Exploration of Plasmonic Copper-Based Nanocrystals Through Various Synthetic Methods

Jonathan B. Rider, Jason E. Kuszynski, Catherine J. Fabiano, Geoffrey F. Strouse
Department of Chemistry and Biochemistry, Florida State University

Introduction

Nanotechnology is a young field of research with applications in electronics, medicine, and energy. Plasmonic nanomaterials scatter and manipulate light in unique ways which make them apt candidates for improved sensors, catalysis, and numerous biotechnical devices. The study centered around two techniques- microwave reactor and round-bottom synthesis. The microwave reactor method involves irradiating the sample with microwave radiation at continuous wattage and programmed temperature, while round bottom uses a traditional, convection heat source with a thermocouple. The particles are cooled, rid of unwanted material, and vacuumed to yield solid nanocrystals. Spectroscopic techniques are then used to reveal the structural and energetic characteristics of the material. X-ray diffraction (XRD) identifies crystalline phases and serves as the initial indicator of synthetic success. Ultraviolet-Visible (UV-VIS) extinction spectroscopy then tests for the presence of a localized surface plasmon. If a plasmon is present, a large, broad extinction is observed.

Methods

Chemical Species:

– Copper (I) Acetate, Cu(OAc), 97%
– Copper (II) Acetylacetonate, $Cu(acac)_2$, 97%
– Chromium (III) Acetylacetonate, $Cr(acac)_3$, 97%
– 1-octadecene, ODE, 90%
– 1-dodecanethiol, DDT, 98%
– Oleylamine, OLAM, 70%

Round-Bottom Synthesis

1) Cu(OAc) and $Cr(acac)_3$ are added to a 50 mL round bottom flask with ODE at room temperature
2) DDT and OLAM are prepared as an injection in a separate vial
3) The solution is heated to 280°C under a nitrogen atmosphere
4) Injection occurs, flask contents are maintained at 280°C for 30 min
5) Particles are cleaned with strong solvents and centrifuged for 10 min

Microwave Reactor Synthesis

1) Cu(OAc) and $Cr(acac)_3$ are added to a microwave vial with ODE at room temperature
2a) For one-vial synthesis, DDT and OLAM are also added to the vial
2b) For injection synthesis, step 2 is completed as described above
3) The solution is placed in the microwave and irradiated with continuous power of 300 W for 10 min
 - For injection synthesis, injection occurs after the first 5 min
4) Particles are cleaned with strong solvents and centrifuged for 10 min

Setup

Figure I: Round-Bottom Flask Reactor
Middle Neck: Condenser
Right Neck: Thermocouple

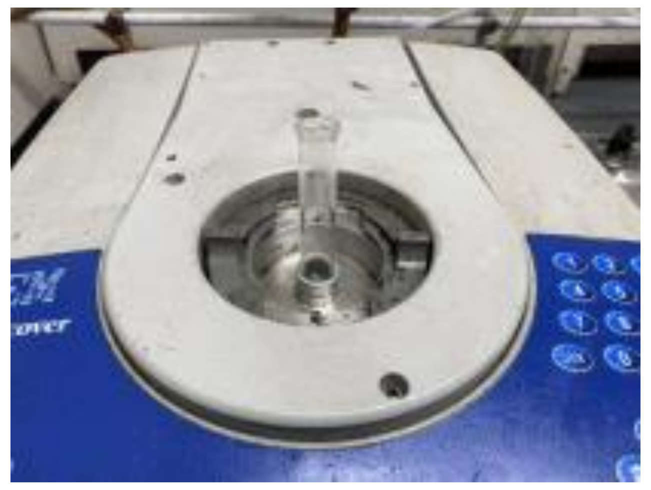

Figure II: CEM *Discover* Microwave Synthesis Reactor

Figure III: $Cu(acac)_2$, DDT, $Cr(acac)_3$ Microwave Vial

Figure IV:
Top: 3 mL Sulfur/OLAM Injection
Bottom: 1 mL DDT Injection

Results

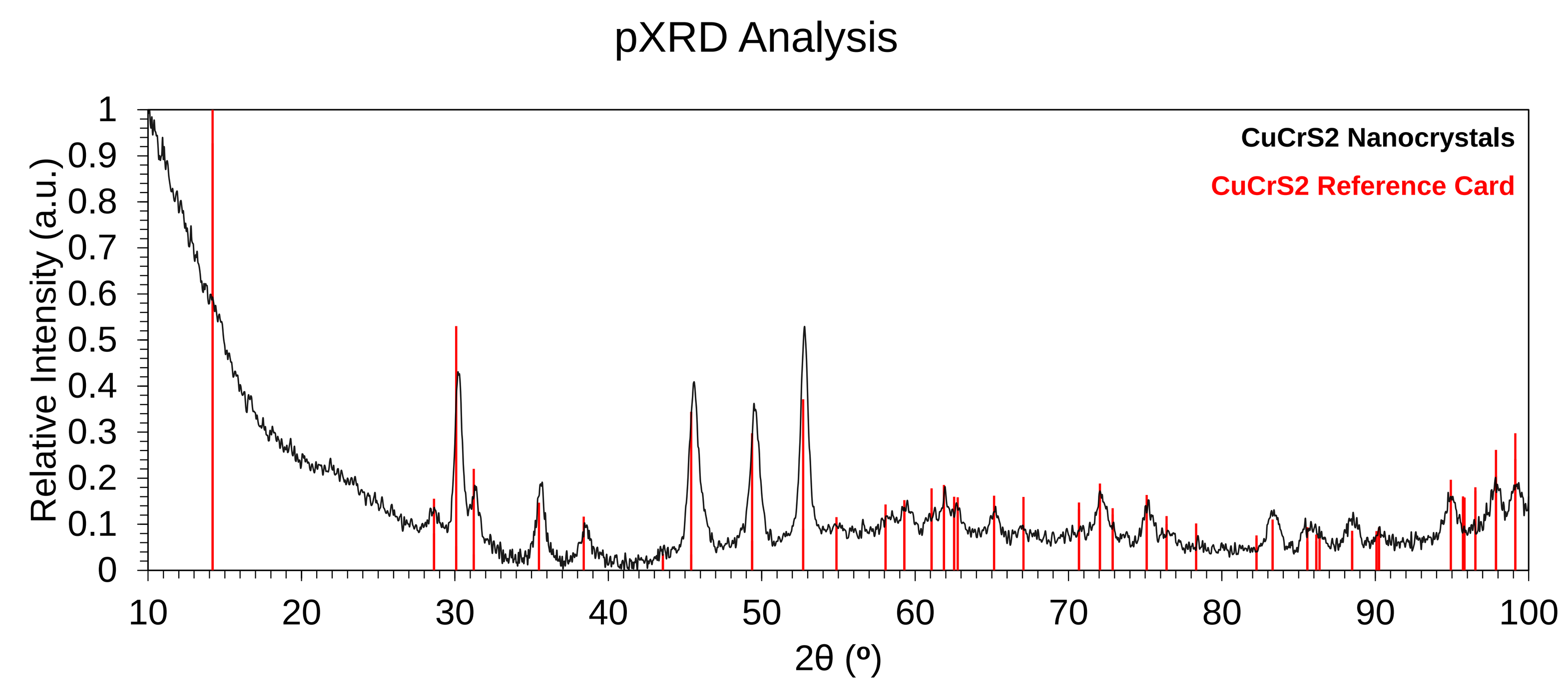

Figure V: pXRD Spectrum, $CuCrS_2$

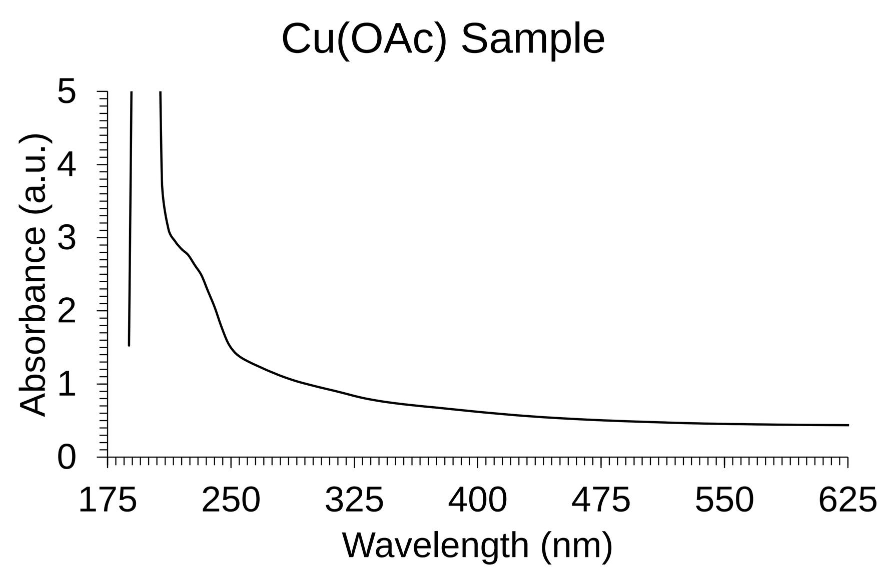

Figure VI: UV-VIS Spectrum, $CuCrS_2$ Prepared With Cu(OAc) Precursor

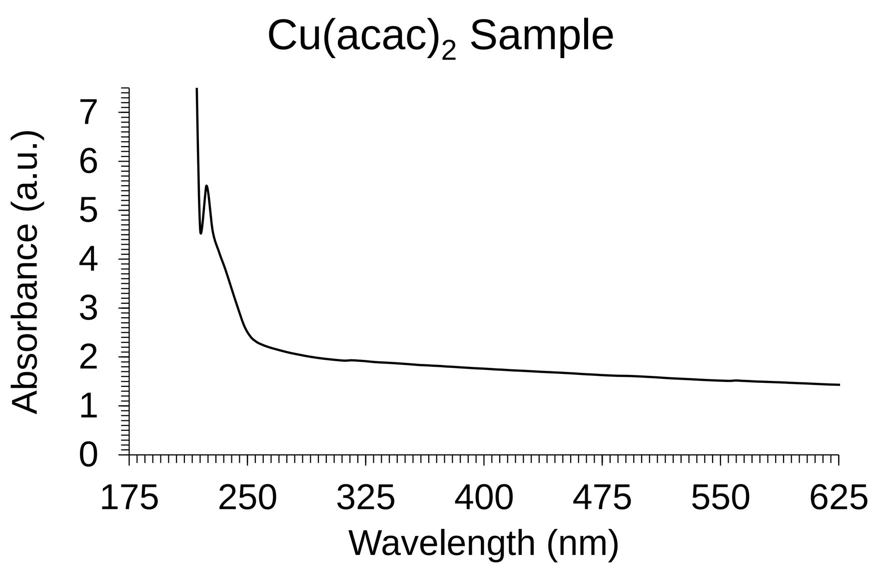

Figure VII: UV-VIS Spectrum, $CuCrS_2$ Prepared With $Cu(acac)_2$ Precursor

Discussion

The round bottom synthesis method was more effective than microwave methods in yielding nanocrystals with localized surface plasmons. XRD data confirmed both methods produced the desired Copper-based product, but preliminary UV-VIS data could only identify extinction characteristic of plasmonic behavior in the crystals made through the round bottom technique.

Changing the initial one-vial microwave technique to include a continuous injection drip appeared to help the reaction proceed to completion. Furthermore, heating the solid components of the reaction into solution before starting injection minimized the release of unwanted gaseous products like Sulfur.

Future work will be dedicated to studying different microwave methods and evaluating alternative copper precursors with the hope of consistently observing plasmonic behavior and tuning particle size.

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