Plasmonic Metal Oxide Nanocrystals

How a Semiconductor acts like a metal

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Defect Engineering

$V_{M/O}$

$M/O_i$

$M_{2M_1}$ (antisite)

carrier density

$n \sim 10^{19} - 10^{21}$ carriers / cm$^3$

MO$_x$

carrier type/ mass

$m^* \sim 0.01 - 2.0 m_e$

$^{113}$Cd

UV-VIS-NIR

EPR

NMR

NSF-DMR #1905757
Plasmonic $\text{MO}_x$ Semiconductor Nanocrystals

$\text{MO}_x$ carrier type/ mass
$m^* \sim 0.01 – 2.0 \text{e}$

Defect Engineering
$n \sim 10^{19} – 10^{21} \text{carriers/ cm}^3$

$V_{M/O_i}$
$M/O_i$
$M2_{M1}$

$\text{MO}_x$ carrier density

FLORIDA STATE UNIVERSITY

E

E_F

metal

semiconductor

insulator

CB

CB

VB

VB

VB

Au

CdSe

In_{2}O_{3}
THE RELATIVE SIZE OF PARTICLES

From the COVID-19 pandemic to the U.S. West Coast wildfires, some of the biggest threats now are also the most microscopic.

A particle needs to be 10 microns (µm) or less before it can be inhaled into your respiratory tract. But just how small are these specks?

Here's a look at the relative sizes of some familiar particles:

- CdSe 6nm
- Respiratory droplets 5-10 µm
- Dust particle (PM2.5) 2.5 µm
- Bacterium 1-3 µm
- Wildfire smoke 0.3-0.7 µm
- Coronavirus 0.1-0.5 µm
- Zika virus 0.045 µm

Wildfire smoke can persist in the air for several days, and even months.

Respiratory droplets have the potential to carry smaller particles within them, such as dust or coronavirus.

The visibility limits for what the naked eye can see hovers around 10-40 µm.

Band gap ($E_g$)

Conduction Band $\text{Cd}(s)$

Valence Band $\text{Se}(p)$

acceptor/holes

CdSe (wurtzite) $P_6\overline{3}mc$

Spin-orbit

Crystal field

$k$-space $0 (\Gamma) \rightarrow \pi/a (\chi)$

Energy $e^-$ $h^+$
LSPR Extinction Spectra for Au

Lycurgus cup, 5th century
Plasmons, Photons, and Permittivity, Oh my

**The Dielectric Function**

(relative permittivity)

\[
\varepsilon_r(\omega) = \varepsilon'_r(\omega) + i\varepsilon''_r(\omega)
\]

\(\varepsilon_r(\omega)\) describes the interactions of materials with applied electric fields.

\[
\varepsilon_r(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \quad \omega_p^2 = \frac{ne^2}{\varepsilon_0 m^*}
\]

Maximum extinction arises at maximum \(\varepsilon''_r\).

Here, a resonance condition is met

\[
\varepsilon_r(\omega) = \frac{\omega_p^2}{\omega^2 + i\omega\Gamma}
\]
Metals:
Localized Surface Plasmon Resonance (LSPR)

\[ d_{NC} \leq \frac{\lambda_{LSPR}}{20} \]

Nobel Metals (metallic)

Plasmons require carriers (or electrons) above the Fermi Energy Level.
Collective oscillation of free carriers at a plasma frequency, $\omega_p$.

Defect Engineering

$n$-type carrier density

$n \approx 10^{19} - 10^{21}$ carriers/cm$^3$

$n$-Sn$_x$:CdO ($V_o$)

$p$-pCu$_x$FeS$_4$ ($Cu_{Cu}$)

$p$-pCu$_x$FeS$_4$ ($Cu_{Cu}$)

$\omega_p \propto n^{1/2}$

$E_g \propto n^{2/3}$

Plasmonic Semiconductor Nanocrystals (PSNC)

n-WO$_{3-x}$ ($V_O$)

n-Cd$_2$SnO$_4$ (Sn$_{Cd}$)

n-Sn:CdO ($V_o$)
Conducting glass: an industrial standard

Indium-Tin Oxide

$n$-In$_2$O$_3$

ITO

$V_o$ and Sn$_{In}$ lead to n-doping
Materials Chemistry at the Boundary of Technology Discovery
Carrier Density, Effective Mass, and Nuclear Relaxation Pathways in Plasmonic SnIn$_2$O$_3$ Nanocrystals

Carl R. Conti III, Giovanni Quiróz-Delfi, Joanna S. Schwarck, Banghao Chen, and Geoffrey F. Strouse

The Drude Model

\[ \omega_p^2 = \frac{n e^2}{m^* \varepsilon_0} \]
Moss-Burstein ($E_g$)

\[
\Delta E_{\text{abs}} = E_{g}^{\text{Sn}} - E_{g}^{0} = \left(\frac{\hbar^2}{2m^*}\right)(3\pi^2 n)^{2/3}
\]

- Band edge (VB $\rightarrow$ CB)
- Plasmon
Can we see the effect of introducing carriers through defect engineering of Sn$_{\text{cd}}$ on ITO?

\[ \text{Spin-Echo Experiment} \]

Bruker AVIII HD 500 MHz WB NMR

\[ ^{119}\text{Sn} \text{ MAS Solid-State NMR} \]
\[ T_{1K}^{-1}(K, T) = \left( \frac{\gamma_n}{\gamma_e} \right)^2 \frac{4\pi K_B T}{h} K^2 \]

Knight-Korringa Relaxation Time

\[ \tau_{\text{Knight}} = \frac{\gamma_n}{\gamma_e} \frac{4\pi K_B T}{h} K^2 \]

\[ T_1, \tau_{\text{Knight}} \sim K^2, \gamma_n - \frac{1}{\gamma_e} \]

\[ \frac{\gamma_n}{\gamma_e} \frac{4\pi K_B T}{h} K^2 \]

\[ 6.3\% \text{ ITO} \]

\[ 231x293 \]

\[ 249x289 \]

\[ 244x301 \]

\[ 354x280 \]

\[ 383x320 \]

\[ 407x308 \]

\[ 419x280 \]

\[ 92x343 \]

\[ 119^{\text{Sn}} \text{ MAS ssNMR spin-echo} \]

\[ \text{Knight-Korringa} \]

\[ a. \]

\[ b. \]
The ternary Cd – Sn – O PSNCs and the impact of structure on plasmonic properties

- **Rock salt**
- **Sn(IV)**
- **Vo**
- Carriers increase with $x$
- CdO = 0.26$m_e$

\[ \text{Vo Driven} \quad O_o^x \leftrightarrow V_o^- + 2 \text{e}^- \]

- **Inverted spinel**
- **Sn(IV)**
- **Sn$_{Cd}$**
- Carriers increase with $x$
- Cd$_{1.86}$Sn$_{1.14}$O$_4$ = 0.022$m_e$

**Sn$_{Cd}$ Driven**


Xingchen Ye *Chem. Mater.*, 2021
(antisite) $M_1^{M_2}$

$\text{Cd}_{Cd}^x \leftrightarrow \text{Sn}_{Cd}^\cdot\cdot\cdot + 2e^-$

$\text{Cd}_{Cd}^x \leftrightarrow V_{Cd}^{\cdot\cdot\cdot} + 2h^+\text{Cd}_{Cd}^x$

$\text{Cd}_{Cd}^x \leftrightarrow C_d^{\cdot\cdot\cdot} + 2e^-\text{Cd}_{Cd}^x$

$\text{Cd}_{Cd}^x \leftrightarrow M_{O_{i}}$

$\text{Cd}_{Cd}^x \leftrightarrow M_{O_{i}}$

$\text{Cd}_{Cd}^x \leftrightarrow M_{O_{x}}$

$\text{Cd}_{Cd}^x \leftrightarrow M_{O_{x}}$

Defect Engineering

carrier density

$n \sim 10^{19} - 10^{21}$ carriers/cm$^3$

$V_{M/O_{x}}$

$M/O_{i}$

$M_{2M_{1}}$

carrier mass

$m^* \sim 0.01 - 2.0 m_e$
Sn: CdO
(V_0 carriers)
Rock salt

**VS.**

Cd₂SnO₄
(antisite carriers)
inverted spinel

Cd(acac)_2 + n SnF₂

Sn: CdO NCs (< 33% Sn)

Cd₂SnO₄ NCs (> 33% Sn)

oleic acid
octadecene
316 °C
70 mins


Rock Salt

Inverted spinel

\[ \text{Cd}_{2-x} \text{Sn}_{1+x} \text{O}_4 \]

\[ \text{Sn}_{\text{Cd}} \]

\[ \text{Cd}_{1.80} \text{Sn}_{1.20} \text{O}_4 \]  
(CTO)  
19 nm

\[ \text{Sn}(10\%) : \text{CdO} \]

21 nm

\[ \text{Cd}_2 \text{SnO}_4 \]

\[ \text{CdO} \]

\[ \text{Sn}_x : \text{CdO} \]

\[ \text{V}_\circ \]
\[ \omega_p = \left( \frac{n}{m^*} \right)^{1/2} \]

- \( \text{Cd}_{2-x}\text{Sn}_{1+x}\text{O}_4 \)
- \( \text{Sn}_{\text{Cd}} \)
- 16 nm
- 21 nm
- \( \text{Sn}_x:\text{CdO} \)
- \( V_0 \)
Cd₂SnO₄

- Raw Data
- Total Fit
- Corner
- Edge
- Face

Normalized Extinction

Frequency, $h\nu$ (cm⁻¹)

$\text{n} = 5 \times 10^{19}$ carriers/cm³

$m^*(\text{Lit}) = 0.022m_e$

10% Sn:CdO

- Raw Data
- Total Fit
- Corner
- Edge
- Face

Normalized Extinction

Frequency, $h\nu$ (cm⁻¹)

$n = 1.5 \times 10^{21}$ carriers/cm³

$m^* (\text{Lit}) = 0.26m_e$
$^{113}\text{Cd}$ solid state NMR to probe site dependent effect in Sn:$\text{CdO}$ vs. CTO

$^{113}\text{Cd}$ of 10% Sn:$\text{CdO}$ PSNCs collected using a WURST-CPMG pulse sequence

$^{113}\text{Cd}$ of CTO PSNCs collected using a WURST-CPMG pulse sequence

ppm
Are the carrier parentage really different?

Electron Paramagnetic Resonance (EPR)

\[ g_{iso} = g_e - \frac{2 |\lambda|}{\sqrt{\lambda^2 + \Delta^2}} \]

\( \lambda \) = spin-orbit coupling
\( \Delta \) = crystal field

\[ \Delta E = h\nu = g\mu_B B \]

\( V_0 \)

(antisite) Sn\textsubscript{Cd}

\[ g_{value} = g_e - \lambda^2 + \Delta^2 \]
Identifying the defect type by EPR

Sn(10%):CdO

\[ g(O_h) \sim 2.005 \]

Cd\textsubscript{2}SnO\textsubscript{4}

\[ g \sim 2.001 \]

CdO  Liu, Z. et al., ACS Nano., 2020

ZnO  Ayoub, I. et al., Nanotechnol. Rev., 2022
Can we increase carrier densities by removal of $V_o$ (Oxygen vacancy) by active etching using SnF$_2$ as reactant instead of Sn(acac)$_2$?
\[ \omega_p^2 = \frac{ne^2}{m^* \varepsilon_0} = \frac{n}{m^*} C \]

**LSPR**

- **F-CTO (Cd_{1.8}Sn_{1.2}O_4)**
- **a-CTO (Cd_{1.86}Sn_{1.14}O_4)**

**Normalized Extinction**

- **Frequency, \( h\nu \) (cm\(^{-1}\))**
- **Raw Data**
- **Total Fit**
- **Corner**
- **Edge**
- **Face**

**Aspect ratio**:
- **1.22**
- **19 x 14 nm**
- **n = 2 x 10^{19} carriers/cm^3**

- **1.36**
- **22 x 18 nm**
- **n = 5 x 10^{19} carriers/cm^3**
Does EPR help us understand?

EPR confirms lower $V_o$ for F-CTO, but why no increase in $n$?
**113Cd – WURST**

- $B_0 = 18.8$ T
- $\nu_0 = 177.371$ MHz
- $\nu_{\text{rot}} = \text{static}$
- $D1 = 6$ sec
- $D6 = 100$ $\mu$s
- 50 Echoes
- WURST SWEEPT = 600 kHz
- 4096 scans (7 hours)

**FCTO**
- $\Gamma(\text{KS}) = 450$ KHz
- $2.0 \times 10^{19}$
- 6% $V_0$

**a-CTO**
- $\Gamma = 300$ KHz
- $5 \times 10^{19}$
- 27% $V_0$

Observe a large increase in Knight Shift (KS)

$KS \propto n^{1/3}$

FCTO has lower carrier density but also lower $V_0$

Slower relaxation, $T_1$

Knight-Korringa
But are we sure it's KS and not CS?

KS frequency shift will be dependent on applied field.
Can we prove it by chemically removing carriers in CTO using the 1-electron oxidant NOBF₄?

\[ \omega_p^2 = \frac{n}{m^*} - C \]

\( y = -0.0051x + 0.5607 \)
\( R^2 = 0.99 \)
Can we be sure it is KS and not CS?

F-CTO Titrated with NOBF$_4$

Spectral change suggests shift arises from metallic like carriers (Knight shift) since CS is site dependent

$KS \propto n^{1/3}$
VT, VH-MCD Experiment

IR Lamp Source
Mechanical Chopper
Linear Polarizer
PEM
Cryostat

$v_L = 211$ Hz
$v_H = 42$ kHz

$B$ to Lock-ins

10 T Cryostat Magnet

Detector
Magnetic Circular Dichroism (MCD)

Extraction of $m^*$

Cyclotron resonance

$$\omega_c = \frac{qB}{m^*m_e}$$

Circularly Polarized Light

$\omega_{\text{circular}} = 0.5\omega_{\text{linear}}$

Zeeman splitting:

$$E_{\text{Zeeman}} = \sigma B^{\text{RCP}} - \sigma B^{\text{LCP}}$$

Is this a question of trapping at donor levels due to $V_o$?

Then it should be reported as a change in $m^*$ measured by MCD

$$m^* = \frac{qBc}{2\pi(E_{Zeeman})m_e}$$

$$\omega^LCP/RCP_B = \omega_0 \pm \frac{qB}{2m^*}$$

$0.022 \text{ m* for a-CTO}$

$0.006 \text{ m* for F-CTO}$
It will also show up in the LSPR Relaxation Processes
Cd$_2$SnO$_4$ fs-TA Data

<table>
<thead>
<tr>
<th>LSPR Pump</th>
<th>Decay (fs)</th>
<th>Decay (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnAc$_2$</td>
<td>184.0 ± 5.8</td>
<td>27.19 ± 3.95</td>
</tr>
<tr>
<td>SnF$_2$</td>
<td>192.2 ± 6.4</td>
<td>99.51 ± 53.51</td>
</tr>
</tbody>
</table>

350 nm Probe (0.99+ R$^2$ Fits)

SnAc$_2$ 1400 nm Pump, Vis Probe

- a-CTO (5 x 10$^{19}$)
- 26% $V_o$

SnF$_2$ 1400 nm Pump, Vis Probe

- F-CTO (2 x 10$^{19}$)
- 6% $V_o$
Does carrier parentage matter?

- Sn\text{cd} or V\text{O} results in change in carrier mobility
  - (XPS, XSTM, TA, NMR and EPR T\text{1} and T\text{2})
- Site and lattice matter (lattice energies) – DFT
- Impacts w\text{d} – surface interface damping
- Impacts LSPR damping/ hot carrier formation

- Way more to do to fully understand carrier parentage in a PSNC shape, concentration, chemical interface damping, T-dependence,