Analyzing Monolayer Graphene Edge-on by Raman Spectroscopy

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Abstract

Nowadays graphene is becoming one of the most potentially promising materials for use in different fields, ranging from composites reinforcement to device fabrication. As nanoscale materials, just one atom thick, whose lateral dimensions can be controlled, the orientation of graphene is of great importance, because of its impact on the final performance. Much work has already been undertaken upon graphene orientation when it is rotated around an axis perpendicular to the graphene basal plane, however methods of characterizing its orientation parallel to the basal plane are still lacking. In this work, the Raman scattering from graphene edge-on has been detected, revealing a dependence of Raman band intensity on the graphene orientation, similar to carbon nanotubes.[1] As a result, when combining this work with the previous orientation studies perpendicular to the graphene basal plane, a systematic methodology dealing with 3D orientation of graphene can be established.

The graphene was prepared by low-pressure chemical vapour deposition (LP-CVD) method.[2] Polarized Raman spectra were obtained from either the cross-section or the top surface of the CVD graphene using the so-called 'VV' polarization configuration, where the polarization of incident and scattered radiation were both parallel to each other. Fig.1 defines the Cartesian coordinate system with X, Y and Z axes used to describe the experimental settings[3] in which the CVD graphene samples were tested. In the 'Z' direction, the propagation of laser is along the Z axis, perpendicular to the top surface of the sample; In the 'X' direction, the specimens were cold mounted and further polished until the sample cross section was exposed. Then they were set vertically with the propagation of the laser along the X axis, perpendicular to the cross section. With the laser polarization configurations fixed, Raman spectra were obtained from the specimens rotated to different angles, θ_X and θ_Z, over the full range of 90° in steps of 10°.

The high ratio of the 2D band intensity (I_{2D}) to the G band intensity (I_G), together with a sharp 2D band, as narrow as 35 cm^{-1} in 'Z' direction, corresponds to monolayer graphene (Fig.2) which was further confirmed by the transmission electron microscope (TEM) diffraction pattern (Fig.3). It is found that as the sample is rotated, I_{2D} behaves differently in 'Z' and 'X' directions. In 'Z' direction, I_{2D} does not vary, consistent with the previous study.[4] While in 'X' direction, it is found that the dependence of the I_{2D} shows a ~cos^4 dependence on the graphene orientation, that is, I_{2D} is of the highest/lowest when the laser polarization is parallel/perpendicular to the graphene basal plane. Similar behavior was also observed with other stacked graphene structures.[5] For the purpose of fitting, a constant was added (Eq.1) to the original theoretical prediction.[5] It is also found that the added constant can be a reflection of the graphene orientation degree. In this case, the graphene orientation is partially affected by the roughness of the substrate polymer surface as well as the uneven Cu substrate, characterized by the height profile by the atomic force microscope (AFM) (Fig.4).

It will be demonstrated how this analysis of graphene in the edge-on orientation with Raman spectroscopy can be employed to quantify the orientation of graphene in bulk composites.

References

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Figures

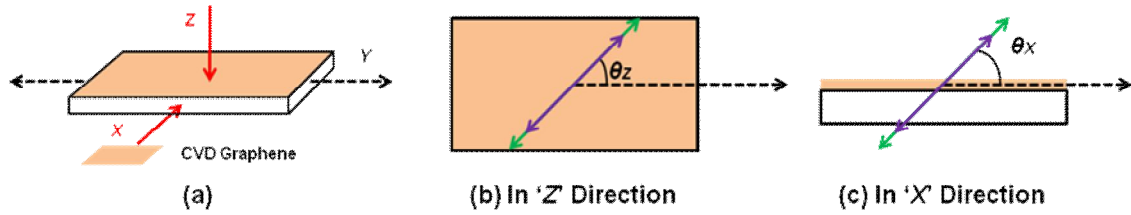(a)   (b) In 'Z' Direction   (c) In 'X' Direction

Figure 1. Schematic illustration of the relationships between the specimen geometries and polarization conditions used in the Raman spectroscopic analysis. The red, purple and green arrows represent the laser propagation, incident radiation and scattered radiation, respectively.
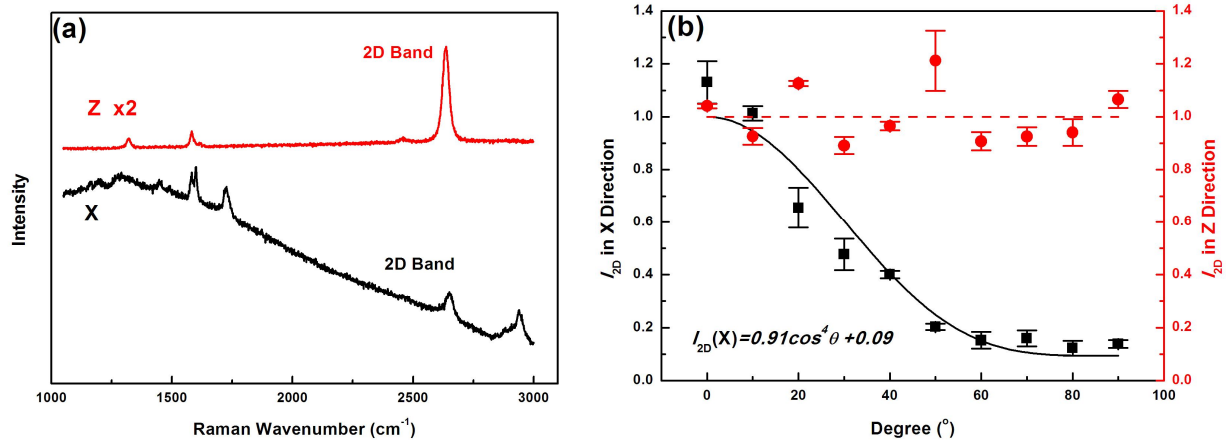

Figure 2. (a) The Raman spectra of the graphene in both 'X' and 'Z' direction. (b) I_{2D} variations of the graphene in both 'X' and 'Z' direction.

Inside figure 2(b): $I_{2D}(X) = 0.91\cos^4\theta + 0.09$
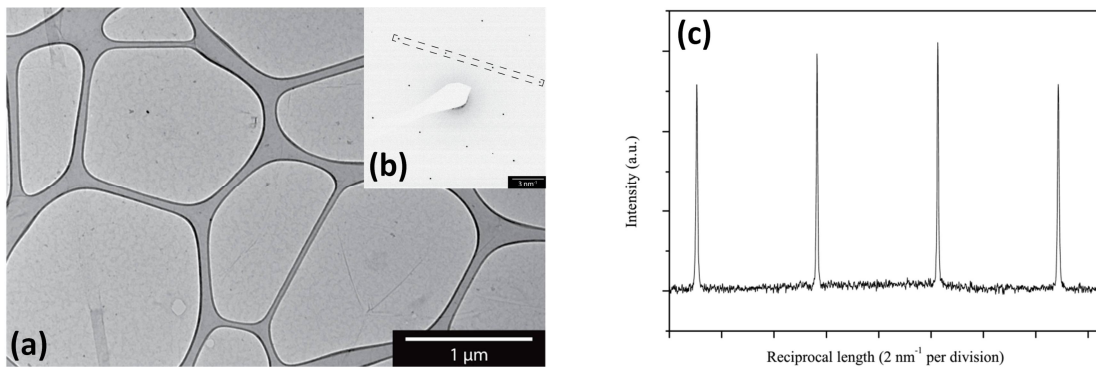

Figure 3. (a) Bright field TEM of graphene after transfer to a lacy carbon grid. (b) TEM diffraction pattern and (c) line profile of the diffraction intensity from the marked area. The outer spots are of comparable intensity to the outer spots indicating single-layer graphene.
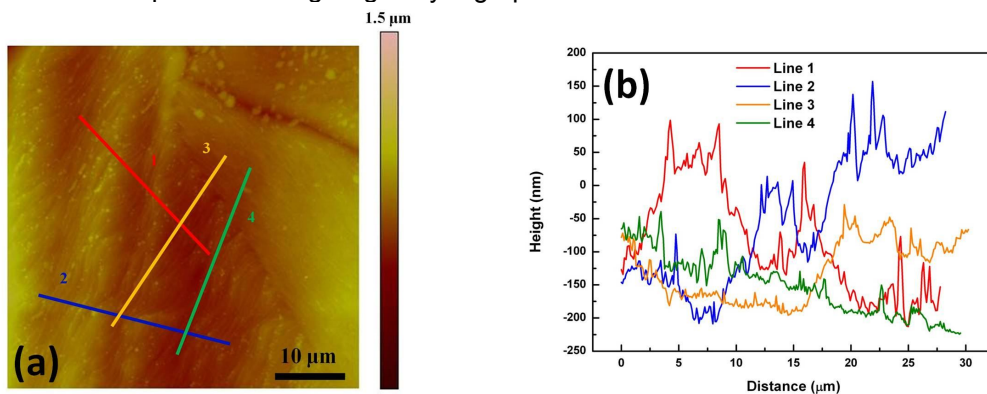

Figure 4. (a) AFM topography and scanning lines. (b) AFM height profile of the scanning lines.

Equation

$$I_{2D}(X) \propto C_1 \cos^4\theta_X + C_2 \qquad\qquad \text{Eq.1}$$