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14. ABSTRACT

We report a new single-aerosol particle scope using an optical trapping-cavity ringdown spectroscopy (OT-CRDS) technique. The scope can not only view physical parameters such as size, motion, restoring force constant of a single aerosol particle trapped in air, but also display time-, particle-, or wavelength-resolved chemical properties such as single aerosol particle extinction. We demonstrate the scope by trapping and walking single carbon-nanotube particles of ?50 µm in size and viewing those properties via changes of ringdown time. This single-

15. SUBJECT TERMS

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Report Title

Annual Progress Report: Physical and chemical study of single aerosol particles using optical trapping-cavity ringdown spectroscopy

ABSTRACT

We report a new single-aerosol particle scope using an optical trapping-cavity ringdown spectroscopy (OT-CRDS) technique. The scope can not only view physical parameters such as size, motion, restoring force constant of a single aerosol particle trapped in air, but also display time-, particle-, or wavelength-resolved chemical properties such as single aerosol particle extinction. We demonstrate the scope by trapping and walking single carbon-nanotube particles of ?50 µm in size and viewing those properties via changes of ringdown time. This single-aerosol particle scope offers a new, powerful tool to study both physical and chemical properties as well as their evolving dynamics.

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)

Received		Paper
10/01/2014	3.00	Chuji Wang, Yong-Le Pan, Mark Coleman. Experimental observation of particle cones formed by optical trapping, Optics Letters, (04 2014): 0. doi: 10.1364/OL.39.002767
10/01/2014	4.00	Brandon Redding, Yong-Le Pan, Chuji Wang, Hui Cao. Polarization-resolved near-backscattering of airborne aggregates composed of different primary particles, Optics Letters, (07 2014): 0. doi: 10.1364/OL.39.004076
10/01/2014	1.00	Chuji Wang, Yong-Le Pan, Deryck James, Alan E. Wetmore, Brandon Redding. Direct on-strip analysis of size- and time-resolved aerosol impactor samples using laser induced fluorescence spectra excited at 263 and 351 nm, Analytica Chimica Acta, (04 2014): 0. doi: 10.1016/j.aca.2014.02.037
10/02/2014	6.00	Yong-Le Pan, Chuji Wang, Steven C. Hill, Mark Coleman, Leonid A. Beresnev, Joshua L. Santarpia. Trapping of individual airborne absorbing particles using a counterflow nozzle and photophoretic trap for continuous sampling and analysis, Applied Physics Letters, (03 2014): 113507. doi:

TOTAL: 4

Number of Papers published in peer-reviewed journals:

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

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 6.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper
08/30/2016 15.00	. Optical trap, manipulation, and characterization of light-absorbing single aerosol particles in air, American Association for Aerosol Research: AAAR, Oct. 2015. 30-AUG-16, Minneapolis, Minnesota USA. : ,
08/30/2016 16.00	. Optical trap for both transparent and absorbing particles in air using a single shaped laser beam for measuring Raman spectra, 2015 AAAR. 30-AUG-16, Minneapolis Minnesota USA. : ,
08/30/2016 17.00	. Laser pushing or pulling of absorbing airborne particles, 2016 AAAR. 31-AUG-16, Portland Oregon USA. : ,
08/30/2016 18.00	. Optical configurations for photophoretic trap of single particles in air, 2016 AAAR. 31-AUG-16, Portland Oregon USA. : ,
08/30/2016 19.00	. Optical trap for both transparent and absorbing particles in air using a single shaped laser beam for bioaerosol characterization, 2016 SPIE Optical Trapping and Manipulations. 30-AUG-16, San Diego USA. : ,
08/30/2016 20.00	. Optical trap and laser spectroscopy for characterizing single airborne aerosol particles, 2016 AAAR. 30-AUG-16, Portland Oregon USA. : ,

TOTAL: **6**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
08/30/2016	5.00	Chuji Wang, Yong-Le Pan, Steven C. Hill, Brandon Redding. Photophoretic trapping-Raman spectroscopy for single pollens and fungal spores trapped in air, Journal of Quantitative Spectroscopy & Radiative Transfer (04 2014)
TOTAL:		**1**

Number of Manuscripts:

Books

Received	Book
TOTAL:	

Received	Book Chapter
TOTAL:	

Patents Submitted

Patents Awarded

Awards

One article is featured on the from cover of Applied Physics Letters

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Zhiyong Gong	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Chuji Wang	0.13	
FTE Equivalent:	**0.13**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Andrew Cameron	0.10	Physics
FTE Equivalent:	**0.10**	
Total Number:	**1**	

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

NAME
Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

None

Annual Progress Report on W911NF-13-1-0429

Annual Report Period: 8/01/2015 – 08/31/2016

Submitted on: 8/30/2016

AMSRD-ARL-RO-SI Proposal Number: 63583-EV

Agreement Number: W911NF-13-1-0429

Principal Investigator: Chuji Wang

Organization: Mississippi State University

ARL Project Mentor: Dr. Yong-Le Pan

Program Manager: Dr. James Parker

Submitted By: Chuji Wang - Principal Investigator

Title: Physical and chemical study of single aerosol particles using optical trapping-cavity ringdown spectroscopy

What are the research goals of the project?

The overarching goal of this project is to pursue a better understanding of physical and chemical properties of aerosol particles. We propose to measure single aerosol particles using the optical trapping-cavity ringdown spectroscopy (OT-CRDS) in combination with conventional aerosol characterization methods/techniques to gain fresh insight into aerosol properties, especially chemical properties.

The proposed specific research objectives include

1) Transport and stabilize a single aerosol particle in air using optical trapping techniques (radiation pressure trapping and photophoretic trapping) in different optical configurations including free-space single laser beam (optical tweezers), counter propagating Bessel beams, and counter propagating hollow beams. Single aerosol particles will be generated to include three optical property groups: optically transparent, low-absorbing, and high-absorbing particles with different chemical constituents (atmospherically and biologically important compositions).

2) Upgrade our existing CRDS system for the study of single aerosol particles via integrating an optical trapping system, a CCD imaging system, and a single aerosol generation system into the CRDS system.

3) Validate the OT-CRDS system using well-defined single aerosol particles for spatial resolution in a single aerosol manipulation, detection limit of extinction coefficient, detection sensitivity of chemical absorption, accuracy of refractive index (both real and imaginary parts), and system temporal resolution.

4) Conduct physical and chemical characterizations of different types of single aerosol particles using the validated OT-CRDS system. Physical properties of aerosol particles to be investigated include size, size equilibrium, refractive index, etc.; chemical properties include surface chemical compositions, spectral fingerprints of selected function groups (i.e. OH, CH, H_2O), aerosol hygroscopicity, wavelength-dependent extinction, scattering, and absorption coefficients, etc.

What was accomplished under these goals?

(For Period: 08/01/2015 – 08/31/2016)

A. Major activities

1. Development of a new aerosol characterization technique: Single-Aerosol-Particle-Scope using Optical Trapping-Cavity Ringdown Spectroscopy (OT-CRDS)

2. Investigation of fundamental light forces and motions of absorbing airborne particles

3. Exploration of diversity of optical trapping schemes and configurations for airborne particles

4. Measurements of size-, particle-, or wavelength-dependent extinction of single aerosol particles optically trapped in air using Optical Trapping-Cavity Ringdown Spectroscopy

5. Improvement of the current experimental system for future work

B. Objectives

1. Develop a new aerosol characterization technique for study of both physical and chemical properties of single aerosol particles trapped in air

2. Understand fundamental light forces and motions of light-absorbing single airborne particles

3. Conduct comprehensive characterization of single trapped aerosol particles using the OT-CRDS system

4. Explore fundamental aerosol science and generate impact on US DoD's missions.

C. Significant results

1. Optical Trap-Cavity Ringdown Spectroscopy (OT-CRDS) as a Single-Aerosol Particle Scope

We have developed a new single-aerosol particle scope using an optical trapping-cavity ringdown spectroscopy (OT-CRDS) technique. We have demonstrated a high-precision and rigid single airborne particle trap-and-transport system combined with the CRDS technique. The OT-CRDS records and displays the single particle's location, motion, and temporal behavior through vivid RD views. So, we tentatively name the technique as an OT-CRDS single-aerosol particle scope. The scope can not only view physical parameters such as size, motion, restoring force constant of a single aerosol particle trapped in air, but also display time-, particle-, or wavelength-resolved chemical properties such as single aerosol particle extinction. This single-aerosol particle scope offers a new, powerful tool to study both physical and chemical properties as well as their evolving dynamics.

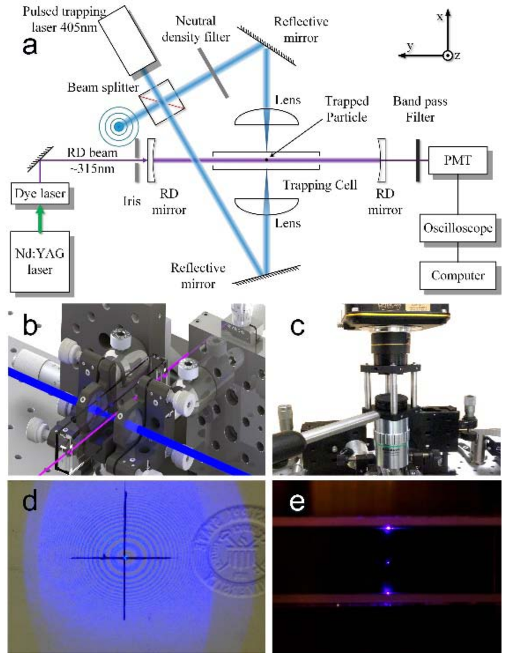

Fig.1 (a) Schematic diagram of the optical trapping-cavity ringdown spectroscopy (OT-CRDS) system using two simply focused pulsed Gaussian beams at 405 nm for trapping and a pulsed beam near 315 nm for RD. (b) Detailed illustration of the trapping device. (c) An imaging system to monitor a trapped particle in live. (d) Interference pattern for the validation of the alignment of the two counter-propagating trapping beams. (e) A single particle (MWCNT) trapped in air.

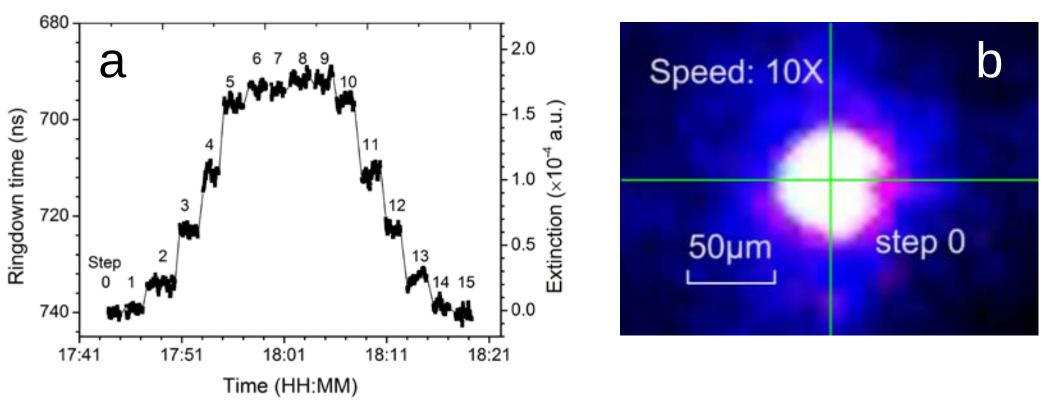

Fig. 2 (a) Response of the OT-CRDS scope that views the trapped particle walking through the ringdown beam step by step. (b) An image that shows the traces of the particle (MWCNT) walking through the RD beam.

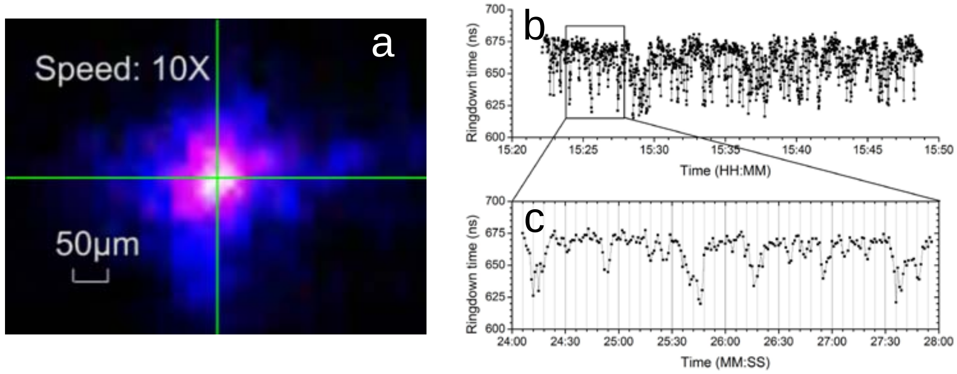

Fig.3 The OT-CRDS single particle scope views oscillations of a trapped particle. (a) Image of a trapped single SWCNT particle. (b) Oscillations of the trapped particle viewed by the OT-CRDS scope. The particle was trapped outside the RD beam, with the longest RDT at the equilibrium position. (c) Enlarged view of the data in (b) for a time window of 5 consecutive thermal oscillation intervals of 39, 42, 46, 36, and 39 s.

In conclusion, (1) we extended the OT-CRDS technique for the study of single aerosol particles of different type, size, and morphology, (2) we report a new OT-CRDS scheme to achieve a simple particle trap and high-precision (~50% of a particle size) particle transport, (3) we have demonstrated for the first time that the OT-CRDS particle scope can view the oscillatory behavior of the local thermal equilibrium, (4) the OT-CRDS scope can directly measure an oscillation restoring force constant of as small as ~10^{-10} N/m when a trapped particle oscillates slowly, e.g., 0.2 Hz, which corresponds to a force of ~10^{-14} N resulting from a change in the trapping force, and (5) further development of this new OT-CRDS single particle scope will potentially generate an all-in-one technology to enable one to directly measure a tiny change (e.g., pN or smaller) in optical trapping forces and its resultant motions and to quantity several key aerosol properties simultaneously.

Part of this work is published in *Applied Physics Letters*, 107, 241903 (2015). The work is featured in the front cover of the issue.

2. Laser Pushing or Pulling of Absorbing Airborne Particles

Optical manipulation of microscopic objects using light is an emerging tool used in diverse research fields such as physics, chemistry, biology, materials. Research related to optical manipulation using optical forces ranges from the early demonstration of particle levitation and trapping in different media such as solution or air to the recent breakthrough in controlled optical manipulation as reported in recent theoretical proposals and experimental demonstrations. Of those significant theoretical or experimental studies in controllable optical manipulation of small particles using light, the fundamental light-particle interaction phenomenon, *light can push and pull a small particle*, has been demonstrated using transparent spherical particles, transparent nonspherical particles, and absorbing spherical particles (all except absorbing nonspherical particles). Whether it is a general fundamental light-particle interaction phenomenon for arbitrary particles lies in a theoretical or experimental breakthrough in controlled optical manipulation for the last category–absorbing nonspherical particles. However, this challenge has been addressed neither theoretically nor experimentally to date.

Here we report our experimental observations of light-controlled pushing or pulling of absorbing irregularly-shaped particles. This observation is made by using a rigid experimental design, so that the fundamental phenomenon of optical forces is revealed without possible external interferences. A single absorbing particle formed by carbon nanotubes in the size range of 10-50 μm is trapped in air by a laser trapping beam and concurrently illuminated by another laser manipulating beam. When the trapping beam is terminated, the motion of the particle is controlled by the manipulating beam. Both pushing and pulling motions are observed. Additionally, the movement direction has little relationship to the particle size and manipulating beam's parameters but is dominated by the particle's orientation and morphology. With this observation, the controllable optical manipulation is now able to be generalized to arbitrary particles regardless of being transparent spherical, transparent nonspherical, absorbing spherical, or absorbing nonspherical that is, for the first time, shown in this work.

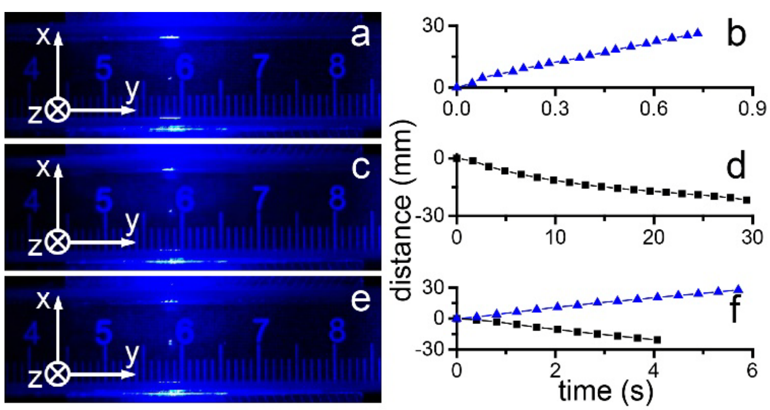

Fig. 4 Images (top view) of the trapped MWCNT particles in air associated with the particle being **a**, pushed; **c**, pulled; and **e**, pushed and pulled simultaneously by the manipulating beam upon blocking the trapping beam, respectively. Media 1, Media 2, and Media 3 show the corresponding motions of the particles in **a**, **c**, and **e**; while **b**, **d**, and **f** show the moving behaviors of the particles in **a**, **c**, and **e** respectively, which are represented in distance versus time, and symbol Δ for pushing motion, □ for pulling motion.

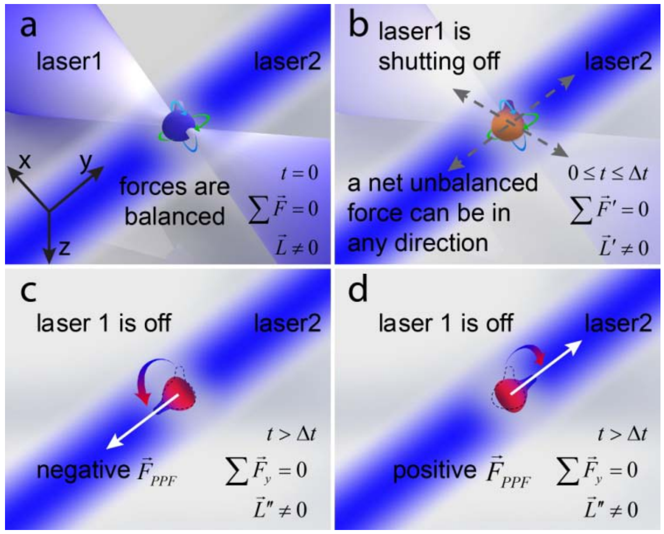

Fig. 5 Illustration of the explanation. The pushing and pulling motion of a single irregularly-shaped absorbing particle in air under the manipulation of a laser beam at **a**, $t = 0$; **b**, $0 \leq t \leq \Delta t$; **c**, **d**, $t > \Delta t$. Laser 1: trapping; laser 2: manipulating.

In summary, we used a specially designed experimental setup to observe the net forces on particles illuminated by a laser. We began the study with the particles levitated and at rest. We observed both pushing and pulling motions of the irregularly shaped particles with equal probability and with zero interference from initial speed, gravitational force, buoyancy force, and drag force. We suggest that the direction of motion is due to the particle orientation and morphology, as there is little dependence on the manipulating beam's parameters and the particle size in the size range studied. This experimental observation poses a challenge in an effort to extend the theories that are limited to spherical particles to irregularly shaped, absorbing particles. A breakthrough in controlling the motion of single particles of arbitrary morphology would be useful in diverse applications such as three-dimensional sorting and manipulating of microscopic objects.

Part of this work is published in *Applied Physics Letters*, 109, 011905 (2016); http://dx.doi.org/10.1063/1.4955476

3. Optical configurations for photophoretic trap of single airborne particles in air

In this work, we discuss six types of photophoretic trapping schemes using: (I) a single Gaussian beam, (II) a single hollow beam, (III) a confocal Gaussian beam, (IV) a confocal hollow beam,

(V) dual CP Gaussian beams, and (VI) dual CP hollow beams. These six types of trapping schemes are sequentially labeled and referred to as Type I-VI in the text below. Key parameters affecting the simplicity, robustness, flexibility, and efficiency of optical traps based on these schemes include trapping laser source, beam power, beam shape, focusing optics, and trapping cell geometry, among others. In total, we explored 21 variants (with 21 configurations) from the six types of schemes by altering those key parameters. Trapping configurations were evaluated with both strongly absorbing (two types of carbon nanotubes and two types of grass smut spores) and weakly absorbing particles (two types of pollen particles). Our results show that the confocal beam traps (Type III and IV), which are reported for the first time in this paper, have well balanced merits and may have a wide application in the future. We then demonstrate the application of confocal beam optical trapping to cavity ringdown spectroscopy (OT-CRDS). We also recommend a procedure to choose a proper trapping scheme for a specific application and discuss the advantages and disadvantages of the schemes for additional applications.

A. Single Gaussian or hollow beam trap scheme

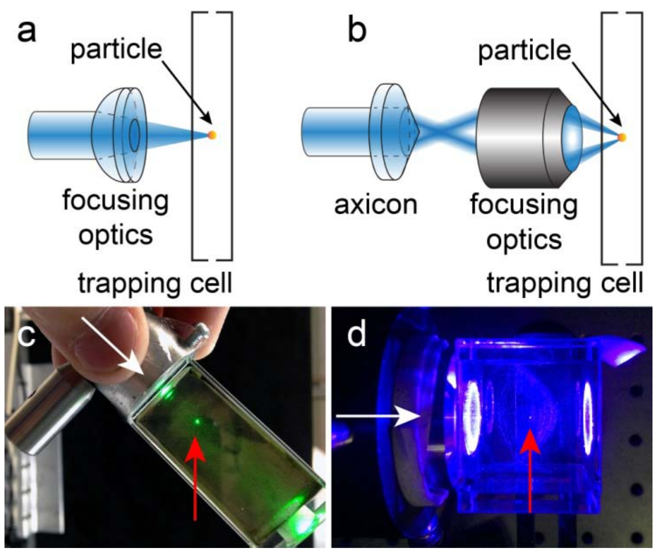

Fig. 6 The trapping schemes using a single beam. (a) Single Gaussian beam trapping scheme. (b) Single hollow beam trapping scheme. (c) A single MWCNT particle is trapped in the single Gaussian beam trap, formed by focusing a 532 nm Gaussian beam using a lens with *f* = 10.0 mm. (d) A single MWCNT particle is trapped in the single hollow beam trap in which a hollow beam is formed from a 445nm Gaussian beam using an axicon, and then focused by a MO50×. Red and white arrows indicate the location of the trapped particle and the direction of the trapping beam, respectively.

B. Confocal Gaussian or hollow beam trap scheme

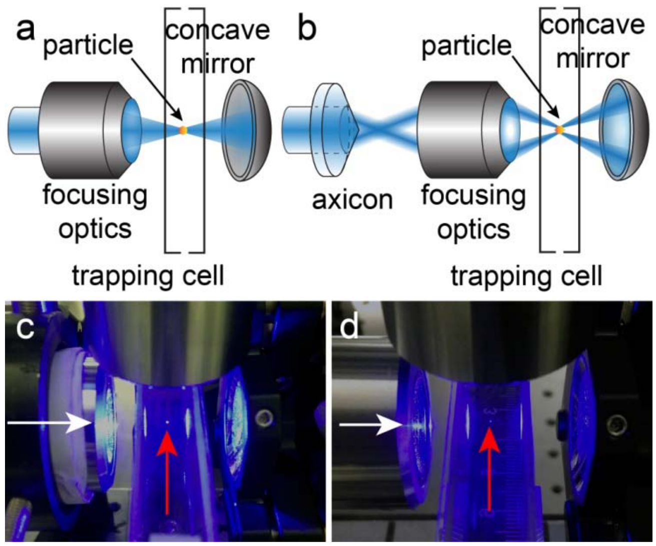

Fig. 7 The confocal trapping scheme using a single beam. (a) The confocal Gaussian beam trapping scheme, (b) the confocal hollow beam trapping scheme. (c) A single MWCNT particle is trapped using the confocal Gaussian beam trap formed by focusing a 445 nm Gaussian beam using a micro objective (MO50×). (d) A single MWCNT particle is trapped using the confocal hollow beam trap. The hollow beam was formed from a 445nm Gaussian beam by an axicon and then focused by a micro objective (MO50×). Red and white arrows indicate the location of the trapped particle and the direction of the trapping laser, respectively.

C. Dual-Gaussian or hollow beam trap scheme

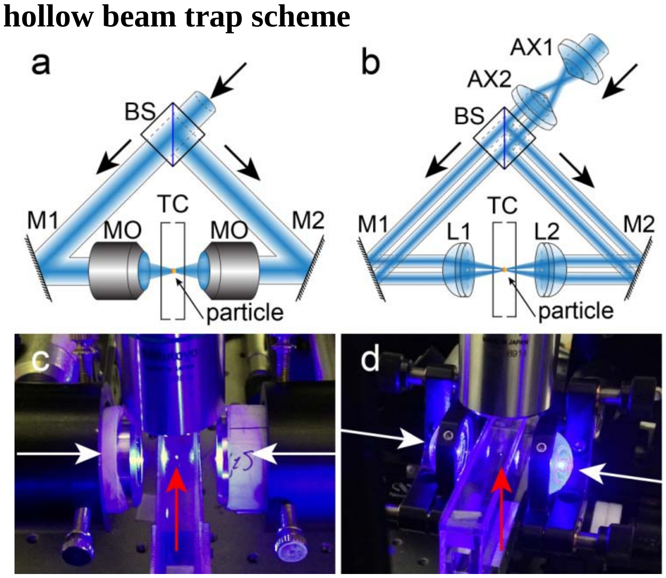

Fig. 8 The dual-beam trapping schemes. (a) The dual-Gaussian beam trapping scheme, (b) the dual-hollow beam trapping scheme. A single MWCNT particle is trapped in (c) the dual-Gaussian beam trap and (d) the dual-hollow beam trap. Red and white/black arrows indicate the location of the trapped particle and the direction of the trapping laser, respectively.

Table 1 lists all trapping schemes and their optical configurations. Their trapping properties are rated based on the four key trapping properties: Simplicity, Robustness, Flexibility, and Efficiency.

TABLE 1. Comparison of the evaluation aspects of the six types of photophoretic trapping schemes.

Type of trapping scheme	Simplicity	Robustness	Flexibility	Efficiency (%)
Single Gaussian beam	simple	loose	moderate	10-30
Single hollow beam	moderate	moderate	high	10-30
Confocal Gaussian beam	simple	rigid	high	>80
Confocal hollow beam	moderate	rigid	high	>80
Dual-Gaussian beam	complex	rigid	moderate	>80
Dual-hollow beam	complex	rigid	low	>80

In conclusion, experimental parameters which include laser source, power, beam shape, and focusing optics affect the quality and performance of an optical trap. Fortunately, there are diverse trapping schemes available for different application purposes. Trapping configurations based on the PPF can be optically and mechanically complicated yet can also be relatively simple. In practice, the key experimental parameters need to be balanced and optimized in the construction of an OT for a specific application. We explored six different trapping schemes that lead to 21 trapping configurations using different laser sources, power, beam shapes, and focusing optics. We experimentally evaluated and rated the six trapping schemes based on the four key aspects: trapping simplicity, robustness, flexibility, and efficiency. Simplicity relates to the time and cost of an applicable optical trapping configuration. Trapping robustness relates to the stability of a trapped particle and time duration of the trapping. Flexibility relates to whether the configuration is spacious, compact, or adaptive to other measuring techniques. Finally we define the trapping efficiency for PPF schemes as the ratio of successful trapping events over the number of the sample injections. Researchers should take their own situations into consideration when constructing a specific optical trap using the four criteria. We believe that the availability of diverse optical trapping configurations will further extend applications of OT.

A manuscript is under review in *Review Scientific Instruments.* Recommended for publication after minor revisions as of August, 2016.

4. Single Aerosol Particle Extinction in the UV Using OT-CRDS

The previously (in the last report period) developed Optical Trapping-Cavity Ringdown Spectroscopy (OT-CRDS) has been further improved. Now this OT-CRDS technique can not only trap various types of airborne particles but also accurately measure size of a trapped particle, single particle extinction in different wavelengths in the UV. A faster imaging system has been integrated into the OT-CRDS system to be able to monitor a trapped particle's locations and motions inside the ringdown beam. The OT-CRDS allows us to measure particle-, size-, or wavelength-dependent single particle extinction. Furthermore, the trapping device is so rigid that we can control exact numbers of particles trapped, followed by OT-CRDS measurements. The sensitivity of the pulsed UV-CRDS system can discriminate extinction of 0, 1, 2, 3, or 4 particles inside the trapping region. This high sensitivity benefits from the stable ringdown baseline stability of this pulsed UV-CRDS system that offers a laser beam in a wide wavelength range from visible to deep UV (200 nm) with a spectral resolution of 0.01 nm or higher. This OT-CRDS system will serve a kind of new platform technique for study of single airborne particles.

Four types of airborne particles have been characterized using the OT-CRDS system in the UV (308 -316 nm). Part of results is outlined below.

A. The upgraded OT-CRDS system

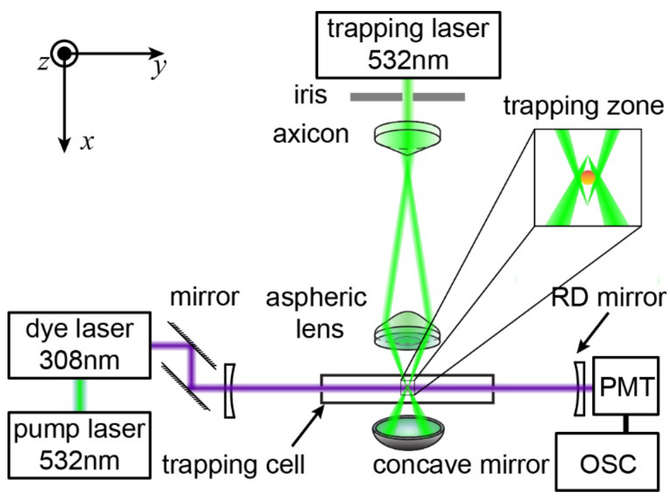

Fig. 9 The upgraded optical trapping-cavity ringdown spectroscopy system. One of the major differences from our previously demonstrated OT-CRDS system is the vertical layout of the trapping optics. The trapped particles are viewed by a microscopic image system and measured by CRDS. The image system consists of a micro objective (NA0.42, x20, Mitutoyo), a set of tube lens (InfiniTube, Edmund optics), and a CMOS camera (GS3-U3-32S4C-C, pixel pitch=3.45 um, point grey). The laser source of the CRDS system is the frequency doubling of a tunable dye laser system (Radiant), pumped by an Nd:YAG laser (DLS8020, Continuum) output at 532 nm. The dye laser operates in the range of 306-315 nm and can be scanned at a step of 0.0001 nm in the current study.

B. Manipulations of number of trapped particles in the trapping region

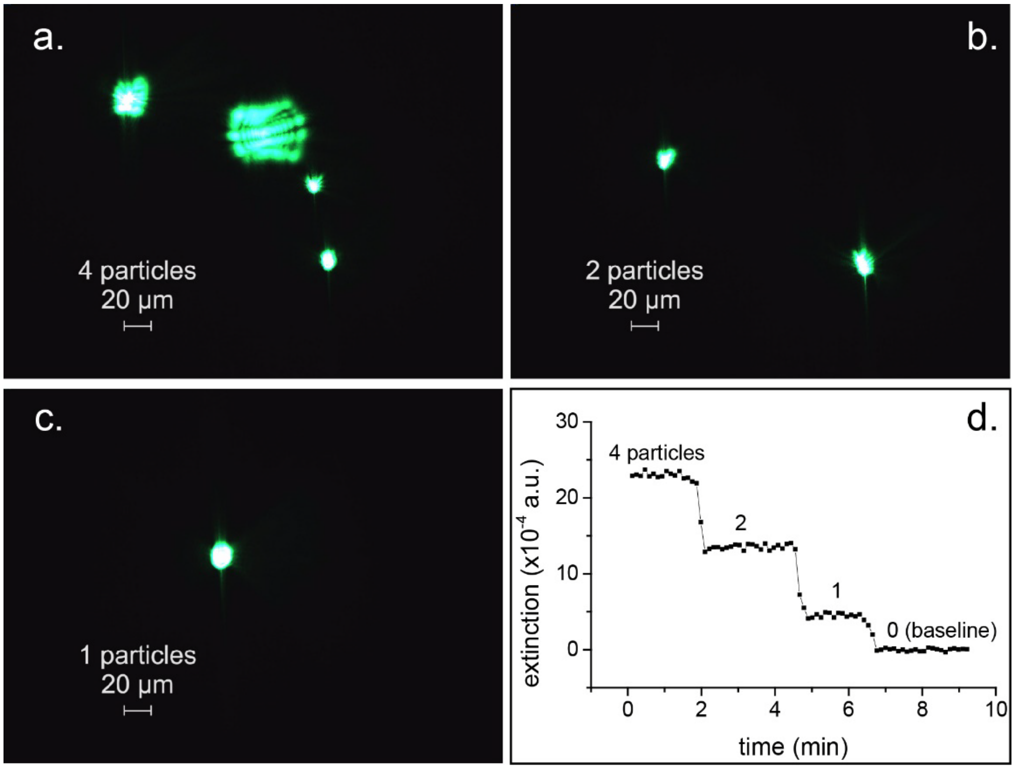

Fig. 10 Manipulations of number of the trapped particles (e.g., Bermuda grass smut spores), changing from 4 particles to 2, 1, or 0. a) 4 Bermuda grass smut spores were trapped in the trapping zone at the beginning. b) 2 particles were trapped after introducing mechanical turbulence. c) A single particle was trapped. d) The corresponding extinctions measured using the OT-CRDS in the UV. To the best of our knowledge, this level of particle manipulation and control is the first attempt ever. The particles are trapped; their numbers are controlled and counted. Size and motions of the particles are monitored by the imaging system. Their individual or combined extinction is measured by the OT-CRDS technique.

C. Spatially-resolved extinction of a single trapped particle

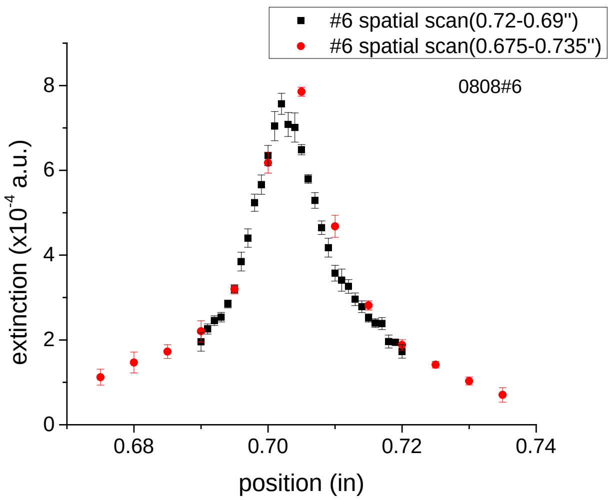

Fig. 11 Spatially-resolved extinction of a single Bermuda particle that is located in different locations inside the ringdown beam that has a diameter of ~500 µm. Two spatial scans were conducted from both +x (square) and –x (dot) directions (the laser beam is propagating in the z-direction in the xyz-coordinates). The steps of the spatial scans from the +x and –x directions are 127.0 and 25.4 µm, respectively.

D. Particle-resolved extinction of a single trapped particle

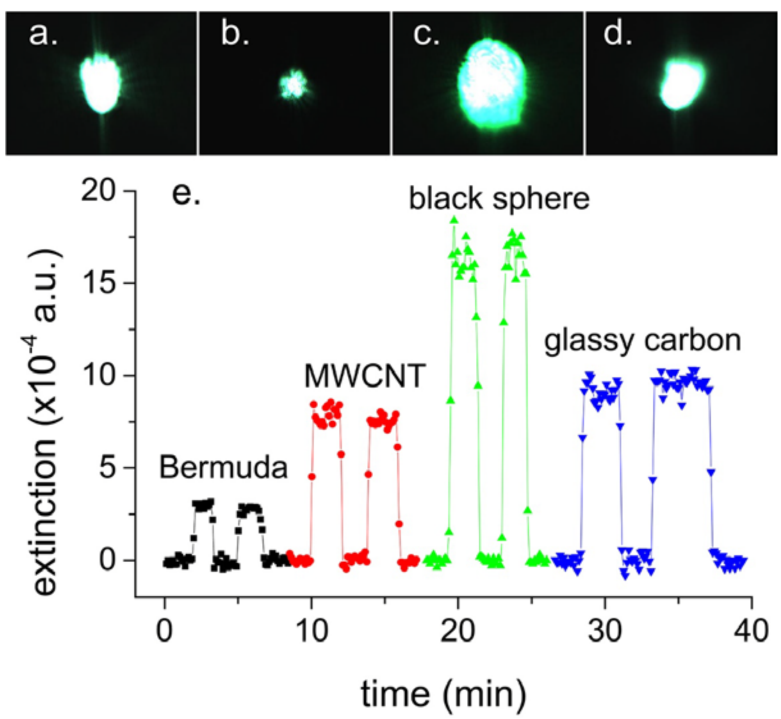

Fig. 12 Extinctions of four different types of particles. Top row are the images of single trapped a) Bermuda grass smut spore, b) multi-walled carbon nanotube (MWCNT), c) black coated polyethylene sphere, and d) glassy carbon sphere. e) The corresponding extinctions of these single particles. The extinction measurements repeat at least twice for each type of particles.

E. Size-dependent single particle extinction

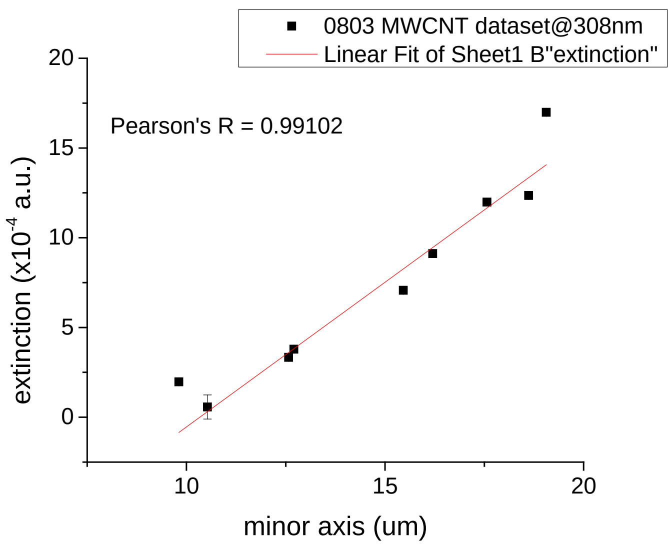

Fig. 13 Single particle extinction versus the particle's dimension. A single multi-walled carbon nanotubes (MWCNT) particle measured at 308 nm. The data shows for the same type of particles, e.g., MWCNT, the single particle extinction is size-dependent. Intuitively, we hypothesize that with the same particle size, single particle extinction is particle- (material) dependent. This hypothesis will be tested.

F. Wavelength-dependent single particle extinction

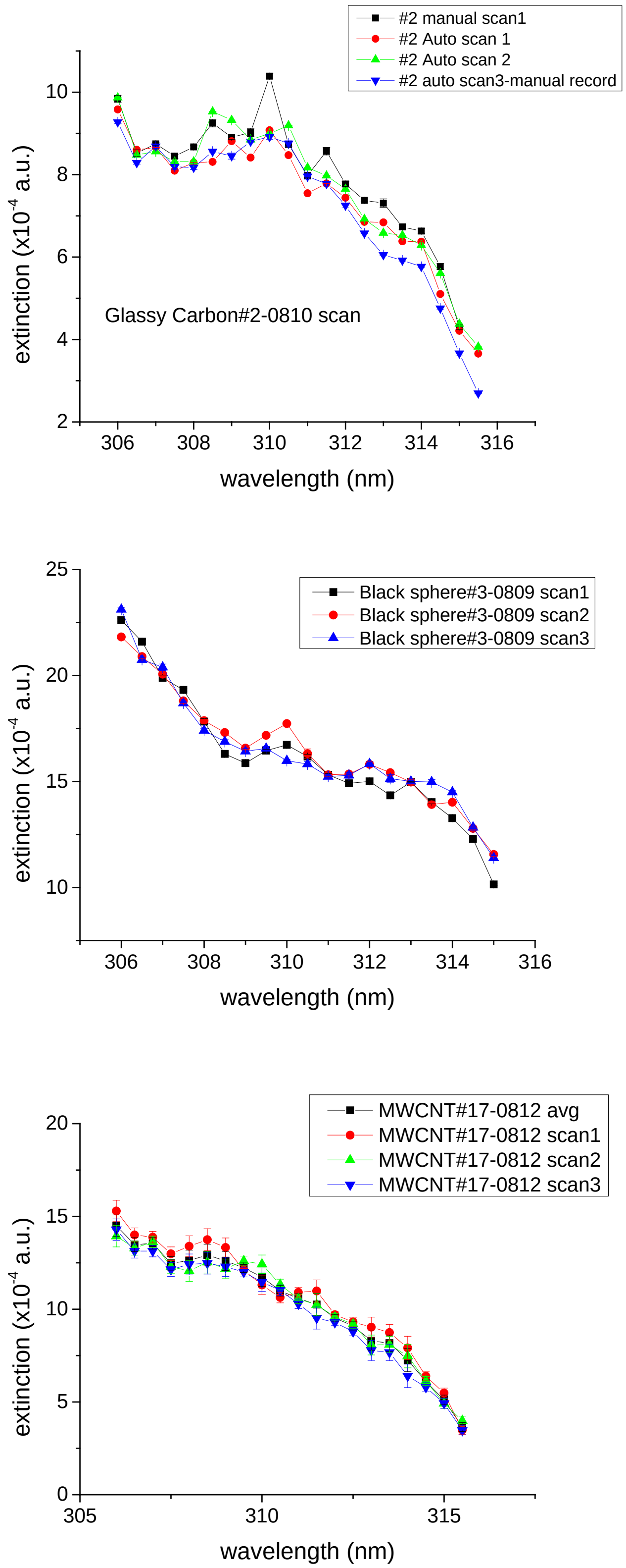

Fig. 14 Wavelength-dependent extinction of single tapped glassy carbon sphere, black coated polyethylene sphere and MWCNT. These results show that given the same particle trapped in the

same location at the same wavelength, the single particle extinction is strongly wavelength-dependent.

In conclusion, the new optical trapping-cavity ringdown (OT-CRDS) technique using a pulsed UV laser has been successfully developed, improved, and applied for single airborne particle study. We have demonstrated the rigid particle trapping, waking, counting, and viewing. Measurements of single particle extinction for four different types of airborne particles have been demonstrated using the OT-CRDS in the UV. We have achieved particle-, material-, or wavelength-dependent single particle extinction. We show that for a given particle trapped, e.g., a MWCNT particle, the single particle extinction is strongly wavelength-dependent in the UV (e.g., 308-316 nm, the wavelength range examined in this work). The high speed imaging system integrated into the OT-CRDS offers live monitoring of particle's motions and vibrations that are related to fundamental phenomena in light-material interactions. This platform technique (OT-CRDS) will serve as a powerful and versatile means for single particle study. Although the OT-CRDS technique is still in infantry, the technique has high potential to be further developed and integrated with light scattering and Raman techniques for comprehensive characterization of aerosol particles.

D. Key outcomes

1. New findings

1a) Laser Pushing or Pulling of Absorbing Airborne Particles Optical manipulation of microscopic objects using light is an emerging tool used in diverse research fields such as physics, chemistry, biology, materials. Research related to optical manipulation using optical forces ranges from the early demonstration of particle levitation and trapping in different media such as solution or air to the recent breakthrough in controlled optical manipulation as reported in recent publications including those reviewed and commented in Nature Photonics and Nature news & views. Of those significant theoretical or experimental studies in controllable optical manipulation of small particles using light, the fundamental light-particle interaction phenomenon, light can push or pull a small particle, has been demonstrated using transparent spherical particles, transparent nonspherical particles, and absorbing spherical particles (all except absorbing nonspherical particles). Whether it is a general fundamental light-particle interaction phenomenon for arbitrary particles lies in a theoretical or experimental breakthrough in controlled optical manipulation for the last yet unexplored category-absorbing nonspherical particles. However, to the best of our knowledge, this challenge has been addressed neither theoretically nor experimentally, as of the submission of this manuscript. We reported our experimental observation that light can push or pull small absorbing nonspherical particles, too. This observation is made by using a rigid experimental design, so that the fundamental phenomenon of optical forces is revealed without possible external interferences. The significance of this work is two-fold: **(1)** "With this observation, the controllable optical manipulation is now able to be generalized to arbitrary particles regardless of being transparent spherical,[1,3-7] transparent nonspherical,[8] absorbing spherical,[2] or absorbing nonspherical that is shown in this work"[9]. **(2)** Our observation shows that the photophoretic force may even be in the opposite direction of that predicted for spherical particles. We show the movement direction has little relationship to the particle size and manipulating beam's parameters but is dominated by the particle's orientation and morphology. Our observation would motivate future theoretical work to be extended for arbitrary particles. By then our understanding of optical forces would be unified.

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1b) Diverse Optical trapping Configurations Today, there are multiple optical trapping schemes in use. We explored six different optical trapping schemes based on the photophoretic force (PPF). Within these schemes we explored 21 variants differing in such details as laser source, power, beam shape, and focusing optics. We experimentally evaluated and rated the six trapping schemes based on the four key aspects: trapping simplicity, robustness, flexibility, and efficiency. Simplicity relates to the time and cost of an applicable optical trapping configuration.

Trapping robustness relates to the stability of a trapped particle and time duration of the trapping. Flexibility relates to whether the configuration is spacious, compact, or adaptive to other measuring techniques. Finally we define the trapping efficiency for PPF schemes as the ratio of successful trapping events over the number of the sample injections. Our research findings show that trapping configurations based on the PPF can be optically and mechanically complicated yet can also be relatively simple. In practice, the key experimental parameters need to be balanced and optimized in the construction of an OT for a specific application. Researchers should take their own situations into consideration when constructing a specific optical trap using the four criteria.

1c) OT-CRDS In 2013, a research group in UK (J.S. Walker, A.E. Carruthers, A.J. Orr-Ewing, and J.P. Reid, J. Phys. Chem. Lett. 4, 1748 (2013)) reported the first study of single optically-trapped aerosol particles (water droplets) using cavity ringdown spectroscopy. The OT-CRDS system developed in the last report period has been further improved in the current report period. This OT-CRDS uses a pulsed UV laser source so that we can measure wavelength-dependent single particle extinction for different types of particles and in different wavelength regions (Visible-UV). We found: (1) particles made of same materials but with different sizes have different single particle extinctions, (2) The same particle has different single particle extinctions in different wavelengths, (3) Particles in the same size but from different materials have different single particle extinctions, (4) For a trapped airborne particle, their wavelength-dependent extinction is reproducible within a period of time, e.g., a few hours, (5) The OT-CRDS system can discriminate extinction among one particle, two particles, three particles, and four particles, (6) The location of a single particle inside a ringdown beam affect the particle's extinction, e.g., it has maximum when the trapped particle is located in the central of the ringdown beam, and (7) The optical trapping device integrated into the OT-CRDS is so rigid that it can control the number of particles trapped, e.g., 1, 2,3,or 4 particles as desired.

1d) Optical Trap-Cavity Ringdown Spectroscopy (OT-CRDS) as a Single-Aerosol Particle Scope The scope can not only view physical parameters such as size, motion, restoring force constant of a single aerosol particle trapped in air, but also display time-, particle-, or wavelength-resolved chemical properties such as single aerosol particle extinction. We have demonstrated the scope by trapping and walking single carbon-nanotube particles of ~50 μm in size and viewing those properties via changes of ringdown time. We have demonstrated for the first time that the OT-CRDS particle scope can view the oscillatory behavior of the local thermal equilibrium. The OT-CRDS scope can directly measure an oscillation restoring force constant of as small as ~10-10 N/m when a trapped particle oscillates slowly, e.g., 0.2 Hz, which corresponds to a force of ~10^{-14} N resulting from a change in the trapping force.

2. Transformative Technology

The OT-CRDS technique developed in this study can be integrated with the light scattering technique, Raman spectroscopy, and a fast imaging system for (1) comprehensive characterization of aerosols in different shape, size, optical property, materials, and absorbance; (2) study of heterogeneous surface chemistry under externally controlled conditions, e.g., exposed to chemical reactants, such as atmospheric radicals, ozone, water etc; and (3) study of time-resolved aerosol particle formation/loss dynamics, hygroscopicity, and surface chemical compositions.

What opportunities for training and professional development has the project provided?

One PhD student has received training in this project. One undergraduate student has received training in the academic year of 2016 (graduated in May 2016). One new undergraduate student has expressed his interest to be involved in this project during this academic year. Four other graduate students, who are working on other projects in the PI's groups, have benefited from the research discussion and exposure to the research work in the lab.

Training and Development:

Graduate student:

Mr. Zhiyong Gong is a third year PhD student. He has committed 100% of his research time to this project. His research efforts are focused on development of optical trapping schemes and integration of an optical trap with a cavity ringdown spectroscopy system. He has been trained to be able to construct optical traps and conduct experimental measurements using cavity ringdown spectroscopy (CRDS). He now plays an important role in the experimental work in this project. He has made significant progresses in data analysis, data presentation, and writing a manuscript. He makes significant contributions to this project. He has fulfilled all requirements for a M.S. degree that is to be awarded this fall.

Undergraduate student:

Mr. Andrew Cameron double majors in physics and geosciences. He graduated in May, 2016 and received a B.S. in physics. He has received trainings in lab safety operation rules, bioaerosol materials handling, laser safety, literature survey, etc. He has been trained with basic knowledge of lasers, aerosol particles, and CRDS from the summer of 2015. He knows how to make a PowerPoint presentation and how to graph experimental data using different software tools. He can conduct estimation of optical trapping forces. The knowledge and experimental skill sets he has gained from the research experience in this project will benefit him for his career developments in the field of atmospheric science. He is now a PhD student at University of Colorado Boulder, studying Atmospheric and Oceanic Sciences.

Mr. Jeff Headley is a Physics junior. He has joined in the PI's research group since the spring of 2016. He wishes to gain some research experience and skill sets for his future graduate study. He has passed lab operation safety training and received an operation certificate. He is ready to be involved in research activities in this project.

<u>How have the results been disseminated to communities of interest?</u>

A. Part of the research results has been presented in the 2015 American Association for Aerosol Research (AAAR) held in October 12-16, 2015, Minneapolis, Minnesota.

- The PI delivered a talk on the recent progresses on single aerosol particle spectroscopy
- Two conference papers have been accepted
- The PI served as chairman for one session in this conference

B. Some results will be presented in Optical Trapping and Optical Micromanipulation 2016 SPIE conference in San Diego, August 28-Sept.1, 2016. One conference paper has been accepted.

C. The PI has organized (with two co-organizers) a special symposium for “Single Aerosol Particle Studies” in 2016 AAAR conference. Recent research results will be presented in three conference presentations and three conference papers.

D. The PI’s research lab and research activities have been exposed to 47 undergraduate students at MSU, who took the PI’s Physics III class in the spring of 2016 and showed great interest in aerosol sciences.

E. During this reporting period, 2 peer-review articles have been published, 1 in production, 2 under review and accepted, and 1 in preparation.

F. Research activities at MSU have been timely and adequately exposed to the US Army Research Lab in Adelphi MD through regular discussion between the PI and his collaborators, Drs. Yongle Pan and Videen Gorden in ARL. This interaction further helps results dissemination to communities of interest.

<u>What do you plan to do during the next reporting period to accomplish the goals?</u>

During the next period (6 months no-cost extension), (1) we will explore the theoretically calculated yet not experimentally confirmed phenomenon that light can control the moment direction of absorbing and non-absorbing spherical particles in air. Achieving this goal would be significant in unifying our understanding of light-particle interactions; (2) we will measure single particle extinction of absorbing and non-absorbing particles using the OT-CRDS technique in the UV, so that scattering and absorption of single irregularly-shaped large airborne particles can be quantified separately; and (3) we will explore OT-CRDS measurements of single particles under exposure of chemicals.

Products

A. Journal Publications

1. Chuji Wang,* Zhiyong Gong, Yong-Le Pan, Gorden Videen,
   Optical Trap-Cavity Ringdown Spectroscopy (OT-CRDS) as a Single-Aerosol Particle Scope
   Applied Physics Letters, 107, 241903 (**2015**). The work is featured in the front cover of the issue.

2. Chuji Wang,* Zhiyong Gong, Yong-Le Pan, Gorden Videen,
   Laser pushing or pulling of absorbing airborne particles
   Applied Physics Letters, 109, 011905 (**2016**); http://dx.doi.org/10.1063/1.4955476

3. Zhiyong Gong, Chuji Wang,* Yong-Le Pan
   Diverse optical trapping schemes for different aerosol particles trapped in air
   Review Scientific Instruments, reviewed, suggested for minor revisions (as of **August 26**, **2016**)

4. Yong-Le Pan,* Chuji Wang, Leonid A. Beresnev, Alex J. Yuffa, Gorden Videen, David Ligon, Joshua L. Santarpia
   Measurement of back-scattering patterns from single laser trapped aerosol particles in air
   Applied Optics, in production (as of **August 12**, **2016**)

5. Richard Fu, Chuji Wang, Olga Muñoz, Gorden Videen, Joshua L. Santarpia, Yong-Le Pan*
   Elastic back-scattering patterns via particle surface roughness and orientation from single trapped airborne aerosol particles
   Journal of Quantitative Spectroscopy and Radiation Transfer, Submitted in **August**, **2016**.

B. Books or Other One-time Publications

None

C. Conference Proceedings, Presentations, and Invited Talks

1. Chuji Wang, Yong-Le Pan, Zhiyong Gong, and Brandon Redding,
   Optical trap, manipulation, and characterization of light-absorbing single aerosol particles in air

American Association for Aerosol Research: AAAR, Oct. **2015**

2. Yong-Le Pan, Brandon Redding, Chuji Wang, Steven C. Hill, Joshua L. Santarpia,
   Optical trap for both transparent and absorbing particles in air using a single trapping laser beam for measuring Raman spectra
   American Association for Aerosol Research: AAAR, Oct. **2015**

3. Yong-Le Pan, Brandon Redding, Chuji Wang, Joshua L. Santarpia,
   Optical trap for both transparent and absorbing particles in air using a single shaped laser beam for bioaerosol characterization
   Optical Trapping and Optical Micromanipulation XII, SPIE **2016**, August 2016

4. Zhiyong Gong, Yong-Le Pan, Chuji Wang
   Optical Configurations for Photophoretic Trap of Single Airborne Particles in Air
   AAAR 35th Annual Conference, October 17 -21, **2016**, Porland, Oregon, USA

5. Chuji wang, Zhiyong Gong, Yong-Le Pan, Gorden Videen
   Light Pushing or Pulling of Absorbing Airborne Particles
   AAAR 35th Annual Conference, October 17 - 21, **2016**, Porland, Oregon, USA

6. Yong-le pan, Chuji Wang, Joshua Santarpia
   Optical Trap and Laser Spectroscopy for Characterizing Single Airborne Aerosol Particles
   AAAR 35th Annual Conference, October 17 - 21, **2016**, Porland, Oregon, USA

Project Participants

Senior Personnel

Name: Chuji Wang

Worked for more than 160 Hours: Yes

Contribution to Project:

Conducted experiments, wrote papers, and advised students

Graduate Student

Name: Zhiyong Gong (PhD candidate)

Worked for more than 160 Hours: Yes

Contribution to Project:

Conducted experiments; collected experimental data; analyzed experimental data.

Undergraduate Student

Name: Andrew Cameron (Physics and Geosciences double major)

Worked for more than 160 Hours: Yes

Contribution to Project:

Research Experience:

Gained research experiences in lasers and cavity ringdown technologies; understood basics of optical trapping.

Impact

A. Outreach and educational Activities

a. Four lab tours were given to 47 undergraduate students who were taking the PI's class of Physics III in Spring 2016
b. A lab research tour was given to two visitors from Savannah River National Laboratory, August 29-30, 2016
c. A lab tour was given to on professor from Jackson State University

B. Impact within Discipline

The research activities will help gain new knowledge of aerosol science and advance enabling technology in aerosol characterization. Our current understanding of aerosol particles mainly remains at the level of ensemble measurements. A single aerosol particle is the fundamental unit of aerosol particle accumulation or particle ensembles and it carries individual chemical properties. Study of single aerosol particles (e.g. light absorbing or nonabsorbing) requires two main technological elements: a single aerosol particle manipulation (trap and transport) and a measuring technique that has sufficient spatial- and time-resolutions to be able to pinpoint the single particle of nano- or micro-meter size and to track its time evolution in seconds. The technique should also have high chemical sensitivity so that a change or a difference in the properties of the single particle can be detected. The integration of an optical trapping technique into an advanced laser spectroscopy method such as cavity ringdown spectroscopy can be an ideal solution that leads to a better understanding of aerosol chemical properties and their time-evolution.

A Special Symposium on *Single aerosol particle studies: From fundamental physics to instrumentation* has been created in 2016 AAAR conference

Organizers:
Chuji Wang, Mississippi State University, Mississippi State, MS
Yongle Pan, Army Research Laboratory, Adelphi, MD
Jian Wang, Brookhaven National Laboratory, Upton, NY

Due to the physical and chemical complexity of aerosol particles and the interdisciplinary nature of aerosol science that involves physics, chemistry, and biology, our knowledge of aerosol particles is rather incomplete; our current understanding of aerosol particles is limited by averaged (over size, composition, shape, and orientation) and/or ensemble (over time, size, and multi-particles) measurements. Physically, single aerosol particles are the fundamental units of any large aerosol ensembles. Chemically, single aerosol particles carry individual chemical components (properties and constituents) in particle ensemble processes. Therefore, study of single aerosol particles can bridge the gap between aerosol ensembles and bulk/surface properties and provide a hierarchical progression from a simple benchmark single component system to a mixed phase multicomponent system. Latest technological advances provide exciting new opportunities to study single aerosol particles and to further develop single aerosol particle instrumentation. The purpose of this special symposium is to bring together an interdisciplinary group of researchers with expertise and interest in single aerosol particle studies including, but not limited to, single aerosol particle manipulation, single aerosol particle measurements, single aerosol particle's physical, chemical and biological properties, and single aerosol particle instrumentation.
This special symposium will generate significant impacts in aerosol science.

C. Impact on Human Resource Development

One graduate student and one undergraduate student have received training in this project. Four other graduate students, who are working on other projects in the PI's groups, have benefited from the research discussion and exposure to the research work in the lab.

D. Impact in a larger community

(1) Research activities conducted in this project are in strong collaboration with several scientists in ARL. Aerosol, especially bioaerosol, is strongly related to missions in the US defense and national security defense. Study of aerosol will help better understand atmospheric conditions and battle field environments that are often strongly time-dependent due to the complex and dynamic mission operations.

(2) One of the publications directly generated from this project is featured on the front cover of Applied Physics Letters.

(3) The project activities were exposed to two technical program directors from Savannah River National Laboratory when they visited the PI's research labs at Mississippi State University. Communications and discussion may lead to broader applications of the OT-CRDS technique in the US Department of Energy.

Changes and Problems

Special reporting requirements: A 6-month no-cost extension has been requested and made to the Technical Program Director, Dr. James Parker. Upon writing this report, the request has been approved by the ARO contract office.

Change in Objectives or Scope: None

Reprints and manuscripts submitted are attached below