A COMPARISON OF THE MICROMECHANICS OF GRAPHENE- AND TRANSITION METAL DICHALCOGENIDE-NANOCOMPOSITES

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Abstract
We have previously studied the micromechanics of graphene composites by using Raman spectroscopy to map the strain in model composite systems comprising of single graphene flakes. The design rules derived from these models have then been applied successfully to bulk composites. Herein, we have adapted our approach to understand the behaviour of transition metal transition metal dichalcogenide (TMDC) reinforcements such as tungsten disulphide (WS_2) and molybdenum disulphide (MoS_2). Few-layer nanoplatelets were produced by mechanical exfoliation, applied to a polymer substrate and then put under uniaxial strain. Small but significant Raman band shifts were observed upon deformation. These strain-induced bands shifts were modeled using density functional perturbation theory with good correlation between the experimental and predicted band shifts. The micromechanical behaviour of these experimental systems were modeled and compared to that of graphene, with the differences being correlated nature of the interfaces and microstructures. Finally, composites were produced using WS_2 nanotubes in order to assess the role of the dimensionality of the reinforcement in the mechanical performance.

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 including (i) matrix additive in conventional fibre reinforced polymers, (ii) additive manufacture, and (iii) coatings. 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* in 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

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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 8/15th compared to 1/5th 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 cm-1/% strain for A_{1g} mode in both mono- and few-layer structures, and −2.1 cm−1/% strain, −1.7 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. Model experimental systems were produced through micromechanical exfoliation and the behavior of the system studied by mechanical testing *in-situ* in a Raman spectrometer. WS_2 composites were also used as comparison to understand the role of dimensionality of the system.

2. Experimental Methods

WS_2 flakes were prepared by the mechanical exfoliation method whereby sellotape was used to repeatedly cleave a bulk crystal until suitable thin crystals were obtained. WS_2 nanotubes were produced by fluidized bed CVD, as described in [14]. The morphology of these nanomaterials was then investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

The flakes and nanotubes were transferred to a PMMA substrate in order to assess the interface of the nanomaterials with a polymer. The flakes are used as a coating on the PMMA substrate (herein denoted as “Flake-coating”), whereas the nanotubes were either applied as a coating (“NT-coating”) or embedded in an epoxy resin applied the top of the substrate (“NT-composite”). These sample configurations are shown in Fig. 1. The substrates were then deformed *in-situ* in a Raman spectrometer using a small 4-point bending rig. The strain was increased stepwise with a Raman spectra collected at each step. A peizoresitive strain gauge being used to measure the strain. Renishaw inVIA and Horiba LabRAM spectrometers were used with an excitation wavelength of 542 nm.

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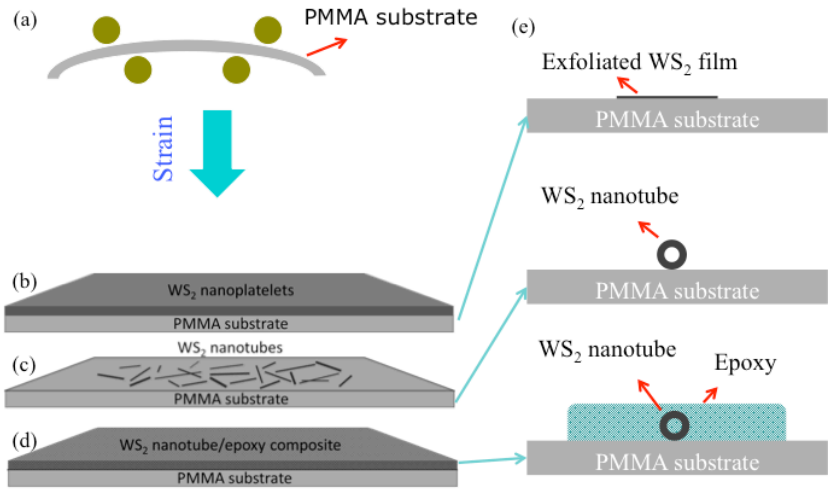

Figure 1. The sample used for the deformation studies. (a) The PMMA substrate in the 4-point bending rig, (b) The "Flake-coating" sample on which WS_2 flakes were deposited on the PMMA, (c) "NT-coating" where WS_2 nanotubes are deposited on the substrate and (d) "NT-composite" where the WS_2 nanotubes are embedded in an epoxy composite which was then coated on the beam. (e) Schematic cross-sections showing the interfaces of the nanomaterials with the polymer.

3. Results and discussion

The AFM and SEM confirmed that the flakes produced were approximately 5 microns in diameter with a thickness of ~ 5.5 nm. The nanotubes were approximately 100 nm in diameter with lengths of the order of tens of microns. Raman spectroscopy revealed the $E_{2g}{}^1$ (~351 cm^{-1}) and A_{1g} bands (~420 cm^{-1}) for the WS_2 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).

Figure 2 shows the change in the Raman spectra as a function of applied strain for the three different samples studied. In particular the graphs on the right-hand side of Figure 2 show the position of each band for a given applied strain. The shift of the band is related to the stress within the flakes and nanotubes, with a decrease in the wavenumber corresponding to a tensile deformation. The rate of the change of the band position with strain (i.e. the gradient of the strain-Raman shift graphs) is proportional to the effective modulus of the reinforcement. It can be seen that a small but significant deformation was observed in the WS_2 flakes, confirming that stress transfer had occurred between the polymer substrate and the flake. However, there was no change in band positions of the NT-coating sample with strain. This result implies that no stress transfer occurred between the nanotubes and the underlying substrate. The NT-composite sample, though, did display a shift in its Raman bands with strain, showing that the stress transfer can occur when the nanotubes were embedded within a composite. These results show the importance of the area of the interface between the nanoreinforcment and the matrix in achieving a good degree of reinforcement; the nanotubes coating on the substrate had a very small interfacial area compared to that of the flakes and the the nanotubes surrounded by polymer.

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a)

b)

c)

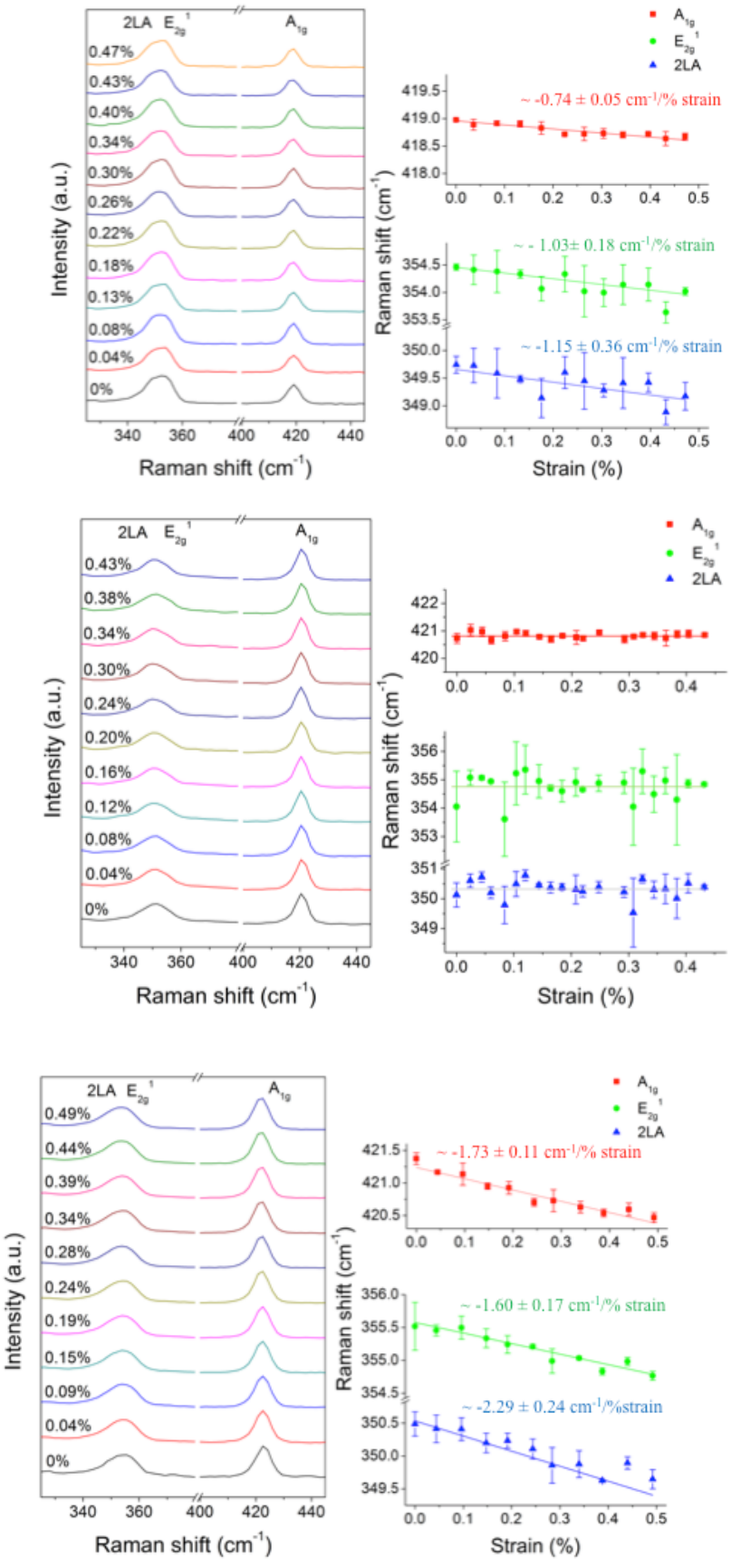

Figure 2. The Raman spectra of the (a) Flake-coating, (b) NT-coating and (c) Flake-coating samples as a function of strain.

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4. Conclusions

Model experimental composite systems were produced using mechanical exfoliated WS_2 flakes and CVD grown WS_2 nanotubes. Raman spectroscopy was used to follow the stress transfer from the polymer substrate into the WS_2 fillers as a function of applied strain. The samples with a relatively high interfacial area (i.e. flakes and embedded nanotubes) showed a good level of stress transfer, whereas the sample with a low interfacial area (nanotubes coated on the surface of the PMMA substrate) did not show any stress transfer. On-going work is using density functional theory to predict the changes in the Raman spectra with strain so that the experimental data can be understood in more detail. The potential of WS_2, MoS_2 and graphene as reinforcements will then be compared.

Acknowledgments

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