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RPPR Final Report
as of 21-Jan-2020

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Major Goals: Carbon-based nanostructures including nanotubes (CNTs) and graphene have superior electronic, optoelectronic and mechanical properties, which provide tremendous opportunities for design of novel optoelectronic devices of extraordinary performance in addition to the benefits of low cost, large abundance, and light weight. Our recent demonstrations of uncooled infrared detectivity D* of 3.4x109 cm?Hz1/2/W on individual multiwall CNT infrared detectors with asymmetric Schottky contacts, D* of 2.3x108 cm?Hz1/2/W in a photoconductor based on semiconductive singe-wall CNTs and conjugated semiconductor Poly(3-hexylthiophene) polymer (s-SWCNT/P3HT) nanohybrid thin films, photoconductive gain up to 108 at zero VBG together with fast photoresponse on graphene field effect transistor with GaSe-nanosheets sensitizer, and responsivity ~1.62 A/W?V on the ZnO nanowire/graphene hybrid ultraviolet detectors, highlight a few examples developed under our prior ARO support and illustrate fresh opportunities in exploration of nanohybrids between carbon nanostructures and other functional materials targeting at unprecedented physical properties demanded for high-performance photodetection.
The proposed research builds upon the discoveries made through our prior ARO project, but aims to take it to the next level of high-performance photonic devices through atomistic interface design of exciton dissociation and charge transfer at the interfaces of nanohybrids through a thorough understanding of the fundamental physics governing the optoelectronic behaviors. Besides high performance and low cost, the proposed nanohybrid approach also has the advantage in its compatibility with Si-based readout circuits with micro/nanofabrication schemes employed for scaling up the proposed devices. Technology transfer for commercialization will be an emphasis of the proposed research. The overall goal of this project is to achieve a thorough understanding of the basic physics underlying the photodetection and to develop higher-performance carbon-based nanohybrid photodetectors for uncooled infrared and ultraviolet detection to meet Army's requirements of high sensitivity, light weight, and low cost.

Accomplishments: The ARO grant: "Fundamental Physics of Carbon-based Nanohybrids for High-performance Infrared and Ultraviolet Detection" is a three-year project started on December 1, 2015 mainly supporting one postdoc and a part-time undergraduate researcher on experimental studies of basic physics that governs the IR, UV and broadband photodetection based on heterojunction CNT and graphene nanohybrids. A no-cost extension to August 31, 2019 was requested to and approved by ARO. The ultimate goal was to develop uncooled IR, UV and broadband detectors with high quantum efficiency much beyond the conventional semiconductor counterparts' through implementation of the novel heterojunction electronic structures.

Significant progress has been made in the two topics proposed originally on CNT-based bulk heterojunction nanohybrids photodetectors and graphene/semiconductor hybrid photodetectors. The major achievements include:

1) development of an novel individual MWCNT IR detector with asymmetric Schottky electrodes to facilitate photocurrent generation/collection from inner CNT shells and demonstrated outstanding D* of 3.4x109 cm?Hz1/2/W, two orders of magnitude higher than previously reported on CNT based IR detectors;
2) demonstration of type II bulk heterojunctions at the interface between CNT and biomolecule cytochrome c (Cty c) based on our earlier success in s-SWCNT/P3HT nanohybrids NIR photodetectors (high D*~2.3x108 cm?Hz1/2/W). The more efficient exciton dissociation and charge transfer in Cty c/CNT nanohybrids allows demonstration of an extraordinary external quantum efficiency in exceeding 90%, high speed photoresponse with time constants as small as sub-ms, together D* >1.0x1010 cm?Hz1/2/W for broadband photodetection in UV-vis-NIR spectra. This is in contrast to the EQE of 1.72% reported in s-SWCNT/P3HT nanohybrid and opens up a new pathway of biomolecule-based nanohybrids with physical properties superior to that of conventional materials for optoelectronics such as IR detection;
3) exploration of sensitizer/graphene nanohybrid photodetectors using nanostructured sensitizers including semiconductor QDs, nanosheets, nanodomes, perovskites thin films. In particular, the high gain in the range of 106-1010, high D* (in exceeding 1014 cm?Hz1/2/W in UV, and 1012 cm?Hz1/2/W together with fast photoresponse time of 10 ms were recently demonstrated for the first time;
4) exploration of novel 2D heterostructures, such as GaTe/InSe vdW heterostructures with type-II band alignment, in which the interlayer transition energy of ~0.55 eV lies in the SWIR light range of 1.0?1.55 ?m beyond the cut-off wavelengths of the individual GaTe and InSe. (not in original proposal) and successfully demonstrated high D* in exceeding 1012 cm?Hz1/2/W at SWIR;
5) development of CVD, solution and printing methods for wafer-size, especially transfer-free synthesis of graphene, nanostructured sensitizers in UV-vis-IR spectra for commercialization.
6) development preliminary result towards flexible focal plane arrays

It should also be mentioned that most of the results obtained from our ARO project represent the best results so far achieved on uncooled photodetection especially in the IR spectra.

Training Opportunities: Integration of research and education has been a major emphasis of this project by providing unique education and training at different levels including post graduate, graduate, undergraduate and K-12. During the reporting period, the grant supported one postdoctoral researcher - Dr. Maogang Gong (100%) on experimental studies of semiconductor sensitizer/graphene based infrared (IR), ultraviolet (UV) and broadband of UV-Vis-IR photodetectors at the University of Kansas (KU). In addition, a few PhD students Brent Cook (a Native American PhD student) and Ryan Goul, were also involved in this project and supported partly in summer. The graduate student Brent Cook passed his PhD candidacy exam with honor during the reporting period and will continue his PhD dissertation research under the ARO support. Three students (Bibek Gautam, Jagaran Acharya and Jamie Wilt) completed their PhD degrees (two with honors) during the project period, and have been employed since then by Intel at Oregon. Three other students Ryan Goul (with honor), Victor Ogunjimi (American African) and Samar Ghopry (female) passed their PhD candidacy exams during the reporting period.

The PI also continued her effort in education/outreach to K-12 and community. She worked with three high school students recruited to the 2017 ARO HSAP program published two manuscripts with these students (Jackson Butler, Karen Shi and Keifer Smith) as co-authors. In addition, the PI has provided advice and support for these students' college applications and all of them are in college now in STEM disciplines. It is particularly worth mentioning that two of the three HSPA students are admitted to/attending the top universities in the nation including Washington University at St. Louis (Jackson Butler) and University of Chicago (Karen Shi). In summer of 2019, PI recruited a local high school student Alex Corbin for an 8-weeks research in nanotechnology. She has a strong interests in STEM and is currently working with PI both on research and on her college application in STEM disciplines.

In summary, during the project period, the this project has supported/co-supported 1 postdoctoral research associate, 3 visiting professors (2 female), 12 graduate students (4 females, 1 Native American, 1 American African), three summer undergraduate students Cherelle Speen (female and Native American from Haskell National Indian University and to enter KU Engineering graduate program since Fall 2019), Brandon Kinn (in KU graduate program jointly by Physics and Chemical Engineering since 2019) and Francisco Alejandro Pedroza Montero (through an international REU program jointly between KU and University of Sorona, Mexico, Francisco plans to come back to KU for his PhD in Physics study), and 4 high school students (2 females).

Results Dissemination: The research result dissemination was mainly through peer-review journal publications and conference presentations. This project has produced 60+ publications and 5 submitted manuscripts. In addition, 3 US patents have been awarded plus several pending. In addition, 30+ invited/keynote presentations and 20+ contributed presentations were made at regional/national/international conferences by the PI's group. All above acknowledge this ARO support.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

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International Collaboration:
International Travel:
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Project Contribution:
International Collaboration:
International Travel:
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International Travel:
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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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Project Contribution:
International Collaboration:
International Travel:
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Project Contribution:
International Collaboration:
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International Travel:
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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

RPPR Final Report
as of 21-Jan-2020

Fundamental Physics of Carbon-based Nanohybrids for High-performance Infrared and Ultraviolet Detection

Final Report (ARO W911NF-16-1-0029)

August 31, 2019

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The reporting period is the last year of this ARO grant that ended originally on December 1, 2018. A no-cost extension was requested by the PI and approved by ARO to complete the proposed research that was delayed slightly by the PI's lab move to the new Integrated Science Building. By the end of the no-cost extension (August 31, 2019), all proposed research was completed. This report therefore covers the progress made in period between the last annual report on September 1, 2018 to August 31, 2019.

The focus of the project was to achieve a thorough understanding of the basic physics that governs the IR, UV and broadband photodetection based on heterojunction CNT and graphene nanohybrids. The ultimate goal was to develop uncooled IR, UV and broadband detectors with high quantum efficiency much beyond the conventional semiconductor counterparts' through implementation of the novel heterojunction electronic structures. The two topics proposed originally have been carried out in parallel during the reporting period and all the proposed research was completed. The following highlights some of the most important results in the last period of the project, while the details can be found in our 21 papers published (1 invited book chapter, 2 on journal cover), plus 7 papers submitted and several in preparation. In addition, 1 US patent was approved during the report period. All of them acknowledge our prior ARO support.

Topic 1- CNT-based Bulk Heterojunction Nanohybrids Photodetectors: Extraordinary Photocurrent Harvesting at Heterojunction Interfaces

Biological macromolecules, such as DNA and protein, exhibit a great advantage in forming heterojunctions with CNTs due to their long molecular chains and large surface areas, which enable helical wrapping with SWCNTs via either covalent or noncovalent interactions to form π-stacking onto the side-walls of SWCNTs. In particular, the concentration of SWCNTs could be increased by more than an order of magnitude in the nanohybrids if each SWCNT is individually wrapped by the molecular chains of diameter of sub-to-few nm. Cytochrome complex (Cyt c) is one of such candidates. Cyt c is a metalloprotein containing heme groups and is highly soluble in water. This provides the critical feasibility for Cyt c wrapping around a semiconductive single-wall CNT (s-SWCNT) to form heterojunctions at the s-SWCNT/Cyt c interface. In addition, as an essential component of the electron transport chain, Cyt c can effectively carry electrical current in the CNT/Cyt c nanohybrid. This CNT/biomolecule hybrid approach is attractive to high-performance and low-cost optoelectronic applications because it allows molecular-scale design of material building blocks that can have light-solid interactive properties superior to conventional materials and large-scale device fabrication with compatibility to existing microfabrication procedures. The proposed projects will focus on understanding the fundamental physics of the s-SWCNT/Cyt c IR detectors as an example system and the knowledge developed through this study will be used to guide design of a new class of hybrid materials using biomolecules for unprecedented functionalities and performance.

Following our success in synthesis of high-performance, uncooled s-SWCNT/Cyt c and MWCNT/Cyt c nanohybrid IR and broadband photodetectors with D* in exceeding 10^{11} Jones reported last year (Gong et al, AOM 2017 and ACSAMI 2017), we further investigated nanohybrids of Cyt c on graphene considering a further improved Cyt c/graphene interface may be achieved for exciton dissociation and charge injection through a control of the Cyt c molecule attachment (Figure 1). On graphene field effect transistors (GFETs), a gate voltage would allow such a control of the Cyt c molecule polarity towards the GFET channel during the Cyt c molecule attachment based on the density function theory simulation of the Cyt c charge distribution and the charge transfer channel in Cyt c. Remarkably, this polarity-controlled Cyt c molecule attachment has indeed been demonstrated in the Cyt c/GFET devices (Gong, et al, *Advanced Functional Materials* **28,** 1704797 (2018). **DOI** 10.1002/adfm.201704797). As we show in this paper, this control is important to design a high performance biomolecule/graphene interface electronic structure for exciton dissociation and charge injection, and extraordinary performance was demonstrated in photodetection above the bandgap of the Cyt c molecules. It should be pointed out this work provides a pathway for design a variety of molecular-carbon nanostructure hybrid devices considering their compatibility, low-cost in device fabrication, and a large selectivity of different optical active molecules. A recently completed work of R6G molecules on GFET is one such example (manuscript in preparation).

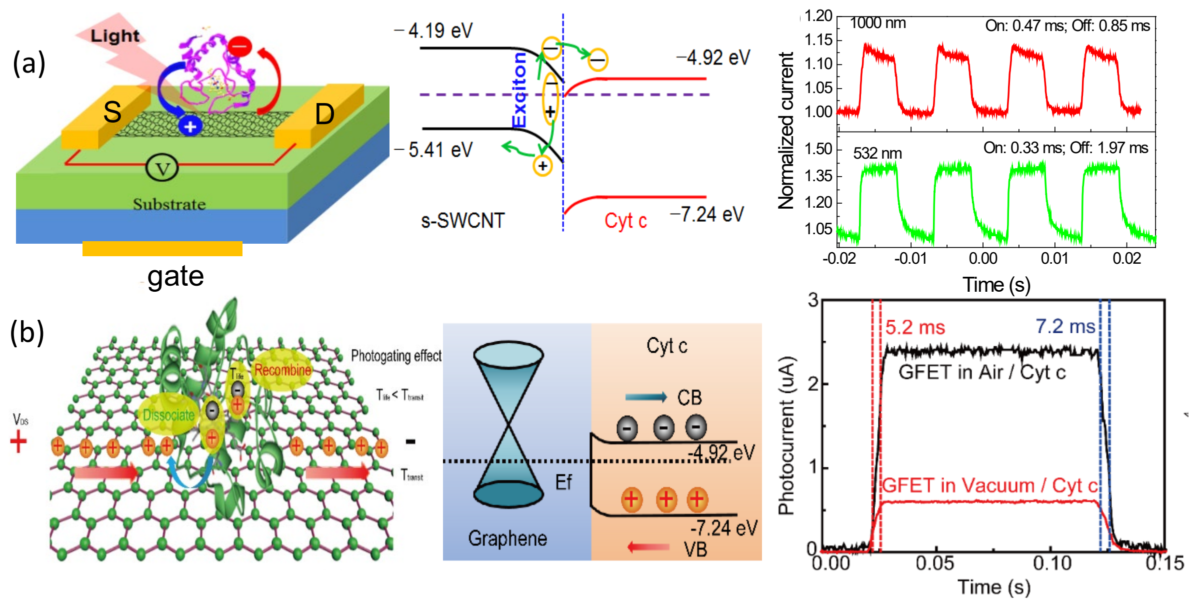

Figure 1 (a) (left) Schematic diagram of the optoelectronic process of the Cyt c/s-SWCNT/nanohybrid photodetector, (middle) band alignment at the s-SWCNT/Cyt c interface and (right) dynamic response of the Cyt c/s-SWCNT nanohybrids; and (b) (Left) schematic image of the photogating effect in the Cyt c/GFET heterojunction devices, (middle) the band energy level diagram of the Cyt c/GFET heterojunctions and the charge transfer facilitated by the built-in electric field, and (right) dynamic response measured on the Cyt c/GFET device.

A unique advantage of the biomolecule/2D inorganic heterostructures is "printability" since the samples can be made in solution processes as we have demonstrated using an inkjet printer. Molecules of Cyt c and R6G, for example, can be well dispersed in water and form heterojunctions with 2D inorganic materials (graphene, TMDC) using layer-by-layer printing.

Specifically, printing cyt c/2D heterojunction optoelectronic devices were explored on electrode arrays fabricated using advanced lithography on substrates, some of them with 2D heterostructures fabricated using CVD. Since cyt c dissolves in water nicely and water suspended cyt c can be used as ink directly in printing, followed with characterization of the electronic and optoelectronic properties. The goal is to achieve high-throughput synthesis of inorganic/biomolecule nanohybrids on flexible substrates and CMOS (several manuscripts are in preparation).

Topic 2-Graphene/Semiconductor Hybrid Photodetectors: Towards High Gain, Fast Photoresponse and Broad Spectrum

Nanostructured sensitizer/graphene heterojunction nanohybrids provide a novel platform for deign of novel optoelectronics. These devices combine the strong quantum confinement in the sensitizers with the superior charge mobility in graphene and can have high photoconductive gain (or external quantum efficiency) by many orders of magnitude higher than that in conventional semiconductors (max. 100%). During the optoelectronic process, excitons (electron-hole pairs) are generated in the sensitizers upon optical absorption and dissociated by the built-in electric field at the van der Waals sensitizer/graphene heterojunction interface. The van der Waals interaction between graphene and semiconductor sensitizer is generally weak and can be affected by any interfacial contamination to block the photocarrier transfer, which is the case of the low performance in most previously reported work.

Our recent success in demonstration of several van der Waals sensitizer/graphene heterojunction optoelectronic devices includes GaSe-nanosheet/GFET (high photoconductive gain in the range of 10^7-10^8 in visible, Lu, et al, Sci. Rep, 2016); ZnO QD/GFET UV detectors (photoconductive gain in exceeding 10^9 and detectivity of $D*$ in exceeding 1×10^{14}Jones for UV detection, Gong et al, ACS Nano 2017), FeS_2-PbS nanocomposite QD sensitizer on GFET for broad band photodetection and demonstrated responsivity > 10^6 A/W in the broad band of UV-Vis-IR (Gong et al, ACS AMI 2017). In this report period, we have explored QDs with broadband absorption much beyond the fundamenetal limit by the semiconductor bandgap via charge doping and facet control in QDs. Using FeS_2 as an example, we have found doping on the "Fe" site can cause the plasmonic resonance of broadband with overall enhanced absorption (Gong *et al*, *Adv. Opt. Mat.* 2018, ACS nano 2017 and 2019). Using these plasmonic semiconductor quantum dots, we have demonstrated the first success of broadband plasmonic QDs/GFET optoelectronic devices with photoresponsivity > 10^6 A/W in the broad band of UV-Vis-IR.

Another sensitizer we studied in the reporting period is the emerging organo-perovskites thin films and nanocrytsals-based optoelectronics. We succeeded in synthesis of highly crystalline samples directly on GFETs and investigated the optoelectronic performance (Qin et al, Adv. Func. Mat. 2017, Wu et al, ACSAMI 2018, plus two manuscripts submitted). It is worth mentioning that the devices were fabricated using inkjet printing, which is important to development of high-performance flexible electronic and optoelectronic devices. In addition, the works in our project pave the way for integrating semiconductor sensitizer/graphene van der Waals heterojunction optoelectronic devices directly on CMOS. Several other sensitizers, such as WO_3, MoS_2, WS_2, etc. were also investigated as shown in the publication list.

Finally, we also carried out research to couple plasmonic nanostructures with semiconductor quantum dots in meta-optoelectronics. This coupling can address the critical issue in much reduced absorption of a thin layer of quantum dots or other semiconductor sensitizers but requires a careful design in the device structure (dielectric layer materials, thickness, interface, etc) to obtain optimized optical coupling while minimizing Ohmic loss. Promising results were obtained (Sadeghi *et al*, Nanoscale 2018; Wilt et al ACSAMI 2018; Acharya *et al*, ACSAMI 2018, Gong et al, Ghopry et al, 2019, Alamri et al, 2018 and 2019). These meta-device designs are important to achieving light management in optoelectronics with unprecedented functionality and high performance.

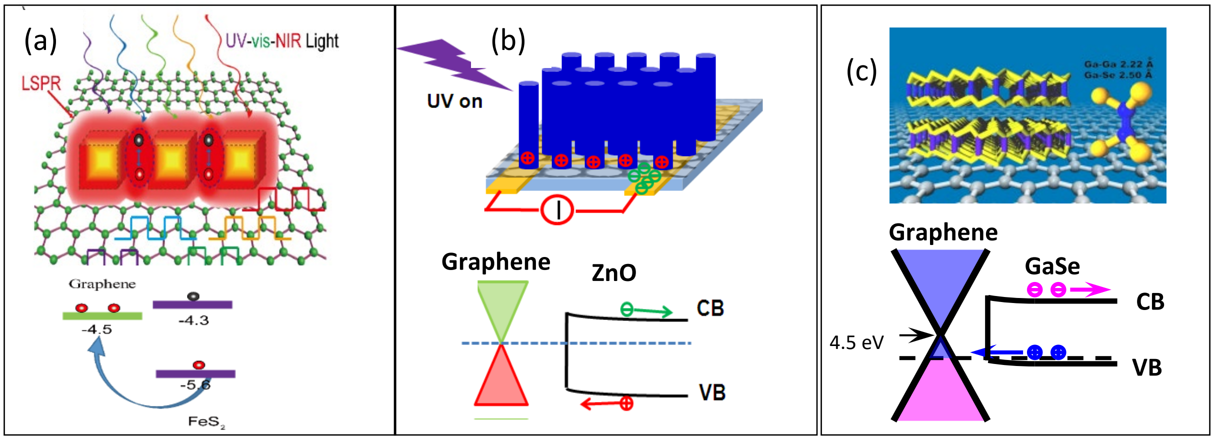

Figure 2. Schematic of three types of sensitizer/graphene nanohybrids photodetectors by PI's group with build-in fields designed at the sensitizer/graphene interface to facilitate exciton separation and charge transfer in: (a) plasmonic 0D FeS_2 quantum dots/graphene; (b) 1D ZnO nanowire/graphene; and (c) 2D GeSe nanosheet/graphene for high gain in the range of 10^6 to 10^{10}.