

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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REPOR	Form Approved OMB No. 0704-0188					
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1. REPORT DATE (DD-MM-YYYY)	2. REPORT	ТҮРЕ			3. DATES COVERED (From - To)	
	Final			52 00	07/01/2015-03/31/2019	
"Characterizing Interactions at Interfaces Critical to the Functions of Ionic			54. 00			
Liquids and Solar Cells"				5b. GR	ANT NUMBER	
				FA955	50-15-1-0213	
				5c. PR	5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Hai-Lung Dai			5d. PR	5d. PROJECT NUMBER		
				5e. TA	SK NUMBER	
			5f. WO	RK UNIT NUMBER		
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230 SOUTH DEARBORN, RM 380 CHICAGO, IL 60605-1595					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 O	F:	17. LIMITATION OF	18. NUMBER	19a. NAME		
a. REPORT b. ABSTRACT c	. THIS PAGE	ABSTRACT	OF	Hai-Lung D	Dai	
			PAGES	19b. TELEP	HONE NUMBER (Include area code)	
				215219795	53	

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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.				
	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 timeresolved 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.

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Statement:

SF298 Form:

Report Document

	 Wilhelm, MJ and Dai, H-L; Collisional Deactivation of Vibrationally Excited Hydrogen Isocyanide <i>Journal of Physical Chemistry A</i>, in press (2019). (Part of the Dai Festschrift)
Archival Publications:	Wilhelm, MJ; Petersson, GA; Smith, JM; Behrendt, D; Ma, J; Letendre, L; and Dai, H-L; <u>UV photolysis of pyrazine and the production of hydrogen isocyanide</u> <i>Journal of Physical Chemistry A</i> , 122 , 9001-9013 (2018).
	Gan, W; Xu, B; and Dai, H-L; <u>Super bright luminescent metallic nanoparticles</u> <i>Journal of Physical Chemistry Letters</i> , 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; <u>Stabilized phase detection of heterodyne sum frequency generation for</u> <u>interfacial studies</u> *Optics Letters*, **40**: 4472-4475 (2015).

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Changes in Research objectives: 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.