

# Raman Spectroscopic Studies of Graphene and Related Nanomaterials

グラフェンおよびナノ材料の顕微ラマン分光解析

Yong P. CHEN

Graphene, the two dimensional carbon, is one of the most actively studied nanomaterials due to its many fascinating properties and potential technological applications. Raman spectroscopy and imaging has become a simple yet powerful, non-invasive method to characterize graphene and a wide range of other nanomaterials. This paper will review examples of using Raman spectroscopy and imaging to study a broad range of structural, phononic, electronic, and thermal properties of graphene, drawing mostly from work in my laboratory on both exfoliated graphene and synthetic graphene grown by chemical vapor deposition. Combining electronic transport and gating with Raman measurements also gives a powerful technique to characterize electron-phonon coupling. Similar experimental techniques can be applied to many other “beyond-graphene” 2D materials and their Van der Waals (VdW) coupled heterostructures.

## Introduction

Graphene is the Two-Dimensional (2D) form of carbon with planar  $sp^2$  bonding in a honeycomb lattice (Figure 1a). Only about 0.5 nm thick, graphene represents a single atomic layer of graphite and is also the building block for many carbon nanomaterials including carbon nanotubes (which are graphene sheets wrapped into cylinders). In the past decade, graphene has received tremendous interests and become one of the most studied and talked about nanomaterials due to a large number of fascinating properties and exciting potential applications.<sup>[1, 2]</sup> For example, graphene claims one of the highest electrical conductivity, current carrying capability, thermal conductivity, and mechanical strength among all materials, while at the same time is highly transparent, flexible and impermeable. Potential applications where graphene can play major roles include high speed and high frequency electronics and communications, flexible electronics and transparent conductors (eg. for touch screens and solar cells), and protective coating for chemical or biological samples, etc. My group has been working on graphene since 2007 on its fabrication and growth, fundamental properties as well as device applications.<sup>1</sup> We produce

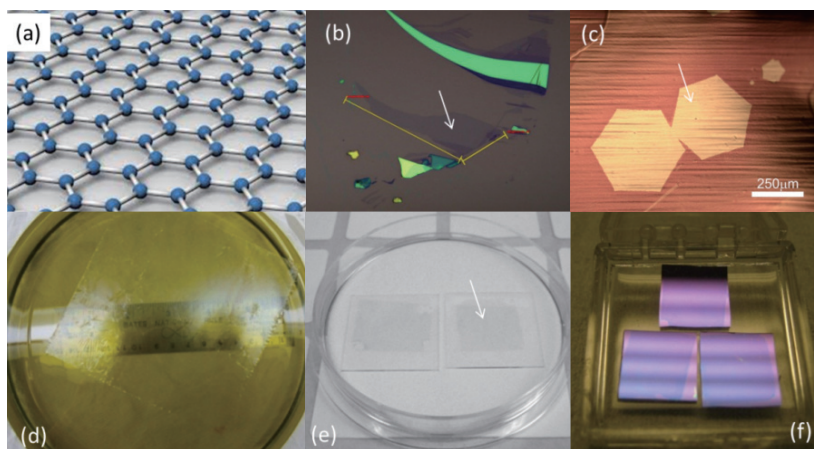


Figure 1 (a) Schematic graphene with its 2D honeycomb lattice of carbon atoms (blue). (b) Optical microscope image of a graphene flake (marked by the arrow) exfoliated using the “scotch tape” method from bulk graphite onto a silicon wafer. (c) Optical image of large graphene single crystals synthesized by CVD on Cu. Figure 1(d-f) Photos of wafer-size CVD-grown graphene films (d) floating on liquid (with graphene covered by a polymer film as support<sup>[5]</sup>), transferred on (e) cover glasses and on (f) silicon wafers.

graphene using both the (top down) “scotch tape” based exfoliation<sup>[2, 3]</sup> from graphite, as well as (bottom up) synthesis from hydrocarbon (e.g.,  $CH_4$ ) using Chemical Vapor Deposition (CVD) on various substrates.<sup>[4, 5]</sup> Figure 1b-1f shows various images of graphene (ranging from microns to centimeters in size) from our work.

Raman spectroscopy<sup>[6]</sup> is a commonly used method, based on inelastic light scattering, to characterize excitations (that give the measured energy or frequency difference, known as the “Raman shift”, between the incident and scattered

light) in diverse systems ranging from molecules to solids and nanomaterials (including graphene<sup>[7, 8]</sup>). In our lab, we have a confocal Raman microscope (HORIBA XploRA), to which we have further added a stage to scan the sample for imaging/mapping of spectral features (“Raman imaging”), and another two optical cryostats with electrical feed-throughs to control the temperature (from 4 K to >800 K) and pressure of the sample and allow electrical connection/gating for simultaneous Raman/optical and electrical measurements (see Figure 2). This system has become an indispensable tool routinely used in our graphene research, and a powerful table-top laboratory and workforce that have supported or enabled many other projects in our lab. As we will demonstrate with various examples below, Raman spectroscopy and imaging offers a noninvasive and efficient technique to characterize and study a broad range of properties of graphene, including (but not limited to) the thickness (number of layers), doping (carrier density/chemical potential), stacking order (between layers in multilayers), defects, edges, grain boundaries, thermal conductivity, and electron-phonon coupling. The measurement methods and techniques we used and developed can be applied to many other nanomaterials, particularly “beyond-graphene” 2D materials that are currently attracting intense interests due to their novel properties and exciting application potentials, and are among a major thrust also in our current and future research.

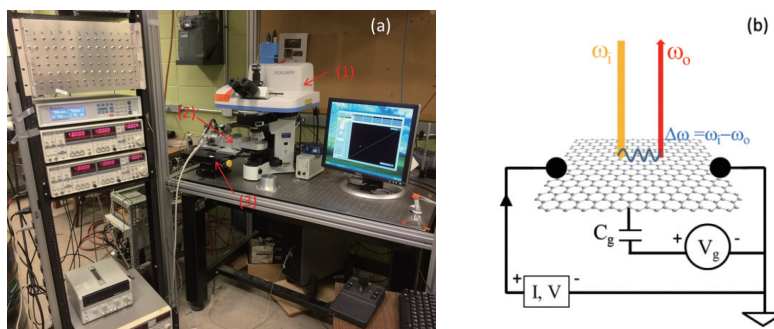


Figure 2 (a) Photo of the Raman spectroscopy and imaging system used in Chen lab. (1): the Raman microscope, (2): an optical cryostat with electrical feedthroughs, (3): scanning stage. (b) Schematic of Raman spectroscopy on graphene ( $\Delta\omega$  is the Raman shift due to some excitation, represented by the blue waves and typically phonons, in graphene). Black round dots represent electrical contacts on graphene that can be used to perform electric transport measurements or pass a current in graphene. We can also apply a gate voltage ( $V_g$ ), typically on a back gate (e.g., doped silicon wafer with  $\text{SiO}_2$  gate dielectric of capacitance  $C_g$ ) to modulate the carrier density (doping) in graphene.

### Raman Spectra of Vibration/Phonon Modes of Graphene and its Multilayers.

The excitations responsible to the Raman shift measured in the Raman spectroscopy on graphene are typically various lattice vibration modes (or phonon modes) of graphene.<sup>[7, 8]</sup> Figure 3a shows a typical Raman spectrum of graphene (middle trace, note in this paper “graphene” means a single layer graphene unless otherwise specified), along with the spectra for a 2-layer graphene (lower trace) with “AB” (or “Bernal”) stacking (similar to the stacking in graphite) and a more disordered graphene (upper trace) where we have used e-beam irradiation to create (a controllable amount of) artificial defects. The right and left insets depict the lattice vibration patterns (optical phonon modes) for two particularly important Raman peaks we study: the “G” peak ( $\sim 1580 \text{ cm}^{-1}$ , seen in all 3 spectra), which is a “(Brillouin) zone-center” ( $\Gamma$ ) phonon, and the

\*1: See for example, <http://www.physics.purdue.edu/quantum/publications.php>

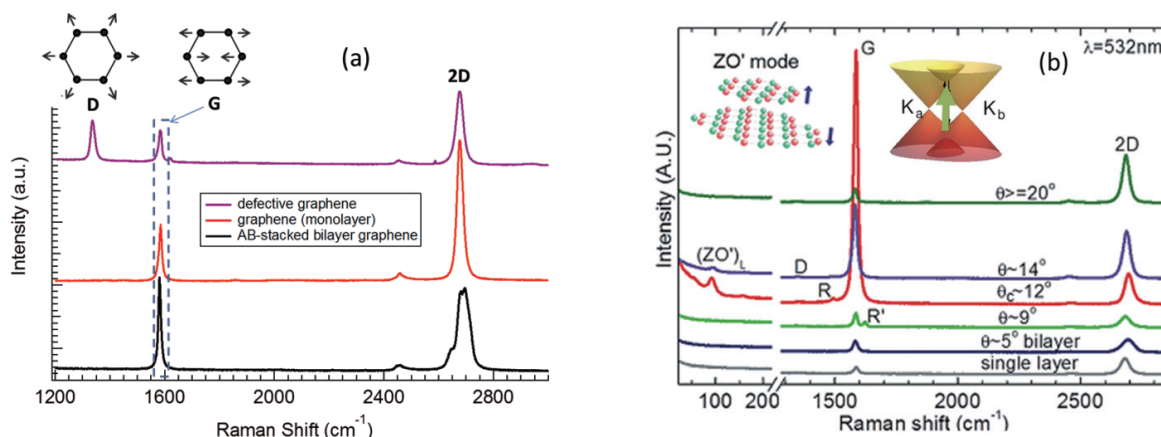


Figure 3 (a) Representative Raman spectra of a graphene (middle red trace), disordered graphene (upper purple trace) and AB-stacked bilayer graphene (lower black trace). Insets depict the atomic lattice vibration patterns corresponding to the Raman “D” and “G” peaks. The defects in the disordered graphene are created by irradiating the graphene with the electron beam in a scanning electron microscope (SEM).<sup>[12]</sup> (b) Raman spectra<sup>2</sup> of a tBLG<sup>[11]</sup> with various twisting angle ( $\theta$ ). A large resonant enhancement<sup>[13]</sup> in the G peak is observed when the excitation photon energy matches the energy separation between the two van Hove singularities (VHs, due to the overlapping Dirac cones in the tBLG electronic band structure, depicted in the right inset). We observe the fundamental layer breathing mode ( $\text{ZO}'_l$ , depicted in left inset) at  $\sim 94 \text{ cm}^{-1}$ . An unexplained, rising low energy background is also observed and might be related to an electronic excitation.<sup>[11]</sup> A single layer graphene spectrum is shown at the bottom for comparison. Spectra in (a) & (b) are vertically offset for clarity. All the Raman data presented in this paper were measured with an excitation laser with wavelength 532 nm.

“D” peak ( $\sim 1350\text{ cm}^{-1}$ ), which is a “zone-edge” (K) phonon and is only activated in the presence of (short-range) defects. The “2D” peak ( $\sim 2700\text{ cm}^{-1}$ , at 2<sup>nd</sup> harmonic of “D”) comes from a double resonance process and requires no defects. The Raman spectrum systematically changes with the number of graphene layers (thickness, and the spectrum for thick multi-layers approaches that of graphite).<sup>[9]</sup> For example, the intensity ratio between the G and 2D peaks and the shape of the 2D peak can be used (and even mapped) to identify single layer graphene (Figure 3a) or single layer regions (in a non-uniform film).<sup>[4, 5, 10]</sup> In contrast to the behavior of usual (bulk) solids (whose Raman spectra should not vary with thickness), the thickness dependence of the Raman spectrum is often seen for nanomaterials such as few-layer graphene, where one or more dimensions (in this case the thickness dimension perpendicular to graphene plane) is highly confined (here only a few atomic spacings) and has a more molecule-like than solid-like character. Multilayer graphene can also have other stacking orders (for example a “random” or “twisted” stacking, with relatively weak coupling between the layers) different from the “Bernal” (or “AB”) stacking in typical graphite. We have recently demonstrated CVD growth of “twisted” Bilayer Graphene (tBLG), whose electronic band structure (which has two sets of interacting Dirac cones with van Hove singularities) and Raman properties are highly tunable by the twisting angle and very different from those of regular Bernal-stacked bilayer graphene (Figure 3). In particular, we have discovered several new, low energy “inter-layer” Raman modes due to inter-layer “breathing” or even “rotation” modes.<sup>[11]</sup> Measuring these low energy modes<sup>2, 3</sup> provides a new way of studying inter-layer interaction in van-der Waals coupled layered materials and hetero-structures.

\*2: The spectra in Figure 3b were measured using a low energy Raman setup in collaborator R. He’s lab that can access such low Raman shift.

\*3: For example, AB-stacked multilayer graphene has a “shear mode” (P. H. Tan et al., *Nature Materials*, **11**, 294 (2012)) that is highly sensitive to the thickness (number of layers).

## Raman Studies of Defects in Graphene

Raman “D” peak ( $\sim 1350\text{ cm}^{-1}$ ) in graphitic materials has been widely used as a measure of the amount of disorder (density of lattice defects) in graphene. For example we have used mapping (imaging) of the D peak intensity to assess the quality of the CVD-grown large scale graphene<sup>[4, 14]</sup>. We also developed two experimental methods --- using electron beam irradiation<sup>[12, 15]</sup> and oxygen plasma etching<sup>[16]</sup> -- to create artificially

disordered graphene with tunable amount of disorder and defect density, and performed systematic Raman studies of how Raman spectra evolve for graphene with variable levels of disorder (complemented by electronic transport measurements). We have discovered that the empirical relation used in the past 30+ years to extract defect density (or correlation length or “domain size”) from the D peak over G peak intensity ratio<sup>[8]</sup> have several fundamental problems and are in fact not complete.<sup>[16-18]</sup> This line of work could lead to new methods of extract defect information and length scale from Raman spectra, and also demonstrated that such e-beam or plasma irradiations can be used to create an artificial, tunable disorder in graphene to study disorder physics and defect chemistry in graphene and other nanomaterials<sup>[19]</sup> in general.

## Studies of Graphene Single Crystals and Grain Boundaries

The macroscopic large-scale graphene films such as those grown by CVD are typically polycrystalline (formed by many graphene single crystals merged together, while the synthesis of large single crystal graphene is an important next frontier).<sup>[20]</sup> We have performed a comprehensive study of CVD graphene single crystals and grain boundaries (between merged single crystals).<sup>[21, 22]</sup> We demonstrated synthetic hexagonal shaped graphene single crystals (an example shown in Figure 1c, and such crystals can even be controllably synthesized in ordered arrays using seeded growth<sup>[23]</sup>) with well-defined (zigzag) oriented edges.<sup>[24]</sup> In particular, we showed that Raman imaging (of Raman D peak intensity) provides a quick and powerful method to visualize nucleation centers (within single crystals) and grain boundaries that are difficult to see in optical image or even other microscopy such as atomic force microscopy. (Figure 4)

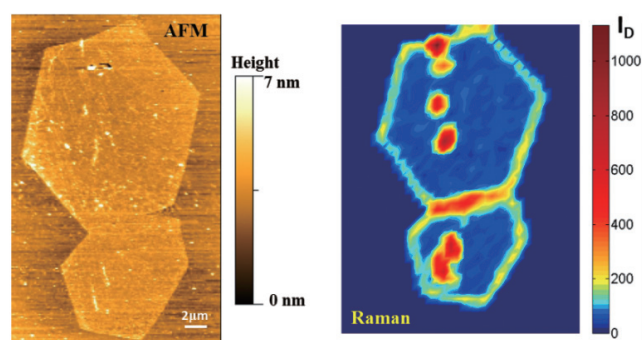


Figure 4 Comparison between an Atomic Force Microscope (AFM) image (left) and Raman image of D peak intensity (right) on two connected graphene single crystal domains with one grain boundary.<sup>[21]</sup>



## Electro-Raman Measurements of Thermal Conductivity of Graphene

Graphene has one of the highest thermal conductivity among all materials known<sup>[25]</sup>, however the precise value of its thermal conductivity has been somewhat debated. We have developed an “electro-Raman” technique (Figure 5)<sup>[26]</sup> to measure the thermal conductivity --- combining electrical transport (using a current to induce Joule heating in a suspended graphene) and Raman spectroscopy (using the temperature dependent Raman spectral peak of graphene as a *thermometry*), and measured the thermal conductivity of both CVD and exfoliated graphene to be  $\sim 2000$  W/mK. Such a method can be generalized to measure thermal conductivity of other nanomaterials (2D materials and nanowires) and also to study energy dissipation of nanomaterial based electronic devices.

## Gate-tunable Raman Spectrum and Electron-phonon Coupling

The Raman spectrum of graphene is known to depend on the doping or carrier density,<sup>[27, 28]</sup> which can be conveniently varied by electrostatic gating in a graphene Field Effect Transistor (FET) device. This reflects the coupling of phonons with the electronic charge carriers in graphene. For example, the G peak will blue-shift and become narrower with increasing carrier density of either n (electrons) or p (holes) type (Figure 6a-6c), a behavior related to such interesting physics as the “Kohn-anomaly”<sup>[27]</sup> as well as the breakdown of the Born-Oppenheimer approximation (due to the absence of

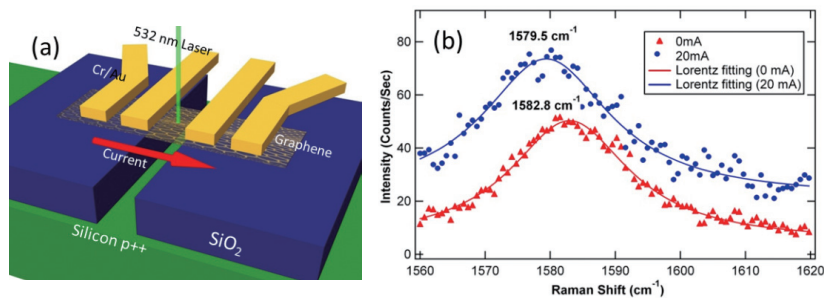


Figure 5 (a) Schematic of measuring thermal conductivity of graphene by combining electrical current Joule heating with Raman spectroscopy. Graphene is suspended over a trench. (b) Raman spectra of graphene near “G” phonon peak without and with 20 mA heating current. The red shift of G peak is used to measure the temperature rise in graphene. Data adapted from Ref. [26]

electronic bandgap in the Dirac cone band structure).<sup>[28]</sup> This dependence can be used to directly extract the Electron-Phonon Coupling (EPC) constant in graphene ( $\sim 1.4 \times 10^{11}$  eV/m).<sup>[27, 17, 30]</sup> Combining Raman spectroscopy and electrostatic gating in a graphene FET device (both with conventional dielectric back-gating, and with ionic liquid gating), we have performed gate-dependent Raman spectroscopy studies also on disordered graphene (defects created by e-beam irradiation) and twisted bilayer graphene and measured systematically the evolution of Raman spectra (esp. D peak in disordered graphene, and G peak resonantly enhanced by van Hove singularity in tBLG) when the carrier density (chemical potential) in graphene is tuned by the gate.<sup>[17, 30]</sup> This has allowed us to perform the first measurement of EPC parameters (important for understanding electronic, thermal, and thermoelectric transport and device operations) in disordered graphene and tBLG, and also observation of novel features such as electric field induced quenching and splitting of resonantly enhanced G peak in tBLG. (Figure 6d) This powerful technique can be applied to study electron-phonon or electron-vibron coupling in other nano/molecular materials.

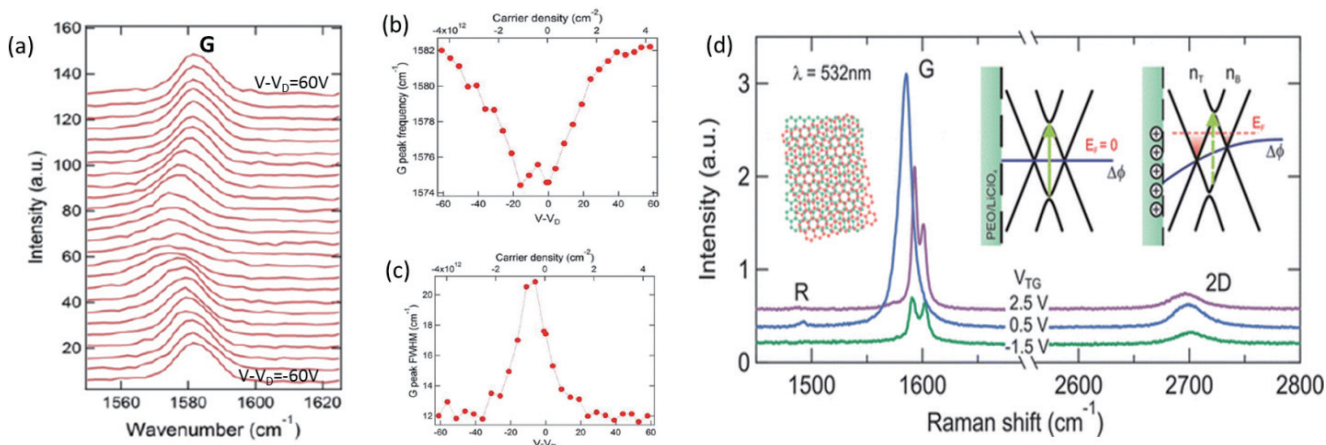


Figure 6 (a) Evolution of graphene Raman spectrum near “G” peak with gate voltage (V, applied to the SiO<sub>2</sub>/Si backgate and ranging from -60 V to 60 V relative to the Dirac point voltage V<sub>D</sub>) that tunes the graphene carrier density.<sup>[17]</sup> The G peak frequency (b) and width (c) as functions of V-V<sub>D</sub> (bottom axis) and carrier density (top axis, positive for electrons, negative for holes). (d) Evolution of Raman spectrum in a tBLG (left inset) when its carrier density is tuned by an ionic gate. Right inset is a model of gate-modulated electronic band structure to explain the splitting and quenching of resonantly enhanced Raman G peak.<sup>[30]</sup>

## Future Directions

There are many interesting further questions one can study with Raman measurements on graphene-based materials (including chemically functionalized graphene and hybrid materials mixing graphene with other (nano) materials). The measurements and techniques developed for graphene can also be extended to study other nanomaterials, particularly a wide range of so called “graphene-like or “beyond graphene” 2D materials --- Van der Waals coupled layered materials that can be reduced to one or few atomic layers, ranging from insulators such as h-BN, semiconductors such as silicene, phosphorene, MoS<sub>2</sub>, topological insulators and thermoelectric materials such as Bi<sub>2</sub>Te<sub>3</sub>, superconductors such as FeSe, and some complex oxides etc.<sup>[3, 31, 32]</sup>. Many Raman-based measurements described above (such as thermal conductivity, electron-phonon coupling in gate-tuned Raman, low energy interlayer Raman modes) have just started to be performed on these 2D materials<sup>[8]</sup>, and this would be a very fertile area of future research. The same experimental setup used for Raman (Figure 2) can also be conveniently used to measure Photoluminescence (PL) and photoconductivity. In addition, by stacking different 2D materials, we can make novel “Van der Waals” stacked heterostructures (such as MoS<sub>2</sub>/graphene as an example) and superlattices that have never existed or been studied before<sup>[32]</sup>, and we plan to apply our techniques (such as interlayer Raman modes) to study these hetero-structures. Such 2D materials and heterostructures have exciting potentials both in terms of fundamental science (new materials with novel properties due to 2D nature or proximity/hybrid-heterostructures) and potential technological applications in electronics/optoelectronics, flexible devices, energy (thermoelectrics, solar cells, and measurements of electron phonon coupling in 2D materials for example will give key insights to the processes involved in such energy conversions).

## Acknowledgments

*I thank my group members, particularly Isaac Childres, Jack T-F. Chung, Luis Jauregui and Helin Cao, for their contribution to the work described here. I also thank Rui He, Qingkai Yu, Wei Wu, and many colleagues for collaboration and discussions, and thank US National Science Foundation, Department of Defense and Department of Homeland Security, American Chemical Society, Miller family endowment and Day & Associates for support of our graphene-related work. We also acknowledge Horiba Inc. for technical support related to our Raman instruments.*

## References

- [1] A. K. Geim, Graphene, "Status and Prospects", *Science*, **324**, 1530 (2009)
- [2] K. S. Novoselov, "Graphene, Materials in the Flatland (Nobel Lecture)", *Angew. Chem. Int. Ed.*, **50**, 6986 (2011)
- [3] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, "Two-dimensional atomic crystals", *Proc. Natl. Acad. Sci. USA*, **102**, 10451 (2005)
- [4] Ting-fung Chung, Tian Shen, Helin Cao, Luis A. Jauregui, Wei Wu, Qingkai Yu, David Newell and Yong P. Chen, Synthetic, "Graphene Grown by Chemical Vapor Deposition on Copper Foils", *International Journal of Modern Physics B*, **27**, 1341002 (2013)
- [5] Helin Cao, Qingkai Yu, Luis Jauregui, Jifa Tian, Wei Wu, Zhihong Liu, Romaneh Jalilian, Daniel K. Benjamin, Zhigang Jiang, Jiming Bao, Steven S. Pei and Yong P. Chen, "Electronic Transport in Chemical Vapor Deposited Graphene Synthesized on Cu: Quantum Hall Effect and Weak Localization", *Applied Physics Letters*, **96**, 122106 (2010)
- [6] *Introductory Raman spectroscopy*, by John R. Ferraro, Kazuo Nakamoto and Chris W. Brown, Academic Press (2003)
- [7] L.M. Malard, M.A. Pimenta, G. Dresselhaus, and M.S. Dresselhaus, "Raman spectroscopy in grapheme", *Physics Reports*, **473**, 51 (2009)
- [8] Andrea C. Ferrari and Denis M. Basko, "Raman spectroscopy as a versatile tool for studying the properties of grapheme", *Nature Nanotechnology*, **8**, 235 (2013)
- [9] A. Gupta, G. Chen, P. Joshi, S. Tadigadapa, and P.C. Eklund, "Raman Scattering from High-Frequency Phonons in Supported n-Graphene Layer Films", *Nano. Lett.*, **6**, 2667 (2006)
- [10] Helin Cao, Qingkai Yu, Robert Colby, Deepak Pandey, C. S. Park, Jie Lian, Dmitry Zemlyanov, Isaac Childres, Vladimir Drachev, Eric A. Stach, Muhammad Hussain, Hao Li, Steven S. Pei, and Yong P. Chen, "Large-scale Graphitic Thin Films Synthesized on Ni and Transferred to Insulators: Structural and Electronic Properties", *Journal of Applied Physics*, **107**, 044310 (2010)
- [11] Rui He, Ting-Fung Chung, Conor Delaney, Courtney Keiser, Luis A. Jauregui, Paul M. Shand, C. C. Chancey, Yanan Wang, Jiming Bao, and Yong P. Chen, "Observation of Low Energy Raman Modes in Twisted Bilayer Graphene", *Nano Letters*, **13**, 3594 (2013)
- [12] Isaac Childres, Luis A. Jauregui, Mike Foxe, Jifa Tian, Romaneh Jalilian, Igor Jovanovic, and Yong P. Chen, "Effect of electron-beam irradiation on graphene field effect devices", *Applied Physics Letters*, **97**, 173109 (2010)
- [13] Kwanpyo Kim, Sinisa Coh, Liang Z. Tan, William Regan, Jong Min Yuk, Eric Chatterjee, M. F. Crommie, Marvin L. Cohen, Steven G. Louie, and A. Zettl, "Raman spectroscopy study of rotated double-layer graphene: Misorientation-angle dependence of electronic structure", *Phys. Rev. Lett.*, **108**, 246103 (2012)
- [14] Wei Wu, Zhihong Liu, Luis A. Jauregui, Qingkai Yu, Jiming Bao, Rajeev Pillai, Helin Cao, Yong P. Chen, and Shin-Shem Pei, "Wafer-scale Synthesis of Graphene by Chemical Vapor Deposition and its Application in Gas Sensing", *Sensors and Actuators B*, **150**, 296 (2010)
- [15] Isaac Childres, Michael Foxe, Igor Jovanovic, and Yong P. Chen, "Effect of energetic electron irradiation on graphene and graphene field-effect transistors", *Proc. SPIE*, **8031**, 803122 (2011)
- [16] Isaac Childres, Luis A. Jauregui, Jifa Tian, and Yong P. Chen, "Effect of oxygen plasma etching on graphene studied with Raman spectroscopy and electronic transport", *New Journal of Physics*, **13**, 025008 (2011)
- [17] Isaac Childres, Luis A. Jauregui, and Yong P. Chen, "Raman spectra and electron-phonon coupling in disordered graphene with gate-tunable doping", *Journal of Applied Physics*, **116**, 233101 (2014)
- [18] Isaac Childres, Luis A. Jauregui, Wonjun Park, Helin Cao, and Yong P. Chen, "Raman Spectroscopy of Graphene and Related Materials", in *New Developments in Photon and Materials Research*, ed. J. I. Jang, Nova Science Publishers (2013)
- [19] Isaac Childres, Jifa Tian, Ireneusz Miotkowski, and Yong P. Chen, "AFM and Raman studies of topological insulator materials subject to argon plasma etching", *Philosophical Magazine*, **93**, 681 (2013)
- [20] Oleg Yazyev, and Yong P. Chen, "Polycrystalline graphene and other two-dimensional materials", *Nature Nanotechnology*, **9**, 755 (2014)
- [21] Qingkai Yu, Luis A. Jauregui, Wei Wu, Robert Colby, Jifa Tian, Zhihua Su, Helin Cao, Zhihong Liu, Deepak Pandey, Dongguang Wei, Jack Chung, Peng Peng, Nathan Guisinger, Eric A. Stach, Jimin Bao, Shin-shem Pei, and Yong P. Chen, "Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition", *Nature Materials*, **10**, 443 (2011)
- [22] Luis A. Jauregui, Helin Cao, Wei Wu, Qingkai Yu, and Yong P. Chen, "Electronic properties of grains and grain boundaries in graphene grown by chemical vapor deposition", *Solid State Communications*, **151**, 1100 (2011)
- [23] Wei Wu, Luis A. Jauregui, Zhihua Su, Zhihong Liu, Jiming Bao, Yong P. Chen, and Qingkai Yu, "Growth of Single Crystal Graphene Arrays by Locally Controlling Nucleation on Polycrystalline Cu using Chemical Vapor Deposition", *Advanced Materials*, **42**, 4898 (2011)
- [24] Jifa Tian, Helin Cao, Wei Wu, Qingkai Yu, and Yong P. Chen, "Direct Imaging of Graphene Edges: Atomic Structure and Electronic Scattering", *Nano Letters*, **11**, 3663 (2011)
- [25] A. A. Balandin, "Thermal properties of graphene and nanostructured carbon materials", *Nature Materials*, **10**, 569 (2011)
- [26] Luis A. Jauregui, Yanan Yue, Anton N. Sidorov, Jiuning Hu, Qingkai Yu, Gabriel Lopez, Romaneh Jalilian, Daniel K. Benjamin, Derek A. Delk, Wei Wu, Zhihong Liu, Xinwei Wang, Zhigang Jiang, Xiulin Ruan, Jiming Bao, Steven S. Pei, and Yong P. Chen, "Thermal Transport in Graphene Nanostructures: Experiments and Simulations", *ECS Transactions*, **28(5)**, 73 (2010)
- [27] Jun Yan, Yuanbo Zhang, Philip Kim, and Aron Pinczuk, "Electric Field Effect Tuning of Electron-Phonon Coupling in Graphene", *Phys. Rev. Lett.*, **98**, 166802 (2007)
- [28] A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S. K. Saha, U. V. Waghmare, K. S. Novoselov, H. R. Krishnamurthy, A. K. Geim, A. C. Ferrari and A. K. "Sood, Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor", *Nature Nanotech.*, **3**, 210 (2008)
- [29] Simone Pisana, Michele Lazzeri, Cinzia Casiraghi, Kostya S. Novoselov, A. K. Geim, Andrea C. Ferrari and Francesco Mauri, "Breakdown of the adiabatic Born-Oppenheimer approximation in grapheme", *Nature Mater.*, **3**, 198 (2007)
- [30] Ting-Fung Chung, Rui He, Tai-Lung Wu, and Yong P. Chen, "Optical Phonons in Twisted Bilayer Graphene with Gate-Induced Asymmetric Doping", *Nano Letters*, **15**, 1203 (2015)
- [31] Sheneve Z. Butler, Shawna M. Hollen, Linyou Cao, Yi Cui, Jay A. Gupta, Humberto R. Gutierrez, Tony F. Heinz, Seung Sae Hong, Jiaxing Huang, Ariel F. Ismach, Ezekiel Johnston-Halperin, Masaru Kuno, Vladimir V. Plashnitsa, Richard D. Robinson, Rodney S. Ruoff, Sayeef Salahuddin, Jie Shan, Li Shi, Michael G. Spencer, Mauricio Terrones, Wolfgang Windl, and Joshua E. Goldberger, "Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene", *ACS Nano*, **7**, 2898 (2013)
- [32] A. K. Geim, and I. V. Grigorieva, "Van der Waals heterostructures", *Nature*, **499**, 419 (2013)



**Yong P. CHEN**

Brick Nanotechnology Center,  
Department of Physics and Astronomy and  
School of Electrical and Computer Engineering  
Purdue University,  
Associate Professor,  
Ph. D.