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Exploration of Carbon-Based Hybrid Nanoarchitectures as a Unique Platform for Managing Excited State Energies and Processes

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14. ABSTRACT
The objective of this project is the development and establishment of the nanoscale carbon-based/derived hybrid nanostructures as a unique nanomaterials platform for managing photoexcited states, properties, and processes that are critical to novel and high-performance optical/photonic materials. With the excellent effort of the project team and the extensive and highly productive collaborations with the AFRL research groups, the objective has been achieved successfully. More specifically, the experimental results from this project have provided convincing evidence for the conclusion that small carbon nanoparticles, including the conceptually and structurally equivalent nanoscale carbon domains in nanocomposites or hybrids, represent the true nanoscale carbon allotrope at the zero-dimension. In fact, also equivalent to the nanoparticles are

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This project has been based on the fundamental hypothesis that nanoscale carbon particles, including also carbon nanostructures that are conceptually, technically, and configuration-wise resemble or equivalent to the small carbon nanoparticles, represent the true nanoscale carbon allotrope at the zero-dimension, and that they serve as the foundation or platform for hybrid nanostructures of unique and/or advantageous properties. For the specific purpose of this project, our emphasis has been on exploring such a unique class of carbon-based/derived hybrid nano-architectures for managing and/or engineering excited state energies and processes, including especially the development of new photoactive nanomaterials by-design, targeting improved and/or new applications in photonic devices and systems for energy conversions, sensing, and others that are critical to Air Force missions. We have reached and exceeded our project objectives, as highlighted in this report.

I. Small Carbon Nanoparticles for Unique/Advantageous Properties and Opportunities

I-1. Known members in the family of nanoscale carbon allotropes (Figure 1):

- Graphenes (2-D);
- Carbon nanotubes (1-D).

These are true nanomaterials, obviously not large molecules. As nanomaterials, they are generally in "distributions" in terms of lengths and/or sizes, single or multiple "layers", electronic structures, and most importantly the inevitable presence of defects. In fact, defects play a critical role in the properties and uses of these nanomaterials. "Defect-free" graphenes and carbon nanotubes are too perfect to allow any processing or manipulation, so mostly or largely useless except for a few special experiments or cases.

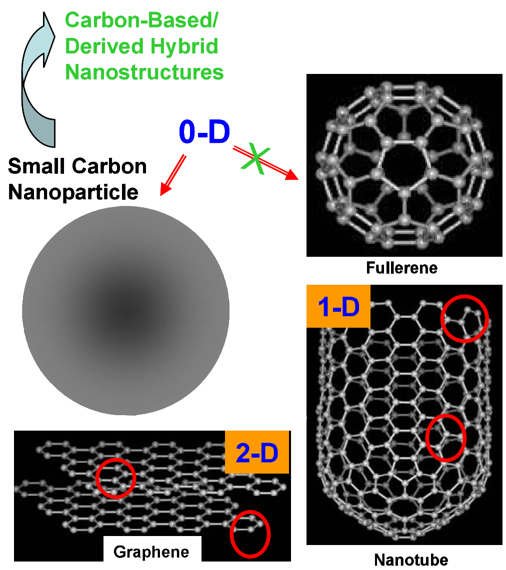


Fig. 1. Cartoon illustration of nanoscale carbon allotropes in different dimensions. The circles make the inevitable presence of defects.

I-2. For the missing member at zero-dimension, our fundamental hypothesis is that small carbon nanoparticles (not fullerenes) deserve the title:

- Fullerenes are stoichiometrically uniquely defined molecules (not "materials") of sizes in nanometers;
- Fullerene molecules, including various derivatives, have distinct electronic structures, fundamentally different from the distribution characteristics in those of graphenes and carbon nanotubes.

In this project we have validated our fundamental hypothesis and provided strong experimental evidence in support of our arguments and conclusions. Equally significantly, we have demonstrated that small carbon nanoparticles compete effectively with not only fullerenes but also conventional nanoscale semiconductors, including "quantum dots" (QDs), in the optical/photonic properties and performances relevant to optoelectronic and related technologies.

- ● Harvesting solar photons effectively;
- ● Ultra-high multi-photon cross-sections (up to 50,000 GM units, orders of magnitude higher than those of molecules, and among the best of all materials/nanomaterials);
- ● Unique photoexcited state properties/processes and redox characteristics;
- ● "Bridging" organic and inorganic, especially valuable for hybrid nano-architectures.

Generally speaking, small carbon nanoparticles are actually nanoscale semiconductor-like in properties and behaviors, and their equivalent structures and functions are also reflected and found in carbon nanotubes and graphenes (Figure 1). Unfortunately, however, they have been extremely underexplored or largely ignored by the research community. Thus, what we have achieved and demonstrated represents a major breakthrough, with likely farreaching implications to the development of carbon-based/derived hybrid nanomaterials for optical/photonic applications and beyond.

II. Defects and Their Passivation for Substantially Enhanced Properties/Performance

II-1. Defects (edge, structural, and other kinds) are ugly or bad to some, but they may actually be very beautiful and valuable to others for their being responsible for many excellent properties and uses. This is particularly true for carbon nanomaterials, in which defects are not only inevitable but also play a critical role in many aspects.

- ● Defects in small carbon nanoparticles (including graphitic, amorphous, and their various mixtures) are particularly abundant;
- ● Conceptually and topologically similar defects to those in the particles are found in graphenes and carbon nanotubes (Figure 1);
- ● All these defects may serve as "trapping sites" for photoexcited state energies, which is in fact responsible for the observed unique photoexcited state properties/processes and redox characteristics.

II-2. The effective passivation of the defects has resulted in dramatically enhanced optical/photonic properties and performance of nanostructures based/derived from small carbon nanoparticles. Specifically, the surface chemical functionalization of small carbon nanoparticles yields "carbon quantum dots" or carbon dots (CDots), dubbed in reference to and competition with conventional semiconductor quantum dots (QDs):

- ♦ Competitive to semiconductor QDs in properties and performance;
- ♦ Mechanistic features similar to those in the exciton model for QDs;
- ♦ Benign and nontoxic (no heavy metals obviously);
- ♦ Excellent versatility and flexibility for hybrid nanostructures (with organic and/or inorganic).

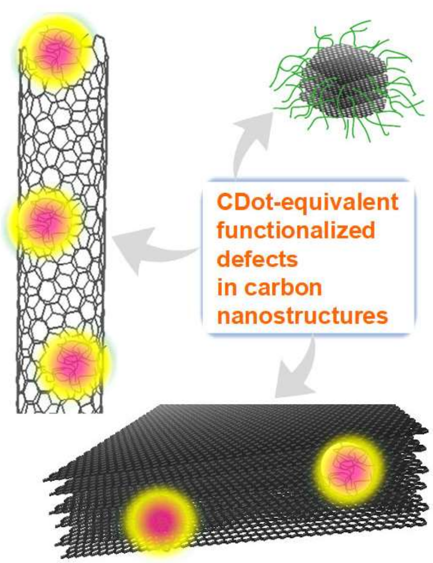


Figure 2

Similarly effective passivation (such as chemical functionalization) of defects in other nanoscale carbon allotropes has resulted in optical/photonic properties and photoinduced redox characteristics similar to those in CDots (Figure 2).

II-3. Successful exploration and demonstration of the photon-harvesting and photoexcited state characteristics:

- Small carbon nanoparticles and CDots share the same strong optical absorptions and similar initial photoexcited state processes;
- For small carbon nanoparticles of 5 nm in diameter, as an example, observed absorptivities in the blue/green are very large, around 5×10^5 per molar nanoparticles per cm;
- Upon photoexcitation, rapid charge transfers and separation, with the electrons and holes trapped at various surface defect sites;
- The separated redox pairs in "naked" small carbon nanoparticles must be very short-lived.

Significant experimental evidence supporting the mechanistic framework and features:

- In CDots, the surface functionalization of the small carbon nanoparticles with organic molecules stabilizes the trapped electrons and holes, which is analogous to the surface capping of conventional semiconductor QDs with wide-bandgap semiconductors (such as ZnS capping CdSe);
- Various productive activities of the separated redox pairs observed experimentally, such as potent photocatalytic reduction of CO_2 and water-splitting, optoelectronic uses, and highly effective antimicrobial functions;
- Radiative recombinations for the emissive excited states, analogous to those in the exciton model for conventional semiconductor QDs;
- The "usual" functions of the emissive excited states, including especially the bright and colorful fluorescence emissions for sensing and other technologies.

III. Carbon-Based/Derived Hybrid Nanostructures for Manipulating/Engineering Excited State Properties-Processes and Redox Characteristics

The purposes as originally proposed and their relevance to optoelectronics and energy conversions:

- ► For "creating/arranging" the excited states in the nanostructures (for a complete harvesting of solar photons, as a representative purpose).
- ► For an understanding of the "communications"/interactions between the different structural domains in the nanostructures, towards optical/photonic nanomaterials of properties by-design.
- ► For the "engineering" of excited states and associated properties/processes, as relevant to the efficient and effective energy conversions.

Our investigations have been on the hybrid nanostructures primarily in the following categories.

III-1. Small carbon nanoparticles with surface chemical functionalization by organic species (dubbed CDots) are essentially special kind of carbon-based/derived hybrid nanostructures. In addition to the properties and mechanistic features highlighted in **section II** above, we have succeeded in the development of new carbon nanoparticle surface functionalization chemistries, including the radical copolymerization (*versus* similar copolymer structures and properties derived from fullerenes), as relevant to potential optoelectronic technologies.

i. The functionalization of small carbon nanoparticles by *N*-ethylcarbazole (NEC) via the radical addition reaction:

- Facile synthesis, with the adducts thoroughly characterized;
- Very stable structures and properties of the adducts;
- Comprehensive optical spectroscopy investigation on the photoexcited state properties and redox characteristics, with the obtained results as predicted;
- With NEC being structurally very close to the precursor for PVK polymer, the sample (as designed) has been shown as being fully compatible with the polymer matrix for homogeneous PVK nanocomposites with the NEC-functionalized carbon nanoparticles, ideally suited for uses in optoelectronic devices;
- Initiated the investigation on the use of same/similar reaction conditions for the functionalization of small carbon nanoparticles with other organic molecules of a similar structural feature to that in NEC, specifically *N*-ethylaniline (an excellent electron donor, thus a redox "dyad" as the targeted product).

ii. PVK copolymers with small carbon nanoparticles *versus* those with fullerenes:

- Fullerenes are known for radical additions, and so can small carbon nanoparticles, including radical copolymerization with vinyl monomers.
- We have targeted PVK copolymers for the popular use of PVK in optoelectronic devices. As we reported, PVK copolymers with small carbon nanoparticles could readily be synthesized just like those of PVK with C_{60}, yet the former exhibited significantly better optical properties, in addition to being considerably cheaper for larger quantities.
- A systematic comparison between the PVK copolymers with carbon nanoparticles and with fullerenes. The available results suggest that the former are mostly better or comparable with the latter in photoexcited state properties and redox characteristics.
- A systematic comparison between the PVK copolymers with small carbon nanoparticles and those with the NEC-functionalized small carbon nanoparticles.
- Recruiting research collaborators/partners for an evaluation of these nanomaterials in optoelectronic devices.
- The exploration of other small carbon nanoparticles-derived copolymers, such as vinyl acetate as monomer for the copolymerization, yielding promising preliminary results.

iii. Small carbon nanoparticles in polymer matrices for optical/photonic nanocomposites:

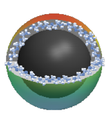
- "Naked" and surface-functionalized small carbon nanoparticles are readily dispersed in polymer matrices for nanocomposites of improved optical/photonic properties, as we reported.
- "Electronic polymers" (PVK, P3HT, etc.) relevant to optoelectronics have been evaluated as matrices for nanocomposites with specifically functionalized small carbon nanoparticles, competing in materials quality and performance with similar nanocomposites embedded with fullerenes.
- Thin films of PVK copolymers with small carbon nanoparticles (diluted with neat PVK for loading variations) have been fabricated and studied in detail for their serving as benchmarks

in the expanded explorations, including those on P3HT nanocomposites with specifically functionalized small carbon nanoparticles.

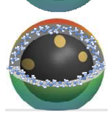
III-2. Carbon/semiconductor (or magnetic oxides) hybrid nanostructures in many different compositions and/or structural arrangements/configurations have been prepared and investigated systematically, from which the experimental results suggest that they may correspond to dramatically different properties/performances, thus excellent "manipulation" or "engineering" opportunities. On the fundamental principles and design/development strategy:

- Small carbon nanoparticles and other nanoscale carbon allotropes serve as the "foundation" in the platform for their effective and efficient photon-harvesting over the solar spectrum to drive the rich excited state processes;
- The nanoscale carbons are structurally fully compatible/miscible with nanoscale conventional semiconductors and/or magnetic metal oxides, as already found experimentally and reported in our publications (on some of the results);
- Much enhanced and/or uniquely advantageous properties in the hybrids:
    - ◊ Hardly simple additions of the components, but instead "1+1 = 3" and beyond;
    - ◊ The strong dependencies on the compositions and structural configurations in the hybrids enable wide tunability in the manipulation of their properties, especially those of the photoexcited states and the related processes and redox characteristics.
- By taking advantage of the extensively studied and well established nanoscale TiO_2 and iron oxides as model systems, we have used them as the starting point in the design, construction and synthesis, characterizations, and property evaluations of the hybrids.

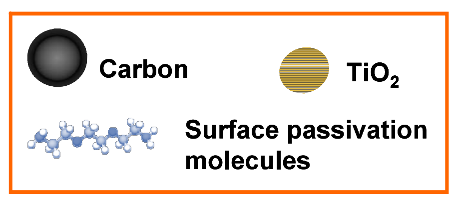
iv. On the various carbon/TiO_2 hybrid nanostructures, the results/outcomes from evaluations based on fluorescence emission properties/parameters and photoinduced redox properties (photocatalytic activities, photodynamic effects, etc.) are highlighted as follows.

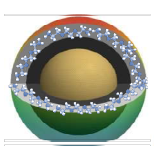


(I) Known properties (bright fluorescence, electron accepting & donating, etc.).

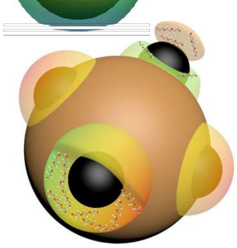


(II) Much enhanced emissions and related performances, with the surface TiO_2 serving the function of co-passivation/functionalization agent.

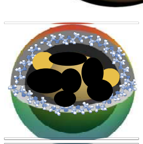




(III) The encapsulated TiO_2 (~8 nm in diameter) quenching the fluorescence emissions, but without significant redox activities (by either components).



(IV) Based on commercial TiO_2 nanoparticles (on the order of 25 nm in diameter):
Solvent dispersible for stable suspensions;
Diminished fluorescence emissions;
Visible excitation resulting in strong redox activities!
Doping with noble metals (simple photolysis) for catalytic activities;
Potent photodynamic effects.



(V) For the core, a composite of carbon with ultra-small (sub-4 nm) TiO_2 nanoparticles (there were some technical issues, which may be addressed in follow-on investigations).

v. On carbon/iron oxides hybrid nanostructures, our various synthesis approaches yielded mixtures of the nanostructures. Some of the components in the mixtures have been isolated by using a magnetic separator, and they have been determined as dot-like nanocomposites of carbon, Fe_3O_4, and organic species. The results along with those from spectroscopic investigations have been published. We have been interested in potentially optical/magnetic couplings in these hybrid nanostructures, but limited by the available resources.

For the mixtures from the various synthesis approaches, about half of each sample was not responsive to the magnetic separation. However, all these samples were found for each to contain a substantial amount of iron. We have been interested in systematic separations of the underlying components for thorough characterizations, but again limited by the available resources.

III-3. Hybrid nanostructures from the carbonization of a wide selection of organic precursors are the most popular in the literature, as reflected by the large number of publications with many naming systems including "graphene quantum dots" and so on. However, many or most of the reported materials contained too little nanoscale carbons due to their preparations under too mild carbonization conditions, so that those samples are often dominated by complex mixtures of organic dye-like species produced thermally under the mild carbonization processing conditions. We have been making corrections on some of the more obvious mistakes in the literature, and we will continue to publish our already acquired experimental results to make the corrections more evident and conclusive for the healthier advances of the relevant research fields.

In our effort described above we came to understand that in the composites of nanoscale carbons with organic species, there are unique interactions of the photoexcited carbons (dubbed "nanoscale carbon domains" in some of our publications) with the organic components, resulting in some interesting and/or highly valuable optical/photonic properties and redox characteristics. We credit the presence of such interactions for what were found in the more correct published studies of carbonized samples discussed above, despite the fact that the authors of those studies were mostly unaware of the presence and consequence of the unique interactions. We have been exploiting such interactions in several hybrid nanostructure configurations for different purposes, as highlighted below on those whose studies are more advanced (some published or being written up for publication). The investigations on others are still being pursued.

vi. Nanoscale carbon/dye hybrids for optical/photonic properties "*By-Design*":

- Various nano-structural configurations, among which we have published some results on nanoscale carbon particles/domains structurally encapsulated/doped with red/near-IR dyes (dubbed "host-guest" in some publications), coupled with the same particle surface chemical functionalization like in CDots.
- The same hybrids applicable to other nano-carbon allotropes, as suggested by preliminary results.
- Optical absorptions are the superposition of those due to the nano-carbons (strong in blue/green) and the selected dye species (strong in red and near-IR), thus covering more completely the solar spectrum from near-UV to near-IR, as designed.
- Upon photoexcitation of the hybrids over the entire covered wavelengths, regardless of the underlying components/entities (the nano-carbons or the selected dyes) being responsible for the optical absorptions, the photoexcited state properties are "shared" or "scrambled" (not superposition of individual component properties anymore), including especially the redox

characteristics to be rather similar to those of the nanoscale carbons, as well studied and understood in CDots.

- Further supporting our published results on one system, our investigations on a series of the hybrids with different dyes and configurations have yielded results that support the same conclusion (to be published).

vii. <u>Other technological relevance beyond solar photon harvesting and energy conversions</u>:

We have been exploring other opportunities for our hybrid nanomaterials platform, among which one unique use is in the development of optical limiters for laser protection and other applications based mechanistically on reverse saturable absorbers (RSA).

- Classical RSA are typically organic dyes such as phthalocyanines, fullerenes, etc., whose performance is limited by the optical properties of the molecules (those determined by Nature).
- We have proposed and experimented with the concept and design of "Supramolecular" RSA ("SupraRSA"): Specifically designed and constructed by combining/connecting two (or more) components, one for the ground state absorptions and the other for much stronger absorptions of the excited states, thus breaking the limit imposed by Nature for unlimited performance improvements.

The nanoscale carbon/dye hybrids – excellent platform for SupraRSA (Figure 3):

- The at/near-record two-photon cross-sections in the near-IR;
- Broad wavelength coverage in the visible by nanoscale carbon domains in the hybrids;
- Versatility/flexibility for unlimited selection of dyes for the desired ultra-strong excited state absorptions, and the facile synthesis of the hybrids;
- The unique excited state properties/processes in the hybrids enable more effective/efficient energy transfers/sharing (confirmed by results on the similar hybrids already available);
- We have been making efforts on the optical limiting measurements of the available hybrids to aid further development, including: (1) seeking external collaborations (AFRL), and (2) trying to refurbish/re-establish the setup in house (acquired some years ago for DoD-funded projects on the same topic).

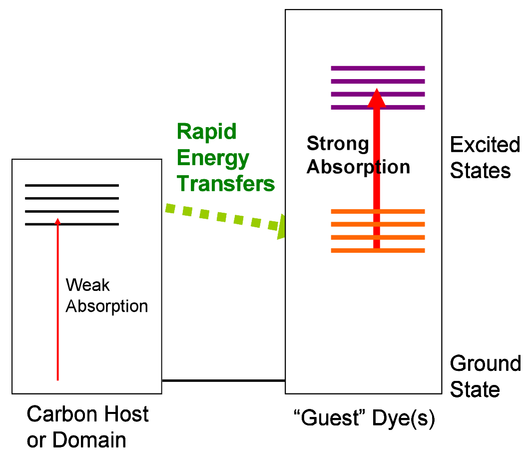


Fig. 3. Carbon/dye hybrid nanostructures for broad-band optical limiters with the "designed" performances.

viii. Critical comparisons of the hybrids in distinctively different configurations (Figure 4) for much expanded opportunities, mechanistic understanding-elucidation, and relevance/competition to the popular dye-functionalized/coupled/decorated conventional semiconductor quantum dots (QDs).

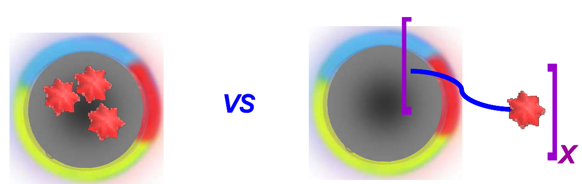


Fig. 4. "Intra-molecular" *versus* "inter-molecular" hybrids.

Some background information/facts:

● The same or similar "intra-molecular"-like configurations of carbon/dye hybrid nanostructures (Figure 4, already designed, synthesized, and studied) are not available to or possible with conventional semiconductor QDs;
● Dye modification of semiconductor QDs has been explored for the purpose of manipulating optical/photonic properties; and similarly small carbon nanoparticles can be functionalized or tethered with selected dye species ("inter-molecular" in Figure 4, rather versatile/flexible and advantageous in synthesis and structures in comparison with their semiconductor QDs-based counterparts);
● Nanoscale carbon/dye hybrids ("intra-") *versus* dye-functionalized carbon nanoparticles ("inter-") shown in Figure 4: Very different photoexcited state properties and processes to enable more effective and flexible "excited state engineering".

Progress made, and very interesting and promising results obtained:

● The successful synthesis and characterization of small carbon nanoparticles functionalized with selected dye species, such as rhodamine 101 and rhodamine 6G;
● Optical spectroscopy studies of the nanostructures, including redox quenching;
● The available results are generally consistent with the expectation that these dye-functionalized carbon nanoparticles are significantly different from the nanoscale carbon/dye hybrids in photoexcited state properties and photoinduced redox characteristics, providing preliminary yet important validation on our design strategy and approach for the carbon-based/derived hybrid nanostructures in different configurations for a variety of purposes and opportunities.

IV. Summary, Conclusions, and Other Positive Outcomes

<u>What are evolutionary and revolutionary about this research project</u>?

Evolutionary: For the project as a whole, the following advances have been accomplished.

∆ The recognition and further experimental validation of the widely held view that nanomaterials offer excellent opportunities in the manipulation of optical/photonic properties (or the "excited state engineering") for ultimately major technological gains in optoelectronics and beyond.
∆ The similar recognition and validation on the potential of carbon-based/derived nanostructures for such purposes.

Revolutionary: This project has resulted in some fundamental/revolutionary ("game-changing") findings/advances and the establishment of new nanomaterials platforms, highlighted as follows.

► The establishment based on solid experimental evidence that small carbon nanoparticles ("dots") instead of fullerene molecules represent the true zero-dimensional carbon allotrope in the family with carbon nanotubes and graphenes.
► The small carbon nanoparticles and other members of the family share similar broad-band optical absorptions with major overlap with the solar spectrum. They also share similar photoexcited state properties and redox characteristics dictated by structural/surface defects ("defect-free" nanotubes/graphenes are rare and practically useless), of which the effective passivation dramatically enhances their performances to be competitive to those of the popular

fullerene-based/derived photonic materials and established nanoscale semiconductors including quantum dots.

► The small carbon nanoparticles (and their conceptually and structurally equivalent nanoscale carbon domains) are miscible with organic species and conventional semiconductors/metal and magnetic oxides for hybrid nanostructures of essentially unlimited selections on compositions and structures/configurations, thus a highly versatile and flexible nanomaterials platform for enhanced and/or new optical/photonic properties, including those by-design.

What scientific areas are impacted with the success of this project?

◊ In optoelectronics, dominating have been semiconductor QDs (even "Q"LED TV sets), and in flexible or similar solar cells especially, fullerenes have been very popular. The QDs-like small carbon nanoparticles-based/derived "dots" are competitive in performance to both of the above, with additional valuable advantages/features such as benign and nontoxic, facile synthesis and processing, and very inexpensive/cheap from mostly renewable precursors. The nanoscale hybrids platform pursued and established in this project offers essentially unlimited opportunities for further enhancements.

◊ Colloidal semiconductors represented by TiO_2 have been extremely popular with broad uses or potential applications in photocatalysis, nano-sensors, photodynamic effects and related biocidal functions, etc. The platform from this project is capable of many/most of those, in addition to the other unique/advantageous features.

Extensive and highly productive collaborations with AFRL:

- Meetings (in person and virtual, including frequent conference calls) with AFRL collaborators led by Dr. Christopher Bunker at WPAFB;
- A large number of graduate student visits to AFRL (WPAFB), including those of many months in duration, to perform some critical experiments and for other collaboration needs.
- Broad and very productive collaborations with AFRL scientists and their associated labs on activities across the entire spectrum of the project, including the planning for the execution of the project tasks, the training and supervision of graduate students, the assistance in the performance of some critical experiments, the data processing and interpretation, and the preparation of joint publications (which in fact represent almost all of those directly related to the project).

Human resource development and other benefits of this project:

- The project has served as an excellent platform for the education and training of graduate and undergraduate students in the technical area important to the needs of Air Force and DoD. For example, the graduate student fully supported by the grant for his participation over almost the entire project period graduated with PhD and took a research job at AFRL.
- The value-added outcomes from the extensive exchanges and sharing of samples, data, and personnel with AFRL collaborators, and also with other groups in the OMC program with projects focusing more on optoelectronic devices and systems.
- Activities of tech-transfer to private industry in the U.S. based on some of the results from this project are in progress.

V. Publications with the Funding of This Project

1. LeCroy, G. E.; Yang, S.-T.; Yang, F.; Liu, Y.; Fernando, K. A. S.; Bunker, C. E.; Hu, Y.; Luo, P. G.; Sun, Y.-P. "Functionalized Carbon Nanoparticles: Syntheses and Applications in Optical Bioimaging and Energy Conversion" *Coordination Chem. Rev*. **2016**, *320–321*, 66–81.

2. Sun, Y.-P.; Wang, P.; Lu, Z.; Yang, F.; Meziani, M. J.; LeCroy, G. E.; Liu, Y.; Qian, H. "Host-Guest Carbon Dots for Enhanced Optical Properties and Beyond" *Scientific Reports* **2015**, *5*, 12354.

3. Anderson, A.; Yang, F.; Cao, L.; Li, H.; Meziani, M. J.; Sun, Y.-P. "Tethered Anthracene Pair as Molecular Tweezers for Post-Production Separation of Single-Walled Carbon Nanotubes" *Chem. Phys. Lett*. **2016**, *657*, 190–194.

4. Yang, F.; LeCroy, G. E.; Wang, P.; Liang, W.; Chen, J.; Fernando, K. A. S.; Bunker, C. E.; Qian, H.; Sun, Y.-P. "Functionalization of Carbon Nanoparticles and Defunctionalization - Towards Structural and Mechanistic Elucidation of Carbon "Quantum" Dots" *J. Phys. Chem. C* **2016**, *120*, 25604–25611.

5. Hu, Y.; Al Awak, M. M.; Yang, F.; Yan, S.; Xiong, Q.; Wang, P.; Tang, Y.; Yang, L.; LeCroy, G. E.; Bunker, C. E.; Xu, L.; Tomlinson, N.; Sun, Y.-P. "Photoexcited State Properties of Carbon Dots from Thermally Induced Functionalization of Carbon Nanoparticles" *J. Mater. Chem. C*. **2016**, *4*, 10554-10561.

6. Liu, Y.; Wang, P.; Fernando, K. A. S.; LeCroy, G. E.; Maimaiti, H.; Harruff-Miller, B. A.; Lewis, W. K.; Bunker, C. E.; Hou, Z.-L.; Sun, Y.-P. "Enhanced Fluorescence Properties of Carbon Dots in Polymer Films" *J. Mater. Chem. C* **2016**, *4*, 6967-6974. Featured as the journal cover.

7. Anderson, A.; Hou, Z.-L.; Song, W.-L.; Meziani, M. J.; Wang, P.; Lu, F.; Lee, J.; Xu, L.; Sun, Y.-P. "Towards Nanostructured Boron Nitride Films" *J. Mater. Sci.: Mater. Electronics* **2017**, *28*, 9048-9055.

8. LeCroy, G. E.; Fernando, K. A. S.; Bunker, C. E.; Wang, P.; Tomlinson, N.; Sun, Y.-P. "Steady-State and Time-Resolved Fluorescence Studies on Interactions of Carbon "Quantum" Dots with Nitrotoluenes" *Inorg. Chim. Acta* **2017**, *468*, 300-307.

9. Hu, Y.; Wang, P.; Bunker, C. E.; Teisl, L. R.; Reibold, M. Yan, S.; Qian, H.; He, D.; Sun, Y.-P. "Preparation and Optical Properties of Magnetic Carbon/Iron Oxide Hybrid Dots" *RSC Adv*. **2017**, *7*, 41304-41310.

10. LeCroy, G. E.; Messina, F.; Sciortino, A.; Bunker, C. E.; Wang, P.; Fernando, K. A. S.; Sun, Y.-P. "Characteristic Excitation Wavelength Dependence of Fluorescence Emissions in Carbon "Quantum" Dots" *J. Phys. Chem. C* **2017**, *121*, 28180–28186.

11. Yang, F.; Ren, X.; LeCroy, G. E.; Song, J.; Wang, P.; Beckerle, L.; Bunker, C. E.; Xiong, Q.; Sun, Y.-P. "Zero-Dimensional Carbon Allotropes – Carbon Nanoparticles *versus* Fullerenes in Functionalization by Electronic Polymers for Different Optical and Redox Properties" *ACS Omega* **2018**, *3*, 5685-5691.

12. Liu, Y.; Liu, Y.; Qian, H.; Wang, P.; LeCroy, G. E.; Bunker, C. E.; Fernando, K. A. S.; Yang, L.; Reibold, M.; Sun, Y.-P. "Carbon-TiO2 Hybrid Dots in Different Configurations – Optical Properties, Redox Characteristics, and Mechanistic Implications" *New J. Chem*. **2018**, *42*, 10798-10806.

13. Ren, X.; Liang, W.; Wang, P.; Bunker, C. E.; Coleman, M.; Teisl, L. R.; Cao, L.; Sun, Y.-P. "A New Approach in Functionalization of Carbon Nanoparticles for Optoelectronically Relevant Carbon Dots and Beyond" *Carbon* **2019**, *141*, 553-560.

14. LeCroy, G. E.; Wang, P.; Bunker, C. E.; Fernando, K. A. S.; Liang, W.; Ge, L.; Reibold, M.; Sun, Y.-P. "Hybrid Carbon Dots Platform Enabling Opportunities for Desired Optical Properties and Redox Characteristics By-Design" *Chem. Phys. Lett*. **2019**, *724*, 8-12. Featured as the journal cover (June, 2019)

15. Cao, L.; Fernando, K. A. S.; Liang, W.; Seilkop, A.; Veca, L. M; Sun, Y.-P.; Bunker, C. E. "Carbon Dots for Energy Conversion Applications" *J. Appl. Phys*. **2019**, *125(22)*, 220903. Featured as Editor's Pick.

16. Liang, W.; Bunker, C. E.; Sun, Y.-P. "Carbon Dots: Zero-Dimensional Carbon Allotrope with Unique Photoinduced Redox Characteristics" *ACS Omega* **2020**, *5*, 965-971.

17. Liang, W.; Ge, L.; Hou, X.; Ren, X.; Yang, L.; Bunker, C. E.; Overton, C. M.; Wang, P.; Sun, Y.-P. "Evaluation of Commercial "Carbon Quantum Dots" Sample on Origins of Red Absorption and Emission Features" *C – J. Carbon Res*. **2019**, *5*, 70; doi:10.3390/c5040070.

18. Sun, Y.-P. "Carbon Dots - Exploring Carbon at Zero-Dimension" Springer Nature (Springer International Publishing, ISBN 978-3-030-41184-8), **2020**.