**Abstract**

Carbon-based nanostructures including nanotubes (CNTs) and graphene have superior electronic, optoelectronic, and mechanical properties, which provide fresh opportunities for designs of novel devices of extraordinary performance in addition to the benefits of low cost, large abundance, and light weight. Our recent demonstrations of uncooled detectivity in exceeding 10^9 cm^2 Hz^{1/2} W on individual multiwall CNT infrared detectors with asymmetric Schottky contacts, responsivity ~1.62 A/W?V on the ZnO nanowire/graphene hybrid ultraviolet detectors, and responsivity above 20 mA/W on thin-gate plasmonic graphene broad-band photo detectors highlight the potential of these materials in a wide range of applications.

**Subject Terms**
- carbon nanotube
- graphene
- photodetector
- nanotechnology
ABSTRACT

Carbon-based nanostructures including nanotubes (CNTs) and graphene have superior electronic, optoelectronic and mechanical properties, which provide fresh opportunities for designs of novel devices of extraordinary performance in addition to the benefits of low cost, large abundance, and light weight. Our recent demonstrations of uncooled detectivity in exceeding 10^9 cm^2Hz^1/2/W on individual multiwall CNT infrared detectors with asymmetric Schottky contacts, responsivity ~1.62 A/W?V on the ZnO nanowire/graphene hybrid ultraviolet detectors, and responsivity above 20 mA/W on thin-gate plasmonic graphene broad-band photo detectors highlight a few examples developed under our prior ARO support. The proposed research aims at understanding the fundamental physics governing the optoelectronic behaviors in these nanostructures, and based on which exploring novel device schemes that enable manipulation of photon absorption, exciton dissociation and charge and phonon transport at nanoscales. Micro/nanofabrication schemes for scaling up these devices will also be in consideration for compatibility with Si-based readout circuits. The overall goal of this project is to achieve a thorough understanding of the basic physics underlying the photo detection and to develop higher-performance carbon-based nanostructure photo detectors for uncooled infrared and ultraviolet detection to meet Army’s requirements of high sensitivity, light weight, and low cost.
Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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<td>37 Jianwei Liu, Qingfeng Liu, Javier Baca, Guowei Xu, Caitlin Rochford, Rongtao Lu, Christina M. Edwards, Cindy L. Berrie, Victor A. Maroni, Judy Wu. Direct graphene growth on (111) Cu2O templates with atomic Cu surface layer, Carbon, ( ): 608. doi: 1,033,113.00</td>
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<td>04/12/2017</td>
<td>35 Steven A. Klankowski, Gaind P. Pandey, Gary A. Malek, Judy Wu, Ronald A. Rojeski, Jun Li. A Novel High-Power Battery-Pseudocapacitor Hybrid Based on Fast Lithium Reactions in Silicon Anode and Titanium Dioxide Cathode Coated on Vertically Aligned Carbon Nanofibers, Electrochimica Acta, ( ): 797. doi: 1,033,112.00</td>
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<td>32 Shima Fardad, Susobhan Das, Alessandro Salandrino, Eric Breckenfeld, Heungsoo Kim, Judy Wu, Rongqing Hui. All-optical short pulse translation through cross-phase modulation in a VO_2 thin film, Optics Letters, ( ): 238. doi: 1,033,109.00</td>
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<td>29 Qingfeng Liu, Youpin Gong, Ti Wang, Wai-Lun Chan, Judy Wu. Metal-catalyst-free and controllable growth of high-quality monolayer and AB-stacked bilayer graphene on silicon dioxide, Carbon, ( ): 203. doi: 1,033,108.00</td>
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<td>28 Ti Wang, Tika R. Kafle, Bhupal Kattel, Qingfeng Liu, Judy Wu, Wai-Lun Chan. Growing Ultra-flat Organic Films on Graphene with a Face-on Stacking via Moderate Molecule-Substrate Interaction, Scientific Reports, ( ): 28895. doi: 1,033,098.00</td>
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<td>30 Rongtao Lu, Jianwei Liu, Hongfu Luo, Viktor Chikan, Judy Z. Wu. Graphene/GaSe-Nanosheet Hybrid: Towards High Gain and Fast Photoresponse, Scientific Reports, ( ): 19161. doi: 1,033,100.00</td>
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<td>34 Gaind P. Pandey, Steven A. Klankowski, Yonghui Li, Xiuzhi Susan Sun, Judy Wu, Ronald A. Rojeski, Jun Li. Effective Infiltration of Gel Polymer Electrolyte into Silicon-Coated Vertically Aligned Carbon Nanofibers as Anodes for Solid-State Lithium-Ion Batteries, ACS Applied Materials &amp; Interfaces, ( ): 20909. doi: 1,033,112.00</td>
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<td>33 Chunrui Ma, Youpin Gong, Rongtao Lu, Emery Brown, Beihai Ma, Jun Li, Judy Wu. Detangling extrinsic and intrinsic hysteresis for detecting dynamic switch of electric dipoles using graphene field-effect transistors on ferroelectric gates, Nanoscale, ( ): 18489. doi: 1,033,111.00</td>
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21 Qingfeng Liu, Youpin Gong, Jamie Samantha Wilt, Ridwan Sakidja, Judy Wu. Synchronous growth of AB-stacked bilayer graphene on Cu by simply controlling hydrogen pressure in CVD process, Carbon, (05 2015): 199. doi: 10.1016/j.carbon.2015.05.063

22 Jamie Samantha Wilt, Maogang Gong, Shengqiang Ren, Judy Wu, Youpin Gong, Qingfeng Liu. Wrapping cytochrome c around single-wall carbon nanotube: engineered nanohybrid building blocks for infrared detection at high quantum efficiency, Scientific Reports, (06 2015): 1. doi: 10.1038/srep11328


5 Chao Ding, Zhenxun Ming, Bing Li, Lianghuan Feng, Judy Wu. Preparation and characterization of pulsed laser deposited CdTe thin films at higher FTO substrate temperature and in Ar+O2 atmosphere, Materials Science and Engineering: B, (06 2013): 0. doi: 10.1016/j.mseb.2013.03.018


08/30/2013 12 Caleb Christianson, Alec Kirkeminde, Shenqiang Ren, Judy Wu, Rongtao Lu. Extraordinary Photocurrent Harvesting at Type-II Heterojunction Interfaces: Toward High Detectivity Carbon Nanotube Infrared Detectors, Nano Letters, (12 2012): 0. doi: 10.1021/nl303302p


08/31/2014 17 Chunrui Ma, Beihai Ma, Shao-Bo Mi, Ming Liu, Judy Wu. Enhanced dielectric nonlinearity in epitaxial Pb0.92La0.08Zr0.52Ti0.48O3 thin films, Applied Physics Letters, (04 2014): 0. doi: 10.1063/1.4872375

08/31/2014 18 Gary A. Malek, Emery Brown, Steven A. Klankowski, Jianwei Liu, Alan J. Elliot, Rongtao Lu, Jun Li, Judy Wu. Atomic Layer Deposition of Al-Doped ZnO/Al, ACS Applied Materials & Interfaces, (05 2014): 0. doi: 10.1021/am5006805

TOTAL: 30

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

08/30/2013 11.00 C. Rochford, N. Kumar, J.W. Liu, R.T. Lu, H. Zhao, J.Z. Wu. Correlation of defect structure and carrier transport in transferred graphene films grown by chemical vapor deposition, Applied Materials and Interfaces, (07 2013): 7176. doi:

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**Patents Submitted**


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### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

- The number of undergraduates funded by this agreement who graduated during this period: 0.00
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields: 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields: 0.00
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: 0.00
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense: 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

### Names of Personnel receiving masters degrees

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### Sub Contractors (DD882)
Atomic Layer Deposition Integrated with Ultra-High Vacuum Physical or Chemical Vapor Deposition

- Patent Filed in US? (5d-1) Y
- Patent Filed in Foreign Countries? (5d-2) N
- Was the assignment forwarded to the contracting officer? (5e) N
- Foreign Countries of application (5g-2):
  - 5a: Alan Elliot
  - 5f-1a: KU, Physics and Astronomy (Department)
  - 5f-c:
  - 5a: Rongtao Lu
  - 5f-1a: KU, Physics and Astronomy (Department)
  - 5f-c:
  - 5a: Judy Wu
  - 5f-1a: KU, Physics and Astronomy (Department)
  - 5f-c:

Biomolecule/carbon nanostructure nanohybrids for high-performance optoelectronics

- Patent Filed in US? (5d-1) Y
- Patent Filed in Foreign Countries? (5d-2) Y
- Was the assignment forwarded to the contracting officer? (5e) N
- Foreign Countries of application (5g-2):
  - 5a: Quingfeng Liu
  - 5f-1a: KU, Physics and Astronomy (Department)
  - 5f-c:
  - 5a: Youpin Gong
  - 5f-1a: KU, Physics and Astronomy (Department)
  - 5f-c:
  - 5a: Judy Wu
  - 5f-1a: KU, Physics and Astronomy (Department)
  - 5f-c:
Semiconductor-graphene hybrids formed using solution growth

Patent Filed in US? (5d-1)  Y
Patent Filed in Foreign Countries? (5d-2)  N
Was the assignment forwarded to the contracting officer? (5e)  N
Foreign Countries of application (5g-2):  
5a:  Jianwei Liu
5f-1a:  Univ. of Kansas
5f-c:

5a:  Judy Wu
5f-1a:  KU, Physics and Astronomy (Department)
5f-c:

Scientific Progress

See Attachment

Technology Transfer
This final report summarizes the progress made in the entire period of the ARO W911NF-12-1-0412 project, which is a three-year project with 6 month no-cost extension. During the project period, the grant mainly supported one postdoctoral researcher. Four postdoctoral researchers have worked for this project including Drs. Rongtao Lu (now in IBM), Chunrui Ma (now on faculty of Xi’an Jiaoting University- a top tier university in China), Youping Gong (now on faculty of South University, Shenzhen, China), and Maogang Gong (the University of Kansas, or KU). The project also supported (part-time) several graduate students Ali Kidham (MS June 2015), Alaa Al-mebir (MS June 2015), Gary Malek (PhD July 2015), Alan Elliot (PhD December 2014), and Ryan Goul. In addition, the project also involved three undergraduate researchers Caleb Christianson (now UC-San Diego), Jake David Meeth (now Cambridge University, UK) and Paul Harrison (now KU), and all graduated from KU during the project period and now in graduate programs for their PhD.

The scope of the project is on experimental studies of carbon nanotubes (CNTs) and graphene based infrared (IR) and ultraviolet (UV) detectors at KU. The focus of the project was to achieve a thorough understanding of the basic physics that governs the optoelectronic process on heterojunction nanohybrids based on CNTs and graphene. The primary approach is to design heterojunction electronic structure to achieve an atomic-scale control over exciton dissociation and charge transfer at the heterojunction interface and device-scale control of the charge carrier transport. The ultimate goal was to develop uncooled CNT/graphene IR/UV detector arrays on Si with high sensitivity, light weight, and low cost that meets the US Army’s updated requirements for anti-terrorist attacks and homeland security.

The three originally proposed topics were completed. The following highlights some of the most important results, while the details can be found in 34 peer-reviewed publications, 5 patents (4 awarded, one pending).

**Topic 1: Semiconducting-SWCNT/polymer nanohybrid IR detector**

**SWCNT/P3HT nanohybrid IR detectors**—Despite the potentials and the efforts put in the development of uncooled carbon nanotube infrared detectors during the past two decades, their figure-of-merit detectivity $D^*$, remains orders of magnitude lower than that of conventional semiconductor counterparts due to the lack of efficient exciton dissociation schemes. We have developed an extraordinary photocurrent harvesting configuration at a semiconducting single-walled carbon nanotube (s-SWCNT)/polymer type-II heterojunction interface, which provides highly efficient exciton dissociation mechanism through the intrinsic energy offset by designing the s-SWCNT/polymer interface band alignment. We picked Poly(3-hexylthiophene) (P3HT) since it is among several semiconducting conjugated polymers that have appropriate band offsets to s-SWCNTs, and large IR photoresponse has been observed in the s-SWCNT/P3HT nanohybrid detector. This results in significantly enhanced near-infrared detectivity of $2.3 \times 10^8$ cm·Hz$^{1/2}$·W,
comparable to that of the many conventional uncooled infrared detectors, together with a small response time of around 1 millisecond, as shown in Figure 1. With further optimization, the s-SWCNT/polymer nanohybrid uncooled infrared detectors could be highly competitive for practical applications (Nano Letters 12, 6244 (2012)].

Figure 1 IR response in semiconducting SWCNT (s-SWCNT)/P3HT type-II heterojunction nanohybrid. (a) Diagram of s-SWCNT/P3HT nanohybrid; (b) Band structure of s-SWCNT/P3HT heterojunction; (c) Temporal response of s-SWCNT/P3HT nanohybrid under 99 Hz IR modulation. (d) Detectivity $D^*$ of s-SWCNT/P3HT nanohybrid as a function of modulation frequency at room temperature, control sample of pure s-SWCNT and suspended SWCNT films are also plotted. [Nano Lett 12, 6244 (2012)].

Photoresponse tuning in CNT film bolometers by forming hybrids with graphene and adjusting the diameter of CNT elements --To simplify the fabrication process and develop new exciton dissociation configurations, we have further explored the implementation of a novel exciton dissociation mechanism through heterojunctions self-assembled at the graphene/MWCNT (multiwall carbon nanotube) interfaces in graphene/MWCNT nanohybrids. Significantly enhanced NIR photoresponsivity by nearly an order of magnitude has been achieved on the graphene/MWCNT nanohybrids as compared to the best achieved so far on carbon nanotube (CNT) only infrared (IR) detectors. This leads to a detectivity up to $1.5 \times 10^7$ cm Hz$^{1/2}$/W in the graphene/MWCNT nanohybrid (Fig. 2), which represents a 500% improvement over the best $D^*$ achieved on pure MWCNT film IR detectors and may be further improved with optimization on the interfacial heterojunctions. This approach of the self-assembly of graphene/CNT nanohybrids provide a pathway towards high-performance and low-cost carbon nanostructure IR detectors (ACS Applied Materials and Interfaces 5, 11703 (2013)). Since the CNT diameter greatly change the band gap, transport property and oxygen adsorption performances, understanding the effect of the CNT diameter on the performance of the CNT film IR detectors via systematic changes of these parameters is important and critical to achieving an optimal device by design. We have investigated that the photoresponse of CNT bolometers can be tuned by adjusting the diameter of CNT elements, and optimized performance can be obtained by using thinner multiwall carbon nanotubes. We prepared and explored CNT films made from a range of CNT diameters from 1 nm (single-wall) to multiwall with diameter up to 50 nm and observed a maximum $D^*$ of $3.3 \times 10^7$ cm $\sqrt{Hz}$/W using 12 nm diameter MWCNTs (Fig. 3), which is believed to be the maximum $D^*$ of a pure CNT IR detector to date (Nanotechnology 25, 425503 (2014)).
Ultrahigh photoresponsivity in novel carbon nanotube/cytochrome c nanohybrid photodetectors -- Both purified semiconductor single-wall CNT (s-SWCNT) and multi-wall CNT (MWCNT) have been employed in the nanohybrids. Infrared photodetector have been fabricated using this nanohybrids and ultrahigh infrared photoresponsivity, especially high $D^* > 10^{10}$ cm-Hz$^{1/2}$/W has been achieved at room temperature. This represents the best result so far achieved in the CNT-based IR detectors, and a two orders of magnitude enhancement over the best resulted reported before in SWCNT/P3HT type II heterojunction nanohybrids. The high quantum efficiency is up to 90%. The high performance of the CNT/Cyt c photodetector derived from a novel exciton dissociation mechanism facilitated by the formation of CNT/Cyt c heterojunctions through a collaboration with Dr. Wai-Yim Ching’s group in computational simulation of the electronic structure and optical properties of Cyt c and Dr. Wai-lun Chan’s group on measurement of these properties using ultraviolet photoemission spectroscopy. This work revealed that the band-edge offset across the CNT/Cyt c heterojunctions was $>2.7V$, which is significantly higher the exciton binding energy in CNTs on the order of 0.3-0.5V, and therefore provides efficient exciton dissociation and charge transfer at the CNT/cytochrome c interface. A measurement of Cyt c sensitized graphene field effect transistors confirmed the efficient charge transfer across the heterojunction. Since Cyt c is also an optical molecule, ultraband photodetection was recently demonstrated across the entire solar spectrum. Our results pioneer a new potential direction to explore carbon-biomaterial nanohybrids photodetection. Several manuscripts are currently in preparation for publication of these results.

The s-SWCNT/Cyt c building blocks with Cyt c molecule wrapping around an individual SWCNT (Fig. 4a) are made via self-assembly in solution prior to the s-SWCNT/Cyt c film formation obtained by vacuum-filtrating the dilute suspension of the SWCNTs/Cyt c solution (Fig. 4b). An AFM analysis has confirmed that the SWCNTs/Cyt c nanohybrid building block has a diameter of 2.1-2.9 nm around individual s-SWCNT of 1.2−1.7 nm in diameter (Fig. 4c), which is anticipated considering the Cyt c is a small molecule, primarily a chain of amino acids of small diameter typically on the order of 1 nm or less. The c-SWCNT and Cyt c in a SWCNTs/Cyt c building block serve respectively as electron donor and acceptor up exciton dissociation at the heterojunction formed at their interface upon NIR photon absorption by SWCNTs (Fig. 4b). In fact, this heterojunction composite structure is similar to bulk inorganic/organic heterojunction structure employed in organic solar cells for efficient exciton dissociation and hence large photocurrent generation. Fig. 4d compares a preliminary study of the optical absorption spectra of pure Cyt c and the s-SWCNTs/Cyt c hybrid solutions. Fig. 4e depicts the schematic of the IR detectors made from the SWCNT/Cyt c nanohybrids.

![Figure 2 Schematic (top) and $D^*$ vs. frequency (bottom) of graphene/MWCNT nanohybrid.](image1)

![Figure 3 Maximum $D^*$ vs. average diameter $\text{dia}_{\text{avg}}$.](image2)
Since pure Cyt c is almost transparent at longer wavelength above ~ 600 nm, the contribution of Cyt C to the RI and EQE is negligible in the s-SWCNT/Cyt c nanohybrids devices, as confirmed in a comparative study using the pure Cyt c control device, its transport property may affect the photoresponse times. As shown in Figs. 5b-c, the response time constants of the SWCNT/Cyt c nanohybrids and the pure Cyt c control devices are in the same range. This suggests that the electron transport in Cyt C limits the response time. Interestingly, in comparison with the case of s-SWCNT/P3HT nanohybrids, a more symmetric dynamic photoresponse with $\tau_{on}$~0.8 ms and $\tau_{off}$~0.7 ms is observed in the s-SWCNT/Cyt c case, suggesting Cyt c out-performs its polymer counterpart by providing a much more efficient electron transport medium in the nanohybrids (Sci. Rep. 5 (2015), doi:10.1016/j.carbon.2015.05.063; Adv. Opt. Mats 5, 2017, DOI: 10.1002/adom.201770002; ACS AMI 9, 11016, (2017)).

Figure 4. Nanohybrid SWCNTs-Cyt c photodetector and its operation mechanism. a, Schematic of a Cyt c-wrapped SWCNTs building block; b, Self-assembled SWCNTs/Cyt c nanohybrid thin films with heterojunctions formed at the SWCNTs/Cyt c interface for exciton dissociation into holes (injected to SWCNT) and electrons (injected to Cyt c); c. AFM image of SWCNTs/Cyt c building blocks. The inset shows the cross section heights of 2.8 nm on two SWCNTs/Cyt c building blocks; d, Optical absorbance spectra of the pure Cyt c and the SWCNTs/Cyt c solution. e, Schematic of a SWCNTs/Cyt c IR detector

Since pure Cyt c is almost transparent at longer wavelength above ~ 600 nm, the contribution of Cyt C to the $R_I$ and EQE is negligible in the s-SWCNT/Cyt c nanohybrids devices, as confirmed in a comparative study using the pure Cyt c control device, its transport property may affect the photoresponse times. As shown in Figs. 5b-c, the response time constants of the SWCNT/Cyt c nanohybrids and the pure Cyt c control devices are in the same range. This suggests that the electron transport in Cyt C limits the response time. Interestingly, in comparison with the case of s-SWCNT/P3HT nanohybrids, a more symmetric dynamic photoresponse with $\tau_{on}$~0.8 ms and $\tau_{off}$~0.7 ms is observed in the s-SWCNT/Cyt c case, suggesting Cyt c out-performs its polymer counterpart by providing a much more efficient electron transport medium in the nanohybrids (Sci. Rep. 5 (2015), doi:10.1016/j.carbon.2015.05.063; Adv. Opt. Mats 5, 2017, DOI: 10.1002/adom.201770002; ACS AMI 9, 11016, (2017)).

Figure 5a. Bias voltage dependence of the photoresponsivity at various incident power density from 15 to 350 mW/cm². Representative dynamic photoresponse measured on b. the SWCNTs/Cyt c and c. the pure Cyt c devices at NIR modulation frequency of 97 Hz.
Top 2: Graphene-based Plasmonic Nanostructures for Enhanced IR Optoelectronics

We have completed our proposed work on development of plasmonic nanostructures on graphene. Besides Ag nanoparticles, we have developed processes for \textit{in situ} generation of Au and transparent conductor (TCO) plasmonic nanostructures. Simulation of the E&M fields around these plasmonic nanostructures has revealed favorable near field distribution upon visible to infrared light illumination and the excited electromagnetic field is enhanced by the localized surface plasmonic resonance (LSPR). It is worth mentioning that such graphene plasmonic nanostructures have broad applications in biosensing, telecommunication, photodetection, etc. A highly sensitive R6G biosensor was demonstrated recently in PI’s lab. The graphene/TCO plasmonic nanostructures we have designed are unique for applications in IR spectrum.

**Coupling Light to Electrical Gating in Graphene Field Effect Transistors with plasmonic nanostructures**—Plasmonic nanostructures may provide a promising scheme for enhanced photoresponse through light trapping and wavelength selectivity via localized surface plasmonic resonance (LSPR). For this project, a novel scheme of photodetection has been developed based on ionic liquid gated GFETs with plasmonic Ag (or Au) nanoparticles (GFET/Ag (or Au)-NP). In these devices, the incident light excites electromagnetic field that is enhanced by the LSPR around the Ag-NPs transduces to the configuration change of the ions in the electric doubly layer in the ionic liquid gate at the GFET (Fig. 6), resulting in efficient variation of the interfacial capacitance of the ionic liquid as well as quantum capacitance of graphene. The corresponding change of the graphene FET channel conductivity as photoresponse, leads to a high photoresponsivity up to $\sim$350 mA/W peaked at the LSPR frequency, which is two orders of magnitude higher than that on Schottky graphene devices with similar plasmonic nanostructures. The strong light wavelength selectivity determined by the LSPR frequency of the plasmonic NPs provides a viable wavelength tuning mechanism via controlling the geometric and material parameters of the plasmonic nanostructures on graphene (Adv. Opt. Mat. 2, 729 (2014)).
**Plasmonic NPs/graphene LSPR** - Photodetectors based on conventional semiconductors suffer from the long-wavelength limit determined by their band gap. With implementation of plasmonic nanostructures of appropriate strong LSPR in the targeted frequency range, GFET/plasmonic-NP hybrids could be a promising candidate for photodetection in an extended optical spectrum. The LSPR frequency may be tuned by selection of the metals or semiconductors with their plasmonic frequency in the targeted range. Cu$_{2-x}$S QDs has been demonstrated to have strong LSPR in NIR spectrum and will be an excellent candidate selection of the plasmonic nanostructure materials. Al-doped ZnO presents another candidate with LSPR frequency varying in NIR to MIR range depending on the charge doping via Al-doping level control. The PI's group has developed atomic layer deposition integrated with ultra-high vacuum sputtering chamber, which is particularly suitable for the fabrication of AZO on graphene and CNTs as we demonstrated recently (Carbon 86, 78, (2015); 96, 203 (2016); 111, 386 (2017); manuscripts under development).

**Topic 3: Graphene/sensitizer Photodetectors**

Combining semiconductor nanostructures with graphene into graphene/sensitizer nanohybrids may provide another scheme for high sensitivity photodetectors by taking advantage of higher photo absorption, band gap tunability, and quantum confinement effects of the semiconductor nanostructures and ballistic charge transport of graphene as electrodes. In these devices, atomic-scale control of the interface is the key to high performance. 2D semiconductors, such as III-VI metal chalcogenide Gallium selenide (GaSe) and transition metal dichalcogenides (TMDC) MoS$_2$ and WSe$_2$ are promising ligand-free sensitizers on graphene via van der Waals interaction due to their layered morphology similar to graphene’s. The band gap tunability via layer numbers and sheet dimension in 2D materials make them excellent photosensitizers on graphene to form a broad-band (UV-IR) graphene/nanosheet hybrid for photodetection. As shown in our recent publication, GFET/GeSe nanoheets hybrid photodetectors on CVD graphene have high photoconductive gain up to $10^8$ at zero $V_{BG}$ and fast photoresponse (both laser on and off time constants of $\sim$10 ms) can be achieved simultaneously by engineering the interface of GFET/GeSe nanoheets using a vacuum cleaning process developed by her group. In addition, the van der Waals interface in ZnO quantum dots and graphene was also demonstrated with a UV photoconductive gain up to $10^{10}$. These results represent the best so far achieved and illustrate the critical role of the graphene/sensitizer interface in affecting the optoelectronic properties of the nanohybrids and provides a pathway for developing high-performance, low-cost graphene-based hybrid photodetectors competitive for commercialization.

**ZnO nanowire/graphene hybrid UV photodetectors**—Graphene holds great promise for optoelectronic applications due to its high carrier mobility at room temperature, however the zero band gap of graphene has presented a major hurdle to electronic and optoelectronic applications. Semiconductor nanomaterials can be integrated with graphene and generated semiconductor/graphene nanohybrid with selected range of photoabsorptions. The ZnO/graphene hybrid is particular interest because it combines the superior wavelength selectivity of ZnO in UV range and the charge mobility of graphene, both of which are critical to applications of UV photodetections. We have developed a seedless solution process to grow crystalline ZnO micro/nanowire arrays directly on single-layer graphene sheets made in chemical vapor deposition (Fig. 6). In particular, the alignment of the ZnO micro/nanowires correlates well with the density of the wires, which is determined by both the sample configuration in solution and the graphene surface cleaning. With increasing wire density, the ZnO micro/nanowire array alignment may be
varied from horizontal to vertical by increasing the physical confinement. Ultraviolet photodetectors based on the vertically aligned ZnO micro/nanowires on graphene show high responsivity of 1.62 A/W per volt, a 500% improvement over epitaxial ZnO sensors, a 300% improvement over ZnO nanoparticle sensors, and a 40% improvement over the previous best results for nanowire/graphene hybrid sensors. This seedless, floating growth process could be scaled up for large scale growth of oriented ZnO micro/nanowires on graphene at low costs (Adv. Func. Mat. 23, 4941 (2013)).

**Graphene/2D-sensitizers phototransistors** — van der Waals interaction between graphene and semiconductor sensitizer is generally weak and can be affected strongly by interfacial contamination, which is the case in most previously reported work. In the GFET/GaSe-nanosheet hybrid (Fig. 7a), we have developed an effective vacuum annealing procedure at room temperature to “cleaning” the interface after the device is fabricated. Hysteresis in source-drain current \( I_D \) vs. gate voltage (\( V_{BG} \)) curves, a signature of the interfacial contamination, can be completely eliminated after 3-day pumping in high vacuum even through the samples were exposed to air afterwards. High gain in the range of \( 10^7 \text{ - } 10^8 \) at \( V_{BG}=0 \) and fast, symmetric response time of 10 ms were achieved simultaneously after the anneal (Fig. 7b). This result suggests the polar molecules trapped on the graphene surface and interfaces to gate or GaSe nanosheets can sensitively affect the optoelectronic properties of the graphene/sensitizer and precise control of the graphene surface and interface with other materials will be a key to achieve high and fast photoresponse (Sci. Rep. 6, 19161 (2016)).

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Figure 6. ZnO-NW/graphene hybrid UV detectors. Top: SEM images; Bottom: Schematic, band structure and photoresponse.

Figure 7. (a) GFET/GaSe nanosheets photodetector and (b) the photocurrent on this device at \( V_{BG}=0 \) and \( V_{SD} \) of 10 mV in response to 532 nm laser pulses.