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Raman spectroscopy and band structure of Pd-hybridized multilayer graphene



Carbon



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ABSTRACT

Graphene sheets prepared through liquid exfoliation of expanded graphite were hybridized with Pd nanoparticles. The impact of these particles on the electronic and physical structure of the graphene is determined through transmission electron microscopy and Raman spectroscopy using 532 and 325 nm excitation wavelengths. Based on the changes to the Raman D and G peaks, insights are provided concerning the deposition mechanism at pristine and defective lattice sites, as well as electronic scattering. These data are compared to *ab initio* band structure computations. For purposes of the model, the graphene/Pd hybrid was approximated by a charged graphene sheet. The resulting structure exhibited π - π * expansion approaching the Γ point of the Brillouin zone which was validated by tracking the Raman D band dispersion.

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1. Introduction

Though graphitic carbon is a long studied material, its unique properties in graphene form have made it a very prolific topic in contemporary research. Various studies have investigated the electronic structure and phonon dispersion of mechanically exfoliated graphene and graphite with great depth [1–5]. These works have helped to establish a very comprehensive understanding of spectroscopic phenomena of carbon-based materials and have produced a broad toolset which can be used to examine these materials.

A current standing need is applying these methods to more application-driven systems. From an applications standpoint, graphene should be easy to produce, patterning should be scalable, and properties should have uniformity at the wafer level. Mechanically exfoliated graphene has presented itself as an incredibly cheap production method which can produce graphene with extremely reliable properties. Indeed, it has been an essential cornerstone of fundamental graphene research. However, with respect to scalability, it is found lacking. Graphene produced through chemical vapor deposition (CVD) is a promising candidate but has limited substrate options during the growth phase, necessitating complex substrate-transfer methods during device fabrication [6]. Liquid-suspended graphene, on the other hand, can be produced in large quantities at very low cost. In addition, methods have been developed to quickly and reliably pattern liquid-suspended graphene onto surface-functionalized substrates, making it scalable on the industrial level [7,8].

Though liquid exfoliation method is capable of producing high-quality graphene with Bernal AB layer stacking, the thermal expansion process produces a vertical strain in the graphene crystal. Under these conditions, the mirror symmetry of the electronic structure of graphene is broken and can result in quenching of double-resonance Raman scattering events [9,10]. In particular, the 2D (or G') Raman peak exhibits

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trends in intensity and peak shape based upon the number of layers of graphene [4,11]. As such, quantification of layers can be made more difficult in exfoliated graphene. As these analytical techniques are developed and refined, they must be examined for effectiveness and validity so that they can be applied to application-level samples.

Further attention is warranted in application of these techniques with graphene hybrids, which is a field of great contemporary interest. The presence of attached particles, functional molecules, linkers, and strain-inducing substrates can break symmetry, distort electronic structure, suppress/ enhance transitions, and alter conductivity [12]. These modifications can be used to great effect in a variety of applications: electrochemical devices and sensors [13]. photocatalysis [14], gas sensing [15], electronics [16], and even functionalized biomedical devices [17]. Numerous methods exist to alter the electronic and optical properties of graphene according to application needs. Processing methods span a broad range: vapor-based doping [18], hydrothermal and solvothermal hybridization [19], as well as substrate-induced strain [20]. Various properties are measured, demonstrating the net impact of hybrids on the host graphene or the guest particles. Over the past several years there has been a systematic effort to explore such hybrids computationally and moreover. to correlate experimental measurements computations of electronic structure [21-23].

This study seeks to unite the aforementioned fields of study by applying the current analytical techniques to hybridized multilayer graphene produced through liquid exfoliation and to further correlate the results to electronic structure. Through this investigation, we will derive information about deposition mechanisms, influence on electronic structure, and defect scattering. It is our hope that such studies can fuel graphene-hybrid research and lead to refined techniques, in addition to the expected benefits towards predictive models.

2. Experimental

Samples of graphene were produced by rapidly heating expandable graphite (low-sulfuric content, 1.5-2.0% wt, 200-350 expansion ratio) to 1000 °C and maintaining temperature for 60 s under the atmosphere of a forming gas (5% H_2 , 95% Ar). Few-layer graphene sheets were subsequently exfoliated from the EG via durative sonication in NMP solvent for 60 min to form a suspension. Finally, the solution was centrifuged at 15,000 RPM for 7 min and separated. This process was repeated until 5 mg of solid, exfoliated material consisting of few-layer graphene sheets was collected. As the remainder of this study focuses exclusively on multilayer graphene, we will omit the "multilayer" descriptor from further discussion for simplicity. Single and bilayer graphene are not explored in this study. Pd nanopartices were deposited onto the surface of the resulting graphene suspended in absolute ethanol using a Pd(acac)₂ precursor. Growth was carried out in Teflon-lined autoclaves at 115 °C for 18 h durations. Measurement samples were prepared by isolating supernatant from a suspended solution of graphene by centrifugation at 10,000 RPM for 5 min. This solution was then drop-cast onto lacey-carbon Cu grids or spin-coated onto Si substrates

at 1500 RPM for 2 min for transmission electron microscopy (TEM) or Raman spectroscopy, respectively.

In order to evaluate morphology and crystalline structure of the graphene and graphene/Pd hybrid, TEM samples were imaged in a FEI Tecnai F20 field emission microscope operated at 80 kV. Bright field imaging (Fig. 1a), followed by particle analysis using ImageJ software [24], showed that the Pd particles are approximately 20 nm in diameter and that the graphene coverage was approximately 38.7%. High resolution TEM imaging (Fig. 1c) showed that the graphene is highly crystalline. Selected area electron diffraction (SAED) was carried out and the resulting pattern is presented in Fig. 1b. Single-crystalline reflections are visible due to the hexagonal graphene lattice. The absence of both Moiré fringes in the HRTEM images and distorted rings in the SAED pattern further supported that the Bernal structure of the graphene was maintained and that there was no rotational stacking [25]. Several polycrystalline rings characteristic of face-centered cubic Pd were observed in the SAED pattern and the principal reflections are indexed in the pattern. Planar spacing measurements were performed by Gaussian fits of a line profile across a radially averaged image. This was carried out with the DiffTools plugin for Gatan Digital Micrograph™ [26]. The planar spacing of the Pd crystal was computed to have 1.87% expansive strain relative to bulk Pd.

Phonon and electronic band dispersion changes were measured by Raman spectroscopy using a Horiba Jobin Yvon HR800 Raman microscope. Spectra were collected from various flakes (Fig. 2) on the substrate with excitation wavelengths of 325 nm (HeCd laser) and 532 nm (diode-pumped solid state laser). Power levels were maintained at approximately 3 mW with a measured spot size of 1.8 μm (the computed ideal spot size was approximately 800 nm) and a spectral resolution of 2.5 cm⁻¹. Spectra which exhibited 2D peak shape characteristic of 1-2 layer graphene and manylayer graphene (more than 6 layers) were discarded from our statistical sample, as bulk graphite properties and layerdependent effects would otherwise dominate spectral features. The vast majority of flakes produced by our synthesis were 4-5 layers, in accordance with our previous findings with these techniques [27]. In addition, flake sizes were limited to approximately 5 µm to limit variations in D-band intensity based on grain size distribution and edge effects [28]. Basic trends in D and G peaks were observed using the 532 nm source. For purposes of these measurements, spectra were collected from 15 individual exfoliated and 15 hybridized flakes (two 3-4 layers, nine 4-5 layers, four 5-6 layers), representative 2D-peaks of which are presented in Fig. 2e. Multiple Lorentzian peaks were fitted to the 2D peaks in order to discriminate between layers in accordance with existing literature [9]. In order to study the D-peak dispersion, 532 nm and 325 nm excitation sources were used to collect Raman spectra from single flakes. These criteria for selecting flakes for these measurements were more stringent. Only flakes which were $5\,\mu m$ in diameter and which exhibited 2D peaks consistent with 4-5 layers of graphene were considered. In total, 6 individual flakes were considered (3 each of exfoliated and hybridized graphene). Representative spectra using the 532 nm source are shown in Fig. 2 and are included in both



Fig. 1 – (a) Bright-field TEM and (b) high-resolution TEM image of graphene-Pd hybrid. (c) Corresponding selected-area electron diffraction pattern.

of the previously mentioned statistical samplings. These spectra have been renormalized and scaled to highlight their differences (Fig. 2). For purposes of peak fitting, backgrounds were removed using a constant offset and single Lorentzian functions were use for the G and D peaks.

The G-peak was observed to have a frequency, ν , of $1582.83 \pm 0.415 \text{ cm}^{-1}$ and $1579.24 \pm 0.281 \text{ cm}^{-1}$ and full-width-at-half-max, Γ_{G} , of $14.97 \pm 0.36 \text{ cm}^{-1}$ and $15.62 \pm 0.40 \text{ cm}^{-1}$ for exfoliated and Pd-hybridized graphene, respectively. In addition, the D/G integrated peak area ratio was observed to decrease on average by 43.5% (from 0.249 ± 0.037 to 0.141 ± 0.023). The 2D peak, on the other hand, exhibited no statistically significant changes after hybridization.

These experimental results were compared to computations using the ABINIT software package [29]. In order to model the exfoliated graphene, a simple 4-layer unit cell was constructed using Bernal AB stacking. The cell had an optimized graphene lattice constant of 2.4612 Å, or carbon-carbon distance of 1.421 Å, and a vacuum region of 20 Å above the graphene sheet. A charge-based model was constructed to approximate the graphene-Pd hybrid structure. Pd atoms were placed on the surface layers of the exfoliated graphene model in a bond-centered configuration. The Madelung energies of the Pd atoms were computed as a function of distance from the graphene surface, as well as the corresponding charge transfer from the Pd atom to each C atom. These results are shown in Fig. 3. The minimum Madelung energy (i.e. the most stable configuration) was found to occur with the Pd atom 2.26 Å from the surface C-C bond and the corresponding donated charge was computed to be 0.0356e per unit cell of graphene (or 0.0178e per surface C atom).

For purposes of the band structure calculation, the Pdhybridized graphene sheet was approximated by a graphene sheet with uniform excess charge on the surface layers. In order to properly compute the surface charge which represented the physical samples, the number of donated electrons needed to be scaled to account for atomic density and Pd coverage area. The graphene unit cell has an area of 5.25 Å^2 and the (111) surface in the FCC-Pd unit cell has an atomic density of 0.153 atoms/Å². Combining these with the 38.7% coverage area measured in TEM analysis resulted in an excess charge of 0.00552e per surface carbon atom in the hybrid model. The (111) surface of Pd was chosen as the contact face for two principal reasons: (1) like the graphene surface, it exhibits six-point symmetry and (2) planes equivalent to the (111) FCC-Pd planes sit perpendicular to the (111) plane and their spacing has <10% mismatch with the graphene (020) planes.

Band structures (Fig. 4) were computed using the two described models (exfoliated graphene and exfoliated graphene with 0.00552e excess charge on each surface carbon atom). The system was modeled using the supercell approach with periodically repeated slabs. A mesh of $20 \times 20 \times 5$ was implemented in Monkhorst–Pack scheme. Several principal observations can be made of the band structure change after hybridization: (1) the Fermi energy increased by 0.166 eV, (2) the π and π^* bands open slightly approaching the high-symmetry Γ point, (3) the individual branches that comprise the π and π^* bands have an increased energy-spread, and (4) the gap between the σ and σ^* bands narrows slightly at the Γ point.

3. Discussion

3.1. Impact of Pd particles on defect sites

The initial observations of the Raman spectra collected using the 532 nm source (contrasting the exfoliated and hybridized graphene) provides some insights into the chemical process and the structural modifications of the graphene sheet. First, the D-peak is quenched by a proportion that is nearly equal to the average Pd coverage area. In order to completely interpret this result, it is first essential to inspect the behavior of the 2D peak. Both the D and 2D peaks are second-order scattering events which involve an electron being excited from the π to the π^* band, subsequently undergoing two scattering events which produces a Raman-shifted photon. The distinction is that the D peak is created by an inelastic scattering event (involving an iTO phonon) and an elastic scattering event (involving a defect), whereas the 2D peak is a result of two inelastic scattering events (involving iTO phonons) [30,31]. The fact that there was a dramatic change in the D peak while the 2D peak remained unchanged suggests that there is little measurable change to the electron-phonon-coupling in the sample and that the suppression of the D peak is due to reduced defect scattering.

Returning to our original observation, the similarity of the D/G ratio quenching to the average Pd coverage area (43.5% and 38.7%, respectively) suggests that the deposition process



Fig. 2 – Raman spectra using 532 nm source of exfoliated and hybridized 4–5 layer graphene showing (a) D and G peaks, (b) 2D peak, and representative optical microscope images of (c) graphene and (d) Pd-hybridized graphene flakes, and (e) Raman layer identification with Lorentzian curve fitting. A color version of this figure can be viewed online.

is not preferential towards defects. The lattice defects are covered by approximately the same fraction as the rest of the sample. Further, the width of the D and G peaks may provide insights concerning the deposition mechanisms at either



Fig. 3 – Madelung energy of bond-centered Pd atom and corresponding donated charge per graphene unit cell.



Fig. 4 – Electronic band structures of 4-layer (a) exfoliated and (b) charged graphene.

lattice site. The broadening of the D peak from 35.44 ± 0.99 to 42.12 ± 1.88 cm⁻¹ may indicate that there is an increased concentration of sp³ carbon atoms [31–33]. However, if sp³ carbon formation also occurred at defect-free regions of the sample, a similar broadening of the G peak would be observed along with an emerging D' peak [31–33]. The G-peak, however, does

not exhibit a significant broadening (the error margins in $\Gamma_{\rm G}$ for either peak overlap). This suggests that the Pd deposition may be linker-driven at the defect sites and non-linker-driven at the pristine lattice sites. Further, the slight down-shift of the G-peak may indicate minor charge doping on the graphene surface [34]. Down-shifting of the G-peak may also suggest the presence of strain, though strain effects should also produce substantial broadening and splitting [35] which, once again, is not observed. Charge doping is typically accompanied by an up-shift in the G peak, though downward shifts are observed for very small Fermi level shifts where the energy of the shift is on the order of the phonon energy [34]. We note that the Fermi level shift of 166 meV predicted by the band structure computations is close to the down-shifting regime. The computed charge transfer results in a charge density of 2.1×10^{13} cm⁻² which, along with the observed Fermi level shift, is in reasonable agreement with some existing experimental studies [36]. Further, we note that the referenced work presents a less dramatic shift of the Raman Gpeak and diminished influence on the 2D/G ratio for bilayer graphene as compared to single layer graphene. We expect these trends to persist progressively greater number of layers in accordance with our observations.

To further refine these quantitative results, we turn to a set of empirically determined formulae which correlate the D/G intensity ratio and excitation wavelength to the defect density and mean distance between defects [37]. Based upon the D/G intensity ratios computed, the defect densities and average defect distances were 2.23×10^{10} cm⁻² and 38.1 nm, and 1.07×10^{10} cm⁻² and 54.9 nm, for exfoliated and hybridized graphene, respectively (a 51.9% reduction in defect density).

From the standpoint of quantifying the change in scattering events, the relative number of occurrences is truly represented by the area of the peak. As such, broadening of the peak will increase the apparent impact of a diminished intensity. In order to refine these results, we scale the area of the Dpeaks collected from the hybridized graphene by the width of the D-peaks observed in the exfoliated graphene to determine the equivalent intensity (the integrated area of a Lorentzian distribution is given by $A = \pi I_0 \Gamma/2$). This yields an average defect density of 1.28×10^{10} cm⁻² and a mean defect distance of 50.4 nm (a 42.8% reduction).

We note that the referenced study is applied towards mechanically exfoliated single-layer graphene only and there may be discrepancies for quantified values, though it may be beneficial in providing relative trends in defect density between the two samples provided that the functional form of the defect density expression follows a similar trend for greater numbers of layers. Indeed, the D-peak widths for exfoliated graphene suggest average defect distances of approximately 5 nm, whereas I_D/I_G ratios predict distances an order of magnitude greater. The two computed values for percent reduction in defect density provide upper and lower bounds on the change in the number of defect scattering sites. These results suggest that the deposition coverage is independent of the defect density which is further validated by our existing synthesis-driven studies which show that the hybridization process can be tuned to provide complete particle coverage [27]. However, to provide a full view of the

role of the lattice defects, it would be necessary to establish a trend in I_D/I_G with respect to Pd coverage area. It may be the case that Pd seed-atoms are initially deposited preferentially on defect sites and subsequent deposition onto pristine sites only occurs after the defect concentration is sufficiently occupied. For an Oswald ripening process, this may provide insight into the preference between nucleation and seed deposition.

3.2. Raman D-peak dispersion

Raman spectra collected at varied excitation energies (Fig. 5) provide further insights into the electronic structure of the graphene. Since the D peak is created by an electron-phonon scattering event, we can jointly probe the band structure and the phonon dispersion relation by inducing this scattering event at different distances from the K-point (pumping the π -to- π^* transition with different photon energies) [34]. Raman spectra show that the Pd-hybridized graphene (Fig. 5b) has a less substantial D-peak shift than the exfoliated graphene (Fig. 5a) when using a 325 nm excitation source. The exact D-peak dispersions were measured to be 44.17 and 36.76 cm⁻¹/eV for the exfoliated and hybridized samples, respectively (a 16.8% change). This indicates that the π - π * gap is greater in the hybridized graphene, causing the phonon frequency to be measured closer to the K-point. This observation is reflected in the computed electronic band structure.



Fig. 5 – Raman spectra collected from single (a) exfoliated and (b) Pd-hybridized graphene flakes using 532 and 325 nm excitation sources. D-peak positions are indicated with lines and averaged values are indicated by single points between the two spectra.

In order to highlight the change in the band structure about the K-point, the bands corresponding to the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the hybridized graphene were subtracted from those of the exfoliated graphene model (Fig. 6). The difference bands are plotted out to $K\Gamma/3$ where the π - π^* gap approaches 8 eV. We note that the computed band opening is relatively small, though these computations consider the donated charge to be averaged throughout the entire graphene sheet. Effects due to more localized regions of high charge density (approximately three times greater than the average, in accordance with our coverage estimate) may contribute towards a greater effective band opening.

While the 2D band would have provided additional insight into the nature of the band structure, there were several associated difficulties which prevented meaningful analysis: (1) the line shape was significantly altered while using the UV excitation source, (2) the peak intensity was drastically reduced, and (3) the graphene samples were predominantly 4-5 layers, and therefore, meaningful peak fitting of the 2D band was not possible. Due to the double-scattering event required to produce the 2D peak, it exhibits splitting which is characteristic of the number of layers in the sample. The observed splitting is not completely explained by the phonon dispersion relation. In fact, from a standpoint of the phonons alone, it is predicted that the positions of the superimposed peaks would only differ by fractions of a wavenumber. The dispersion of the band structure, on the other hand, predicts scattering events which are further separated in k-space, resulting in the discernable components of the 2D peak [9]. The separation of these peaks relative to one another would therefore provide insights concerning the magnitude of the π and π^* splitting due to increased layer quantities. Our band structure computations predicted an increase in this band splitting, which would have been interesting to measure directly with the Raman 2D band.

Since the number of peak components increases with the square of the number of layers, the 2D peak and its components can only be reliably tracked for single and bi-layer graphene (which our samples did not have in great quantity).



Fig. 6 – Difference between electronic band structure of charged graphene (from Fig. 4b) and exfoliated graphene (from Fig. 4a).

These scattering events are less likely to occur further from the K point and are thereby quenched quite severely when collecting Raman spectra using an ultraviolet source [38]. Further, the probability of scattering for each peak component changes and alters the line shape of the 2D band. The compounding of these effects makes it difficult to track the individual peak positions and to discern broadening from increased dispersion of the 2D components, which prevents this avenue of investigation in this study. However, the relatively large source interval facilitated the subtle change to the D-peak dispersion and allowed the relative D-peak shifts to be of sufficient statistical significance.

Finally, to address the validity of the charge-based model, we note several observations in relation to existing literature and provide additional information concerning preliminary computations. The computed charge transfer and Pd-C equilibrium distance is in agreement with existing literature which has used a variety of methods [21,22,39]. The Fermi energy shift is as predicted from the charge donation standpoint (an increase in electron concentration fills higher energy states causing an upward shift) and according to predictions based upon work function [22]. Further, the change in Fermi energy and donated charge contributions were in line with existing experimental works [36]. In the construction of the hybridized model for use with ABINIT, vacancy-centered, atom-centered, and bond-centered Pd configurations were all considered, though minimal difference was observed in the resulting donated charge (within the error margins of experimental measurements).

4. Conclusions

Raman spectra were measured for exfoliated and Pd-hybridized graphene, allowing us to conclude that the deposition process is not preferential towards defects, and that the deposition mechanism may be different at pristine and defective lattice sites. The dispersion of the D-peak also validated the band opening predicted by electronic band structure calculations on a charge-based model. This demonstrates that such simplified models may be more widely applicable in the prediction of electronic properties for applications. While the ultraviolet source used to measure D-peak dispersion resulted in significantly reduced intensities (preventing the use of 2D peaks), it provided a relative large range in k-space to be probed. This allowed the relatively subtle dispersion to be measured.

Based upon the results of this study, we note several further investigations of merit: (1) Since the secondary excitation source used in this study is well into the ultraviolet range, we were unable to validate the wavelength dependence of the Raman defect quantification relations for the exfoliated and hybridized samples (as the formulae presented in the original work were deemed valid for the visible range alone). It would be of great interest to extend the defect quantification study to multilayer and exfoliated graphene so that it can be more widely applied as an absolute measurement, rather than as a relative one, as implemented herein. (2) Adjusting the liquid exfoliation process to produce graphene that is predominantly 2 layers and collecting Raman spectra using an excitation source which is tunable over the visible range would allow for accurate tracking of the 2D peak components, enabling a direct measurement of the relative dispersion of the π and π^* branches. (3) A true defect-dependent hybridization study which observes the trends in the Raman spectra. This would provide a clear insight as to whether or not the defect density can be tuned to increase hybrid particle coverage. In addition, such a study may increase understanding of the nature of the apparent disparity in deposition mechanism between pristine and defective lattice sites. (4) The nature of the substrate-specimen interaction for graphene hybrids has not yet been carefully considered in a systematic study. It would be of great interest to understand whether there are parasitic effects towards the charge transfer between the graphene and its hybrid particles due effects at the particle-substrate junction.

Such studies which provide insights into computational techniques/approximations and adapt idealized analytical methods to applied systems will be highly beneficial towards the field of graphene hybrids as a whole. By addressing these techniques generally, these studies may benefit a variety of graphene hybrid systems, such as those in our previous work which have shown promise in a variety of applications, including supercapacitors [27] and methanol fuel cells [40].

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