AFRL-AFOSR-VA-TR-2019-0205

Characterizing Interactions at Interfaces Critical to the Functions of Ionic Liquids and Solar Cells

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07/11/2019
Final Report

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AF Office Of Scientific Research (AFOSR)/ RTB2
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*

2. REPORT TYPE
Final

3. DATES COVERED *(From - To)*
07/01/2015-03/31/2019

4. TITLE AND SUBTITLE
"Characterizing Interactions at Interfaces Critical to the Functions of Ionic Liquids and Solar Cells"

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-15-1-0213

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
OFC OF NAVAL RSCH
CHICAGO REGIONAL OFFICE
230 SOUTH DEARBORN, RM 380
CHICAGO, IL 60605-1595

10. SPONSOR/MONITOR'S ACRONYM(S)
ONRRO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
We have developed a spectroscopic probe based on Sum Frequency Light Scattering (SFLS) that will enable us to conduct spectroscopic examination of colloidal surfaces to gain molecular level understanding at the colloidal surface. Through characterizing the surface properties of metallic nanoparticle, we have discovered a way to make super-bright luminescent metallic nanoparticles for sensing purposes. While working on the project stated in the original proposal, a discussion with the Program Officer prompted us to develop a new research aimed at solving a great mystery in astrophysics – why there is inexplicable amount of HNC in excess of thermal equilibrium of HCN in interstellar media.

15. SUBJECT TERMS
Second harmonic generation; Sum frequency generation, metallic nanoparticles, Interstellar chemistry, photochemistry of cyano containing molecules

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Hai-Lung Dai
					19b. TELEPHONE NUMBER *(Include area code)*
					2152197953

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Grant/Contract Title:	Characterizing Interactions at Interfaces Critical to the Functions of Ionic Liquids and Solar Cells
Grant/Contract Number:	FA9550-15-1-0213
Program Manager:	Michael Berman
Report Type:	Final Report
Reporting Period Start Date:	07/01/2015
Reporting Period End Date:	03/31/2019

Abstract:

A major goal of this project is to develop experimental capabilities for examining the surfaces/interfaces of materials important to new technology development. The materials of interests include dye coated semiconductor particles, ionic liquids, ultrathin films, composite materials, and nanoparticles. The surfaces/interfaces are critical to the properties of these systems as they have high surface to bulk ratios. But because these surfaces/interfaces are buried within a liquid or solid medium it is difficult to experimentally probe them.

We have in the past decade with the support of AFOSR developed a unique capability based on the nonlinear optical phenomenon Second Harmonic Light Scattering (SHLS) for probing the structure, kinetics and energetics of surfaces/interfaces buried in a colloidal medium. In this current project we have accomplished the following:

1) We have developed a spectroscopic probe based on Sum Frequency Light Scattering (SFLS) for structural characterization of molecules on particle

surfaces. In this new probe, a collinear heterodyne scheme has been demonstrated for more sensitive detection of SFLS. Furthermore, we have developed a new laser source for high resolution SFLS spectroscopy. In this new laser source, a single femtosecond oscillator is used as the seed for two regenerative amplifiers, of which one is femtosecond and the other is picosecond. The output of the femtosecond regenerative amplifier is used for an OPA to generate broadband IR light while part of the picosecond regenerative amplifier is sent to a home-built pulse shaper to obtain a spectrally narrowed visible beam. The new light source can currently provide a resolution of 1.4 cm-1 resolution and has the potential to provide sub-wavenumber resolution. Eventually, the more sensitive collinear heterodyne detection scheme combined with the high resolution light source will enable us to conduct spectroscopic examination of colloidal surfaces to gain molecular level understanding of processes and functions at the colloidal surface.

2) Through characterizing the surface properties of metallic nanoparticle, we have discovered a way to make super-bright luminescent metallic nanoparticles for sensing purposes. It is found that by curing the surface defects that quench photo-excited carriers, luminescence efficiency of metallic nanoparticles can be dramatically increased. For Ag nanoparticles, as much as 300 times increase in photo-excitation induced luminescence is observed upon surface adsorption of ethanethiol. The same treatment increases Au nanoparticle luminescence efficiency by a factor of three. A model based on the elimination of surface defects by the sulphur-metal bond formed upon thiol adsorption can quantitatively account for the observations, which also indicate that nanoparticles without proper surface treatment typically have low luminescence quantum yields.

While working on the project stated in the original proposal, a discussion between the PI and the Program Officer prompted us to develop a new research that is of Air Force interests. This new effort is based on the unique experimental capability – Time Resolved FTIR Emission Spectroscopy – developed in the PI's lab. This technique enables us to detect the IR emission from a small amount of excited molecules in gaseous environments for characterizing their identity and energy content. A new goal is about solving a great mystery in astrophysics – why there is inexplicable amount of HNC in excess of thermal equilibrium of HCN in interstellar media.

Motivated by the possibility that cyano containing hydrocarbons may act as photolytic sources for HCN and HNC in astrophysical environments, we conducted a combined experimental and theoretical investigation of the 193 nm photolysis of the cyano-ester, methyl cyanoformate (MCF). Experimentally, nanosecond time-resolved infrared emission spectroscopy was used to detect the emission from nascent products generated in the photolysis reaction. The time-resolved spectra were analyzed using a recently developed spectral reconstruction analysis, which revealed spectral bands assignable to HCN and HNC. Fitting of the emission band shape and intensity allowed determination of the photolysis quantum yield, and the ratio of photolysis products HNC/HCN as 0.074, a number many orders of magnitude higher than the thermal equilibrium. This work along with previous studies in our laboratory illustrates the propensity for cyano-containing hydrocarbons as photolytic sources of HCN and the overly abundant HNC in astrophysical environments.

Subsequently we have characterized the UV photolysis of pyrazine, another CN containing molecule, and found similarly high HNC/HCN ratio. Furthermore, using the IR emission from HNC as a signature of its internal energy content, we have determined the collisional energy transfer kinetics of this molecule with vibrational excitation. The feasibility of efficient collisional deactivation also serves as a contributing factor to the observed overabundance of astrophysical HNC.

Distribution Statement:

SF298 Form:

Report Document

Archival Publications:

Wilhelm, MJ and Dai, H-L;
Collisional Deactivation of Vibrationally Excited Hydrogen Isocyanide
Journal of Physical Chemistry A, in press (2019).
(Part of the Dai Festschrift)

Wilhelm, MJ; Petersson, GA; Smith, JM; Behrendt, D; Ma, J; Letendre, L; and Dai, H-L;
UV photolysis of pyrazine and the production of hydrogen isocyanide
Journal of Physical Chemistry A, **122**, 9001-9013 (2018).

Gan, W; Xu, B; and Dai, H-L;
Super bright luminescent metallic nanoparticles
Journal of Physical Chemistry Letters, **9**, 4155-4159 (2018).

Wilhelm, M.J.; Martinez-Nunez, E.; Gonzalez-Vazquez, J.; Vazquez, S.A.; Smith, J.M.; and Dai, H-L.;

Is photolytic production a viable source of HCN and HNC in astrophysical environments? A laboratory based feasibility study of methyl cyanoformate
Astrophysical Journal, **849**, 15 (2017)

Xu, B; Wu, Y; Sun, D; Dai, H-L; and Rao, Y;
Stabilized phase detection of heterodyne sum frequency generation for interfacial studies
Optics Letters, **40**: 4472-4475 (2015).

Changes in Research objectives:

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Extensions Granted: A request for a nine month extension to March 31, 2019 with additional funding $51,443 was granted. The additional fund and the extension Has enabled us to replace and upgrade a failing diode laser module in the laser system we use for routine nonlinear optical measurements, so we can carry out additional measurements to confirm the observation of a 300 times enhancement of the luminescence of silver nanoparticles (see description in Abstract) which is important for many applications in sensing and imaging technologies.