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14. ABSTRACT
The purpose of this project was to exploit linear and nonlinear plasmonics in the gold nanorod aerosols (GNRA) in a lab based aerosol environment. The GNRA was produced employing a TSI-3079A Atomizer, with adjustable flowrate for high concentrations, and with TSI-3062(Diffusion Dryer with blue desiccant). The suspension of GNR were in a gas phase. The GNRA were to be characterized in situ using a Herriot cell integrated with a Shack-Hartmann sensor for the nonlinear optical characterization.

15. SUBJECT TERMS
Gold nanorods, aerosol, optical nonlinearity

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Award: N629092012028 Period of Performance: 04/01/2020 03/31/2022

Award: **N629092012028 Modification P00002**

Period of Performance: 04/01/2020 05/31/2023

Project Title: Energy harvesting and aerosol nonlinear plasmonics in gold nanorods

Dynamically control the orientational order of gold nanorods in liquid and gas phases.

Reporting Period: 04/01/2020 to 05/31/2023

Isabel Carvalho, PUC-Rio (PI) and Anderson Gomes, UFPE(co-PI)
In collaboration with Dr Jake Fontana (NRL-USA)

UNIVERSIDADE FEDERAL DE PERNAMBUCO

PUC RIO

Major Goals

This project aims to exploit gold nanorods (GNR) as a platform to study linear and nonlinear optical phenomena in plasmonic nanoparticle aerosols, both in free air in a lab based aerosol environment. To develop novel sensing and signaling capabilities with switchable plasmonic nanomaterials, enabling new technologies with implications to nonlinear optics, geoengineering, nanojet printing, molecular diagnostics and nanomedicine.

Accomplishments Under Goals

Due to pandemic restrictions, the access to the lab March 2020 until July 2021, was very limited and the pace of research slowed down, although the students and post-docs were continuing work when it was possible to access the universities**.**

Achievements:

- Gold Nanorods (Au NRs) synthetized
- Equipment acquisition: Wavefront Sensors - Shack Hartmann (2 units) TSI-3079A (Atomizer withadjustable flowrate for high concentrations) (1unit) TSI-3062(Diffusion Dryer with blue desiccant) (1 unit)
- Built a home-made Herriott Cell to perform measurements of the wavefront of the light wave, passing through the aerosol, with a Shack-Hartmann sensor.
- The aerosol setup for the measurement of the nonlinear refractive index of the

Au NRs aerosol using the Shack Hartman equipment and the Herriot Cell was mounted at the lab at PUC-Rio. Set up implemented with a white light source that allows to measure the absorbance spectrum, as well as with He-Ne laser and Nd-YAG Laser (nanosecond, 10 Hz) at 532 nm, the latter required for nonlinear optical measurements.

- Tests with aerosol containing Au-NRs and using a nanosecond green light (10 Hz) as a pumping source.
- The nonlinear optical characterization of the gold nanorods were not achieved as the sensor Shack-Hartman was broken during the period of the project. A modification of the award was done for the period of 03/31/2022 to 05/31/2023 in an attempt to be acquired a new Shack-Hartmann sensor, but unfortunately, many occurrences avoid the final acquisition of this device.

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Training Opportunities

Within the scope of the project, the opportunities for training and professional development were present with the participation of undergraduate students, graduate students, post docs and technicians. The participants learned the following skills:

a) Preparation of gold nanorods (one post-doc (Andreia Monteiro) self-trained from literature)
b) Use of Hartmann-Schack wavefront detectors (one post-doc, Edwin Colonel, self-trained and trained a PhD student, Gleice Germano)
c) Measurements of Nonlinear response of the gold nanorods aerosol (two post-doc, Melissa Maldonado and Avishek Das)

Participants

Name	Role
Germano,Gleice	Graduate Student (PhD student)
Carvalho, Isabel	PD/PI
Gomes, Anderson	PD/PI
Coronel Sánchez,Edwin	Postdoctoral
Das, Avishek	Postdoctoral
Maldonado, Melissa	Postdoctoral
Gutierrez, Fredy Giovany	Technician
Machado, Yan	Undergraduate Student

Proposed work: Gas (Aerosol) Phase and Detection System

The experimental work was based on the work by Geldmeier et al [J. Geldmeier, P. Johns, N. J. Greybush, J. Naciri, and Jake Fontana, Phys. Rev. B 99, 081112(R) (2019)]. On August 19-24, 2019, there was a scientific visit to the Dr Jake Fontana´s lab (NRL-USA) of 2 post-docs, 1 PhD student and Prof Isabel Carvalho, under the project Award No.N62909-15-1-NO16. During this visit, among other activities, there was a training activity on how to produce gold plasmonic aerosol and to characterize using FTIR. The technique learned at that time was implemented at the Laboratory of Optoeletronics of the Physics Department -PUC-Rio under the scope of the present project.
To generate the aerosol particles a commercial aerosol generator (0.1µm - 3µm) was bought (Fig.1) and a homemade Herriot Cell was made.

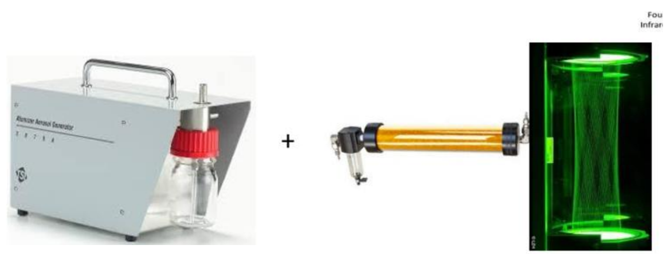


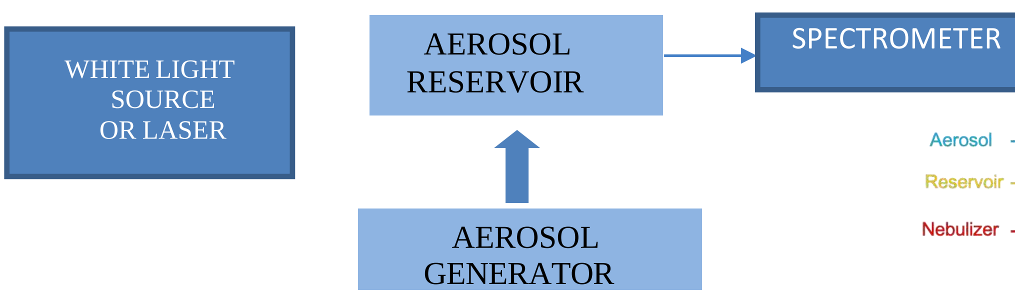
Fig1: Aerosol Generator (left)), Herriot Cell (right).

To investigate the nonlinear optical response of the plasmonic aerosol a Hartman-Shack detector was bought. This detector exploits the laser intensity dependent wavefront change in the presence of the plasmonic aerosol.

The team had already experience in measuring the nonlinear refractive index using the Shack- Hartman detector in electric field aligned Au nanorods [M. Maldonado, Isabel C. S. Carvalho, Jake Fontana, Cid B. De Araújo and Anderson S. L. Gomes,Opt. Express 26, 20298-20305 (2018)]. In the case of the present work, the light source used was a pulsed Q-Switched Nd:YAG laser (Brio -Quantel, 10Hertz, 6 ns, λ=532 nm).

Activity : Generating Aerosol

In the mean (pandemic) time and before the acquisition of the aerosol generator a few experiments were performed with a homemade device. A commercial nebulizer was used to produce aerosol particles and the aerosol was placed in a plastic bottle (Fig. 2).



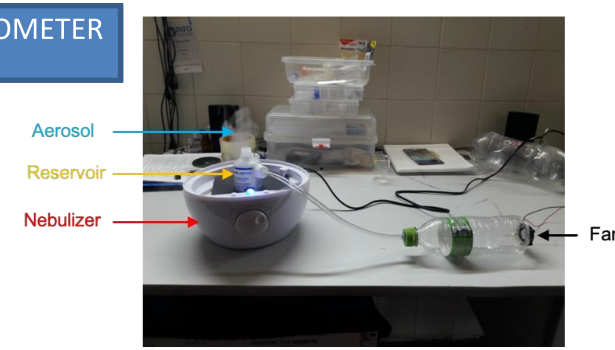


Fig. 2: Scheme of the home made aerosol generator

Also, for the aerosol (bubbles diameter~4µm) formed by a solution of water and Rhodamine 6G it was possible to measure the absorption and emission spectra (Fig.3).

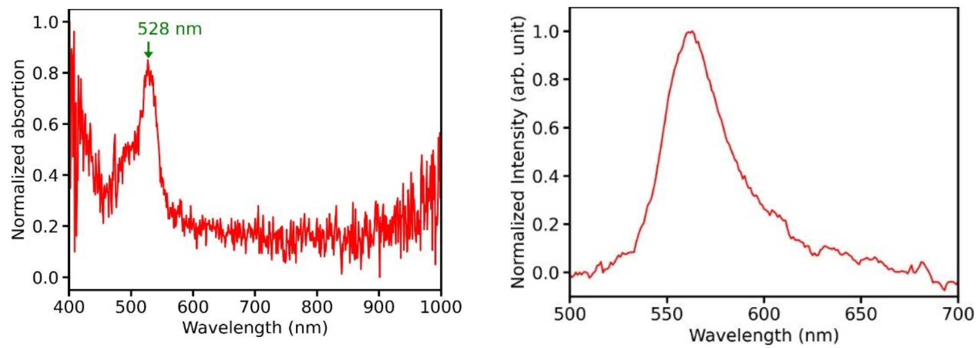


Fig 3: Absorption (left), emission (right) spectra of the aerosol formed with Rhodamine 6G.

Tests were also performed showing that the storage time and the durability of the aerosol with silica nanoparticles presents better results when compared only with water (Fig.4).

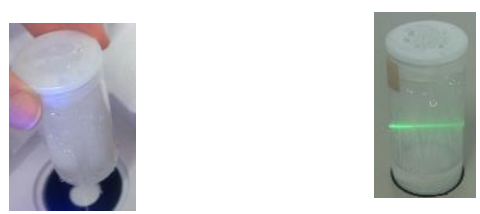


Fig.4: Aerosol hold in a bottle from the vaporizer (left) and laser incident in a bottle containing silica nanoparticles aerosol.

Activity: Building a Home-made Herriott Cell for the characterization of the plasmonic aerosol

A home-made Herriott cell was built to perform measurements of the wavefront of the light wave, passing through the aerosol with the Shack-Hartmann sensor (Fig.5).

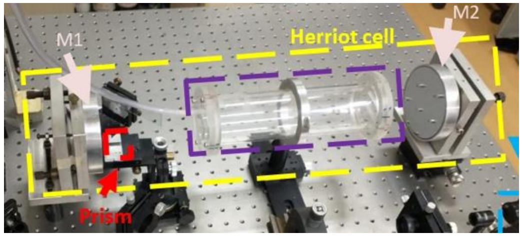
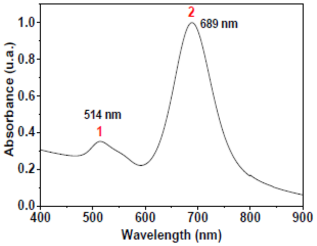


Fig 5: Home-made Herriot Cell(yellow dashed line): 2 concave mirrors (M1 and M2) and-prism (red dashed line).

Activitiy : Synthetize Au nanorods

The Au nanorods samples were synthetized by the pos-doc Dr Andreia Monteiro (Fig. 6).



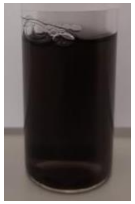


Fig. 6: Au nanorods absorption spectra as a function wavelength showing the typical LSPR absorption bands (left), and an image of the sample (right).

Activitiy : Equipment acquisition with the project budget

- Shack-Hartmann sensor
- TSI-3079A (Atomizer with adjustable flowrate for high concentrations
- TSI-3062(Diffusion Dryer with blue desiccant)

Activitiy: Experimental Set up

The experimental set up for the generation and measurement of the nonlinear characteristics of the de Au nanorods aerosol was mounted at PUC-Rio (Fig. 7).

The set up constitutes of

- He-Ne laser at 630 nm or Nd-YAG Laser (nanosecond, 10 Hz at 532 nm)
- Homemade Herriot Cell (yellow dashed line)
- 2 concave mirrors (M 1 and M 2)
- Prism (red dashed line)
- Atomizer (green dashed line): generates aerosol
- Storage of the aerosol: an acrylic tube (purple dashed line)
- Aerosol pumped with a Laser
- Shack Hartmann sensor: detects changes in the light wavefront after passing along the acrylic tube

Aditionally: setup implemented with a white light source that allows to measure the absorbance spectrum.

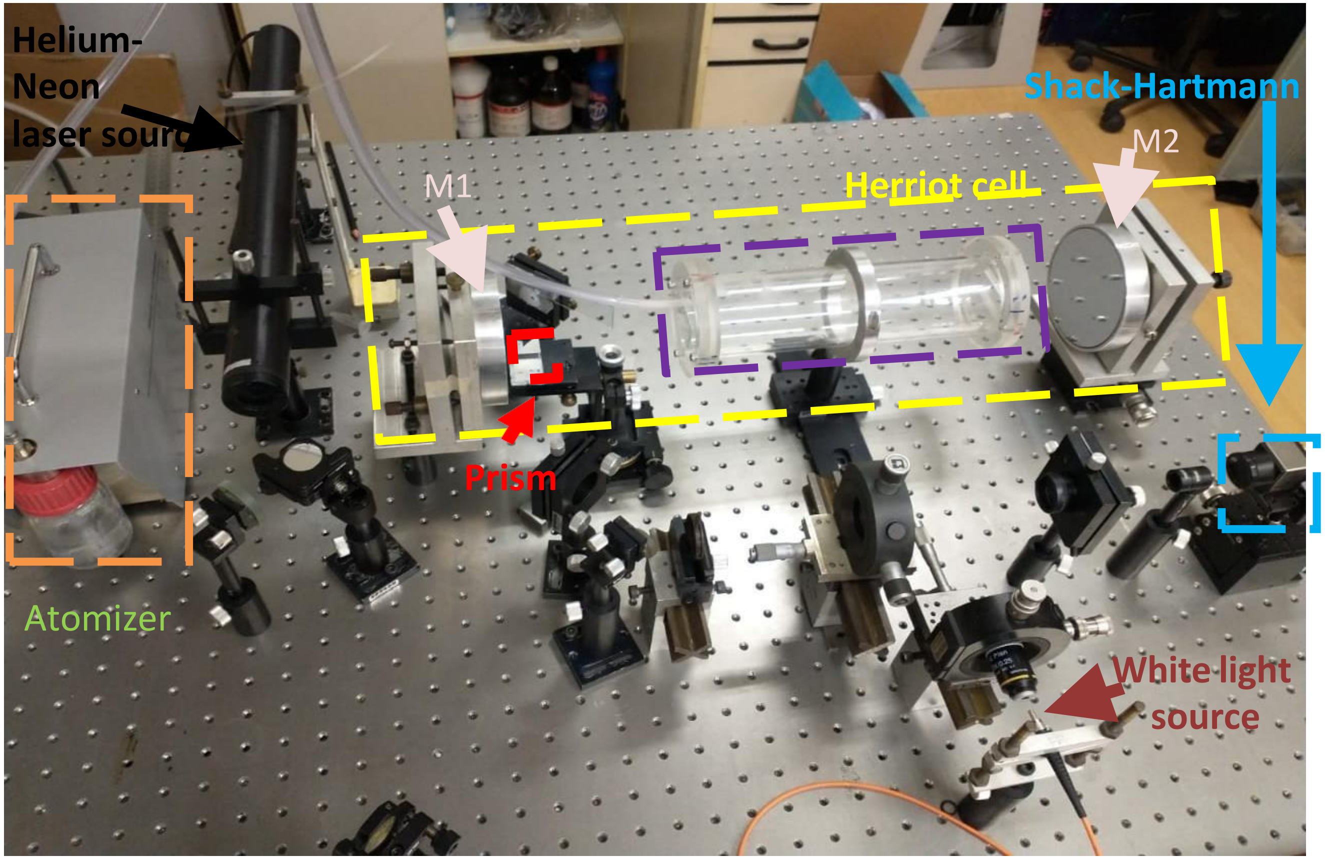


Fig. 7: Experimental set up for the generation and measurement of the nonlinear characteristics of the de Au nanorods aerosol mounted at PUC-Rio.

The experimental set up is versatile as it is possible to use different laser radiations, as tested with He-Ne laser (at 630 nm) to calibrate the system and the 2nd Harmonic of the Nd-YAG (at 532 nm) laser for nonlinear measurements (Fig. 8).

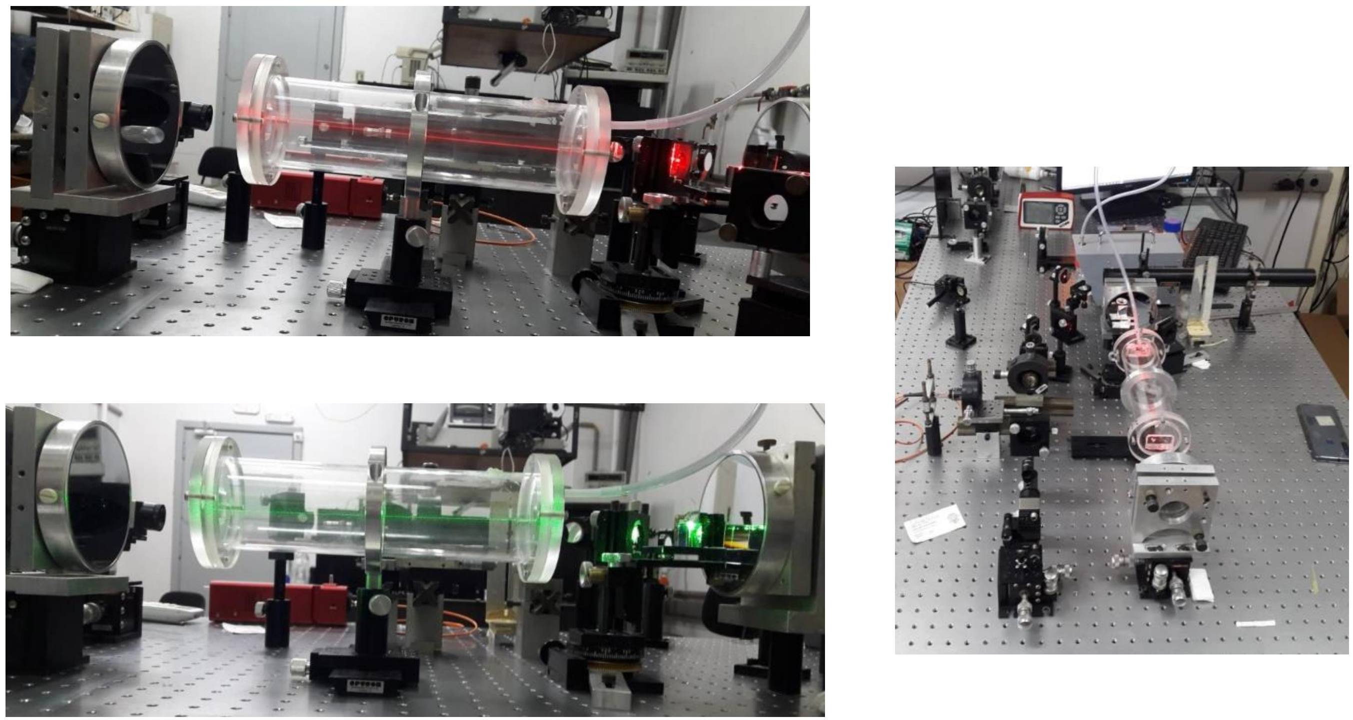


Fig. 8: Herriott-cell using a He-Ne laser (at 630 nm) (top left), Herriott-cell with the 2nd Harmonic Nd-YAG (at 532 nm) laser (bottom left) and top view of the set up (right).

Activitiy: Preliminary Results

Preliminary results were performed of the wavefront variation, using the He-Ne laser light source and the Shack –Hartmann sensor, after the light passes the tube with air, water aerosol and AuNRs aerosol. As can be seen in Fig.9 the wavefront respond to the laser radiation differently according to the aerosol that is present in the tube.
As can be seen the system was operating correctly. The next step of the experiment was to use the Nd-YAG (at 532 nm) laser for the nonlinear optical characterization of the Au nanorods aerosol.
Unfortunately, as the Shack-Hartmann was broken and we were not able to characterize the nonlinear response of the Au nanorods aerosol.

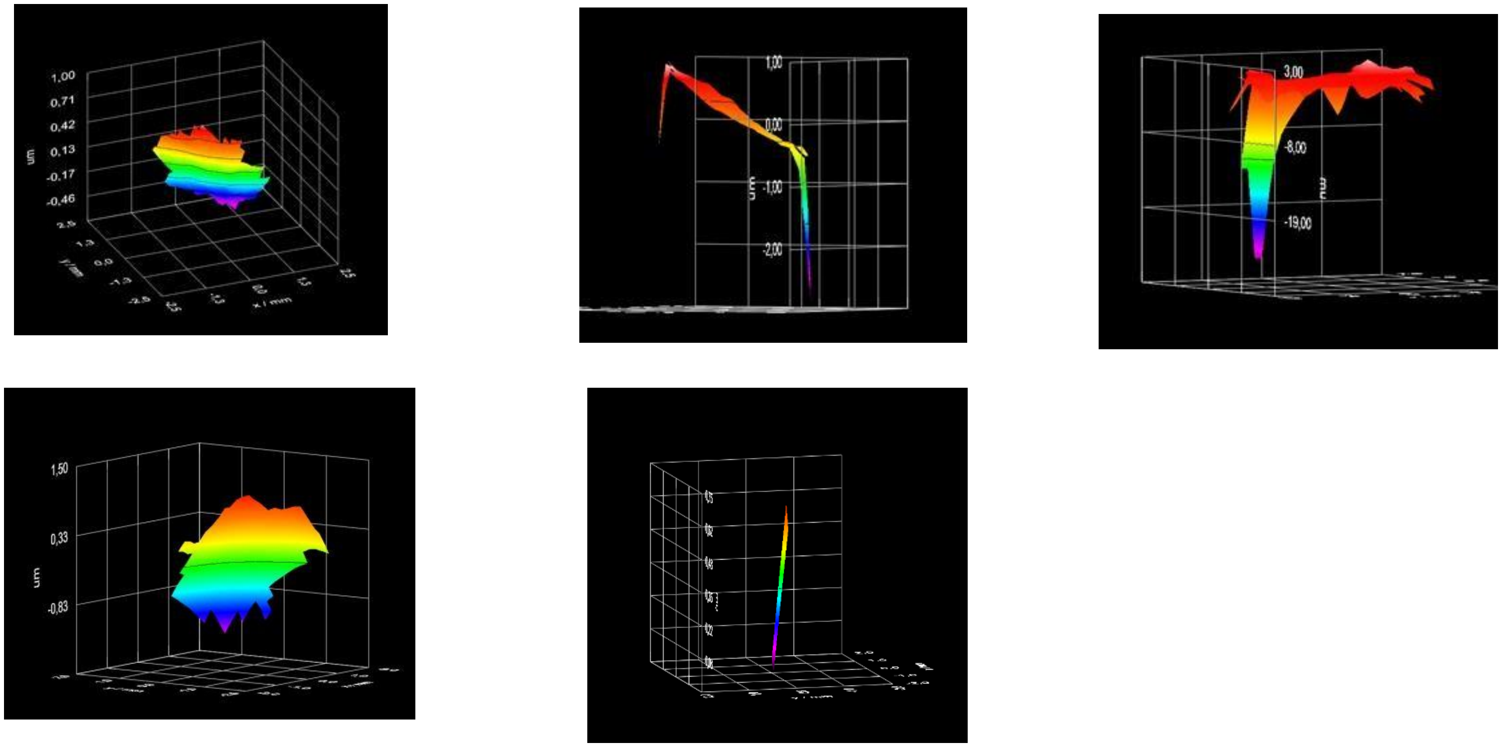


Fig. 9: He-Ne light source wavefront after passing the tube with (left) air, (center) water aerosol, (right) AuNRs aerosol; X and Y-axis indicate the position of the beam and Z indicates the Zernike coefficients