Characterization of CdSe and CdTe nanocrystals by ICP-MS

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Introduction

Semiconductor Nanoparticles

- Have widespread applications in photovoltaics, thermoelectrics, nanoelectronics, biological imaging and catalytic materials

- Possess unique properties:
  - Small hydrodynamic radius
  - Variable surface functionality
  - Tunable bandgap emission
  - High surface-to-volume ratio

CdTe & CdSe Nanocrystals

- CdTe & CdSe, group II-IV semiconductors, have size-dependent band gap energy and can be easily studied across the visible region

Fluorescence of CdTe and CdSe nanocrystals

1. Bolotin, L.L.; Asunskis, DJ; Jawaid, A.M.; Liu, Y.; Snee, P.T.; Hanley, L. “Effects of Surface Chemistry on Nonlinear Absorption, Scattering, and Refraction of PbSe Nanocrystals.” Proc. SPIE 7935, 79350P, 2011
2. Asunskis, DJ; Bolotin, L.L.; Haley, J.E.; Urbas, A. Hanley, L. “Effects of Surface Chemistry on Nonlinear Absorption, Scattering, and Refraction of PbS Nanocrystals.” J.Phys. Chem. C (2009) 113:19824-19829.
3. Li, L.; Qian, H.; Fang, N.; Ren, J. Significant enhancement of the quantum yield of CdTe nanocrystals synthesized in aqueous phase by controlling the pH and concentrations of precursor solutions. *JOL* (2006) 116: 59-66.

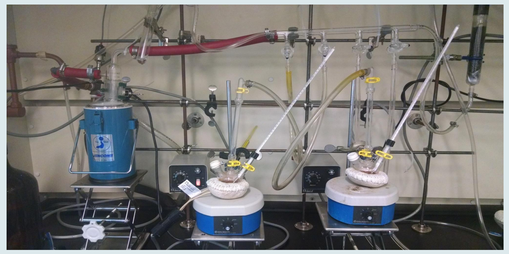
Purpose

The goal of this research is to characterize CdSe and CdTe nanocrystals by ICP-MS and evaluate their use for future cytotoxicity experiments.

Methods

Synthesis of Nanocrystals

- Cadmium oxide was reacted with oleic acid, 1-dodecanethiol, and 1-octadecene (under vacuum, ~85 °C) to create the metal precursor
- *n*-trioctylphosphine:selenide/tellurium was injected (under N_2 gas, between 200-250 °C) and reaction monitored for 10 min
- Nanocrystal formation verified by UV/VIS spectrometry



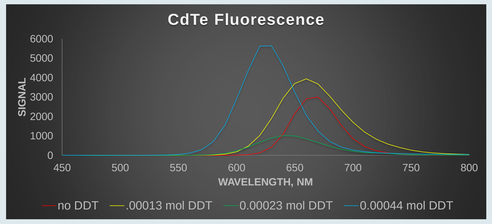
Analysis by Agilient 7900 ICP-MS

- Precipitation of nanocrystals by adding minimal amounts of 200 proof ethanol, centrifuging, and vacuum drying.
- EPA Method 3050 B: Acid Digestion of Sediments, Sludges, and Soils was followed:
  - Dried nanocrystals were re-dispersed in chloroform, transferred to digestion vessels, dried and weighed, and reacted with nitric acid overnight.
  - Nanocrystals were refluxed on a hotblock at 95 °C with additions of nitric acid and hydrogen peroxide, then serially diluted.

Results

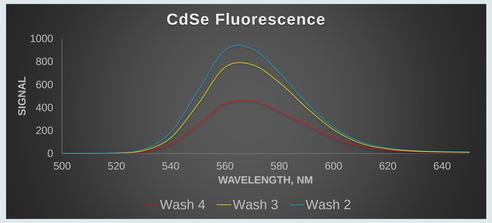
Optical Analysis

Effects of Varying 1-dodecanethiol (DDT)



Fluorescence spectra of CdTe nanocrystals collected at λ*= 680nm shows that increasing the concentration of 1-dodecanthiol (DDT) results in a blueshift.

Effects of Repeated Washing



Fluorescence spectra of CdSe nanocrystals collected at λ*= 680 nm shows that continual washing of CdSe nanocrystals reduced photoluminescence.

ICP-MS Analysis

Cadmium to Tellurium Ratio

Concentration of DDT, mol	Average Cd	Average % Te
0.00021	61 ± 3	39 ± 3

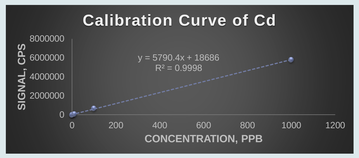
- Analysis of CdTe nanocrystals was impeded by several instrumental set-backs.

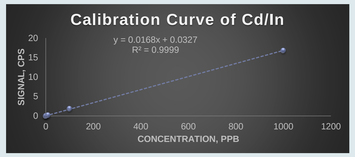
Cadmium to Selenium Ratio

Washes	Average % Cd	Average % Se
2	56.1 ± 0.5	43.9 ± 0.5
3	56.2 ± 0.7	43.8 ± 0.7
4	54 ± 2	46 ± 2

- As samples were washed, a decrease in the amount of cadmium was seen. This is a result of surfactant removal at the nanocrystal surface. As surfactants are removed, the Cd atoms which the surfactants were bound to are also removed. This leads to defects in the nanocrystal surface and loss of photoluminescence.

Method Validation





All calibration curves possessed R^2 values greater than or equal to 0.9998.

Element	Detection Limit, µg/L	% Spike Recovery
Cd	0.0416	93.5
Se	0.4414	101
Te	0.0045	95.8

Conclusion

Changing the concentration of 1-dodecanethiol (DDT) impacted the optical properties of the nanoparticles. Increasing the amount of DDT caused a decrease in the size of the nanocrystals, evident by a blueshift in the photoluminescence emission.

The ICP-MS data supported the optical results of the washed CdSe nanocrystals. The decrease in surface cadmium correlates with the loss of photoluminescence as defects in the nanocrystal surface increased. This phenomenon is most noticeable in the fourth wash where the amount of selenium was noticeably greater than the amount of cadmium.

Acknowledgements

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