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# **RPPR Final Report**

as of 03-Jun-2020

Agency Code:

Proposal Number: 73940MSRIP Agreement Number: W911NF-19-1-0255

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Report Date: 30-Apr-2020 Date Received: 03-Jun-2020

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Title: COMPACT: A Customizable System for Characterization Of Materials Processing And Chemical

Transformations

Begin Performance Period: 01-Apr-2019 End Performance Period: 31-Mar-2020

Report Term: 0-Other

Submitted By: B. Reeja Jayan Email: bjayan@andrew.cmu.edu

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**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1 STEM Participants: 1

**Major Goals:** The overall objective of this project was to build an in-situ characterization system to observe the dynamics involved in EM field-assisted materials processing. To achieve this objective, the project was divided into the following tasks:

- 1. Identify, purchase, and integrate each piece of equipment hardware required to set-up the COMPACT system (COMPLETED)
- 2. Perform an ex-situ measurement using reference materials (i.e. polymer, ceramic) to confirm the successful set-up of COMPACT system. (COMPLETED)
- Perform an in-situ measurement to understand the mechanism of the field-assisted synthesis. (IN PROGRESS)

Please see uploaded PDF document for details.

**Accomplishments:** Please see attached PDF document for detailed description about the accomplishments and delays caused by COVID-19.

**Training Opportunities:** One postdoctoral scholar (Dr. Kyungho Kim) and one MS student (Yashaswin Harathi) received training on equipment set up for Raman and FTIR as well as Interferometry.

Results Dissemination: Nothing to Report

**Honors and Awards:** PI Jayan received the following awards and honors:

Promoted to Associate Professor of Mechanical Engineering at Carnegie Mellon University

Invited attendee at Roundtable on Biomedical Engineering Materials and Applications (BEMA), National Academy of Engineering (NAE) 2020

U.S. Department of Energy (DOE) Faculty Research Program Participant - National Energy Technology Laboratory (NETL), ORISE/ORAU 2020

Faculty Fellow, Scott Institute for Energy Innovation 2019

George Tallman Ladd Research Award 2019

# **RPPR Final Report**

as of 03-Jun-2020

**Protocol Activity Status:** 

**Technology Transfer:** Nothing to Report

**PARTICIPANTS:** 

Participant Type: PD/PI
Participant: B. Reeja Jayan
Person Months Worked: 1.00

**Funding Support:** 

Project Contribution: International Collaboration: International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Kyungho Kim Person Months Worked: 1.00

**Funding Support:** 

Project Contribution: International Collaboration: International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Yashaswin Harathi

Person Months Worked: 1.00 Funding Support:

Project Contribution: International Collaboration: International Travel:

National Academy Member: N

Other Collaborators:

# Report

# COMPACT: A Customizable System for Characterization of Materials Processing and Chemical Transformations

Principle Investigator: Prof. B. Reeja Jayan Department of Mechanical Engineering Carnegie Mellon University

#### 1. Introduction

Materials synthesized under electromagnetic (EM) field show unique structure and phases which are not observed in materials synthesized by conventional method (i.e. high temperature sintering). Nakamura et al. has studied the effect of microwave synthesis by pair distribution function (PDF) [1]. Microwave synthesized TiO<sub>2</sub> below 200 °C formed a long-range crystalline anatase region with a short-range amorphous region, while a furnace grown TiO<sub>2</sub> are amorphous at similar temperatures. Low-temperature densification, anisotropic lattice expansion, metastable phases, and dislocation are other characteristics observed in EM field-assisted synthesis [2,3]. Researchers have suggested that this phenomenon can be explained by far-from-equilibrium "non-thermal" effects.

However, the fundamental mechanism behind EM field-assisted synthesis remains questionable. While ex-situ characterizations on post-processed materials have provided information to study the field-assisted process, these characterizations cannot provide insights about the phenomena during the field-assisted process. To understand processing-structure-property correlation under EM field and to explain how EM field can lower processing temperature, a viable characterization technique is essential. Researchers have made efforts to develop in-situ monitoring and characterization to explain the dynamics during field-assisted processing. Sprouster *et al* studied the dynamics in uranium dioxide during flash sintering via in-situ X-ray diffraction (XRD) [4]. Despite the promising approach using in-situ XRD, more precise characterization technique is required to study nanoscale materials and lattice disorder.

In this project, we developed a 'Characterization Of Material Processing and Chemical Transformation (COMPACT)' system to study synthesis dynamics under EM field by integrating Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and laser interferometry. Raman spectroscopy is a powerful tool due to its ability to detect changes in

bonding environment. The peak intensities, positions, and broadening can provide information about the dynamics of material during EM field exposure. However, Raman has difficulty detecting dipole moment change of molecules and is not capable of detecting materials with fluorescence. To compensate for this, FTIR is integrated into the system. FTIR detects the dipole moment change of molecules and is not affected by fluorescence. In addition, we have integrated laser interferometry to observe material growth parameters like thickness changes during EM-field assisted (e.g., thin film) processing.

# 2. Objectives

The overall objective of this project was to build an in-situ characterization system to observe the dynamics involved in EM field-assisted materials processing. To achieve this objective, the project was divided into the following tasks:

- 1. Identify, purchase, and integrate each piece of equipment hardware required to set-up the COMPACT system *(COMPLETED)*
- 2. Perform an ex-situ measurement using reference materials (i.e. polymer, ceramic) to confirm the successful set-up of COMPACT system. *(COMPLETED)*
- 3. Perform an in-situ measurement to understand the mechanism of the field-assisted synthesis. (IN PROGRESS)

# 3. Components of COMPACT system

Figure 1 shows a schematic diagram of the complete COMPACT system. The COMPACT system is composed of an iXR Raman (Thermo Fisher), an iG50 FTIR (Thermo Fisher), and a laser interferometry parts (Thor lab and National Instrument). Details of each component is described in the following sections.

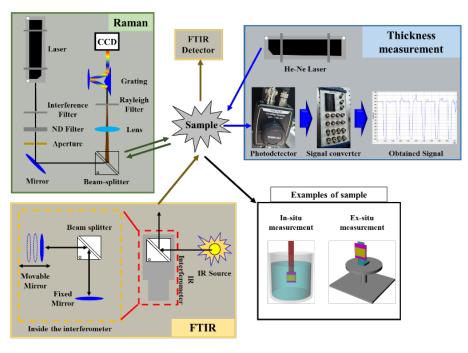


Figure 1. Schematic diagram of COMPACT system.

#### 3.1. Raman System

A general schematic of the iXR Raman system in COMPACT is depicted in Figure 1. Depending on the mode of configuration of the Raman optics, components inside the system may be different. However, a general Raman system contains the parts described in Figure 1. The interference filter reflects one or more spectral bands and transmit a band of interest. This filter improves the monochromaticity of laser emitted from the laser source. A Neural density (ND) filter reduces the intensity of transmitted light from the interference filter. The ND filter reduces the risk of possible damage to the system due to strong light intensity. The Rayleigh filter removes a specific wavelength to collect only the Raman shift from sample. If the measurement is conducted by 785 nm laser, the Rayleigh filter removes the 785 nm light.

Details of our iXR Raman (purchased from Thermo Fisher) are described in Table 1. Pricing details are listed in the appendix.

Table 1. Part information of iXR Raman

| Product Description                         | Part Number |
|---|-------------|
| iXR Raman Spectrometer                      | 912A0908    |
| English Language Kit                        | 699-135500  |
| Power Cord North American 120v, 3 Conductor | 085-703800  |

| DXR 785 nm (NIR) High Power Excitation Laser Set for iXR        | 840-286000 |
|---|------------|
| DXR 532 nm (green) Excitation Laser Set for iXR                 | 840-285600 |
| Laser Safety Goggles 455 nm, 532nm                              | 122-802800 |
| Laser Safety Goggles 633nm, 780nm, 785nm                        | 122-802900 |
| Lens Tube 3 inches  | 840-295300 |
| Lens Tube 6 inches  | 840-295400 |
| Lens Tube Clamp   | 840-295500 |
| 20x Long Working Distance Objective - Brightfield Only          | 222-203300 |
| 10x Long Working Distance Objective - Brightfield Only          | 222-203200 |
| 4X Glass Infinity Corrected Objective - Brightfield Only        | 0045-455   |
| Tube to Brightfield Objective Adapter for iXR lens tube Assys   | 840-294600 |
| Series Data Collect for OMNIC 9                                 | 834-088500 |
| Dell Optiplex Workstation Windows 10 Professional 64 Bit Loaded | 912A0917   |
| 22" Flat Panel Widescreen Monitor                               | 840-223900 |

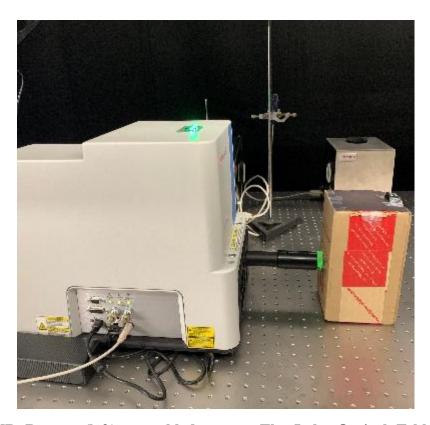


Figure 2. iXR Raman (left) assembled onto a ThorLabs Optical Table as part of

# COMPACT. Cardboard box (right) protects a sample from ambient light during calibration tests.

# 3.2. FTIR System

FTIR consists of an IR source, interferometer, and detector (Figure 1). Light with a wide range of frequencies is emitted from the IR source, which enters the interferometer. Inside the interferometer, the beam splitter transmits half of the light and reflects the other half. One beam hits the fixed mirror and the second one hits the moving mirror. The two beams reflected from each mirror combines into one beam at the beam splitter. The combined beam travels to the detector. The signal format acquired by an FTIR is named as interferogram (Figure 3). Different intensities are attributed to a change in optical path difference (OPD). The maximum intensity is where two beams have no wavelength differences. Details of the parts for our iG50 FTIR system from Thermo Fisher are described in Table 2. Pricing details are listed in the appendix.

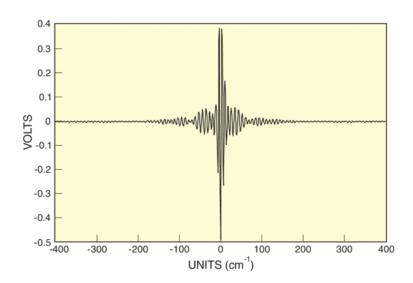


Figure 3. An example of interferogram (https://www.newport.com/n/introduction-to-ftir-spectroscopy).

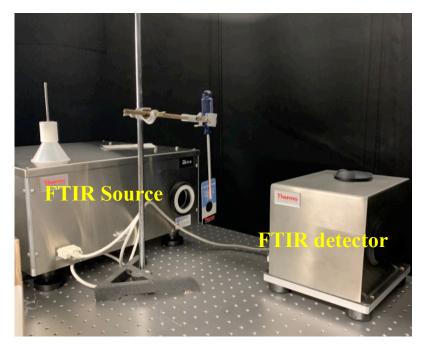


Figure 4. iG50 in COMPACT system. It should be noted that source and detector are modular in nature, allowing plug-and-play style re-arrangements depending on the type of experiment/synthesis (e.g., thin film, powder) we are studying.

Table 2. Parts information for iG50 FTIR

| Product Description   | Part Number |
|---|-------------|
| Nicolet iG50 Standard Mid-IR Spectrometer                       | 840-274600  |
| Nicolet iG50 External Detector Module with Elliptical Mirror    | 840-275800  |
| LN2 Cool Wide Range MCT-B Detector wKRS-5 window                | 840-233800  |
| Liquid N2 Cooled MCT-A Detector with CdTe window                | 840-229200  |
| Ge-on-KBr On-Axis Beamsplitter (7800 - 350 cm-1)                | 840-128900  |
| Nicolet iG50 English Language Kit                               | 699-133700  |
| Power Cord North American 120v, 3 Conductor                     | 085-703800  |
| Standard Purged System  | 470-151400  |
| iG50 Field Service Installation                                 | 701-054812  |
| IR Polarizer  | 0045-347    |
| Dell Optiplex Workstation Windows 10 Professional 64 Bit Loaded | 912A0917    |
| 22" Flat Panel Widescreen Monitor                               | 840-223900  |

# 3.3. Laser interferometry

The laser emitted from the He-Ne source hits the sample and reflects off from the surface. The reflected light enters the photodetector which reads the intensity of light. There is no one specific product for this characterization technique. Therefore, we have built our own system by purchasing parts from different vendors. Table 3 shows the various part information.

Table 3. Parts information of laser interferometry

| Product Description               | Part Number |
|-----------------------------------|-------------|
| Photodetector (Thorlabs)          | PDA100A2    |
| He-Ne Laser (Thorlabs)            | HNLS008L    |
| BNC Cable                         | 2249-C-36   |
| DAQ USB6212 (National Instrument) | 781003-01   |

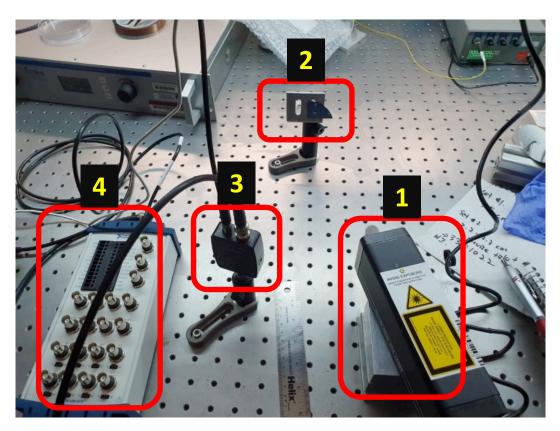


Figure 5. Laser interferometry set-up. #1 is He-Ne laser source, #2 is sample (thin film on silicon wafer) attached to L-bracket, #3 is photodetector, and #4 is a signal converter.

# 4. Technical Approach and Status of Tasks

To set up the COMPACT system set-up, two major approaches were devised. First, understand the basic operation procedure and specifications (specs) of each equipment, and then perform an ex-situ measurement on reference materials. Second, integrate the system and perform insitu measurement during a field-assisted synthesis experiment.

# 4.1. Set-up of COMPACT system

To initiate the set-up of the COMPACT system, a technician from Thermo Fisher visited our lab to provide training on iXR Raman and iG50 FTIR. The technician performed the initial set-up as shown in Figure 2 and 4. After the initial set-up, we worked to calibrate and test each system, as described below.

#### 4.1.1. iXR Raman

When light is incident on a sample, it will interact with the sample (i.e. get reflected, absorbed, or scattered). Raman detects the scattered light. Depending on the characteristic energy of a vibrating molecule, the light is scattered at a specific wavelength. This specific wavelength provides the chemical and structural information of the measured sample. Below are the specifications with which we set up the iXR Raman in COMPACT to do Raman analysis. Please refer to Figure 2 for optical image of iXR Raman.

- ① Working distance: The working distance of Raman is 2 cm. This value is obtained by manual observation of Raman peak intensity. Purchasing an optical camera to improve the quality of measurement is being considered.
- 2 Laser source: There are 2 lasers available in our system, a 532 and 785 nm wavelength laser. The selection of laser depends on the sample condition. Lower wavelength (532 nm) has high excitation efficiency, high fluorescence, and low heat absorption, while 785 nm laser has medium efficiency, fluorescence, and heat absorption. In short, 532 nm laser has benefit in obtaining better Raman signal (resolution) while 785 nm laser can reduce the occurrence of background fluorescence. Samples obtained from microwave radiation are sensitive to fluorescence which can be attributed to the organic compounds attached on the material. Therefore, 785 nm laser is preferable in studying field-assisted synthesis.
- (3) Laser power: The 532 nm laser has a maximum power limit of 10 mW while 785 nm laser has a limit of 150 mW.
- (4) Calibration and alignment: iXR Raman uses an auto-calibration and alignment system.

After auto alignment, we use silicon wafer to confirm that alignment is successful.

(5) **Lens tube:** As shown in Figure 2, the signal is collected by a lens sticking out from the iXR Raman. We have 3" and 6" lens tube. The length of tube does not affect the Raman measurement result.

#### 4.1.2. iG50 FTIR

When IR light is irradiated into the interferometer, an interfered light (sinusoidal wave with different intensity) is produced. As this interfered light transmits through the sample, those frequencies matching the bonding energy of the sample will be absorbed. Subsequently, the detector will read this information and convert the sinusoidal wave information into a spectrum. The basic specifications of our iG50 FTIR set-up are described below. Please refer to Figure 4 for optical image of iG50 FTIR.

- 1) 1.5" (38 mm) collimated front output beam
- 2 **Different detectors:** We have a MCT-A and MCT-B detector. MCT-A has better resolution but shorter detection ranges from 600 11,700 cm<sup>-1</sup>. MCT-B has poorer resolution but larger detection ranges from 400 11,700 cm<sup>-1</sup>. The ceramic oxides (e.g., TiO<sub>2</sub>) we study are generally detected between 400 700 cm<sup>-1</sup>. Therefore, the MCT-B is preferred.
- (3) Since the source and detector is independent, there is minimal restriction for positioning the sample.
- (4) Normally the size of our sample is smaller than 20 mm. Therefore, focusing the beam is necessary to reduce unwanted noise from surrounding environment. Details are described in Section 6.

#### 4.1.3. Laser Interferometry

When a laser hits the sample, the reflected laser intensity changes depending on the thickness of the sample. This reflected beam intensity is measured. The general specifications of this equipment is described below.

- (1) **Reflection angle:** The reflection angle of laser interferometry can be controlled from 1 to 89°. This is done manually.
- (2) **Control program:** NI Max program offers numerous measurement methods (e.g. continuous mode, step mode, etc). We are still working on this equipment to understand the control parameters. Details in Section 6.

#### 4.2. Ex-situ measurement

We first performed test measurements on ex-situ samples as described below:

- 1 Verify the calibration of each equipment: Even though the equipment was initially setup by a technician, it is essential to measure reference samples to test if the equipment is working properly with real samples.
- (2) A preliminary study for in-situ measurement. An in-situ measurement set-up is complicated as we need to install a reactor where the sample will be housed. In addition, the reaction time of ceramic material under EM field varies from 30 mins to 2 hours. A preliminary study on EM field synthesized ex-situ samples will provide us insights on how to design an in-situ experiment in terms of sample position, working distance, laser power, laser type, and reflection angle.

# 4.2.1. Sample types

In this project we have selected two sample preparation methods to perform ex-situ measurement. First, ceramic oxide materials synthesized by microwave radiation (MWR). The goal of this project is to understand the dynamics during EM field-assisted synthesis. A preliminary ex-situ study on EM field synthesized materials can provide information about the feasibility of using Raman/FTIR measurement to detect changes in EM field grown sample's final structure and phase information. To grow TiO<sub>2</sub> using 2.45 GHz microwave radiation, 3 ml of tetrabutyl orthotitanate sol-gel and 12 ml of tetraethylene glycol (TEG) was injected into a glass vial (G30 from Anton Paar). Subsequently the glass vial was placed inside a Monowave 300 (Anton Paar microwave reactor). The reaction was performed at 180 °C.

Second sample type is a chemical vapor deposition (CVD) coated polymer thin film. Our group studies the effect of CVD grown polymers on electrochemical performance of lithium ion batteries. CVD polymerization has many advantages over other coating methods like spin coating, including the ability to engineer uniform coating on complex structures, over large areas in a cost-effective manner. Su et al., studied the effect of CVD coated polymers on the electrochemical performance of ceramic oxide cathodes like LiMn<sub>2</sub>O<sub>4</sub> (LMO) [5]. This study shows that conducting polymer coated on LMO cathode improves the electrochemical performance. The COMPACT system can further benefit this study by providing insights on how the CVD coated polymer changes during the electrochemical charge-discharge cycle.

PEDOT (polyethylene dioxythiophene) and polythiophene (PT) were selected for ex-situ

measurement.

## 4.3. Integration and in-situ measurement

After equipment set-up and ex-situ measurement, the following tasks were conducted to integrate the system.

- 1 Set-up Raman on the optical table
- (2) Position sample within proper distance of the Raman (working distance)
- (3) Position FTIR and ensure IR beam pathway is not disturbed
- 4 Position He-Ne laser first and then place photodetector depending on the reflection angle.

After integrating the system, a tetrabutyl orthotitanate sol-gel combined with tetraethylene glycol (TEG) are mixed inside a KBr cavity cell. KBr is used as a container for its high transparency to IR beam in a range of 400 to 4000 cm<sup>-1</sup>. In addition, as FTIR is extremely sensitive to water, the reaction is performed inside an organic solvent (i.e. TEG). After sample set-up, we apply external microwave radiation (MWR) with different parameters (i.e. temperature, power, and radiation time). In-situ mode Raman, FTIR, and laser interferometry are operated to study the structural changes in the materials during this EM field-assisted synthesis. However, this in-situ work is pending due to COVID-19 shutdown. See Section 5 for details. Table 4 describes the tasks of this project and the completion status to date.

Table 4. Progress of tasks of COMPACT project

|    | Project schedule and task  |                |       |  |  |  |  |  |
|----|--|----------------|-------|--|--|--|--|--|
| #  | #1. Set-up and ex-situ measurement   |                |       |  |  |  |  |  |
|    |  | 100 %          |       |  |  |  |  |  |
|    | Task 1.1 Understanding the general requirement of each system and setting-up the system    | FTIR           | 100 % |  |  |  |  |  |
|    | 2002 29 2002 Wall 2001 20 29 20 29 20 20 20 20 20 20 20 20 20 20 20 20 20                  | Interferometry | 80 %  |  |  |  |  |  |
|    |  | Raman          | 100 % |  |  |  |  |  |
|    | Task 1.2 Performing ex-situ measurement using reference materials (e.g. polymer thin film) | FTIR           | 100 % |  |  |  |  |  |
|    | (vig. porjanor unit mini)  | Interferometry | 80 %  |  |  |  |  |  |
| #2 | #2. Integrating the system and in-situ measurement   |                |       |  |  |  |  |  |
|    | 66 %   |                |       |  |  |  |  |  |
|    | Task 2.2 Perform in-situ characterization  |                | 0 %   |  |  |  |  |  |

# 5. Project delay due to COVID-19

CMU labs were shut-down in middle of March due to the outbreak of COVID-19. All researchers were ordered to work remotely from home. Due to the limited access to facilities, COMPACT project is currently on hold. CMU has recently announced (May 22<sup>nd</sup>) that the school is planning to open facility for a limited number of researchers. We have applied for this opening and are waiting for the school's decision. If we gain this access, task 1.1, 1.2, and 2.1 is expected to be finished in 2 weeks, while 2 months is required to finish task 2.2 tasks.

# 6. Progress and Accomplishments

This section describes our progress and accomplishments prior to COVID-19 shut down.

# (a) Successful set-up of Raman and FTIR

CVD coated PEDOT and PT on silicon wafer, and MW-assisted grown TiO<sub>2</sub> on glass substrate were prepared and measured (preparation method was described in Section 4).

The Raman spectra (Figure 6a for PEDOT and 7a for PT) and FTIR spectra (Figure 6b for PEDOT and 7b for PT) clearly shows that COMPACT system is functioning properly. Raman detects the polarization change while FTIR detects the dipole moment change of molecule. This difference in the working principle causes a slightly different spectra when measuring the same material. For example, PEDOT C-H bonding is detected by FTIR while a different C-C bonding mode is detected by Raman. This difference corroborates that Raman and FTIR can be a complementary technique.

MWR synthesized TiO<sub>2</sub> was measured by both Raman and FTIR (Figure 8). Raman peaks appear at 150, 390, 514, and 640 cm<sup>-1</sup>, indicating a formation of anatase TiO<sub>2</sub>. However, FTIR did not show clear Ti-O bonding information. This can be attributed to the IR beam absorption by glass substrate. The transmission range of IR beam through quartz is 2200 – 25000 cm<sup>-1</sup>, which affects the bonding information at wavenumbers below 2200 cm<sup>-1</sup>. To resolve this issue, TiO<sub>2</sub> powder on Ge, KBr, CsI, and CdTe substrate can be considered. The appearance of C-O and C=O can be attributed to organic solvents (TEG during reaction) and/or atmosphere CO<sub>2</sub>. Nevertheless, we have successfully confirmed that our system is functioning properly.

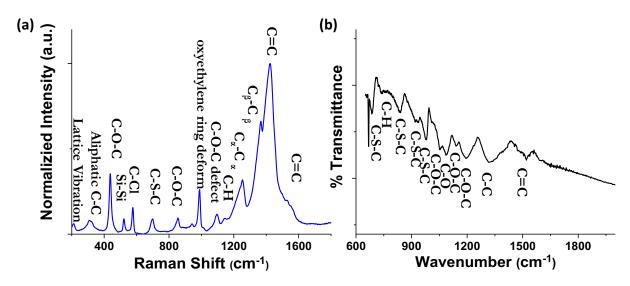


Figure 6. PEDOT ex-situ characterization by (a) Raman and (b) FTIR

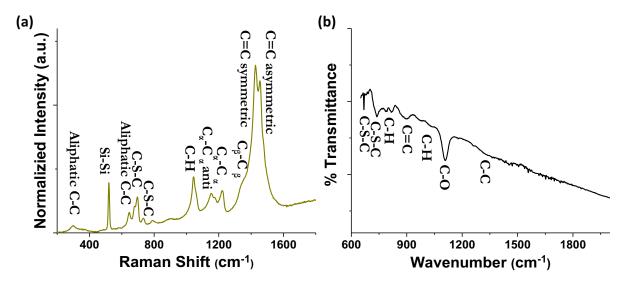


Figure 7. PT ex-situ characterization by (a) Raman and (b) FTIR

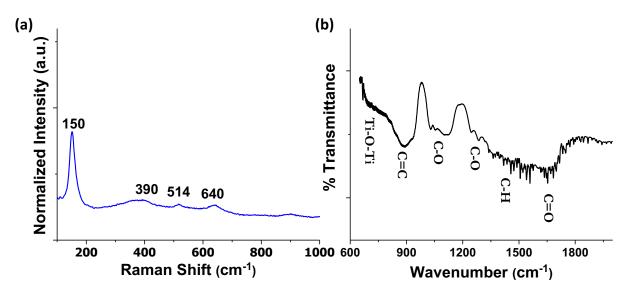


Figure 8. Ex-situ characterization of microwave radiation grown TiO2 by (a) Raman and (b) FTIR.

After ex-situ measurement, Raman and FTIR were integrated. Adjusting the working distance of Raman and focusing the collimated beam of FTIR are the main tasks for successful integration. The working distance of Raman should be 2 cm. In addition, focusing the 1.5 inches collimated IR light onto the sample is necessary to block-out unwanted signal from surrounding. To accommodate both requirements, two set up arrangements were considered:

# **1** The reflection mode FTIR

As shown in Figure 9, reflection mode focuses both Raman and FTIR on the same spot. The FTIR source releases a 1.5 inches diameter collimated beam which is much larger than the sample size (below 10 mm) resulting in unwanted information being collected from the surrounding. To tackle this issue, a confocal mirror was placed in front of the FTIR source box to focus the IR beam on the sample. As shown in Figure 9b inset, the two lasers from Raman and FTIR are successfully focused on the sample. The upper laser beam is from FTIR and the lower one is from Raman. The two beams are not focused on same spot due to the possibility of sample heating from one laser that can affect the other equipment's measurement.

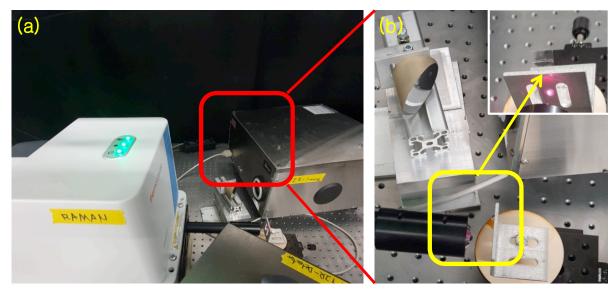


Figure 9. The reflection set-up of Raman and FTIR.

# **2** The transmission mode FTIR

The second mode is the transmission mode. The benefit of this mode is that implementing laser interferometry is simple. For reflection mode, it is difficult to implement the laser interferometry to point the same side of the sample. The main concept of transmission mode is the rotation of sample. As shown in Figure 10, the L-bracket (sample holder) is attached on a rotating disk. During Raman measurement the sample face toward Raman (Figure 10b) and during FTIR the sample face toward FTIR. Later the laser interferometry can be installed on the right side of the picture (opposite to Raman).

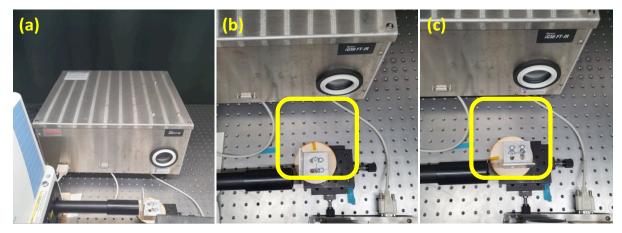


Figure 10. The transmittance set-up of COMPACT system.

# (3) Comparison of set-up modes

A CVD coated PEDOT on silicon wafer was tested in both modes (Figure 11). The

transmittance and reflection mode show difference FTIR spectra. This is attributed to the silicon wafer. Silicon transmits IR beam in the range of  $120 - 360 \text{ cm}^{-1}$  and  $1500 - 8300 \text{ cm}^{-1}$ . The absorption occurring in the range of  $360 - 1500 \text{ cm}^{-1}$  can deteriorate the IR spectra. To avoid such issue, transmittance set-up is beneficial for our study.

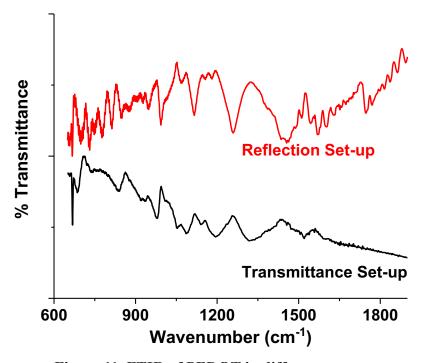


Figure 11. FTIR of PEDOT in different set-up

#### (b) Implementing laser interferometry into the COMPACT system

Our experiments to investigate the effect of EM field on materials relies on ceramic thin film when external fields (i.e. microwave radiation) are localized to a substrate. Real-time monitoring of film thickness is essential to understand the phenomenon of EM field-assisted ceramic growth. A light emitted by He-Ne laser reflects off the sample onto a photodetector that measure the intensity of reflected light. As the film thickness changes, the amount of light absorbed by the interferometer varies. As a preliminary study, we performed an ex-situ study on different film thickness of same materials. Three different PEDOT film thickness (20, 35, and 75 nm) were measured and the amplitude difference is about 25, 24, and 16, respectively (Figure 12). The preliminary study showed that depending on the film thickness, the intensity of light changes.

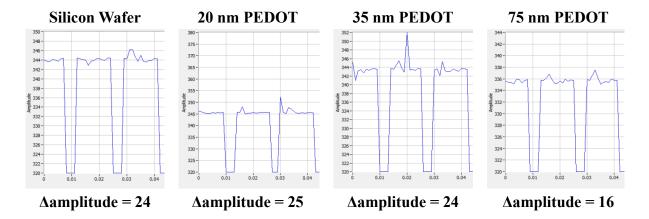


Figure 12. Laser interferometry measurement of PEDOT thin film with different thickness.

Two troubleshooting steps will be performed before we move onto the in-situ characterization tasks.

#### 1 Build a library

We need to build a library of different material thickness before we start an in-situ measurement. The laser interferometry can only detect the change of light intensity. Based on the change of light intensity, we need to reference this library to determine the film thickness.

## 2 Sinusoidal pattern

Generally, a sinusoidal pattern is expected. However, our set-up produced a step pattern. After we gain access to our lab, we will work with the vendor to resolve the issue.

#### 7. Summary

Prior to the COVID-19 outbreak, we have completed the set-up of Raman and FTIR and have tested its feasibility by performing ex-situ characterization. We made considerable progress in setting-up the laser interferometry, which needs a few more steps to complete. Ex-situ characterization of polymer film and ceramic film have been successfully performed by COMPACT system. After CMU reopens our research lab, we will work on in-situ characterization of EM field-assisted material growth.

#### 8. References

- [1] N. Nakamura et al., *Journal of Materials Chemistry A*, 2017, 5(35), 18434-18441.
- [2] B. Reeja-Jayan et al., Sci. Rep. 2012, 2, 1003

- [3] R. Wroe and A.T. Rowley, *Journal of Materials Science* 31 (1996), 2019-2026
  [4] D. Sprouster et al., *Materialia* 2 (2018) 176 182
  [5] L. Su et al., *ACS Applied materials & interfaces* 10 (32), 27063 27073

# **APPENDIX**

# 1. Raman

| Thermo Fisher Scientific  |             |               |                             |  |  |  |  |
|---|-------------|---------------|-----------------------------|--|--|--|--|
| Product description   | Part number | Price         | Comments                    |  |  |  |  |
| iXR Raman Spectrometer  | 912A0908    | \$43,800      | Obtained from updated quote |  |  |  |  |
| English Language Kit  | 699-135500  | \$0           | Obtained from updated quote |  |  |  |  |
| Power Cord North American<br>120v, 3 Conductor                        | 085-703800  | \$0           | Obtained from updated quote |  |  |  |  |
| DXR 785 nm (NIR) High Power Excitation Laser Set for iXR              | 840-286000  | \$23,900      | Obtained from updated quote |  |  |  |  |
| DXR 532 nm (green) Excitation<br>Laser Set for iXR                    | 840-285600  | \$18,700      | Obtained from updated quote |  |  |  |  |
| Laser Safety Goggles 455 nm,  | 122-802800  | \$420         | Obtained from updated       |  |  |  |  |
| 532nm   | 122 002000  | ψ. <b>2</b> ψ | quote                       |  |  |  |  |
| Laser Safety Goggles 633nm, 780nm, 785nm                              | 122-802900  | \$907         | Obtained from updated quote |  |  |  |  |
| Lens Tube 3 inches  | 840-295300  | \$59          | Obtained from updated quote |  |  |  |  |
| Lens Tube 6 inches  | 840-295400  | \$98.00       | Obtained from updated quote |  |  |  |  |
| Lens Tube Clamp   | 840-295500  | \$225         | Obtained from updated quote |  |  |  |  |
| 20x Long Working Distance Objective - Brightfield Only                | 222-203300  | \$2,800       | Obtained from updated quote |  |  |  |  |
| 10x Long Working Distance<br>Objective - Brightfield Only             | 222-203200  | \$1,920       | Obtained from updated quote |  |  |  |  |
| 4X Glass Infinity Corrected Objective - Brightfield Only              | 0045-455    | \$328         | Obtained from updated quote |  |  |  |  |
| Tube to Brightfield Objective Adapter for iXR lens tube Assys         | 840-294600  | \$160         | Obtained from updated quote |  |  |  |  |
| Series Data Collect for OMNIC 9                                       | 834-088500  | \$2,890       | Obtained from updated quote |  |  |  |  |
| Dell Optiplex Workstation<br>Windows 10 Professional 64 Bit<br>Loaded | 912A0917    | \$1,340       | Obtained from updated quote |  |  |  |  |
| 22" Flat Panel Widescreen<br>Monitor                                  | 840-223900  | \$395         | Obtained from updated quote |  |  |  |  |

| Shipping charges |       | \$125      | Obtained from updated quote |
|------------------|-------|------------|-----------------------------|
| Less Discount    |       | (\$15,393) | Obtained from updated quote |
|                  | Total | \$82,674   |                             |

# 2. FTIR

| Thermo Fisher Scientific   |             |           |                             |  |  |  |  |
|--|-------------|-----------|-----------------------------|--|--|--|--|
| Product description  | Part number | Price     | Comments                    |  |  |  |  |
| Nicolet iG50 Standard Mid-IR<br>Spectrometer                           | 840-274600  | \$26,900  | Obtained from updated quote |  |  |  |  |
| Nicolet iG50 External Detector<br>Module with Elliptical Mirror        | 840-275800  | \$2,780   | Obtained from updated quote |  |  |  |  |
| LN2 Cool Wide Range MCT-B<br>Detector wKRS-5 window (11,700-<br>400cm- | 840-233800  | \$5,775   | Obtained from updated quote |  |  |  |  |
| Liquid N2 Cooled MCT-A Detector with CdTe window (11,700-600 cm-1)     | 840-229200  | \$5,675   | Obtained from updated quote |  |  |  |  |
| Ge-on-KBr On-Axis Beamsplitter (7800 - 350 cm-1)                       | 840-128900  | \$5,850   | Obtained from updated quote |  |  |  |  |
| Nicolet iG50 English Language Kit                                      | 699-133700  | \$0       | Obtained from updated quote |  |  |  |  |
| Power Cord North American 120v, 3<br>Conductor                         | 085-703800  | \$0.00    | Obtained from updated quote |  |  |  |  |
| Standard Purged System   | 470-151400  | \$665     | Obtained from updated quote |  |  |  |  |
| iG50 Field Service Installation  | 701-054812  | \$1,748   | Obtained from updated quote |  |  |  |  |
| IR Polarizer   | 0045-347    | \$3,470   | Obtained from updated quote |  |  |  |  |
| Dell Optiplex Workstation Windows<br>10 Professional 64 Bit Loaded     | 912A0917    | \$1,340   | Obtained from updated quote |  |  |  |  |
| 22" Flat Panel Widescreen Monitor                                      | 840-223900  | \$395     | Obtained from updated quote |  |  |  |  |
| Shipping   |             | \$150     | Obtained from updated quote |  |  |  |  |
| Discount   |             | (\$8,347) | Obtained from updated quote |  |  |  |  |
|  | Total       | \$46,401  |                             |  |  |  |  |

# 3. Laser interferometry

| Product description                              | Vendor                 | Part number | Qty | Unit<br>Price | Total   | Comments   |
|--|------------------------|-------------|-----|---------------|---------|--|
| Si Switchable<br>Gain Detector,<br>320 - 1100 nm |                        | PDA100A2    | 1   | \$371         | \$371   | photodetector; Comes with<br>power supply; BNC cable<br>needed for data collection |
| Self-Contained<br>HeNe Laser,<br>632.8 nm        |                        | HNLS008L    | 1   | \$916         | \$916   | Red laser  |
| RG-58 BNC<br>Coaxial Cable                       | Thorlabs               | 2249-C-36   | 2   | \$18          | \$35    |  |
| USB-6212<br>BNC                                  | National<br>Instrument | 781003-01   | 1   | \$1,766       | \$1,766 | DAQ card to connect<br>PDA100A2 to the computer                                    |
|  |                        |             |     | Total         | \$3,088 |  |

# 4. Aluminum Chamber

| Part number | Qty | Unit Price | Total   | Comments                                |
|-------------|-----|------------|---------|---|
| PTA281      | 1   | \$2,318    | \$2,318 |   |
| BX1224S     | 1   | \$6,755    | \$6,755 | 12" X 24" X 12" Aluminum<br>Box chamber |
|             |     | Total      | \$9,073 |   |

# 5. Auxiliary System & Amazon Purchase

| Product description                   | Vendor            | Part number     | Qty | Unit<br>Price | Total      | Comments            |
|---------------------------------------|-------------------|-----------------|-----|---------------|------------|---------------------|
| ND Filter                             | ThorLabs          | NE01A           | 2   | \$51          | \$102.96   |                     |
| PbSe Photodetector                    | ThorLabs          | PDA20H          | 2   | \$470         | \$939.24   |                     |
| Visible Free Space<br>Isolator        | ThorLabs          | IO-3-532-<br>LP | 1   | \$1,693       | \$1,692.52 |                     |
| 1/2" Optical Post                     | ThorLabs          | TR3-P5          | 1   | \$24          | \$24.39    |                     |
| 1/2" Pedestal Post<br>Holder          | ThorLabs          | PH2E            | 5   | \$25          | \$126.05   |                     |
| Clamping fork                         | ThorLabs          | CF175-P5        | 1   | \$50          | \$50.38    |                     |
| Laser Curtain Kit                     | Thorlabs          | TFL1225N        | 1   | \$9,219       | \$9,219    |                     |
| Optical Table                         | Thorlabs          | T48HK           | 1   | \$8,267       | \$8,267    |                     |
| Laser Safety<br>Glasses               | ThorLabs          | LG3             | 2   | \$161         | \$321.36   |                     |
| Keithley 6500 -<br>Digital Multimeter | TestEquity<br>LLC |                 | 1   | \$1,734       | \$1,733.60 | Obtained from quote |
| Laser                                 | Coherent Inc.     |                 | 1   | \$9,390       | \$9,390.00 | Obtained from quote |
|                                       |                   |                 |     | Total         | \$31,866   |                     |

| Product description                          | Vendor | Part number | Qty | Unit Price | Total | Comments              |
|--|--------|-------------|-----|------------|-------|-----------------------|
| Caddy Cart<br>Presentation<br>Station, black |        | B07F6P7LRZ  | 1   | \$149      | \$149 | For computers         |
| Dual Monitor<br>Mount                        | Amazon | B0756WPVZJ  | 1   | \$100      | \$100 | For computer monitors |
|  |        |             |     | Total      | \$249 |                       |