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Tailored Growth of Nanostructured Cadmium Sulfide Thin Films

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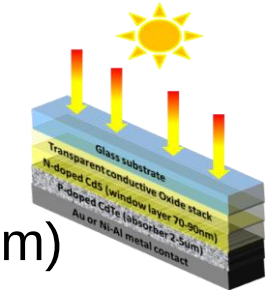
Materials Selection: CdS



Cadmium sulfide (CdS)

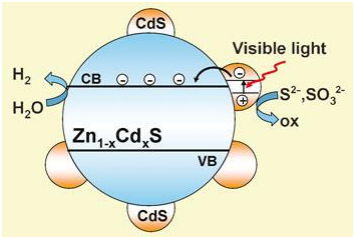
Band gap: E_g = 2.4-2.5 eV (absorbs UV to ~500nm)

Crystallographic polymorphs:

- Hexagonal (a = 0.413 nm, c = 0.671 nm)
- Cubic (a = 0.583 nm)

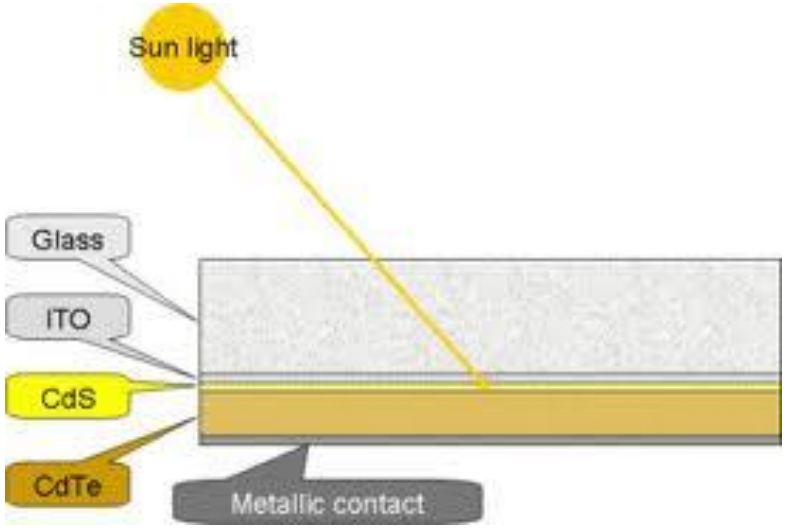
Applications:

- Photocatalyst
- Photoresistors
- Pigments (Van Gogh, Monet, Matisse)
- Photovoltaics
  - CIGS
  - InP
  - CdTe*

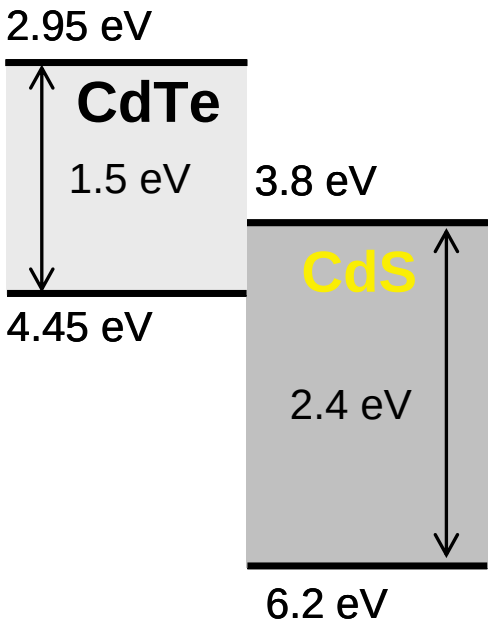


CdS in CdTe Solar Cells

- CdTe/CdS have been identified as among the most promising systems in the drive for $1/Watt solar power:
  - CdTe has excellent band gap for solar absorption (~1.5 eV)
  - Relies on n-CdS/p-CdTe heterojunction
  - Light is absorbed by the CdTe layer, and photogenerated excitons are are separated into electrons and holes at the CdTe/CdS interface.
  - CdS (~2.4eV) layer then serves as the electron transport layer in the device.

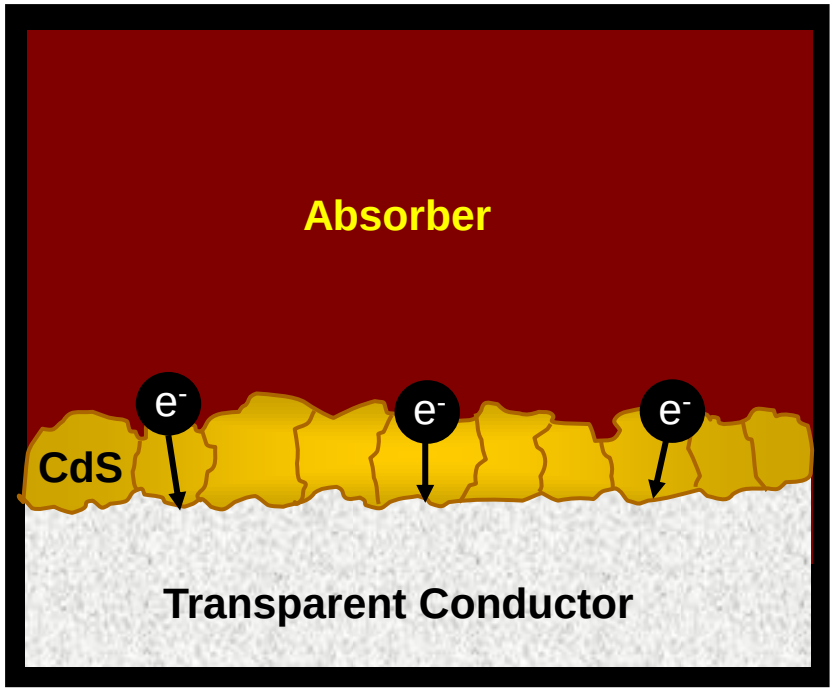


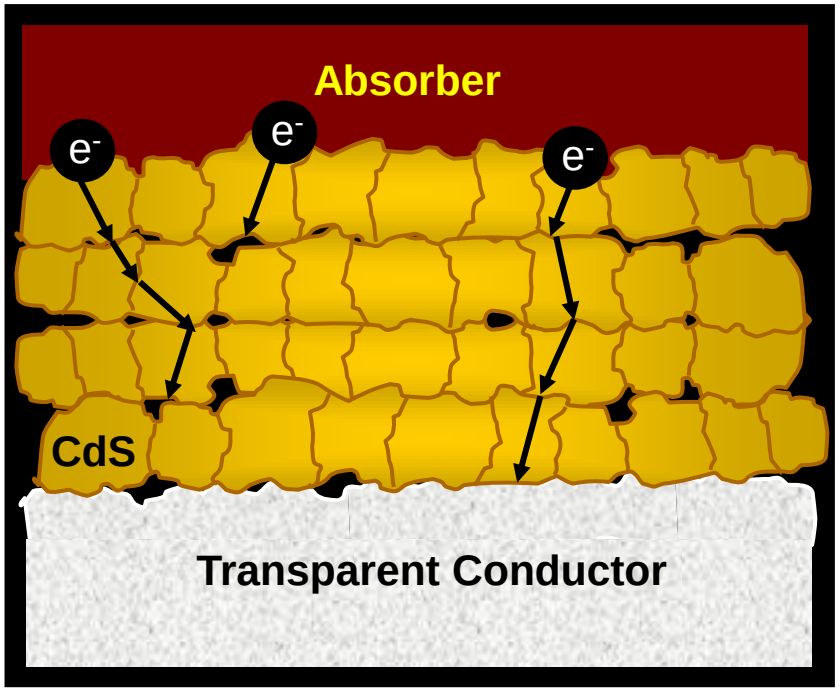
Schematic of CdTe/CdS solar cell

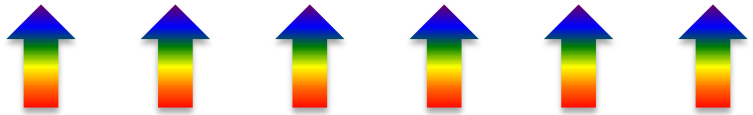


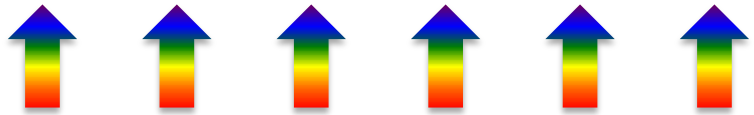
CdS Thickness is Critical

CdS thickness and density affect both light transmission and charge transport.





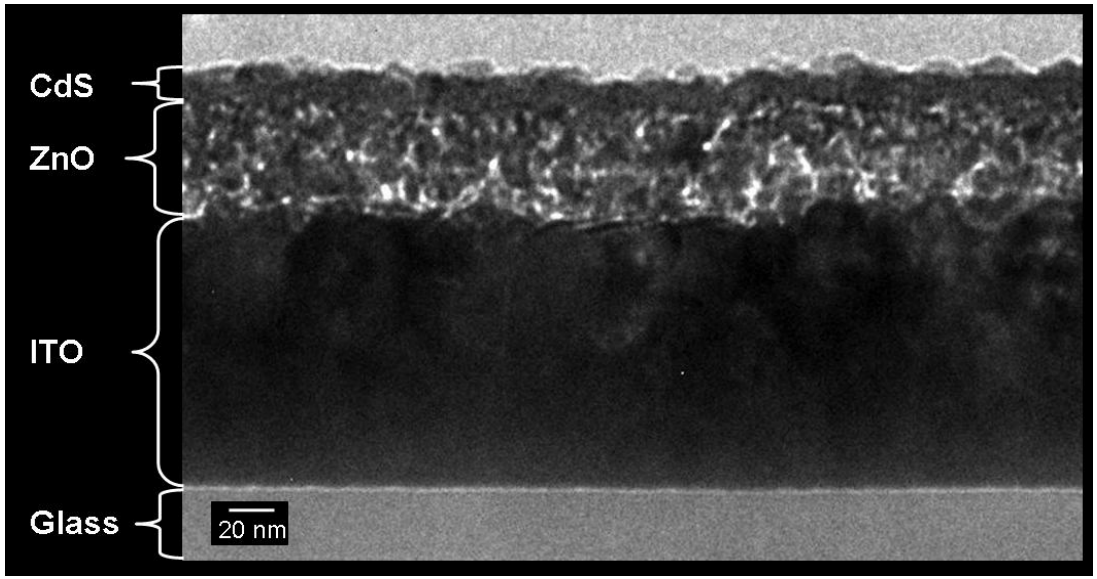




Nanocrystal Layer Deposition (NCLD) of CdS on ZnO

Room temperature, aqueous synthesis

$$CH_3C(S)NH_2 + Cd(OH)_2 \longrightarrow CH_3C(O)NH_2 + CdS + H_2O$$

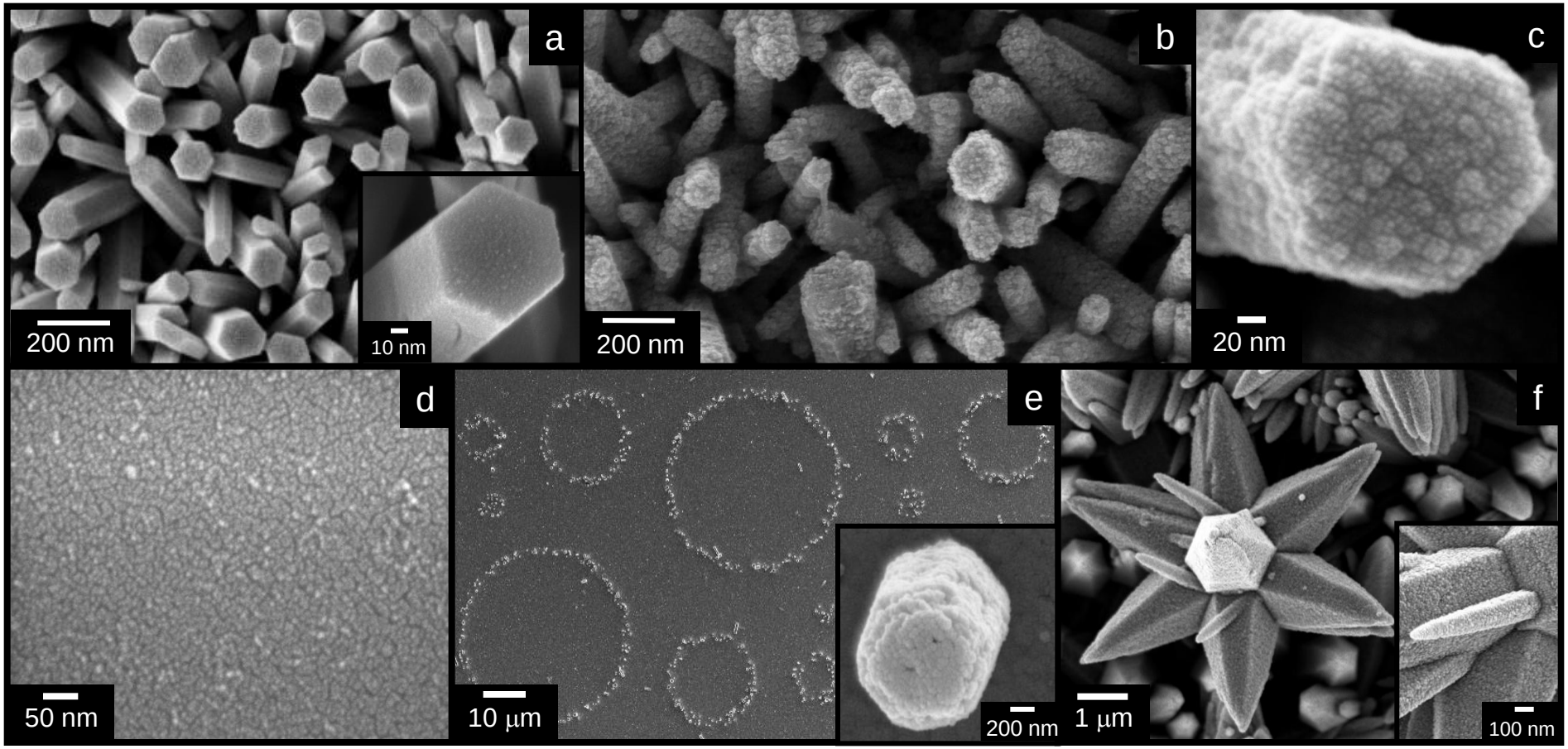


NCLD grows a thin (~10-20 nm), dense film of CdS on ZnO surfaces.

Spoerke, et al. J. Phys. Chem. C. 113, 16329 (2009)

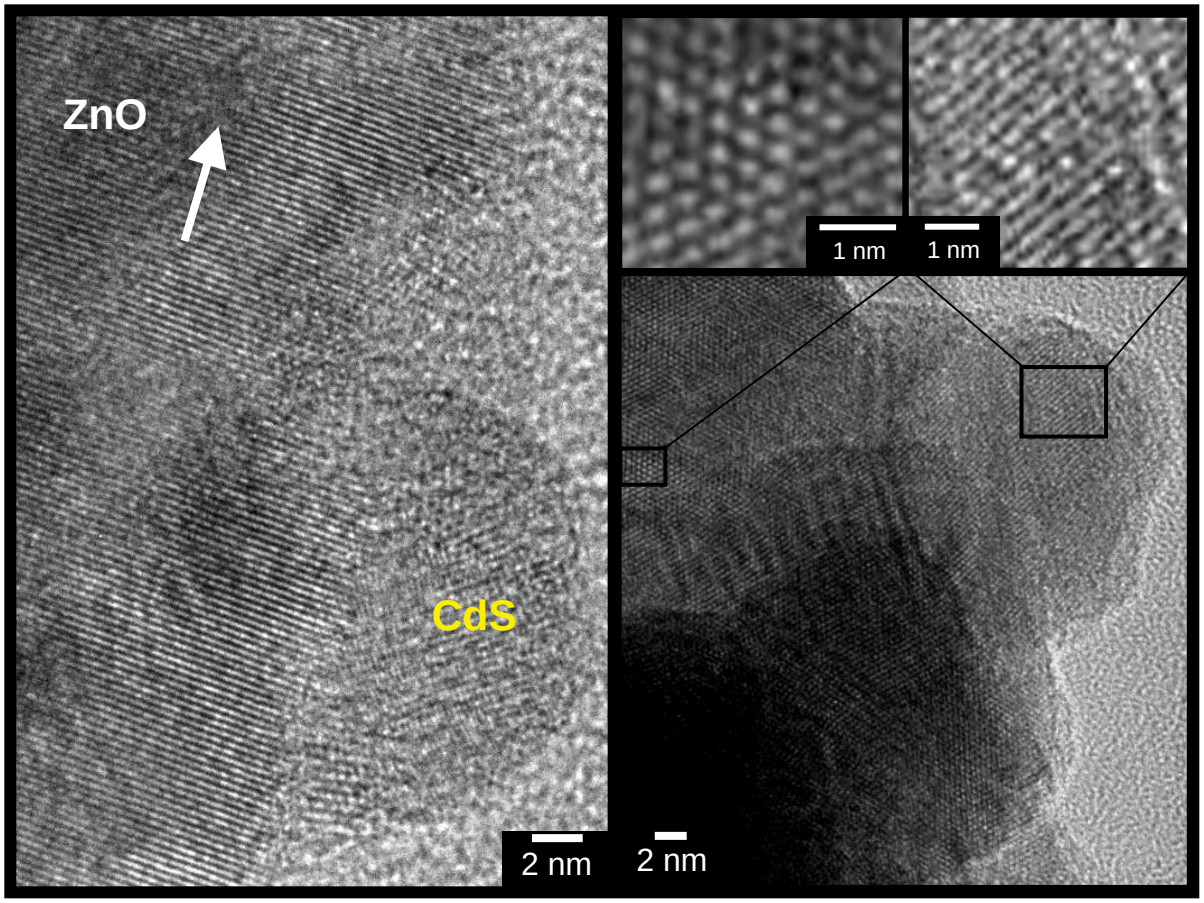
Nanocrystal Layer Deposition (NCLD) of CdS on ZnO

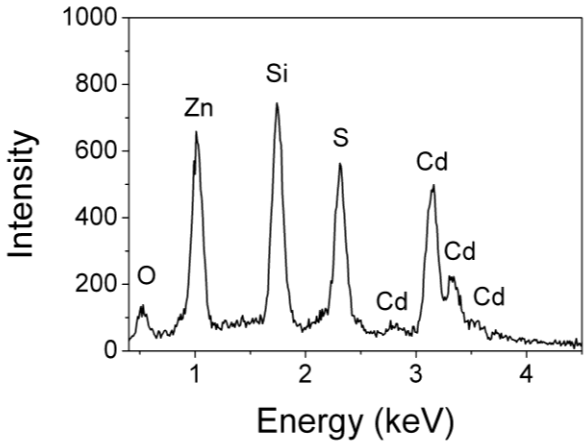
NCLD can be used to grow thin, conformal CdS on a variety of nanostructures

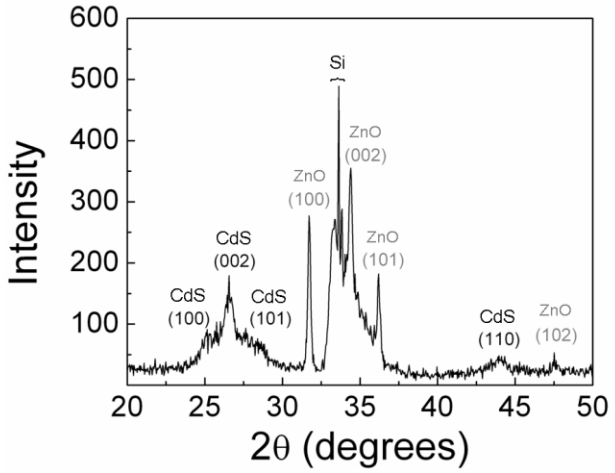


CdS Thin Film Characterization

Detailed characterization confirms the crystallography and composition of the ZnO/CdS nanocomposites

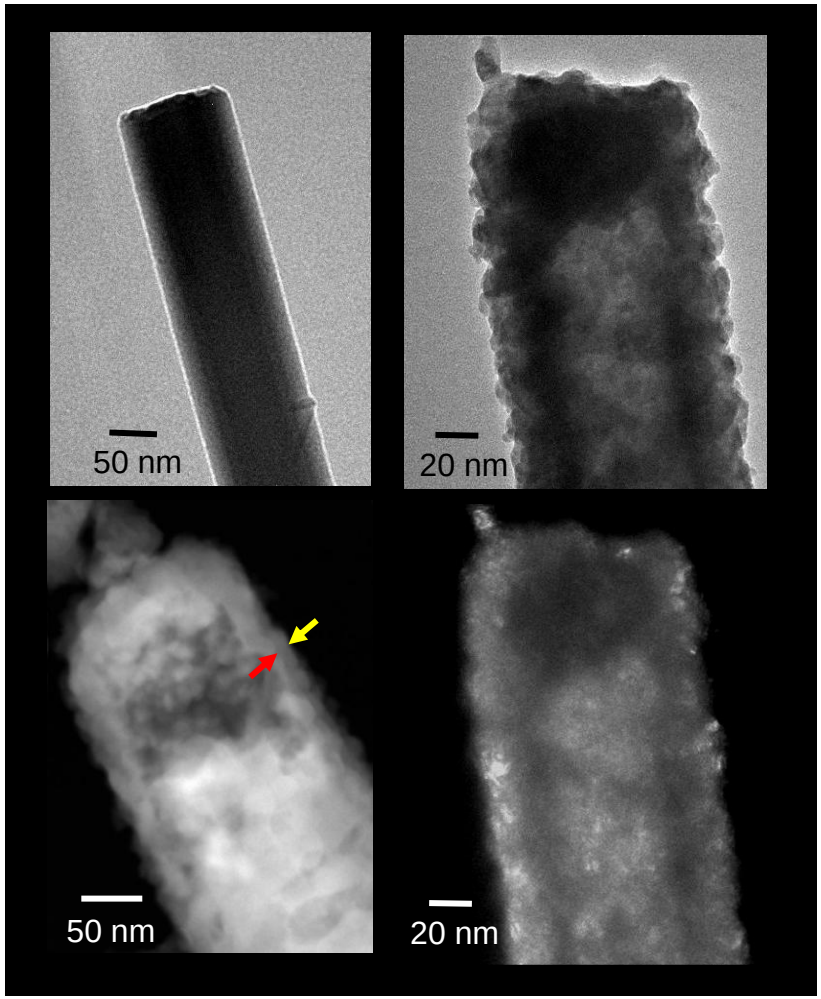




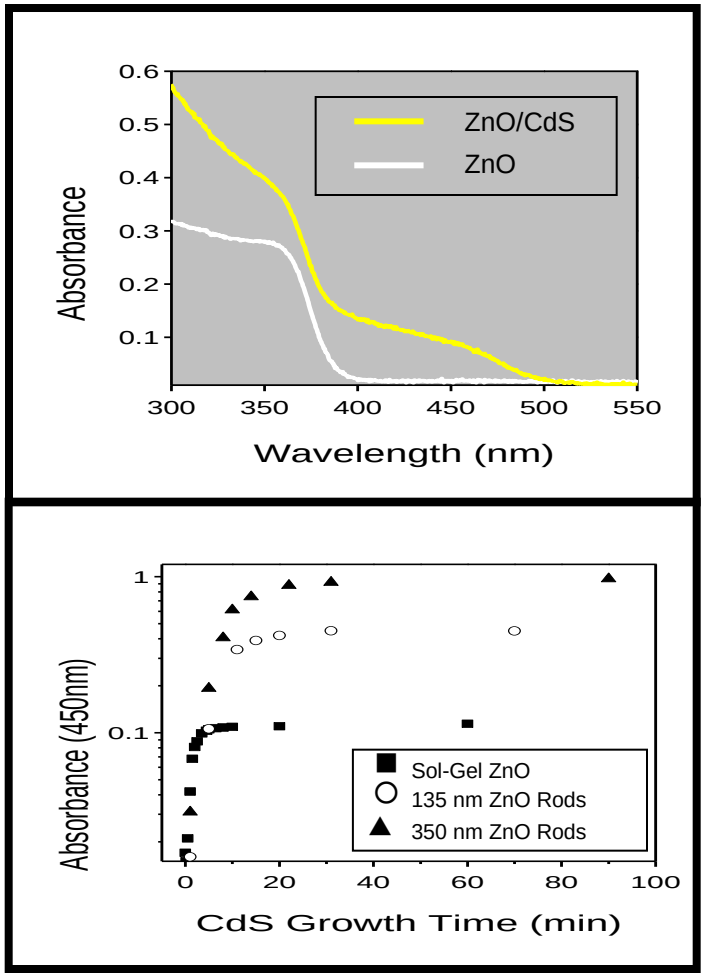


Templated CdS Nucleation and Growth

Nanocrystalline CdS layer is only ~10-20 nm thick

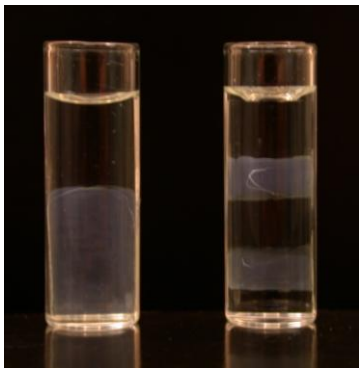


CdS growth is *self-limiting!*



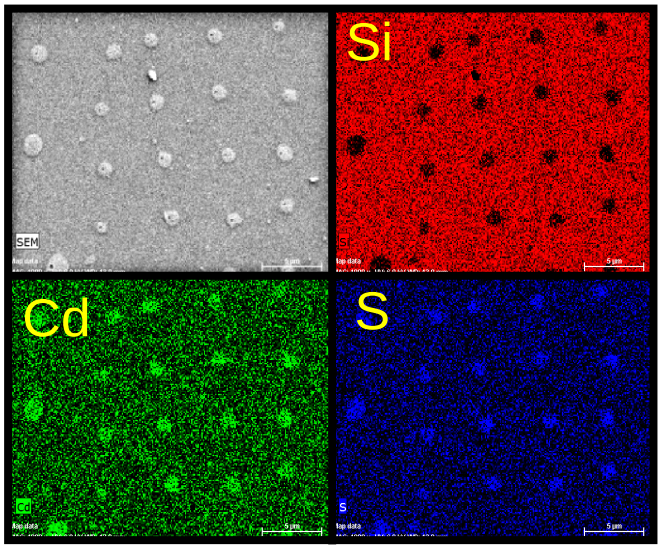
Selective CdS Growth

CdS growth on ZnO is selective on both macro- and microscales

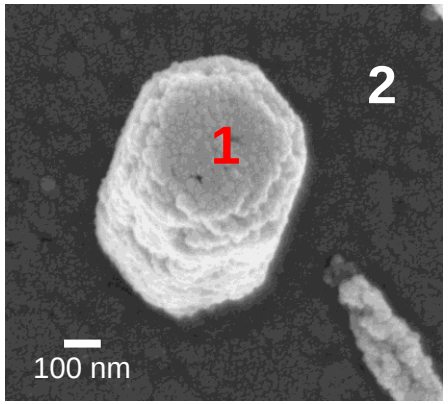


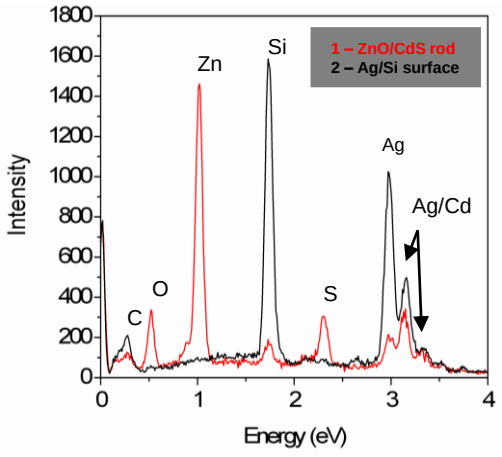
ZnO coated on glass slides at t_0 in CdS reaction solution.

CdS (yellow) selectively grown on ZnO-covered regions after 10 minutes growth.



Stamped “micro-dots” of ZnO produce selective CdS growth





ZnO nanorods on Ag selectively template CdS

The Mechanism of NCLD

Why is CdS Selective for ZnO Surfaces?

At pH 5.5

- Very few cadmium hydroxide species
- ZnO will be heavily decorated with bridging hydroxyls

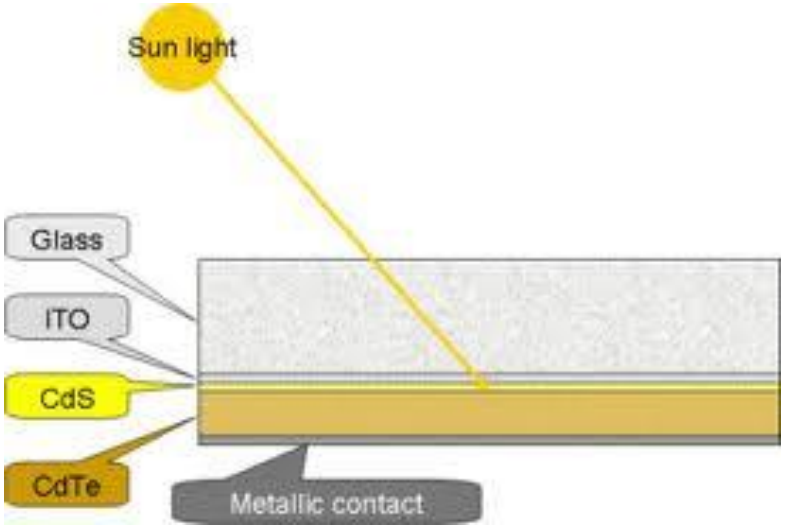
$$CH_3C(S)NH_2 + Cd(OH)_2 \longrightarrow CH_3C(O)NH_2 + CdS + H_2O$$

$$CH_3C(S)NH_2 + Zn(OH)_2 \longrightarrow CH_3C(O)NH_2 + ZnS + H_2O$$

ZnO will bind cadmium ions, forming activated $Cd(OH)_x$ complexes capable of nucleating CdS directly on ZnO surface!

Alternative Oxide Templates

Will CdS grow on other basic oxides?

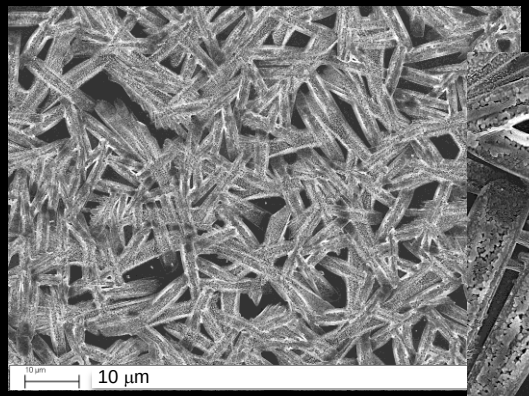


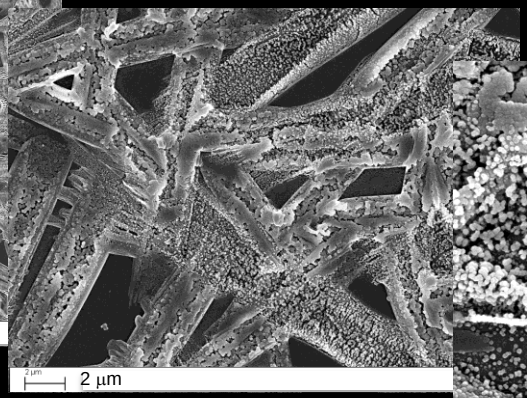
Schematic of CdTe/CdS solar cell

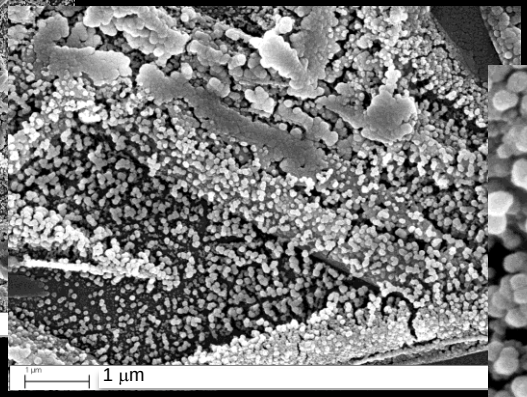
Consider MgO

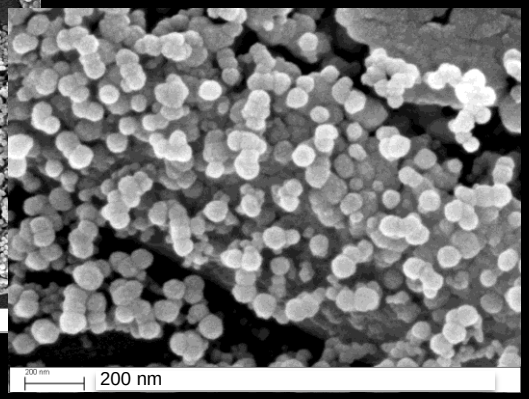
MgO-Templating of CdS

MgO sol-gel

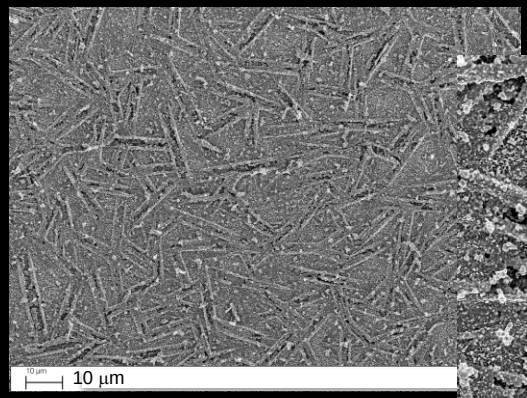


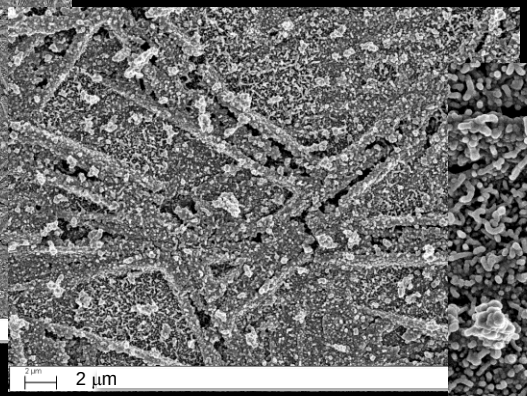


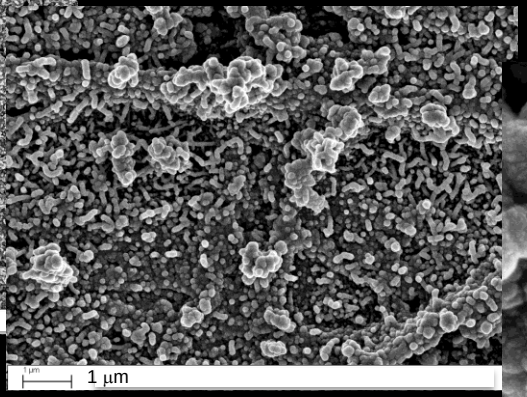


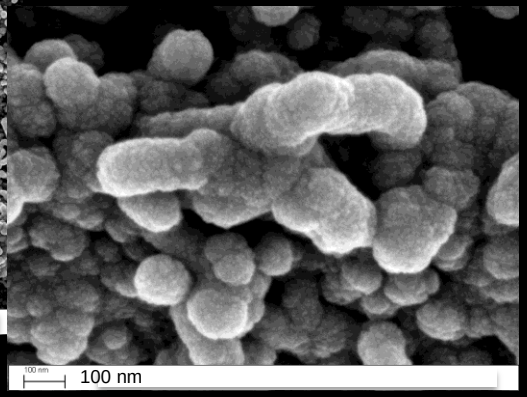


MgO-CdS



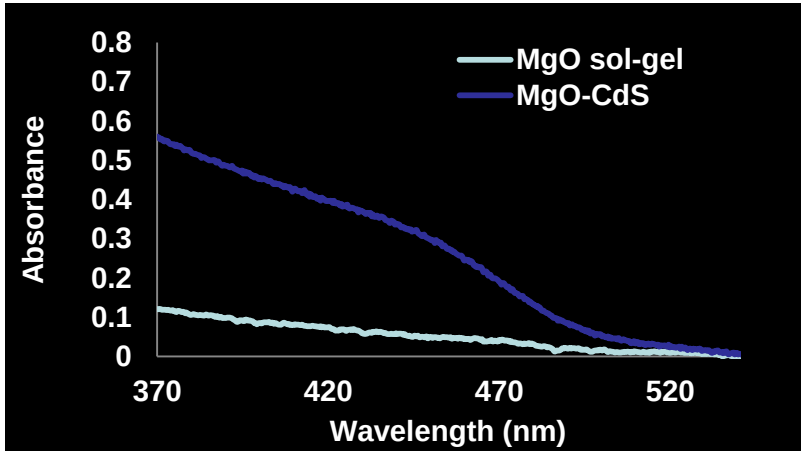


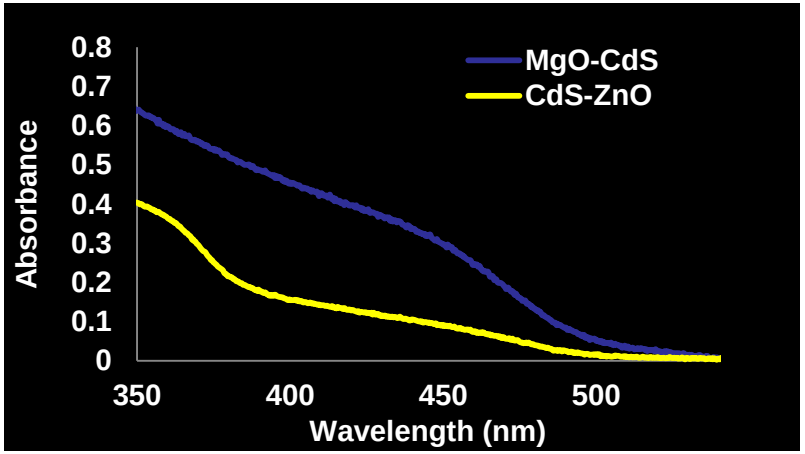


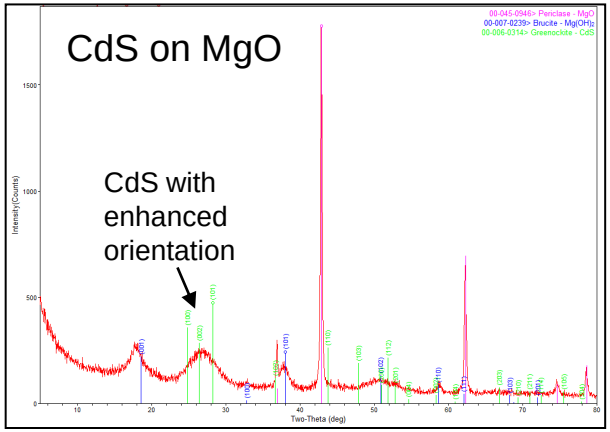


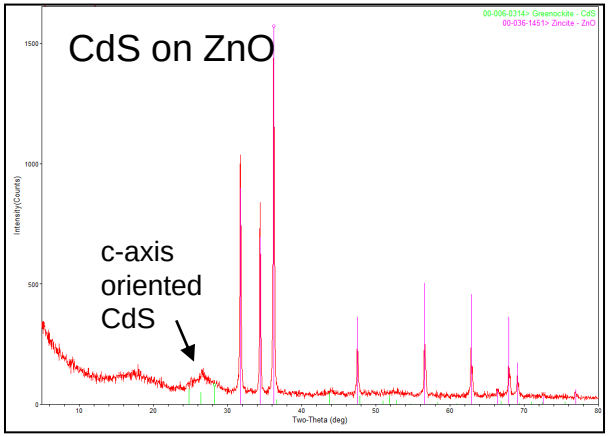
MgO-Templating of CdS

Compared to ZnO, MgO templates CdS with the same band gap, but measurably thicker.



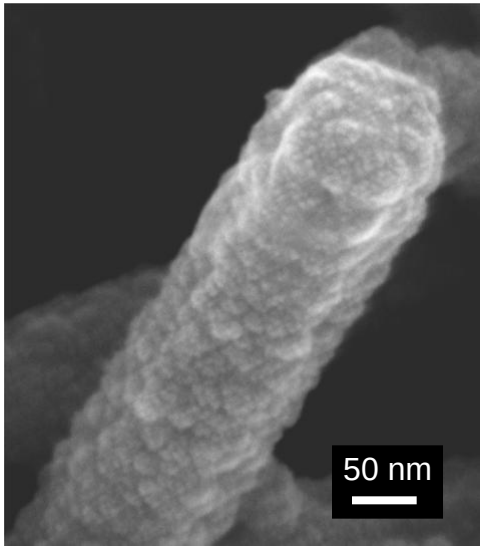




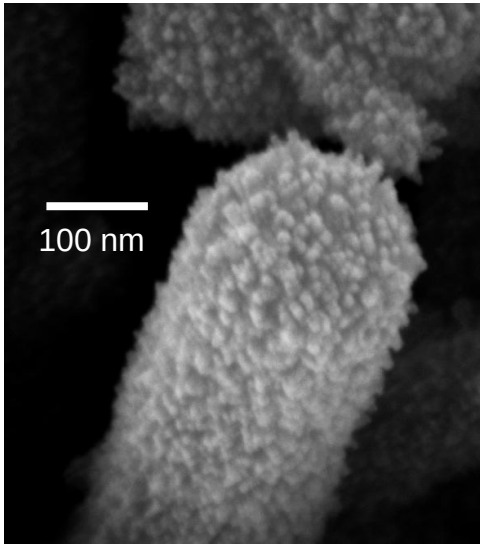


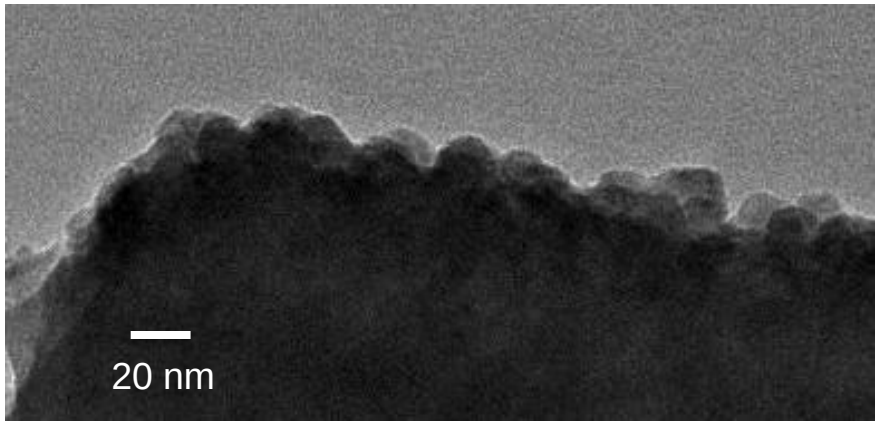
MgO-templated CdS shows enhanced (002) crystallographic orientation

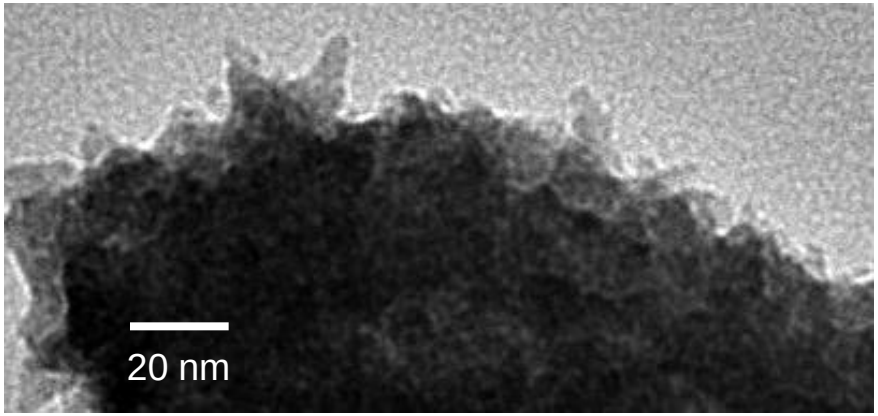
Organic Crystal Growth Modifiers



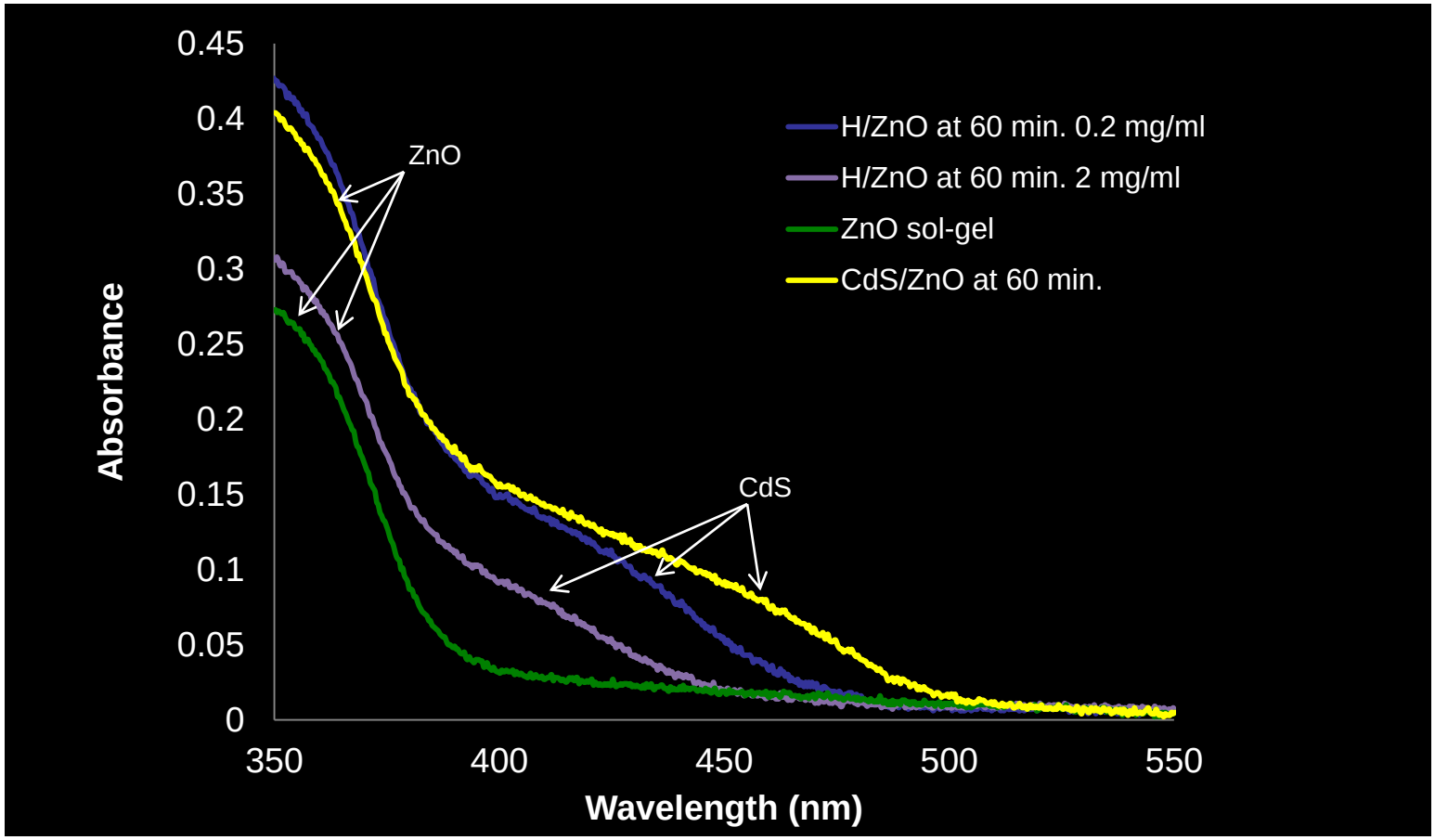
Introducing amino acids (e.g. histidine) to the crystal growth reaction dramatically changes the CdS nanocrystalline morphology.







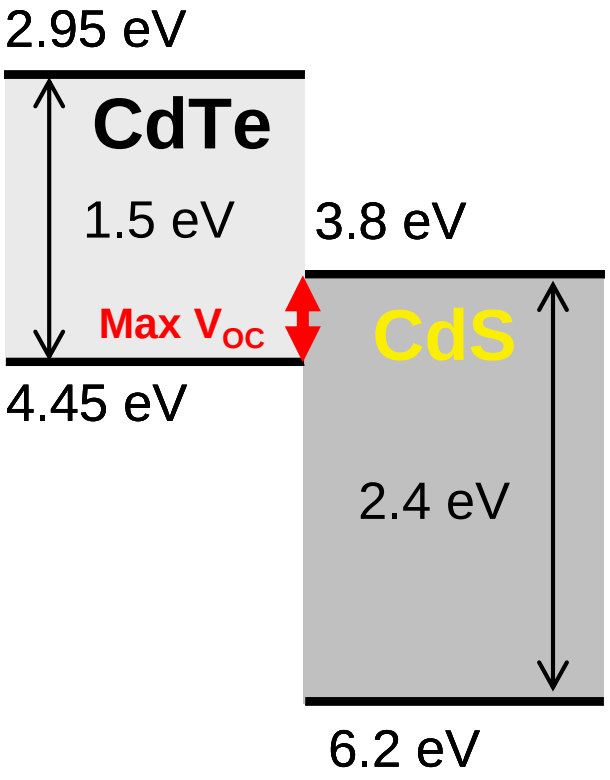
Histidine Influence on Optoelectronics



Incorporation of histidine into CdS growth results in a dramatic blue shift in absorbance. This effect reduces parasitic absorbance and E_g increases by ~ 0.3 eV!

Band Gap Influence on PV Efficiency

Device Efficiency Depends Strongly on the Open Circuit Voltage (V_{OC}).



$$\eta \propto V_{OC}$$

Increasing the band gap of CdS could increase V_{OC}

Summary

NanoCrystal Layer Deposition (NCLD)

- Room temperature, aqueous synthesis
- Self-initiated, self-limited growth process
- Thin, dense, conformal nanocrystalline coating
- Selective for basic oxides (ZnO, MgO)
- CdS growth can be influenced by the templating oxide
- Organic modifiers (e.g. Histidine) modify the nanoscale morphology and optoelectronic properties of the CdS films

Integrating solution-phase chemistry with surface-templating processes can be used to tailor nanocrystalline thin film growth.

Thanks

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