Electron Paramagnetic Resonance (EPR) Investigation of Plasmonic In:CdO nanoparticles

Dianna Pledger, Catherine Fabiano, Geoffrey Strouse

Abstract

A plasmon is a phenomenon that occurs when an electron oscillates on the surface of a conductor. Localized surface plasmon resonances (LSPRs) refer to free carriers oscillating at a frequency of light. Historically, experiments exploring LSPR characteristics have focused on gold (Au) and silver (Ag). However, these noble metals have limited LSPR tunability and are costly. Metal Oxides can be tuned via doping, size, and shape, while noble metals can only be tuned via size and shape. This means that LSPRs can be observed in metal oxides across a wide range of frequencies, from visible (Vis) to far-infrared (FIR), which is useful for telecommunication (MIR-FIR), photothermal therapy (NIR), and electrochromic windows (UV-Vis-NIR). This project examines indium doped cadmium oxide (In:CdO) nanoparticles and how relationships between the structures and properties of different concentrations of indium in cadmium oxide lattice.

Introduction

Plasmons are the oscillation of an electron on the surface of a nanoparticle, and LSPRs are specific to a localized area of a semiconductor material. The Strouse lab uses metal oxides as nanocrystal semiconductors, which include a wide range composed of different metals. Electron Paramagnetic Resonance (EPR) is a form of spectroscopy which observes atoms and molecules that have an unpaired electron. Electromagnetic radiation is applied to and absorbed by the sample, which is contained in a high magnetic field. The absorption of wavelengths is observed to assess the energy and frequency of absorption. The Strouse lab uses indium doping, as it has been suggested to increase the LSPR in cadmium oxide. Thus, it is important to understand the benefits that indium provides in tuning the CdO LSPR frequency.

Nanoparticle Synthesis

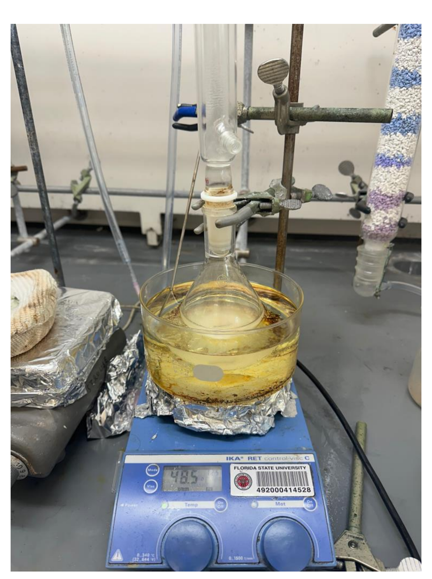

Figure 1. Setup of In:CdO prior to degassing

Figure 2. In:CdO after cooling

1. According to the % FICO, calculate the amounts of its metal precursors needed according to 1.5 mmol. (This includes $Cd(acac)_2$ and InF_3).
2. Add the materials measured in Step 1 and place into a 250 mL one-neck flask along with 7.5 mmol Oleic Acid and 150 mL of 1-Octadecene.
3. Degass under a vacuum for an hour at 125℃.
4. Heat the solution until it begins refluxing at around 316℃.
5. After 30-45 minutes of refluxing, the reaction turns brownish green. This indicates the synthesis of FICO nanocrystals.
6. Ten minutes after the color change, cool the flask to room temperature.
7. Add isopropanol (IPA) until the reaction mixture turns cloudy.
8. Run the sample through the centrifuge three times: for the first trial, at 7000 rpm for 5 minutes. For the second trial, at 3000 rpm for 3 minutes. For the third trial, at 7000 rpm for 5 minutes. This will crash out the nanocrystals for characterization.

Nanoparticle Characterization

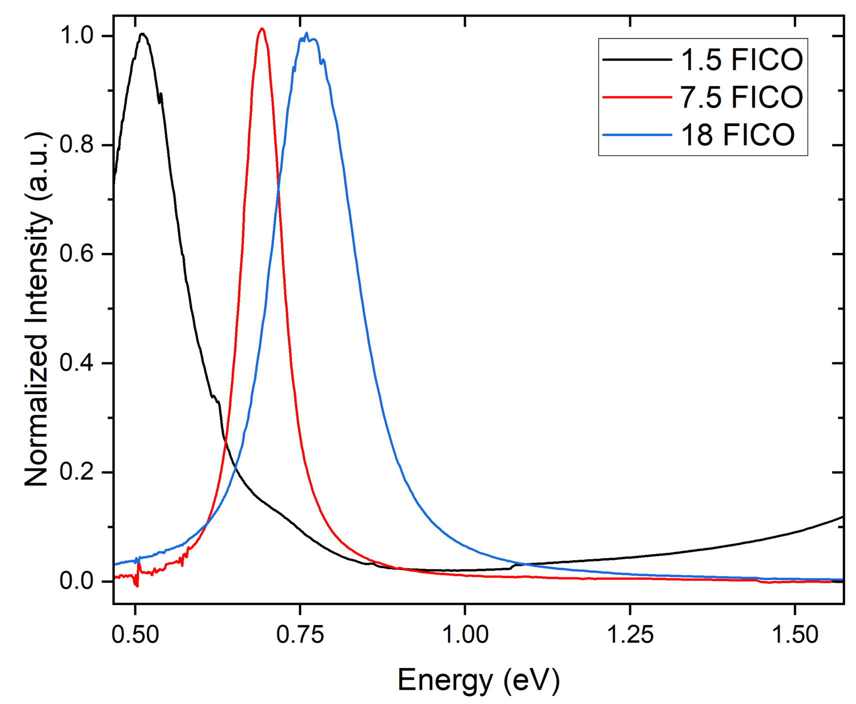

Figure 3. Extinction Spectrum of In:CdO at 1.5, 7.5 and 18% In concentration taken on a Perkin Elmer Lambda 950 UV/VIS/NIR

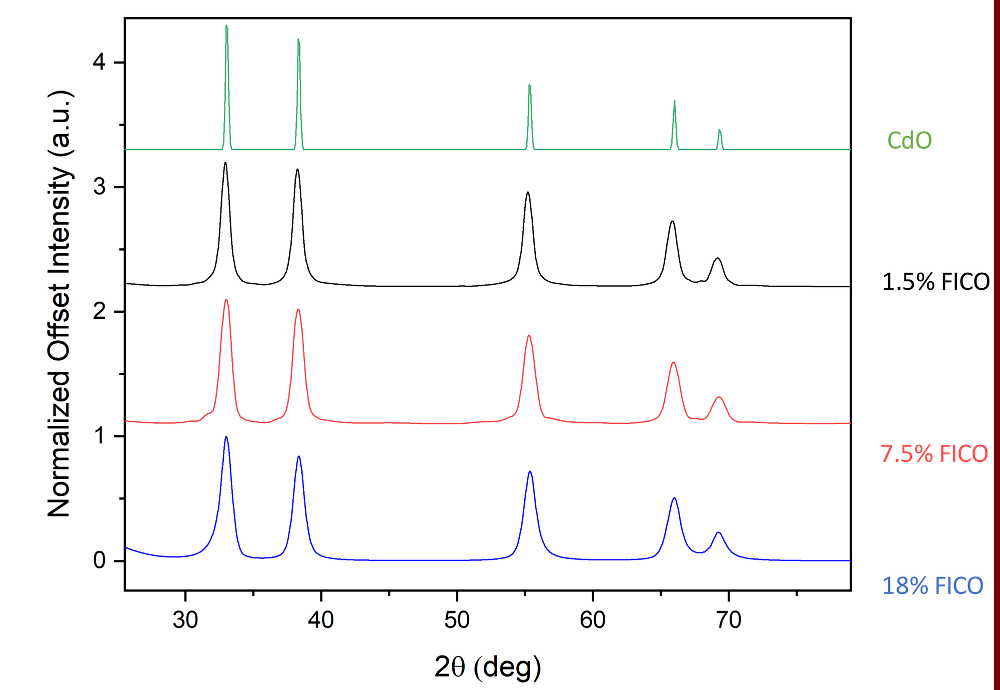

Figure 4. X-ray diffraction pattern of In:CdO at 1.5 (black), 7.5 (red) and 18% (blue) In concentration compared to CdO (green) rock salt phase taken on a Rigaku MiniFlex X-ray diffractometer.

Table 1. LSPR peak energy (λ) and Bandgap (E_g), Quality Factor (Q) of LSPR for 10 nm Spherical FICO NCs

Sample	λ (eV)	E_g (eV)	Q	Carrier Density (cm^{-3}) Assuming m* = 0.21	Nanocrystal Size (nm)
1.5% FICO	0.58	2.51	3.51	2.73E20	10
7.5% FICO	0.6212	2.96	1.59	3.69E20	10
18% FICO	0.7598	3.27	5.11	5.72E20	10

Electron Paramagnetic Resonance (EPR)

Electron Paramagnetic Resonance (EPR) is a form of spectroscopy that specifically focuses monitoring unpaired electrons. EPR is a helpful tool to analyze low concentration defects in nanoparticles. The sample absorbs a single or multiple wavelengths of EM radiation, and the unpaired electron occupies either a +1/2 or -1/2 m_s value. Then, either the magnetic field holding the sample, or the EM radiation is changed. This allows researchers to find the point at which electrons jump from m_s=-1/2 to m_s=+1/2. Using the absorbance value in comparison to its associated wavelength in an equation will produce a graph displaying the relationship between absorption and the frequency of the EM radiation.

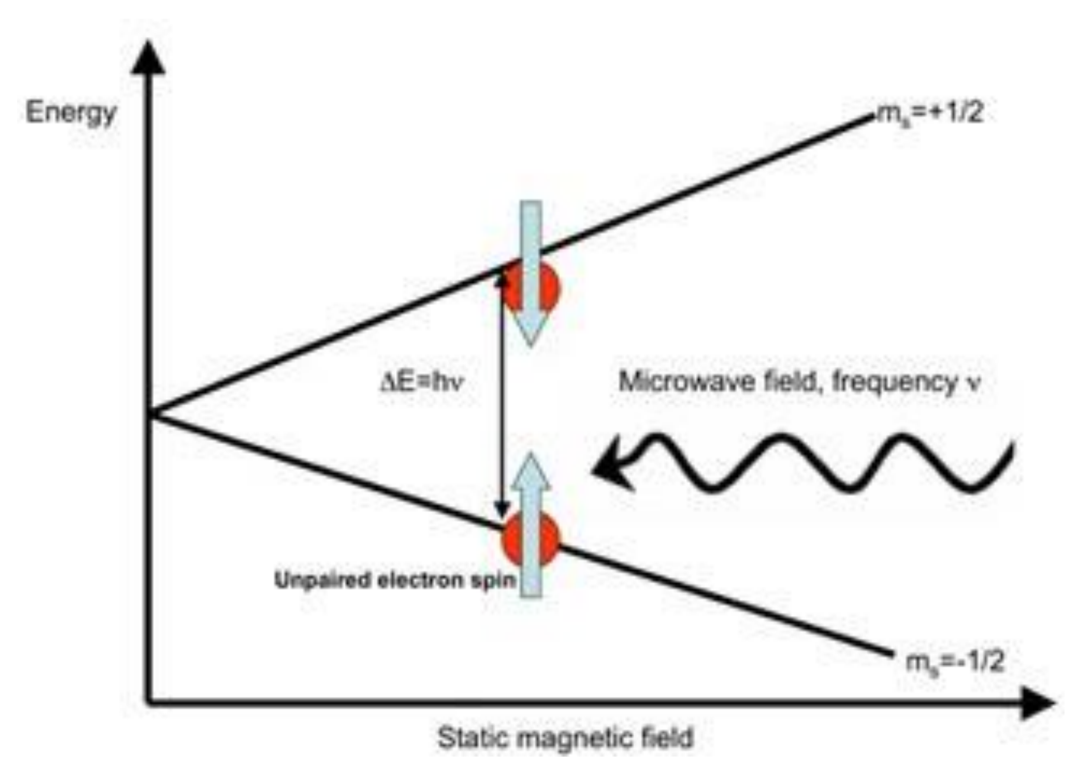

Figure 5. Schematic of Zeeman Splitting taken from the University of Chicago

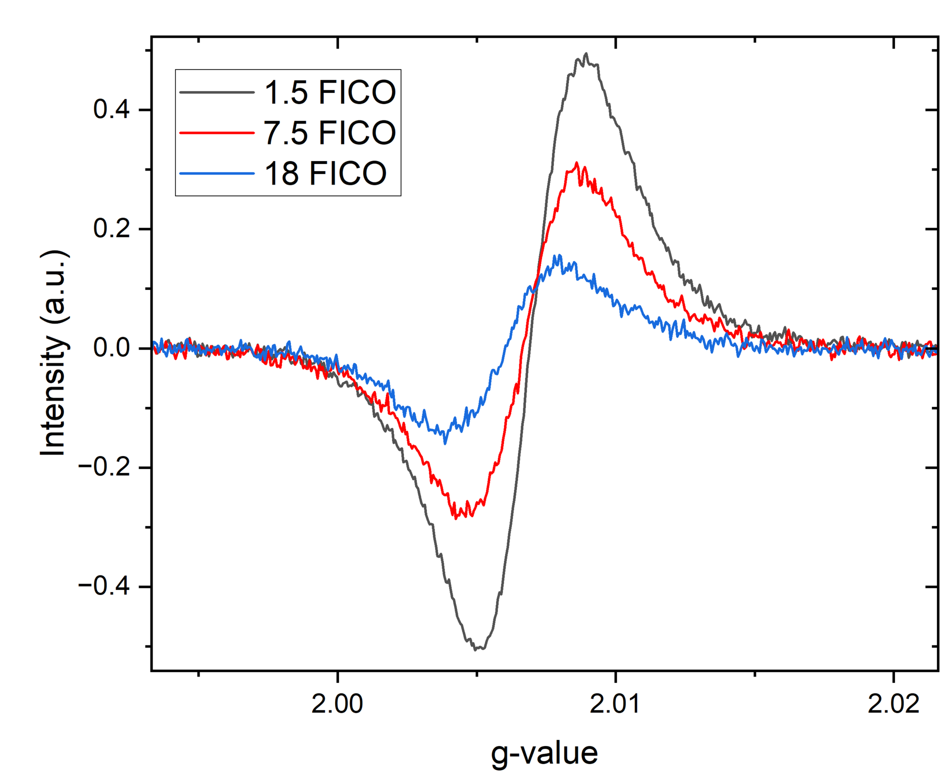

Figure 6. X-Band EPR spectra of doped In:CdO as a function of concentration, 1.5 (black), 7.5 (red), 18 (blue) at room temperature.

Applications

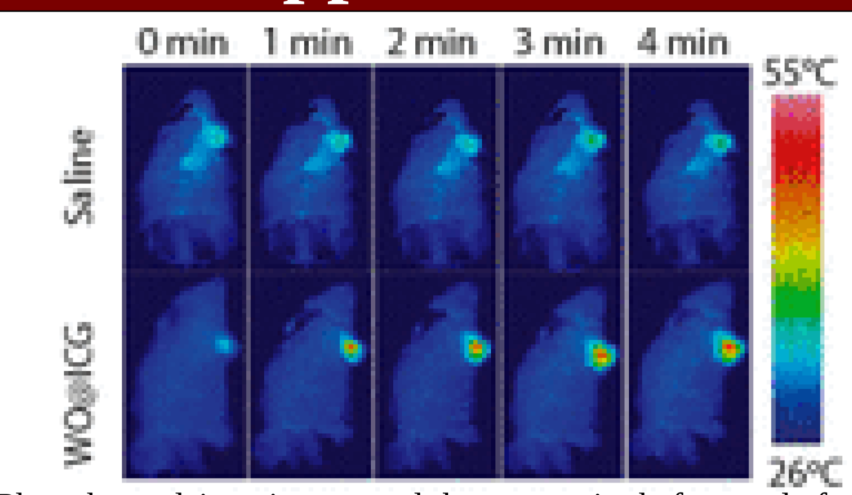

Figure 7. Photothermal imaging around the tumor site before and after injection of WO_{3-x} nanocrystals. There is a rise in local temperature after injection. Taken from Agrawal et al.

A few applications of plasmons include:

1. **Electrochromics**
The electrochromic properties of plasmons affect what types of light rays are absorbed by temperature-controlled windows. This helps to prevent overheating.
2. **Photothermal therapy**
The high absorption of light of plasmonic nanocrystals results in the release of heat, making nanocrystals a local heat source. Research has shown that LSPR materials such as copper sulfide and tungsten oxide have decreased tumor sizes around 50% within a month.
3. **Waste Heat Management**
Plasmonic nanocrystals with high absorption in the MIR allows for heat waste to be managed efficiently between a hot and cold surface. Specifically, metal oxides with broader plasmons have been shown to have high cumulative heat transfer.

References

1. Libretexts. EPR: Introduction chem.libretexts.org/Bookshelves Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Magnetic_Resonance_Spectroscopies/Electron_Paramagnetic_Resonance/EPR%3A_Introduction.
2. Ankit Agrawal, Shin Hum Cho, Omid Zandi, Sandeep Ghosh, Robert W. Johns, and Delia J. Milliron. Localized Surface Plasmon Resonance in Semiconductor Nanocrystals. Chemical Reviews, 2018, 118 (6), 3121-3207, 10.1021/acs.chemrev.7b00613.
3. Carl R. Conti III, Giovanni Quiroz-Delfi, Joanna S. Schwarck, Banghao Chen, and Geoffrey F. Strouse. Carrier Density, Effective Mass, and Nuclear Relaxation Pathways in Plasmonic Sn:In2O3 Nanocrystals. The Journal of Physical Chemistry, C 2020, 124 (51), 28220-28229, 10.1021/acs.jpcc.0c09448.
4. What is Electron Paramagnetic Electron Resonance? The Department of Radiation & Cellular Oncology | The University of Chicago, radonc.uchicago.edu/research/what-electron-paramagnetic-resonance.
5. Xingchen Ye, Jiayang Fei, Benjamin T. Diroll, Taejong Paik, and Christopher B. Murray. Expanding the spectral tunability of plasmonic resonances in doped metal-oxide nanocrystals through cooperative cation-anion codoping. Journal of the American Chemical Society, U.S. National Library of Medicine, pubmed.ncbi.nlm.nih.gov/25066599/.

Acknowledgments

NSF-DMR #1905757

Thank you to Dr. Geoffrey Strouse for giving me the opportunity to research in his lab.