

Development of a Visible Photoluminescence Microspectrometer

by
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Abstract

Photoluminescence (PL) emission is an important characteristic measurement in the field of solid-state physics research. It reveals information about the electron band structure of molecules, and is particularly useful in studying thin-film materials on micron spatial scales. This work sought to design and build a simple instrument which can accurately measure PL in thin-film materials by applying targeted, monochromatic illumination to the sample.

By coupling a diode laser system into a metallurgical microscope, we were able to apply sufficiently energetic, monochromatic light to a small area and achieve sample excitation. Using optical filters to block reflected laser light, we collect emissions with a commercial spectrometer. The resulting PL emission spectra have low noise, and accurately identify spectral features found in literature for test materials of organic photovoltaic crystals and transition-metal dichalcogenide thin films.

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1 Introduction

Photoluminescence (PL) is the process by which materials will absorb a photon, exciting an electron to a higher-energy "excited state," then emit a photon as the electron relaxes back to a lower-energy state. Measuring PL in different ways is a common method for characterizing semiconducting materials.

Basic PL measurements are emission and excitation, and differ by their independent variables. Emission measurements use one wavelength to excite the material, and measure the intensity of light emitted across a chosen spectrum. Excitation measurements use many wavelengths to excite the material, and measure the intensity of light emitted at a particular wavelength. This project is centered around PL emission measurements.

The Micro-Femto Energetics (μfE) group at Oregon State University uses advanced optoelectronic methods to characterize materials, especially thin-layer materials and micron-scale semiconducting devices.

The group's workhorse when it comes to PL measurements is a Horiba **Something?** fluorimeter, coupled to a **[TODO: model?]** microscope. The instrument uses a **[TODO: specs?]** xenon-arc lamp and double-monochromator to illuminate a wide field with a tunable wavelength. The light source is coupled to the microscope with a fiber optic cable. The instrument can be configured for reflection or transmission microscopy depending on the application. With the aid of computer software, the instrument is able to measure both PL emission and excitation. However, there are a few distinct challenges to using this instrument.

Because the fiber optic delivers a large beam, a large area on samples is illuminated whether the instrument is in a reflection or transmission mode. The wide-field illumination is excellent for imaging, but makes it hard to isolate emissions from small spatial domains.

[TODO: Something about the system takes a long time to warmup before the light source is stable.]

[TODO: Check specs for monochromator. What is it's spectrum like vs. laser diode? More or less monochromatic?]

[TODO: Something about training time and the learning curve for using the device. Software is kinda complicated. Takes a really long time to take a measurement.]

This project offers a solution to these challenges by designing and assembling a new PL microspectrometer that can measure the PL emission of samples accurately, quickly, and with the ability to illuminate small spatial domains.

Naturally, the new instrument has fewer applications. It only measures emission (not excitation), and reconfiguration for other measurements requires more consideration to optical design. The goal of this project, however, is to design an instrument that is simple to use for PL measurement when use of the

fluorimeter is impractical, too time consuming, or the instrument is in use for another experiment.

2 Background

2.1 Optoelectronic Materials

2.1.1 Organic Photovoltaics: ADT

2.1.2 Quantum Dots: CdSe

2.1.3 Transition Metal Dichalcogenides: MoS₂

2.2 Photoluminescence

Photoluminescence (PL) is a mechanism by which materials absorb and emit photons. The process can be described with respect to electronic transitions within an atom or molecule.

The absorptive transition occurs first, when a photon interacts with a molecule and is absorbed. The photon's energy must be approximately equal to the bandgap of the absorbing molecule to satisfy the energy transitions allowed by quantum mechanics. When that condition is met, the photon's energy raises an electron to an excited state, where it stays for a short time.

Some number of vibronic transitions occur as the electron loses energy to radiation and vibration. **[TODO: How do we measure these transitions, or their lifetimes?]**

Finally, the radiative transition occurs when the electron decays back to a ground state. During the radiative transition, a photon is emitted at the bandgap energy as the electron moves from the lowest vibronic state in the conduction band to the highest vibronic state in the valence band. **[TODO: This needs some work.]**

2.3 PL as a Characteristic Measurement

[TODO: Why is PL a useful measurement in solid state? In biological sciences? In general?]

3 Methods

3.1 Design

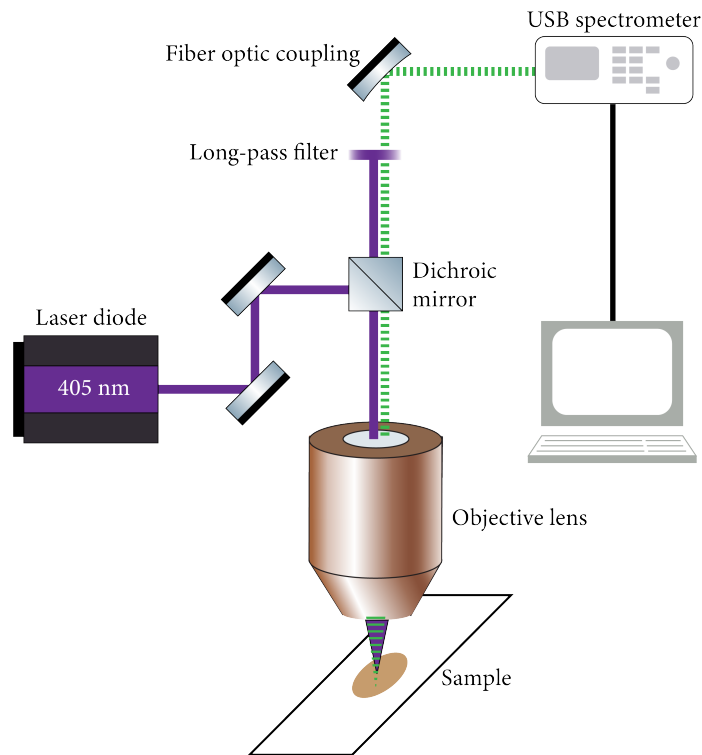


Figure 3.1: Schematic diagram of the new PL microspectrometer.

3.1.1 Microscope

[TODO: Schematic diagram of Olympus microscope]

The starting point of the project was an Olympus BX60M fluorescence microscope. The BX60M is built for reflection microscopy, and includes a housing for brightfield and darkfield mirrors. For the new instrument, we added a mirror cube housing between the brightfield/darkfield mirror housing and the observation tube. This additional component housed a dichroic mirror, which enabled us to couple an external light source into the instrument and filter that light out of the path through the observation tube.

3.1.2 Illumination and Optics

The BX60M is equipped with a xenon arc lamp, which is used for general observations under white light illumination. In order to measure photoluminescence, we require the use of a (mostly) monochromatic light source which is energetic enough to cause electron excitation in the sample. **[TODO: Discuss the mechanics of this, and requirements for a light source in the Background section.]**

Our PL microspectrometer uses a diode laser as its light source. Specifically, we used ThorLabs **[TODO: model?]** laser diode (405 nm), **[TODO: model?]** housing, **[TODO: model?]** laser diode controller, and **[TODO: model?]** temperature controller. To couple the laser and microscope, we used a set of two mirrors in a vertical Z-fold [1] configuration. This allowed for precise alignment of the laser to the optical axis of the microscope, which allows for maximal transmission of excitation light through the objective lens and onto the sample stage.

The laser diode housing and first mirror were mounted to an optical table. The laser starts parallel to the surface of the table, and the first mirror directs the beam upward. The second mirror in the Z-fold configuration was mounted to the end of a tube that extends out the side of the mirror cube housing. This mirror directs the vertical beam horizontally into the mirror. It seems preferable to mount both mirrors to the optical table for stability, but we were successful with this method by mounting the microscope to the table so that it and the second mirror did not move relative to the laser beam during normal operation.

Due to limited space on the optical table, it was not feasible to align the laser diode housing and mirror cube housing in the plane of the table. To overcome this, our Z-fold configuration also turns the beam 90 degrees in the plane of the table. The configuration we used has the laser beam initially pointed in the direction of the operator, then directed upward by the first mirror, then directed into the side of the mirror cube housing. While in operation, but particularly during laser alignment, precautions must be taken to protect the operator's eyes from direct exposure to the laser beam.

The laser was aligned to the microscope's optical axis in two iterative steps. First, we adjust the position of the laser as it enters the mirror cube housing by moving the first mirror. A reticle made of photoluminescent laser viewing material was a particularly useful target when fixed to the opening on the side of the housing. Then, in place of an objective lens, we fix an iris diaphragm to the microscope nosepiece. We adjust the second mirror to position the laser in the center of the mostly-closed iris. This process is repeated until the laser spot is centered on both targets.

[TODO: Pictures/diagrams of the laser configuration/alignment. I have some pictures already that may be useful for this.]

3.1.3 Measuring Spectra

3.1.4 Imaging

3.2 Operating Procedure

3.2.1 Laser Startup

3.2.2 Selecting a Region of Interest

3.2.3 Measuring PL Spectra

3.2.4 PL Imaging

4 Results and Discussion

In general, results from the microspectrometer are much smoother than results from the fluorimeter, which include quite a lot of noise. **[TODO: Something about excitation power and noise? Sources?]** We suspect that this is a consequence of wide-field illumination used by the fluorimeter, in which molecules outside the region of interest (or otherwise, with some defects) are excited and emit spectra different from that of the region of interest. **[NOTE: Maybe not, depending on the power thing.]**

4.1 ADT TES-F

For a drop-cast sample of ADT TES-F on glass, we selected a region of interest which appeared to be a single crystal, with few visually distinguishable defects. The crystal was also selected such that its surface area was larger than the area illuminated by the microspectrometer’s laser spot. The emission spectra of the region of interest are shown in Figure 4.1.

[TODO: Convert wavelength from nm to eV? This seems to be a more common unit in solid state.]

Both spectra in Figure 4.1 show a clear peak around 630nm, which has been shown in other research.[2][3] The spectra measured by the microspectrometer also shows a secondary peak just below 600 nm, which is not evident in the spectrum taken by the fluorimeter. **[TODO: Additional sources that back up the peaks I’m showing?]**

4.2 CdSe Quantum Dots

Figure 4.2 shows the PL emission of CdSe quantum dots **[TODO: in solution? on substrate?]**. There is one broad, clear peak that aligns well with the same measurement taken on the fluorimeter, between 520 and 620 nm. This peak seems to agree with other studies of CdSe quantum structures.[4]

Unlike the same measurement taken on ADT, this measurement was taken in a region of interest which is sparsely populated with quantum dots, with one target grouping illuminated by the laser.

[TODO: What else do I write about here? Need to find more resources on analysis of PL, i.e. what information we get about the material. This will also be useful for Background section.]

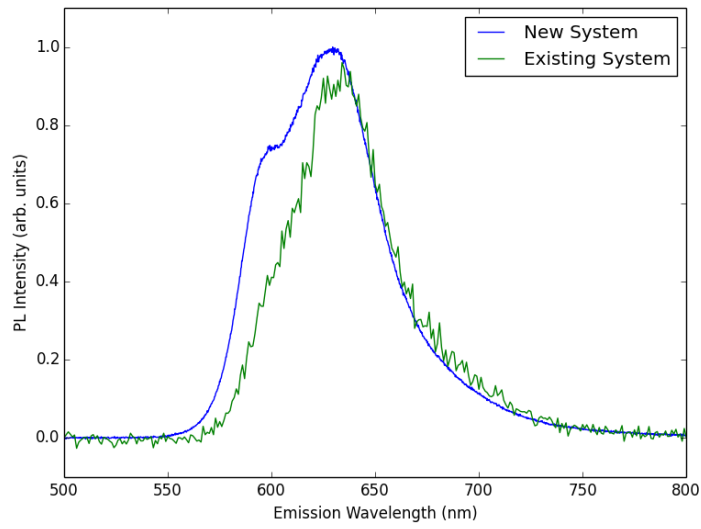


Figure 4.1: PL emission spectrum of ADT TES-F, excited at 405 nm. Wide-field illumination used by the existing system to excite the sample yields a noisy spectrum, and does not excite the secondary peak that is shown clearly in the results from the new system. A single crystal, larger than the laser spot, was selected among smaller neighboring crystals for this measurement.

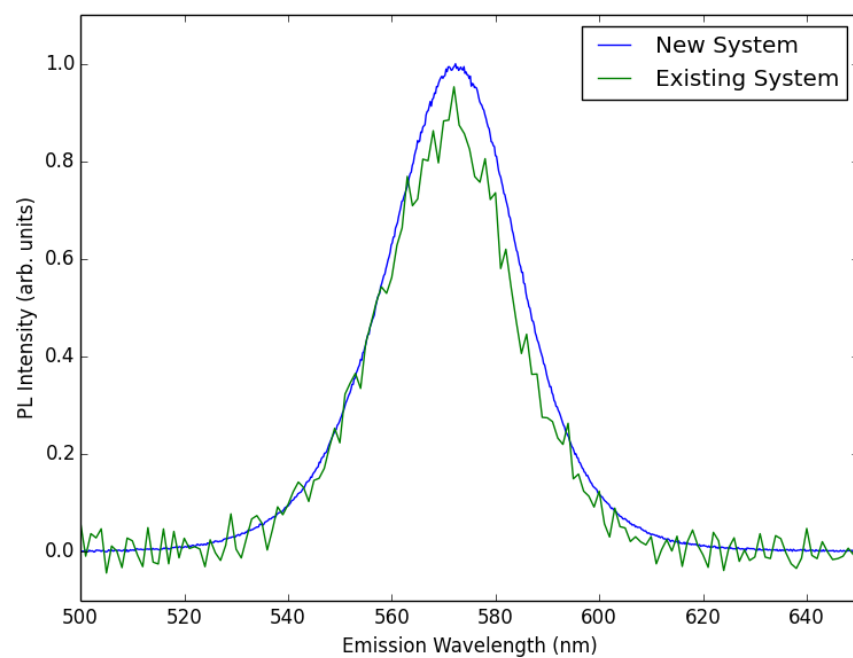


Figure 4.2: PL emission spectrum of a cluster of CdSe quantum dots on ?? substrate, excited at 405 nm.

5 Conclusion

Acknowledgements

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- ²A. Lam, “Polarization dependent spectral analysis reveals dipole alignment and intermolecular coupling in anthradithiophene organic semiconducting crystals”, June 11, 2018.
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A Code