the Raman band shifts were converted to strain using a shift rate of $-2.18 \text{ cm}^{-1}/\%$ for E_{2g}^1 , which was derived from DFPT calculations [our paper]. However, since there is no theoretically derived shift rate for few layer WS_2 , it was assumed that the strain in the middle of the flake matched that of the matrix beneath it. Given that the band position was constant for the majority of the length of the crystal, this assumption was considered appropriate as critical length appeared to have been achieved.

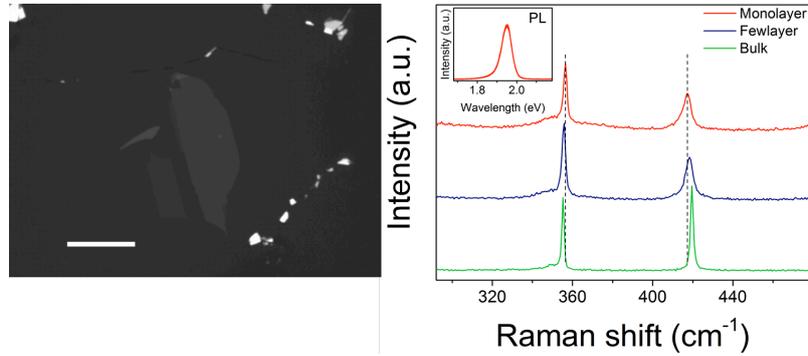


Figure 2: (Left) Optical image and (right) Raman spectra of the monolayer and few layer graphene flakes. The monolayer flake is on the left handside. The bulk WS_2 spectra is shown for reference and the insert shows the PL of the monolayer flake.

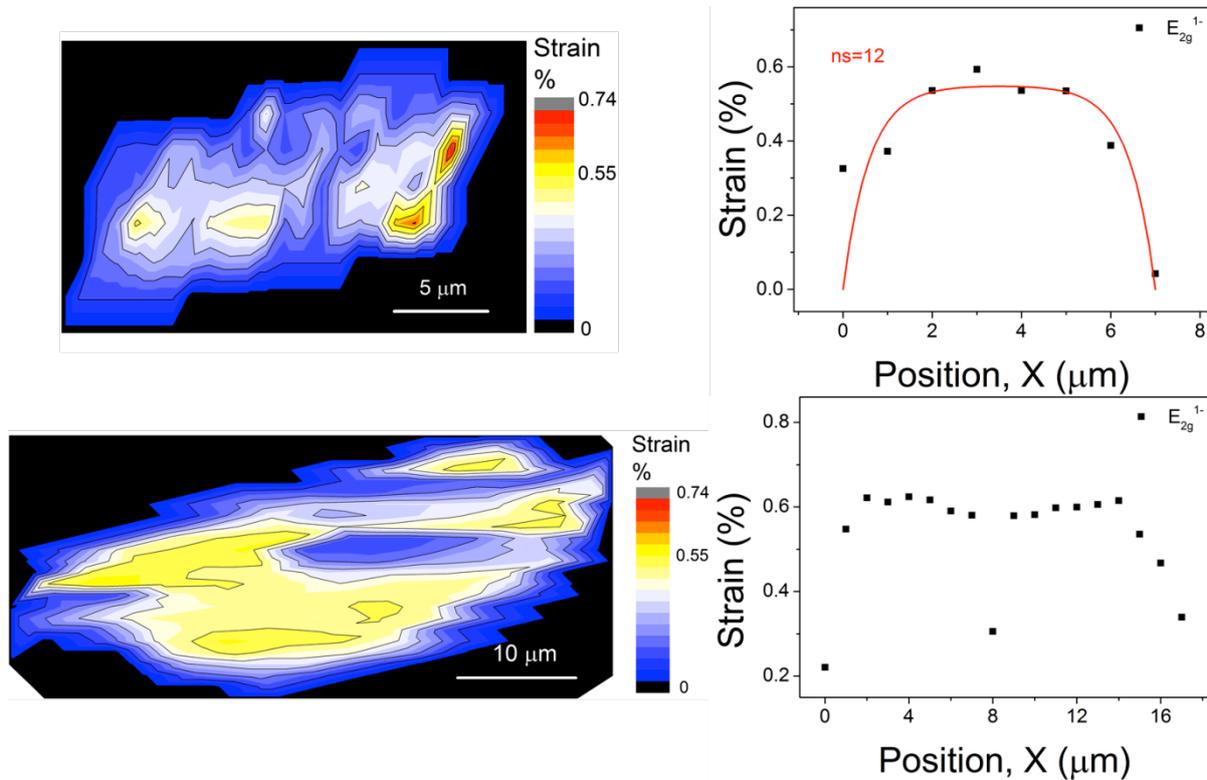


Figure 3: The Raman map and associated line profile from (top) the monolayer flake and (bottom) the few layer flake in Fig. 3. Note that the direction of the applied load was vertical relative to the map and along the x direction in the strain profile.

According to the shear lag theory, the variation of the strain, ϵ_f , along a 2D flake in the direction of applied force, x , can be given by [10]:

$$\varepsilon_f = \varepsilon_m \left[1 - \frac{\cosh\left(\frac{nsx}{l}\right)}{\cosh(ns/2)} \right] \quad (1)$$

where:

$$n = \sqrt{\frac{2G_m}{E_f} \left(\frac{t}{T}\right)} \quad (2)$$

and ε_m is the given level of strain in the matrix, E_f is the Young's modulus of the WS₂ flake, G_m is the matrix shear modulus, l is the length of WS₂ crystal in the measurement region, t and T are the thickness of WS₂ crystal and substrate respectively and s is the aspect ratio (l/t) in the x direction. The parameter n is widely accepted as an indication of efficiency of the stress transfer. It can be seen that the strain profile in the monolayer sample matches this prediction, with zero strain at the edges of the flake, increasing to that of the matrix going towards the centre of the flake. The critical flake length is approximately 4 microns, similar to that found in pristine graphene [10]. A reasonable fitting is found for $ns = 12$ at matrix strain level of 0.55 %. This suggests that the maximum interfacial shear stress at the edge of the crystal is ~ 1.7 MPa ($ns = 12$, $E_f = 272$ GPa and $t = 0.65$ nm). The relatively low level of interfacial shear strength suggests a poor adhesive between WS₂ crystal and polymer matrix. The few layer flake showed similar behavior to the monolayer flake, with a similar critical length. Interestingly the strain dropped to nearly zero at one place near the centre of the few layer flake, suggesting local debonding from the beam or fracture in either the beam or the flake.

3.2 Bulk composites

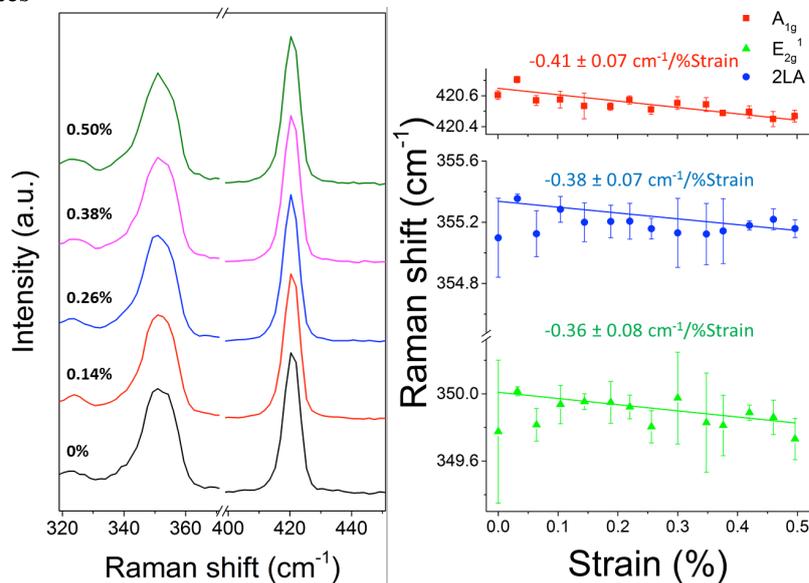


Figure 3: (Left) The Raman spectra of the bulk WS₂-PVA composites produced with the large diameter flakes (diameter = 8.1 ± 4.7 μm) as a function of applied strain and (right) the shift rate of the bands with strain.

Scanning electron microscopy was used to measure the size distribution of three fractions of the liquid exfoliated WS₂ flakes. Mean and standard deviations of 8.1 ± 4.7 μm , 2.3 ± 2.1 μm and 1.1 ± 0.5 μm were measured for the large, medium and small flakes respectively, meaning that only the large flakes were predominately above the critical length of ~ 4 microns found earlier. The composites were deformed in the *in-situ* four point-bending rig under the Raman spectrometer. For these composites, it

was no possible to focus on a particular flake, but rather the spectra were collected from the general surface of the composite. Figure 3 shows the Raman spectra as a function of applied strain for the large diameter flake composites. The bands were found to move with strain, showing that reinforcement had occurred. However, the shift rate of the E_{2g}^1 band was only $0.36 \text{ cm}^{-1}/\%$, compared to theoretical maximum rate of $-2.1 \text{ cm}^{-1}/\%$. This discrepancy can be due to either orientation effects or, more plausibly, that the stress transfer was poor since the average flake diameter was similar to the critical length, whereas typically 10 times the critical length is considered the minimum to get full reinforcement. The Raman band positions of the other two smaller flake samples was found to be independent of composite strain, showing that no stress transfer occurred, confirming the critical flake length found by the shear lag theory (Figure 4).

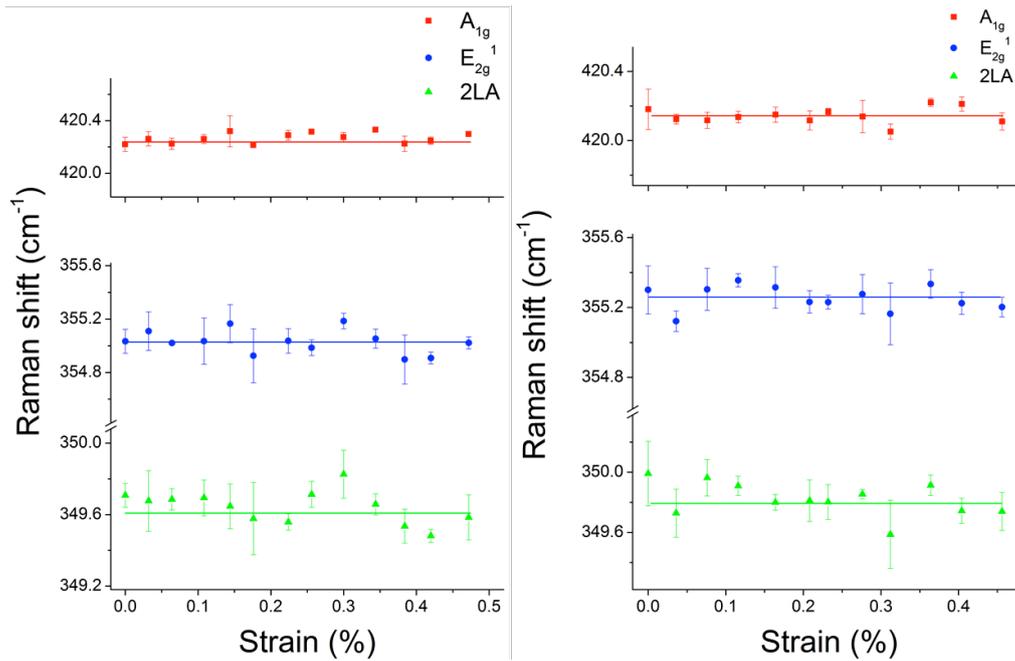


Figure 4: The Raman band positions of the (left) the medium diameter WS_2 flakes and (right) small diameter WS_2 flakes in a bulk PVA composite. Note the flake diameters were $2.3 \pm 2.1 \mu\text{m}$ and $1.1 \pm 0.5 \mu\text{m}$ for the medium and small flakes respectively.

4. CONCLUSIONS

The Raman band shift rate with strain was measured on micromechanically exfoliated WS_2 flakes held on a PMMA beam. Spatial line profiles of the band positions at the maximum applied strain of 0.55 % showed that the strain within the flakes could be described using shear lag theory, despite the sub-nanometre thickness of the flakes. The critical length was found to be $\sim 4 \mu\text{m}$ and the interfacial strength was only 1.7 MPa. Bulk composites were produced using size-fractionated WS_2 flakes. Raman band shifts were only observed in the samples in which the average flake size exceed the critical flake size, confirming the micromechanical approach to such composites.

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