Molecular-Scale Processes Involving Nanoparticulate Minerals in Biogeochemical Systems

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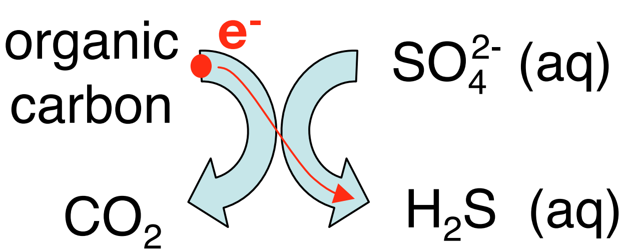
Overview

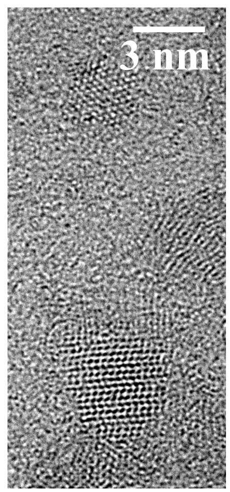
- Sources of environmental nanoparticles
  - Biological & abiotic pathways
- Properties of mineral nanoparticles
  - Size effects on reactivity
- Geochemical cycles
  - Photochemical reactions — sulfides
  - Surface-mediated reactions — oxides
  - Biomolecule - nanoparticle interactions — oxides
- Conclusions & Outlook

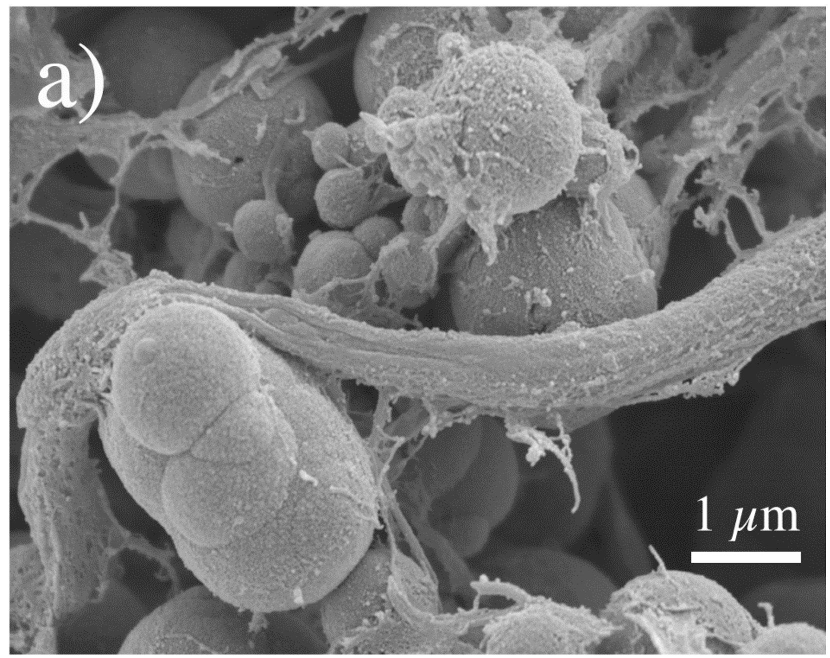
Examples of biogenic nanoparticles

- Sulfate reducing bacteria
  - metabolic energy generation
  - d ≈ 2 - 10 nm



ZnS nanoparticles





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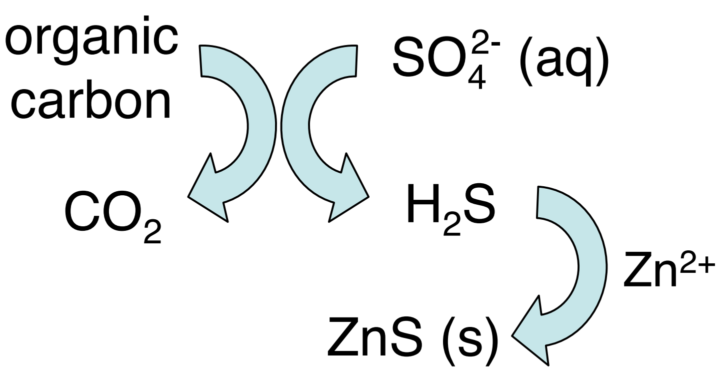

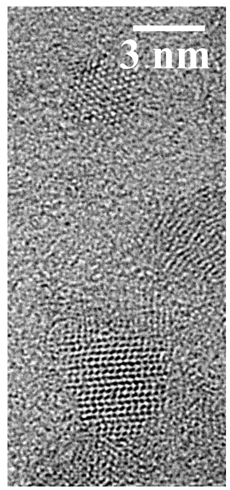

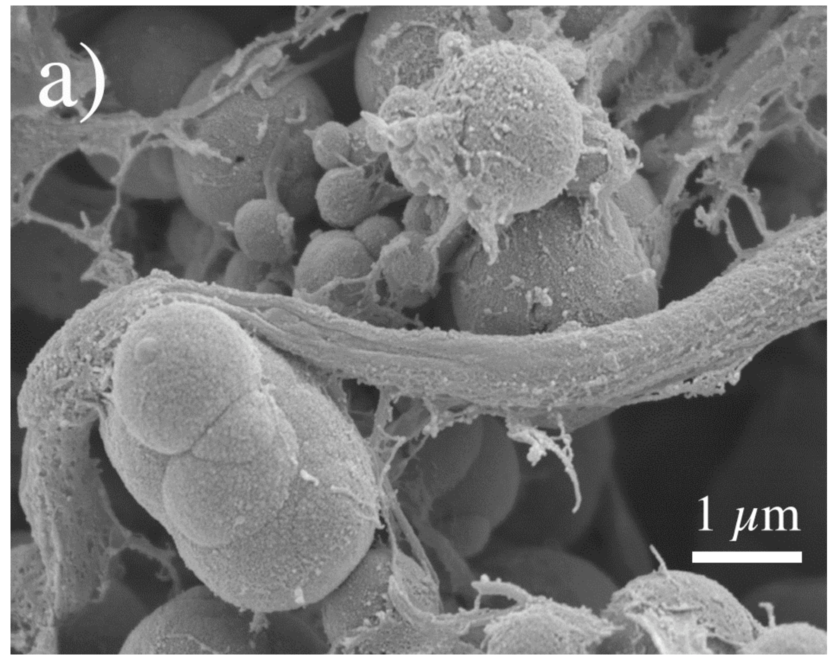

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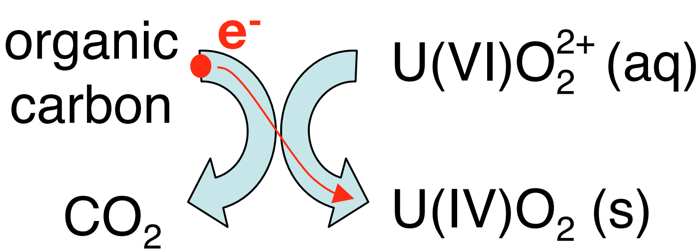
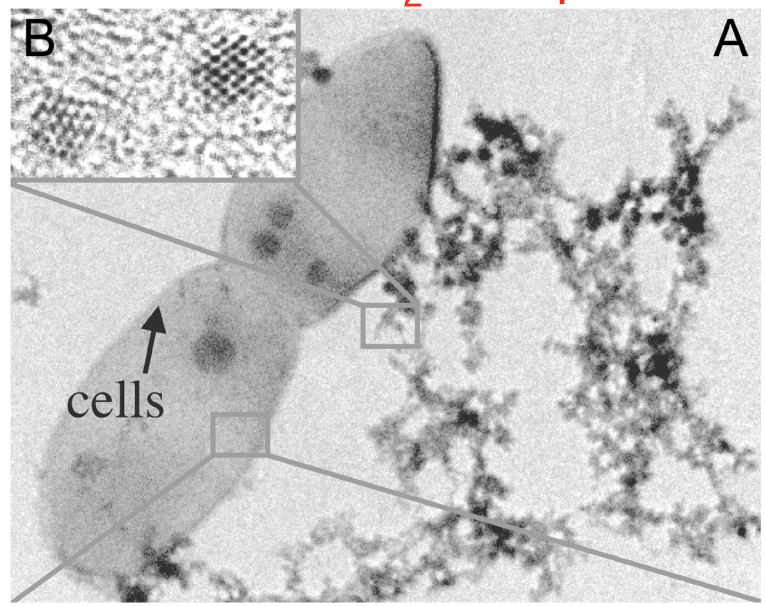
Examples of biogenic nanoparticles

- Sulfate reducing bacteria
  - co-metabolic process
  - d ≈ 1 - 5 nm



UO_2 nanoparticles



Suzuki et al.,
Nature **419**, 134 (2002)

Examples of biogenic nanoparticles

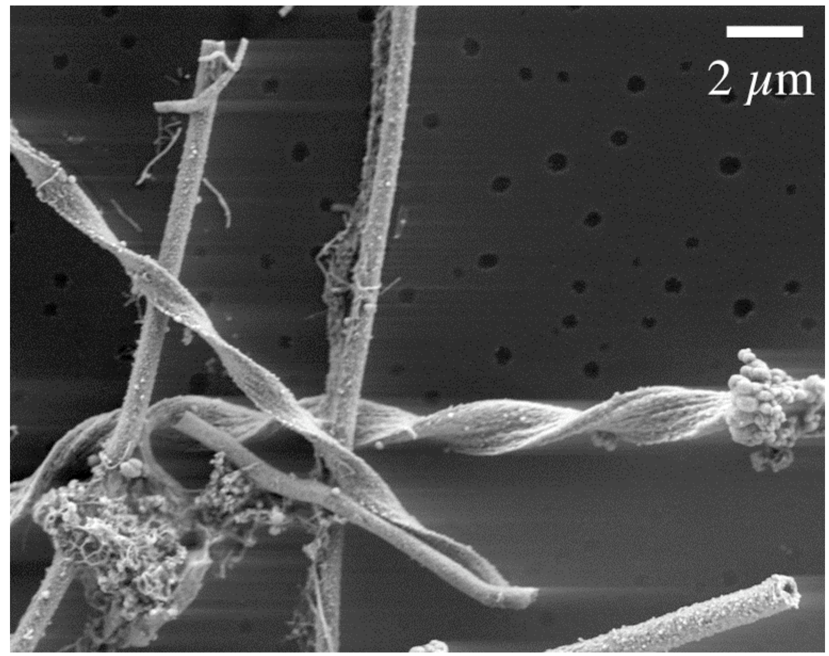
- Iron oxidation
  - energy generation
  - d ≈ 3 nm

enzyme

Fe^{2+} (aq) + O_2 + H_2O

Fe(III)OOH (s)

FeOOH nanoparticles



Chan, De Stasio et al.,
Science **303**, … (2004)

Examples of biogenic nanoparticles

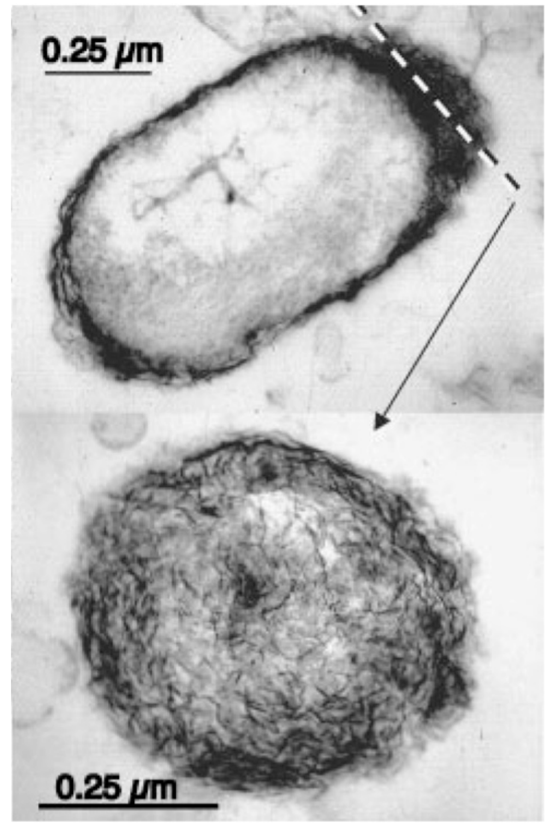
- Manganese oxidizing bacteria
  - enzymatic oxidation
  - d ≈ few nm

enzyme

Mn^{2+} (aq) + O_2 + H_2O

MnO_2 (s)

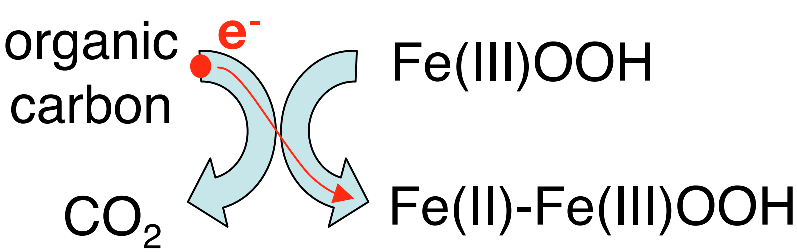
MnO_2 & MnOOH nanoparticles



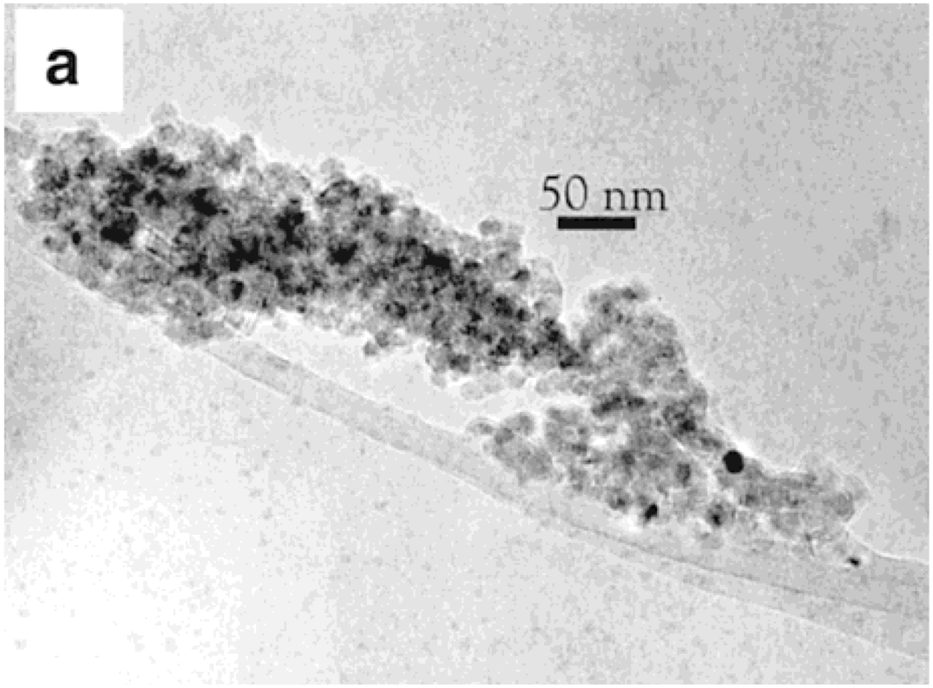
Tebo et al., *Ann. Rev. Earth Planet. Sci.* **32**, 287 (2004)

Examples of biogenic nanoparticles

- iron reducing bacteria
  - terminal electron acceptor
  - d ≈ 5-10 nm



Fe_3O_4 nanoparticles



McCormick & Adriaens, *Env. Sci. Technol.* **38**, 1045 (2004)

Examples of biogenic nanoparticles

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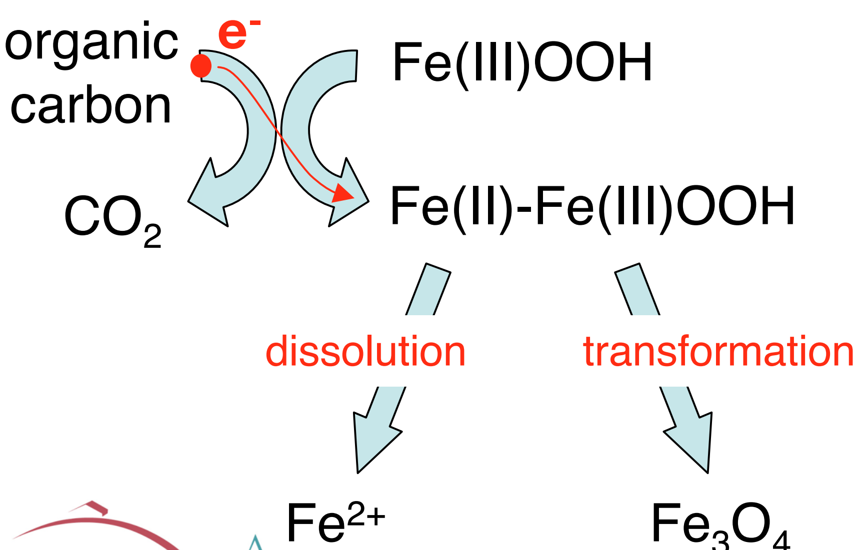
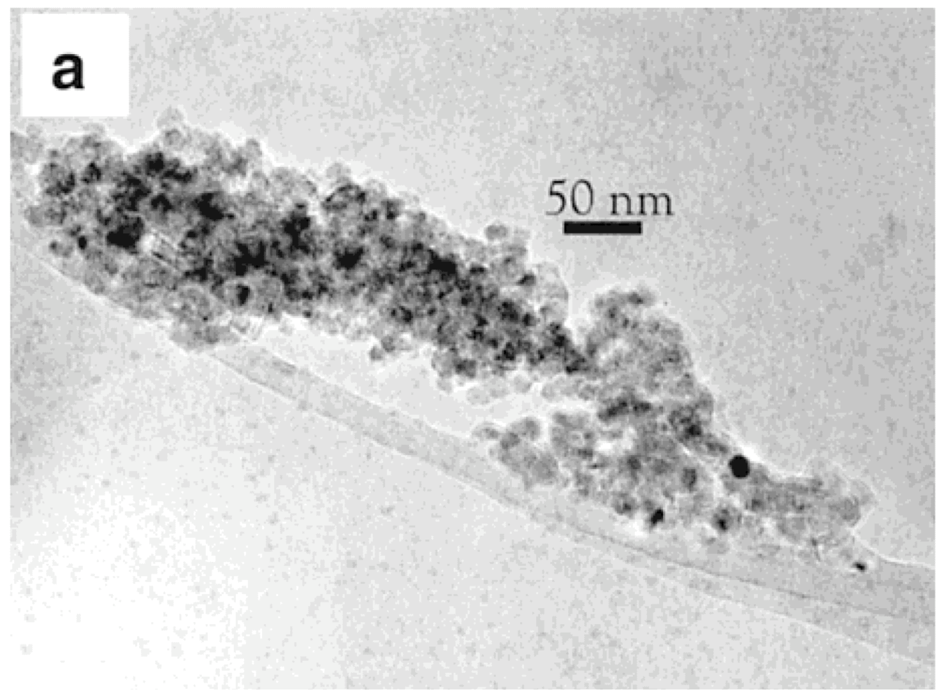


Fe_3O_4 nanoparticles



McCormick & Adriaens, *Env. Sci. Technol.* **38**, 1045 (2004)

Examples of abiotic nanoparticles

- Ferric iron precipitation
  - acid mine drainage
  - d ≈ few nm

FeOOH/ferrihydrite nanoparticles

Acid mine drainage, Iron Mountain, Redding, CA

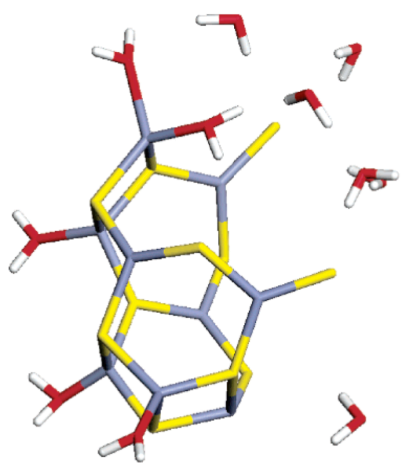
Lakewater species:

"Nanogoethite is the dominant reactive oxyhydroxide phase in lake and marine sediments"

van der Zee et al., *Geology* **31**, 993 (2003)

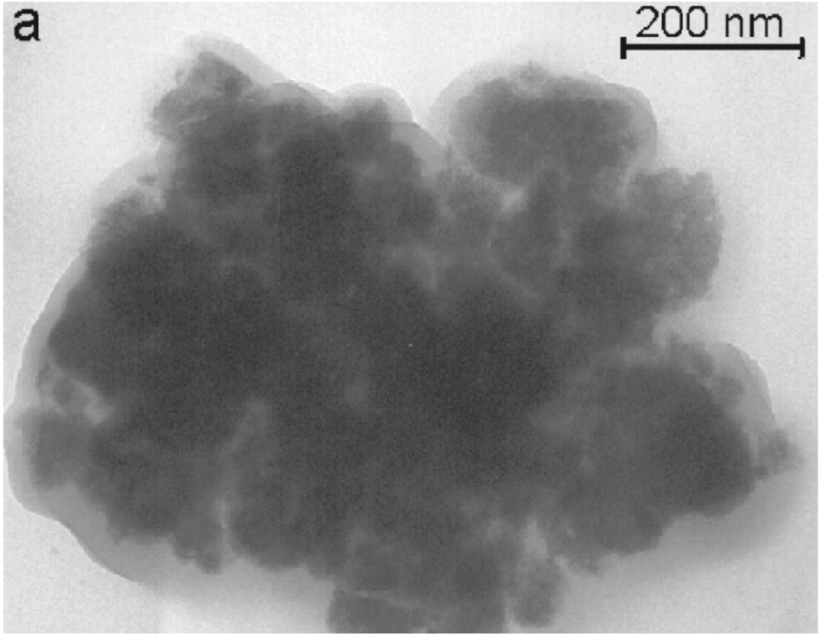
Examples of abiotic nanoparticles

- Sulfide precipitation
  - d ≈ 4 nm



Hamad et al.,
J. Am. Chem. Soc. **127**, 2580 (2005)

FeS nanoparticles



Wolthers et al.,
Am. Mineral. **88**, 2007 (2003)

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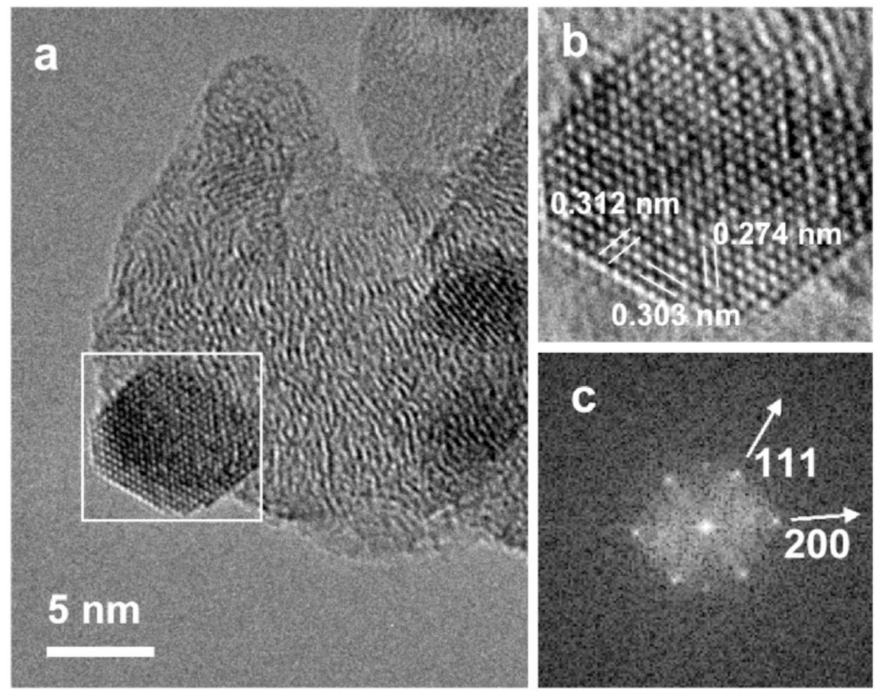
Examples of anthropic nanoparticles

- Combustion
  - UO_2
  - fullerenes
  - CeO_2

UO_2 nanoparticles



Utsonomiya et al.,
Env. Sci. Technol. **36**, 4943 (2002)

Ernest Orlando Lawrence
Berkeley National Laboratory
Berkeley Lab

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Biogeochemical interactions of nanoparticles

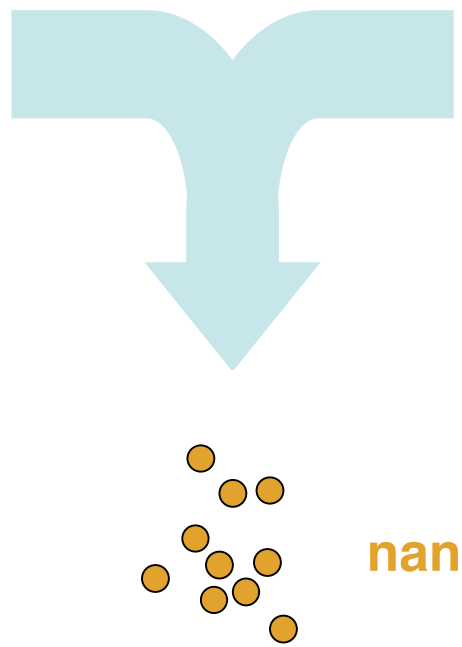
Significant elemental sinks via:

precipitation

adsorption

anions

cations



nanoparticles

Biogeochemical interactions of nanoparticles

Significant elemental sinks via:

precipitation

adsorption

Nutrients

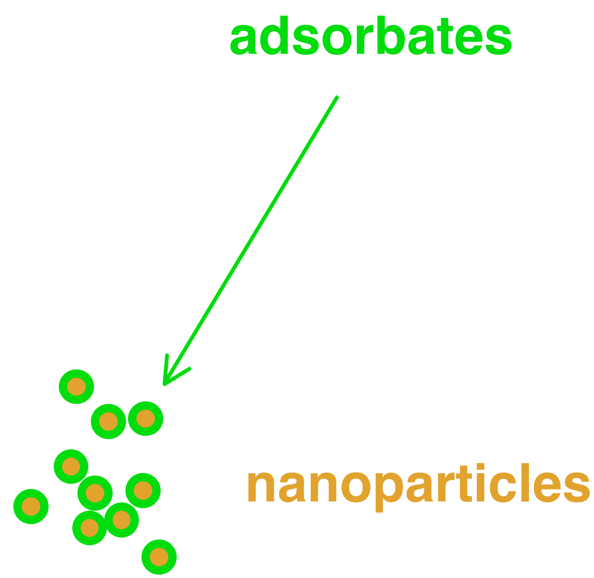
e.g. PO_4

Heavy metals

e.g. Pb, Cr, U

Organic molecules

e.g. humic acids

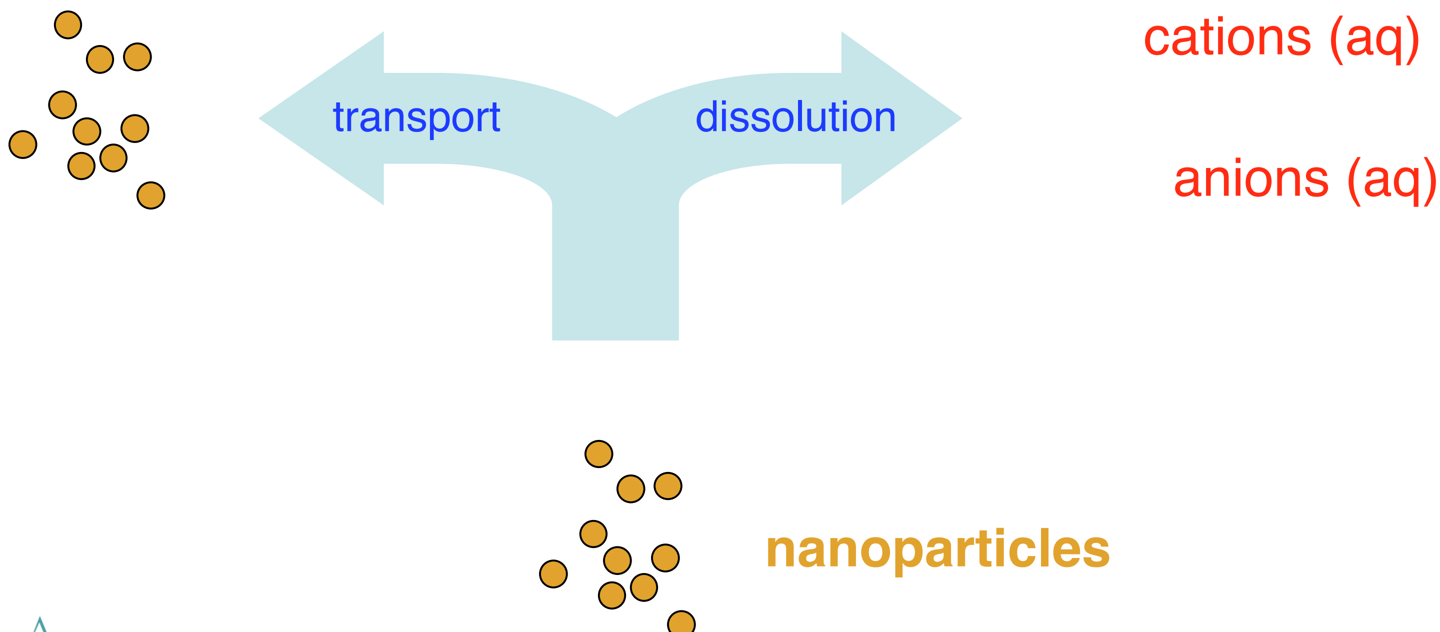


Biogeochemical interactions of nanoparticles

Geochemical cycling:

transportation

dissolution



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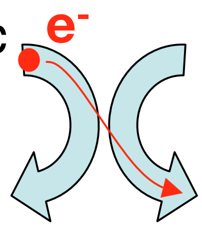
Biogeochemical interactions of nanoparticles

Microbial electron transfer:

e.g. terminal electron acceptors during anaerobic respiration of organic carbon

organic carbon



CO_2

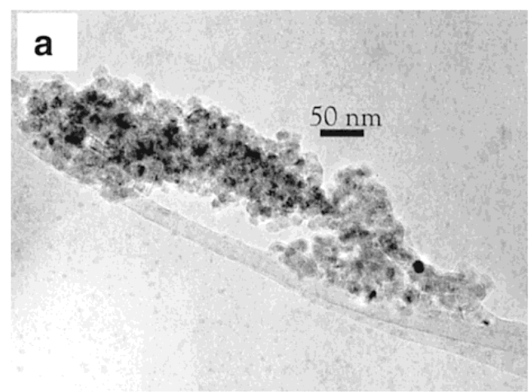
Fe^{3+} in FeOOH (s)

Fe^{2+} in Fe_3O_4 (s)

+ Fe^{2+} (aq)

Ferrihydrite nanoparticles

Magnetite nanoparticles

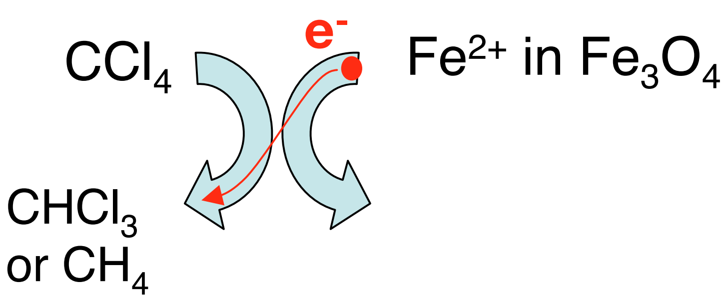


McCormick & Adriaens, *Env. Sci. Technol.* **38**, 1045 (2004)

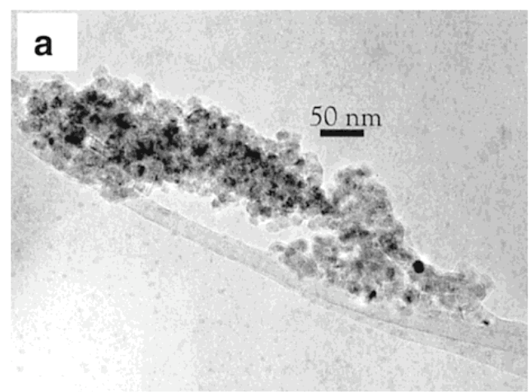
Biogeochemical interactions of nanoparticles

Redox transformation of aqueous species:

e.g. reduction of halogenated hydrocarbons



Magnetite nanoparticles



McCormick & Adriaens,
Env. Sci. Technol. **38**, 1045 (2004)

Properties of nanoparticles

Composition &
crystal structure
impurities
polymorphism

Electronic structure
redox properties
- sulfides
- oxides

reactivity

Surface structure
& sorbates

Stability
dissolution
growth

Aggregation
& transport

Properties of nanoparticles

Composition &
crystal structure
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polymorphism

Electronic structure
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Surface structure
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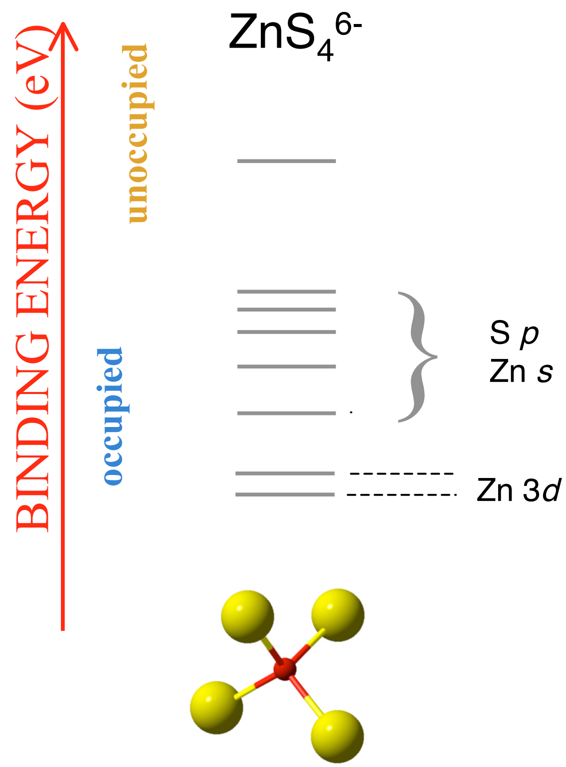
Electronic structure of semiconductor minerals

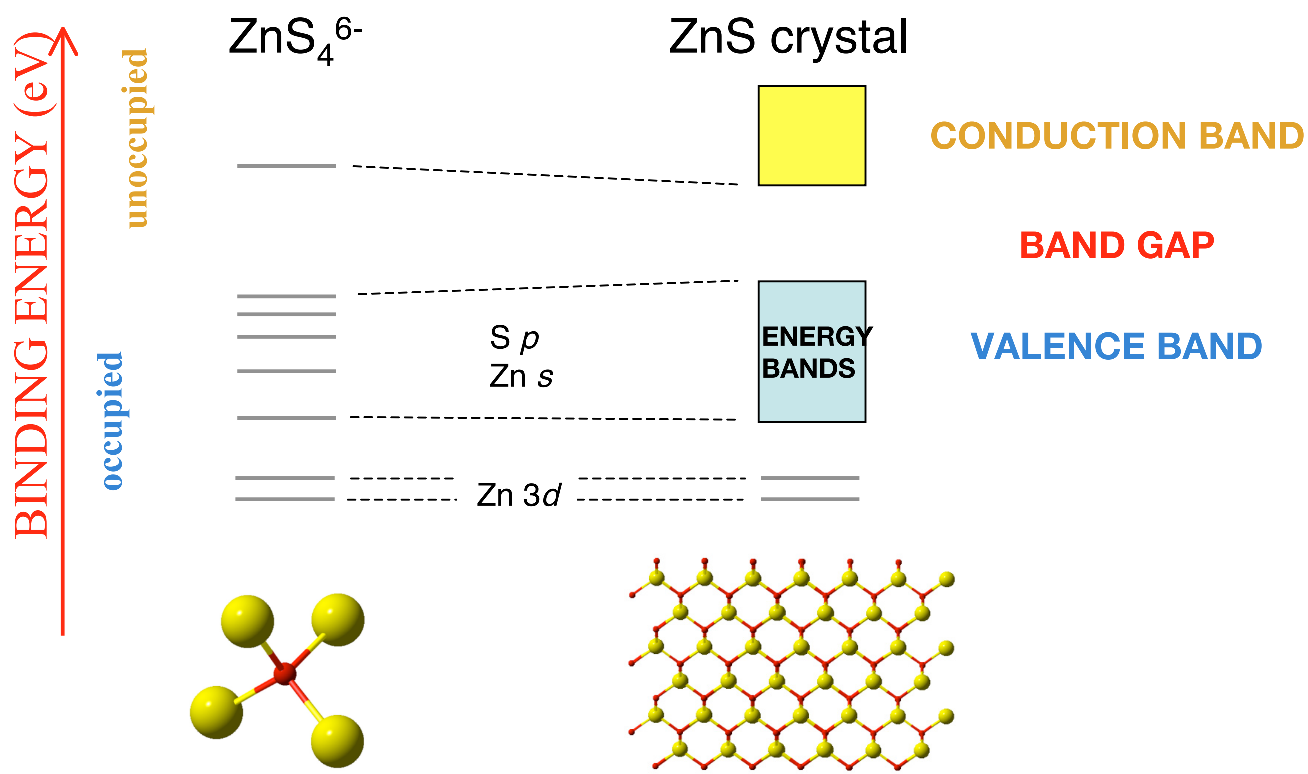
CLUSTER MODEL



Electronic structure of semiconductor minerals

CLUSTER MODEL

CRYSTAL MODEL



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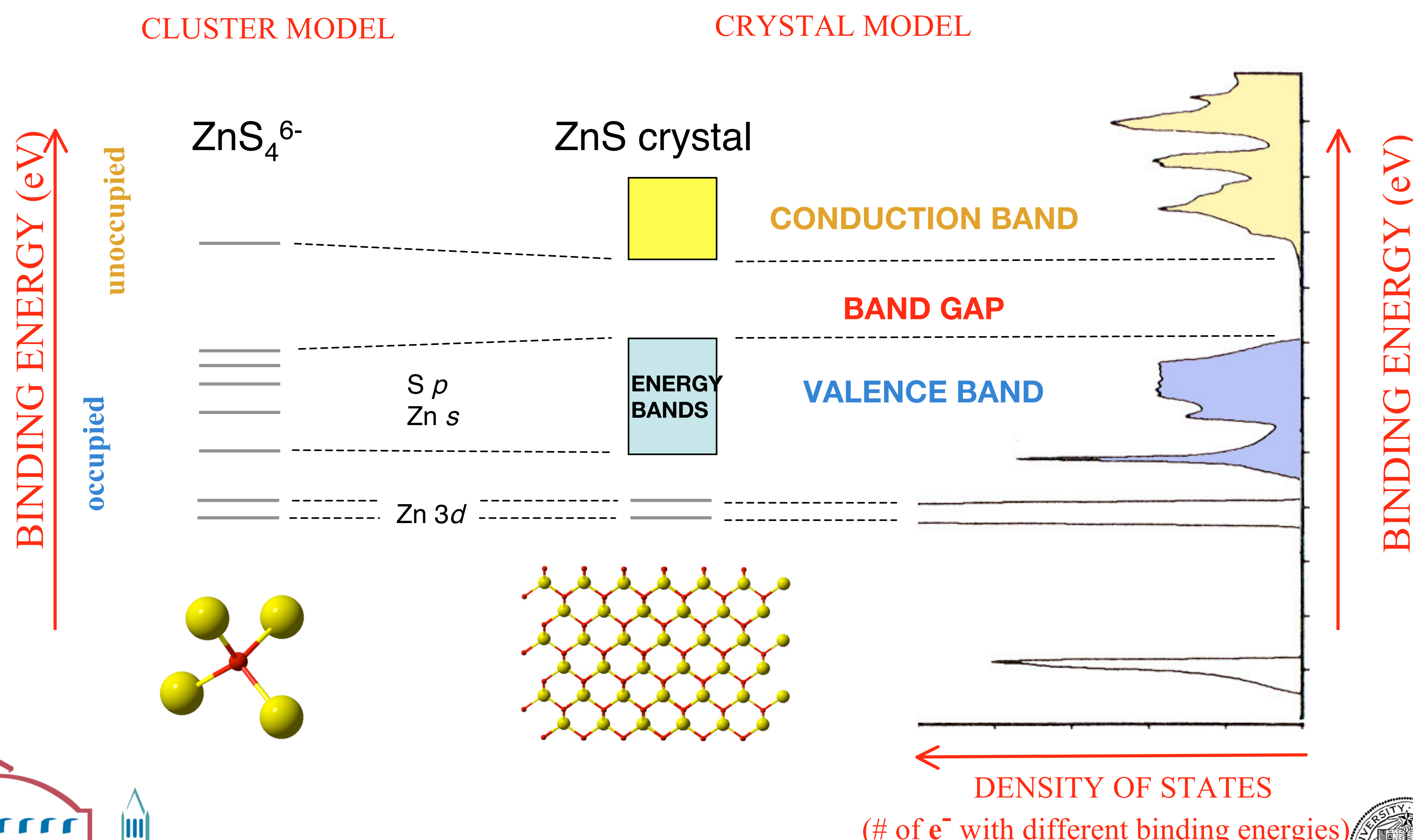
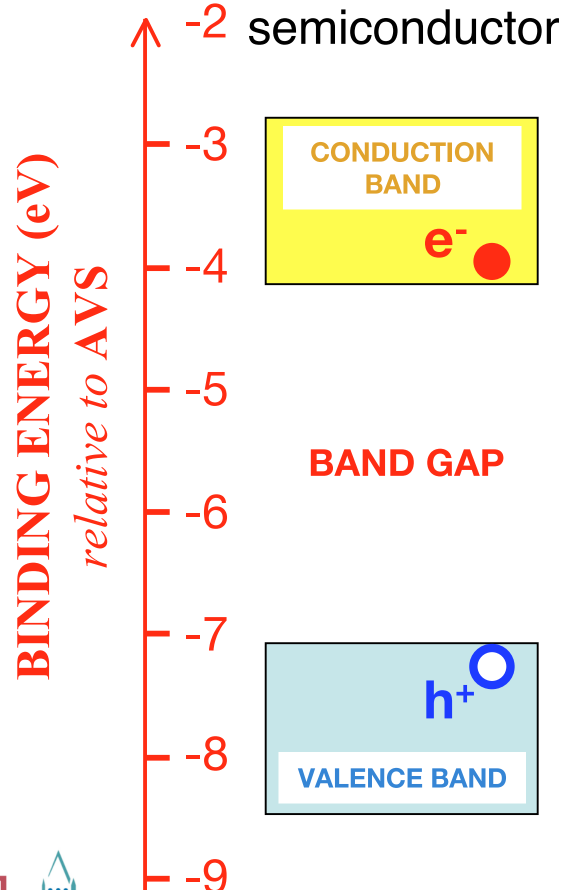
Electronic structure of semiconductor minerals



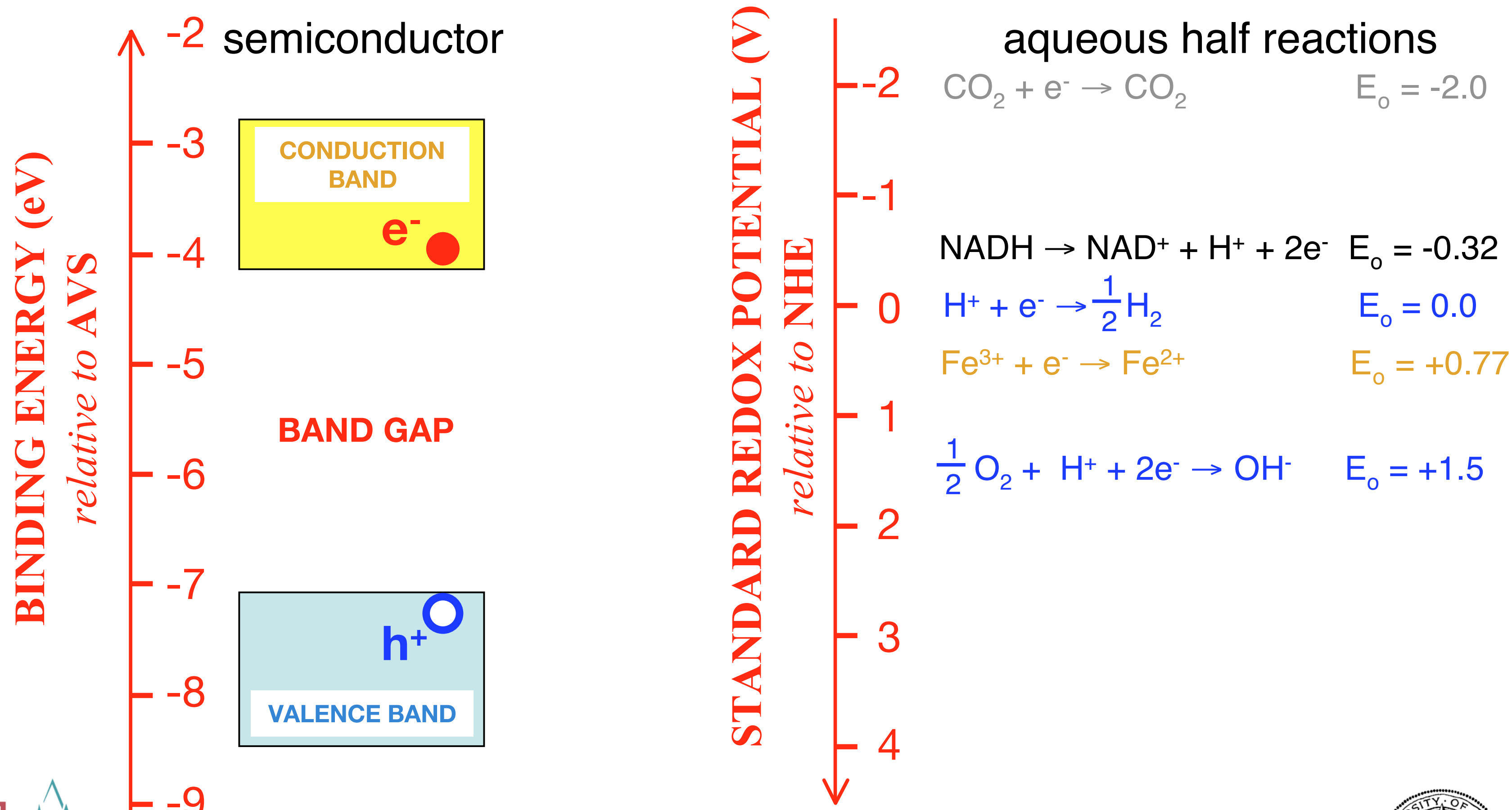
Electronic structure of semiconductor minerals

Redox potential of electrons and holes



Electronic structure of semiconductor minerals

Redox potential of electrons and holes

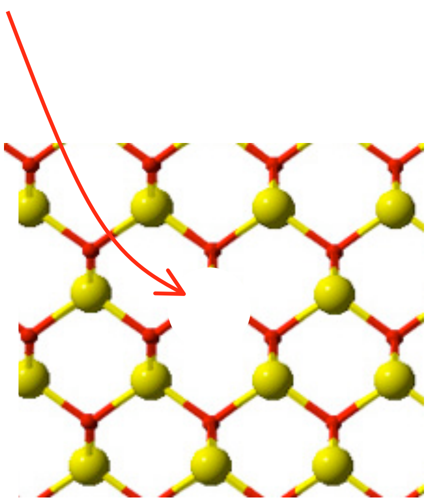


Creating redox active electrons and holes

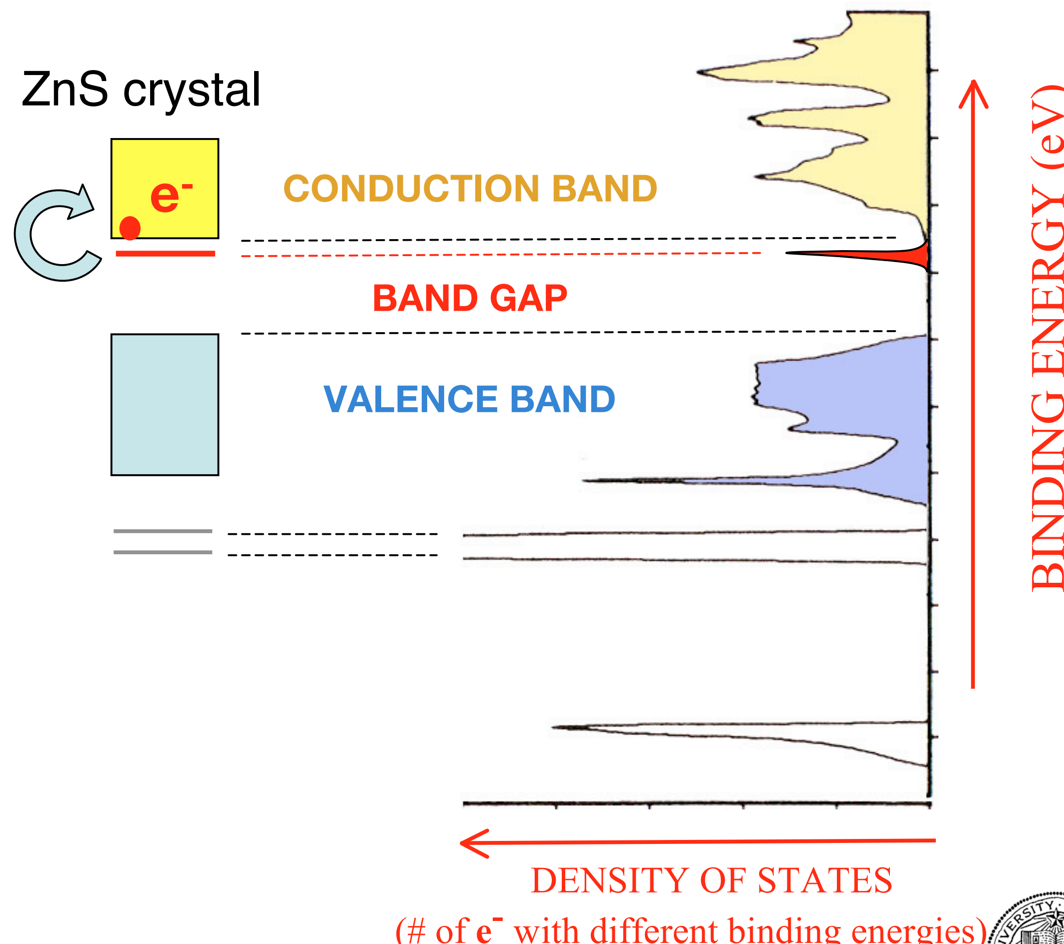
Defects

- **vacancies**
- impurity atoms

vacancy



CRYSTAL MODEL



Creating redox active electrons and holes

Defects

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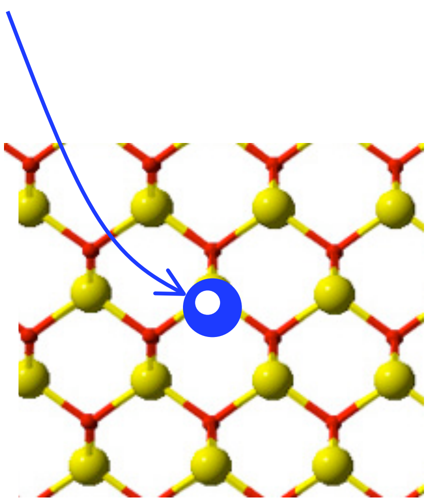
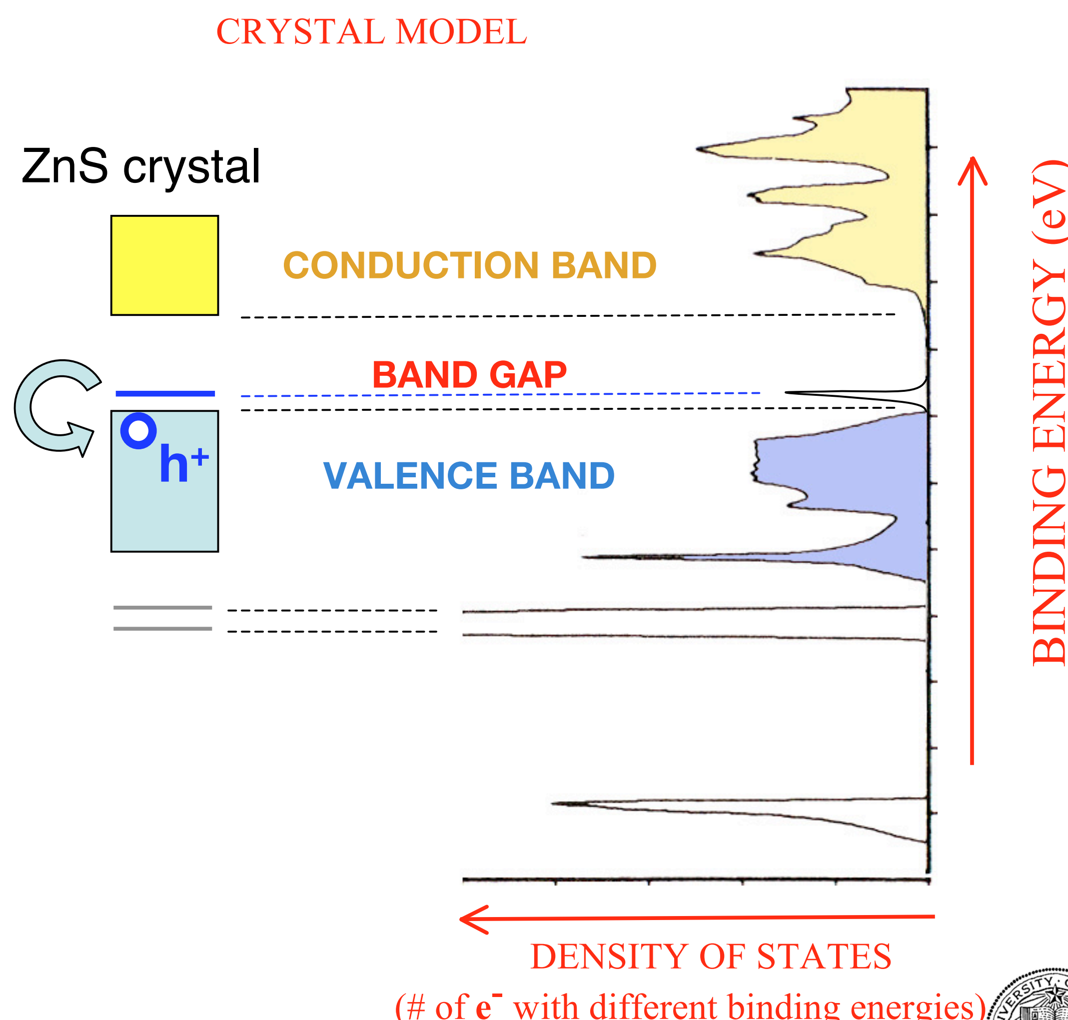
impurity



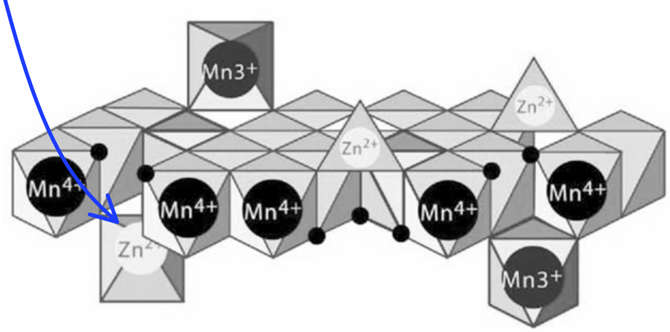


Creating redox active electrons and holes

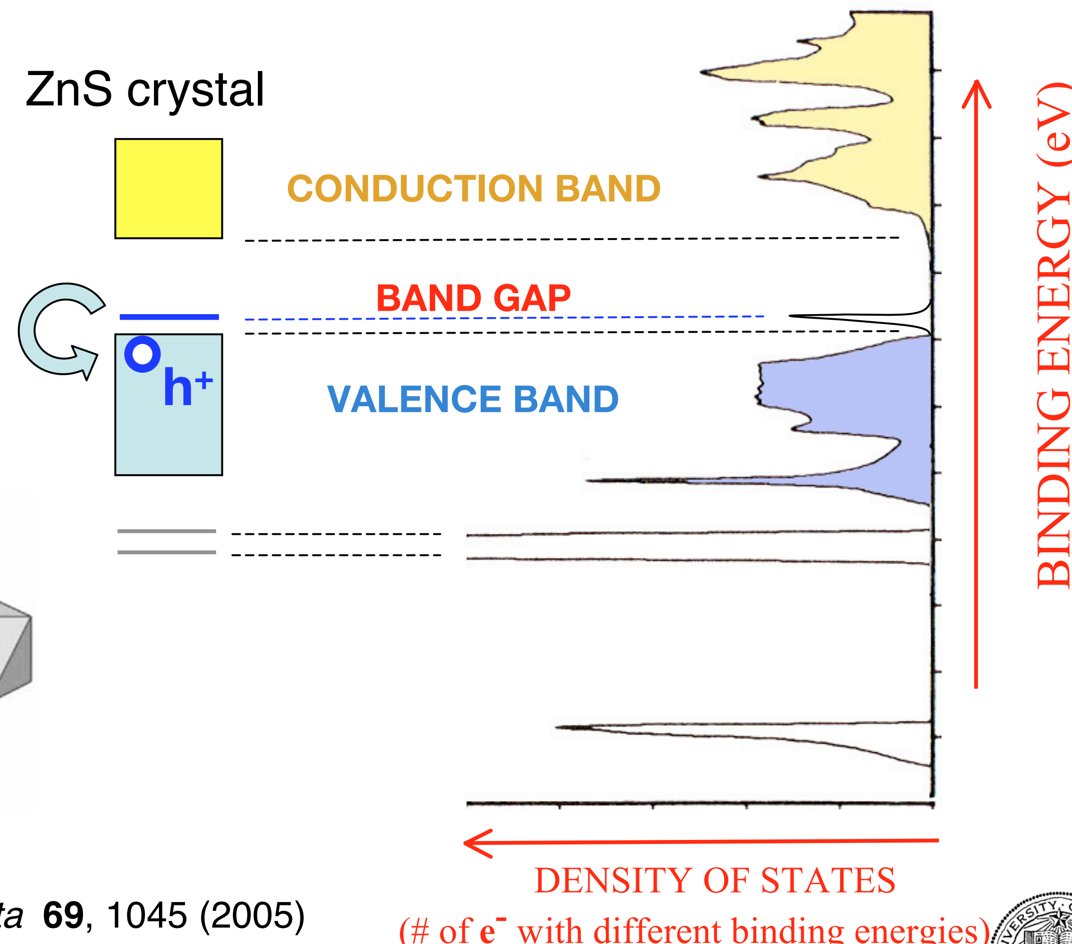
Defects

- vacancies
- **impurity atoms**

Zn impurity



CRYSTAL MODEL



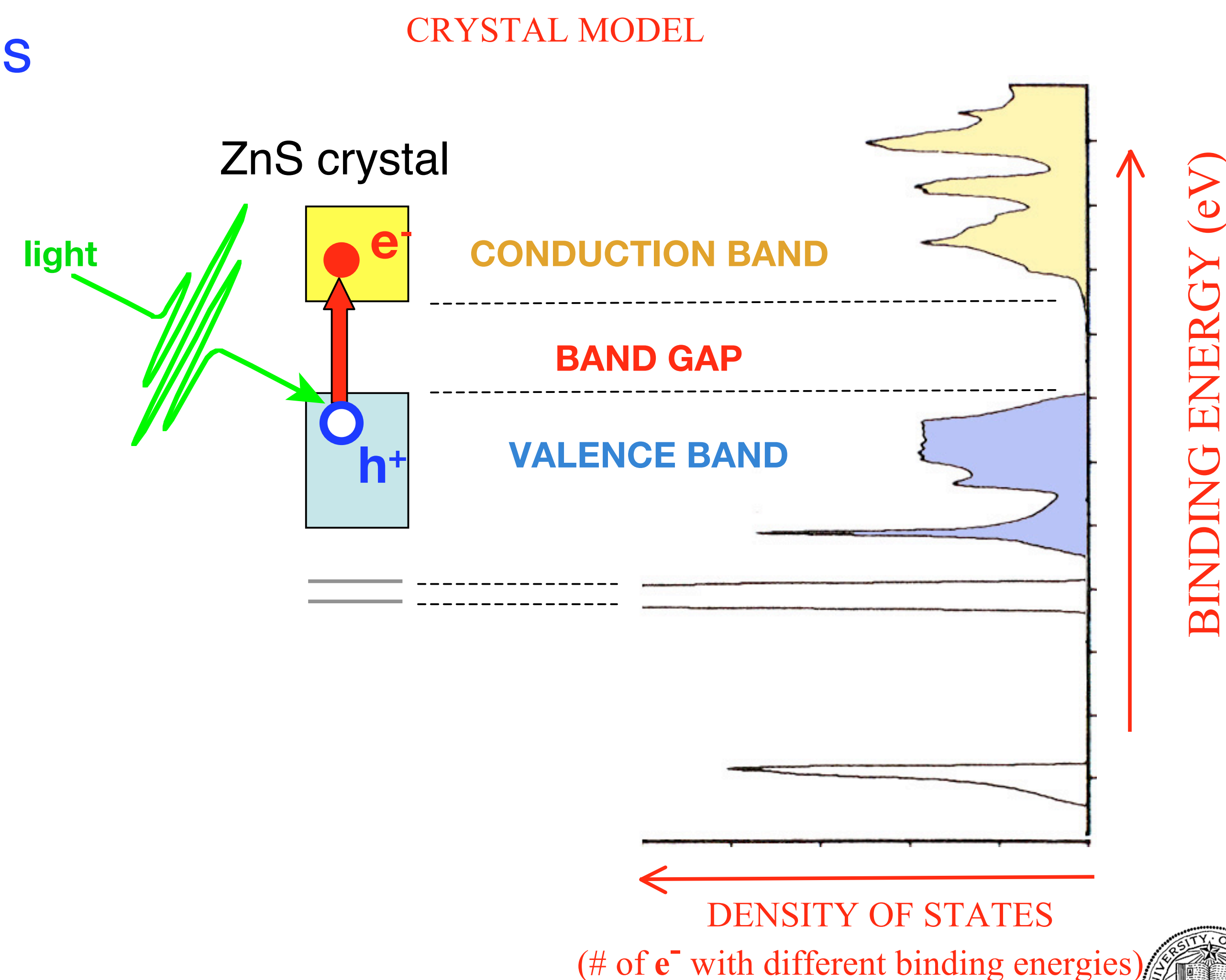
Isaure et al.,
Geochim. Cosmochim. Acta **69**, 1045 (2005)

Creating redox active electrons and holes

Optical transitions

photochemistry

detect **band gap**



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Electronic structure of semiconductor nanoparticles

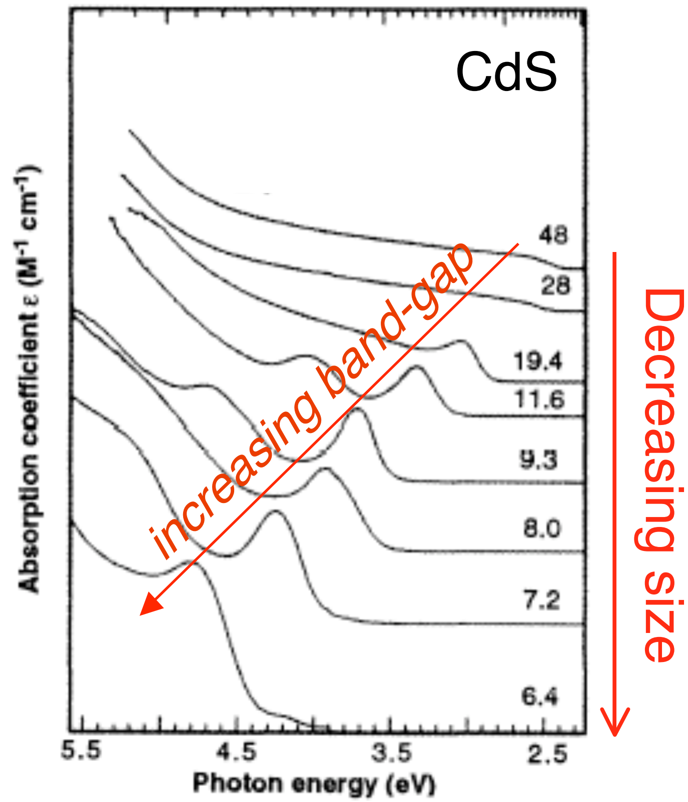
Band gap

may have a

size dependence

Nanoparticle band gap > Bulk mineral band gap

Optical Absorption



Vossmeyer et al., *J. Phys. Chem.* **98**, 7665 (1994)

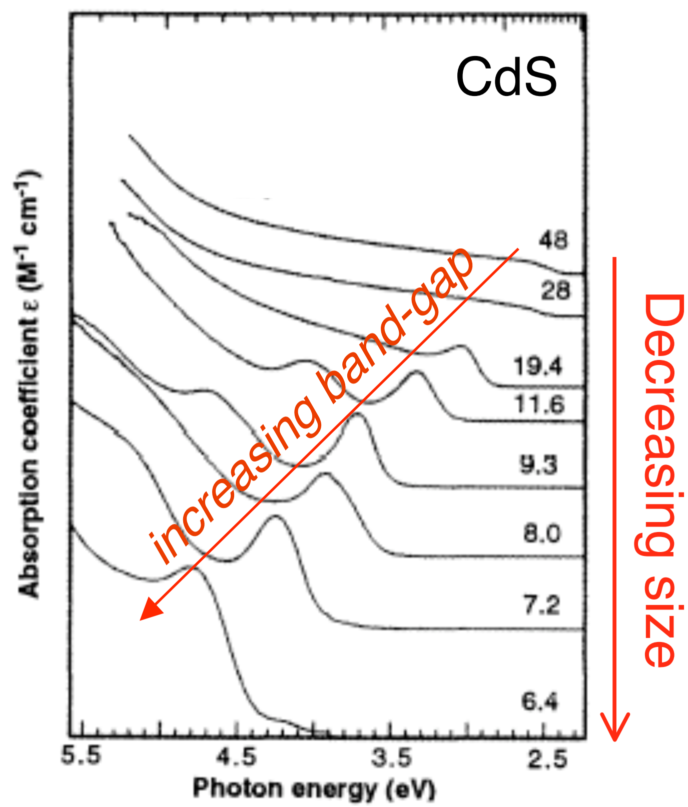
Electronic structure of semiconductor nanoparticles

Band gap
may have a
size dependence

Nanoparticle band gap > Bulk mineral band gap

How are CB and VB affected?

Optical Absorption



Vossmeyer et al.,
J. Phys. Chem. **98**, 7665 (1994)

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Electronic structure of semiconductor minerals

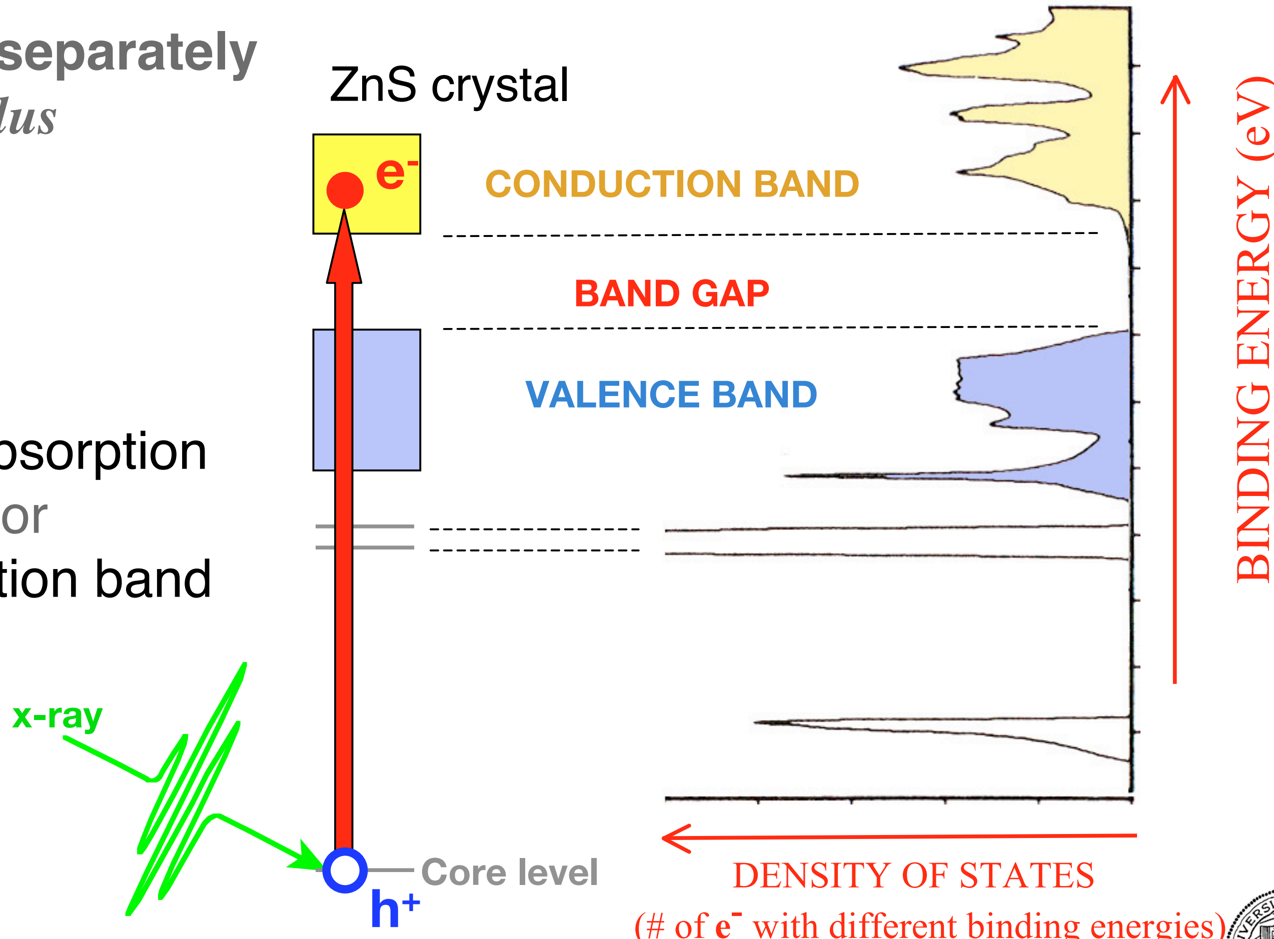
X-ray transitions

show CB & VB separately

⇒ band gap *plus*

⇒ band position

x-ray absorption
for
conduction band



Electronic structure of semiconductor minerals

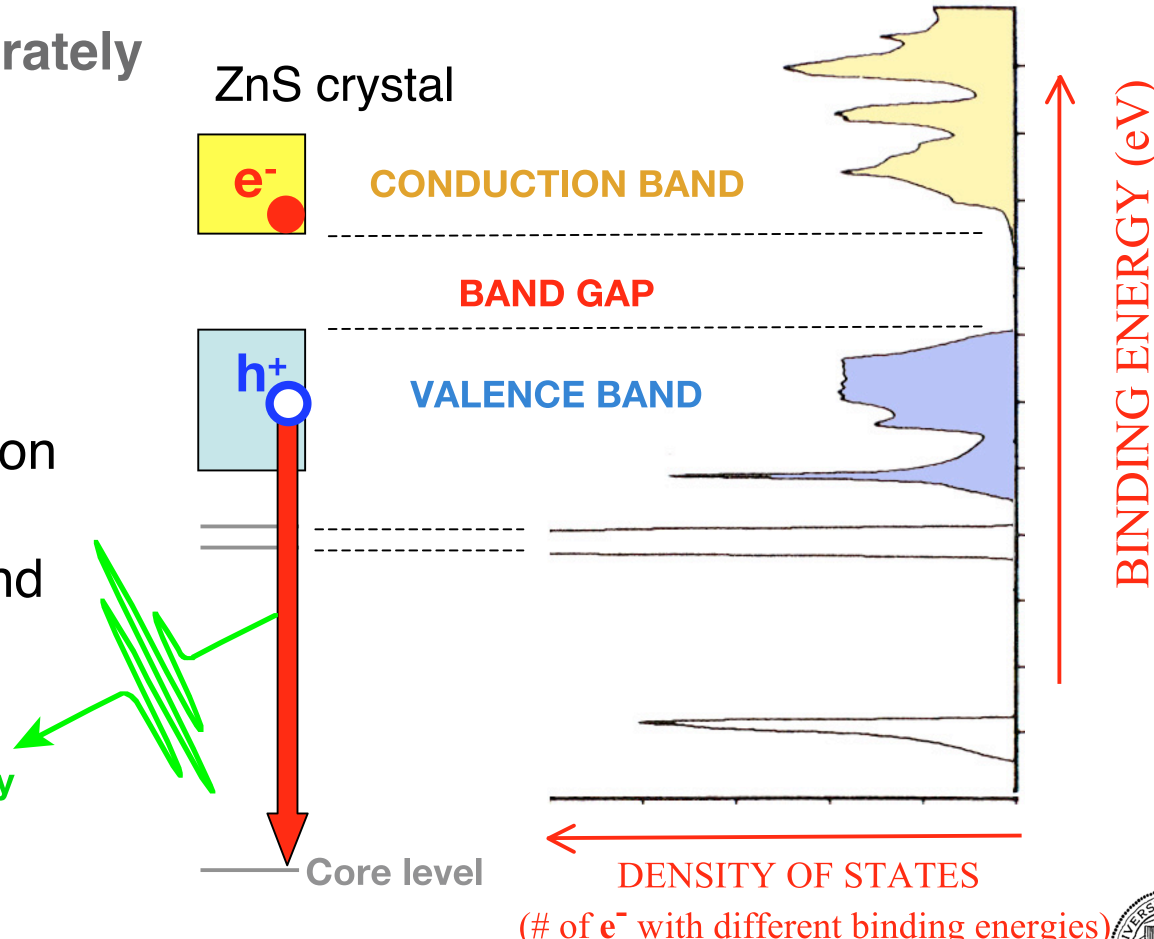
X-ray transitions

show CB & VB separately

⇒ band gap *plus*

⇒ band position

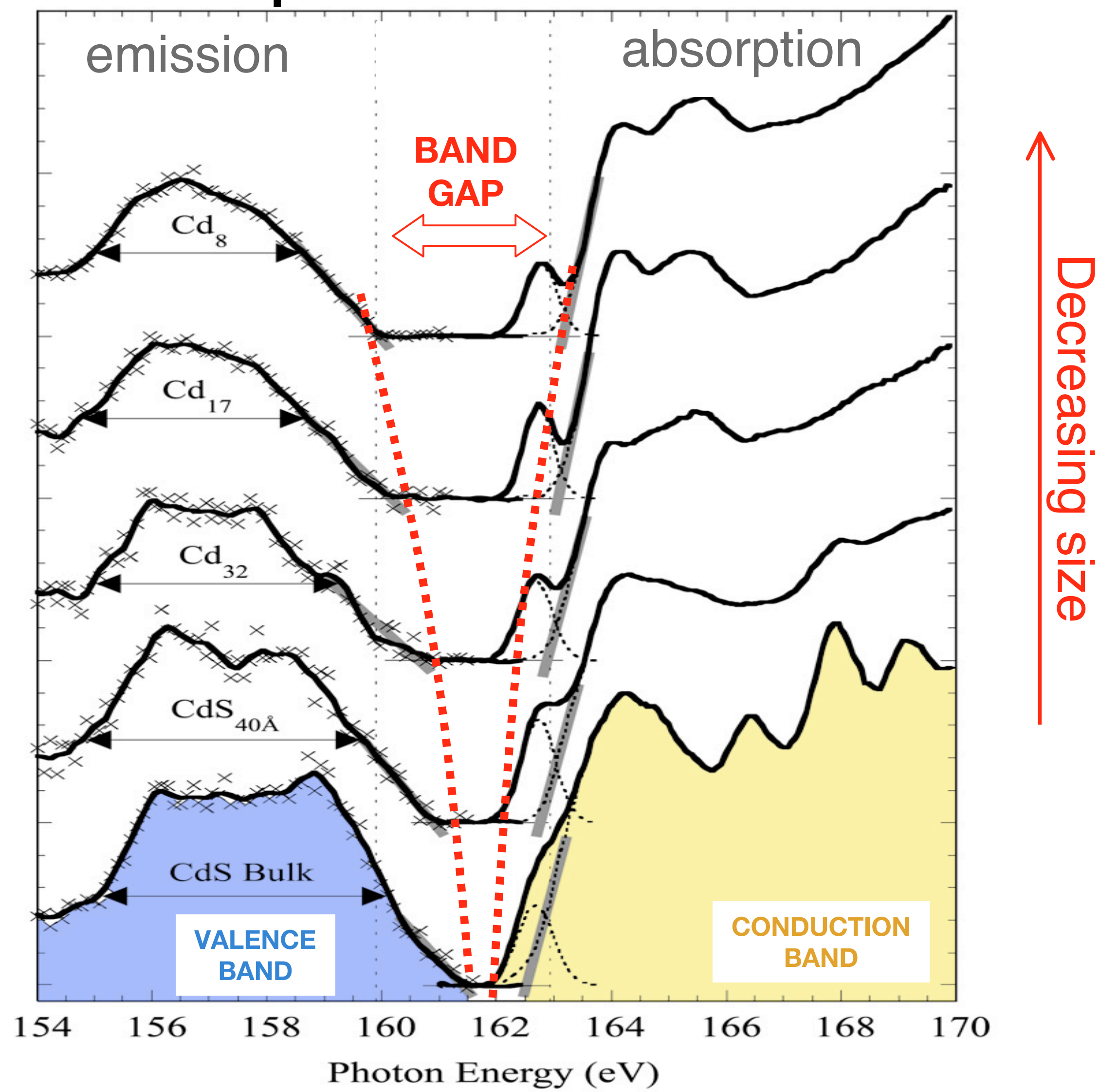
x-ray emission
for
valence band



Electronic structure of semiconductor nanoparticles

CdS Nanoparticle:

CdS Bulk:



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Electronic structure of semiconductor nanoparticles

CdS Nanoparticle:

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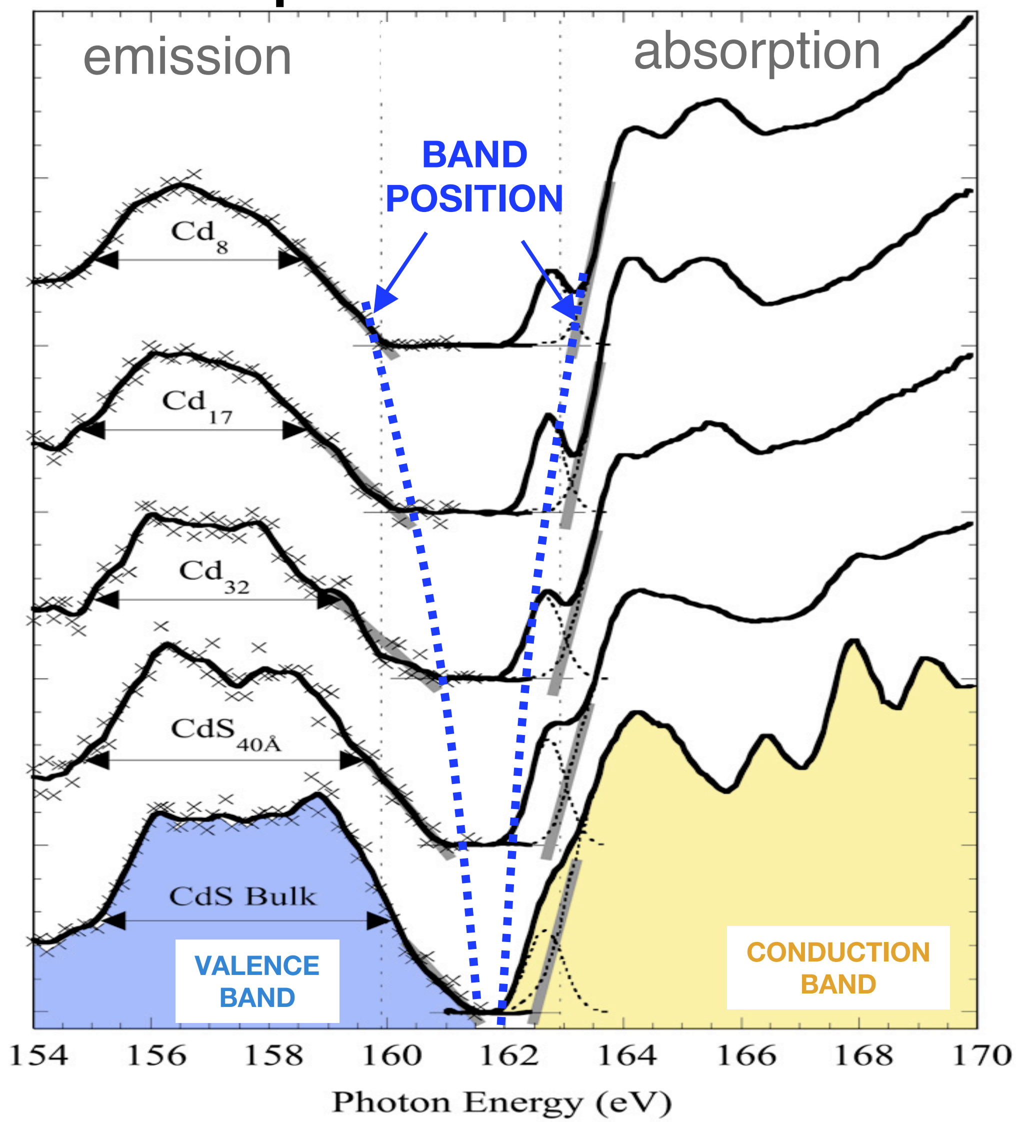

Decreasing size

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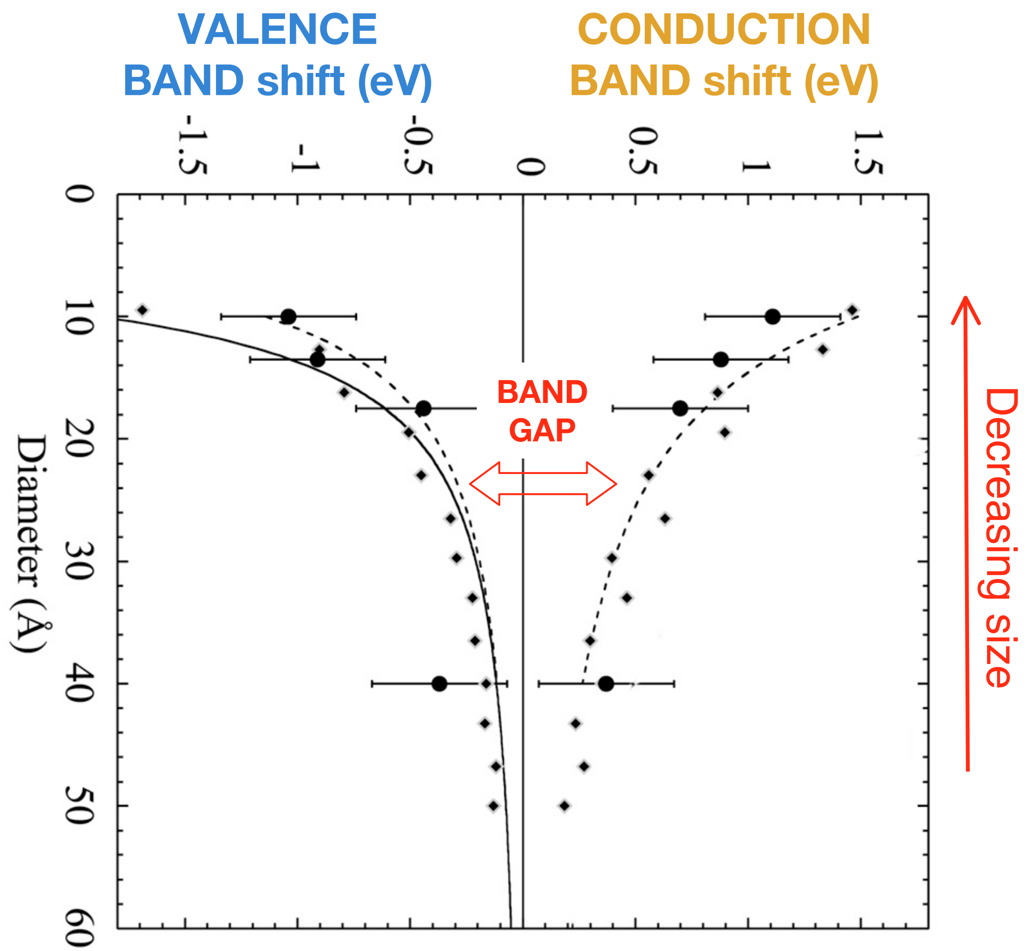
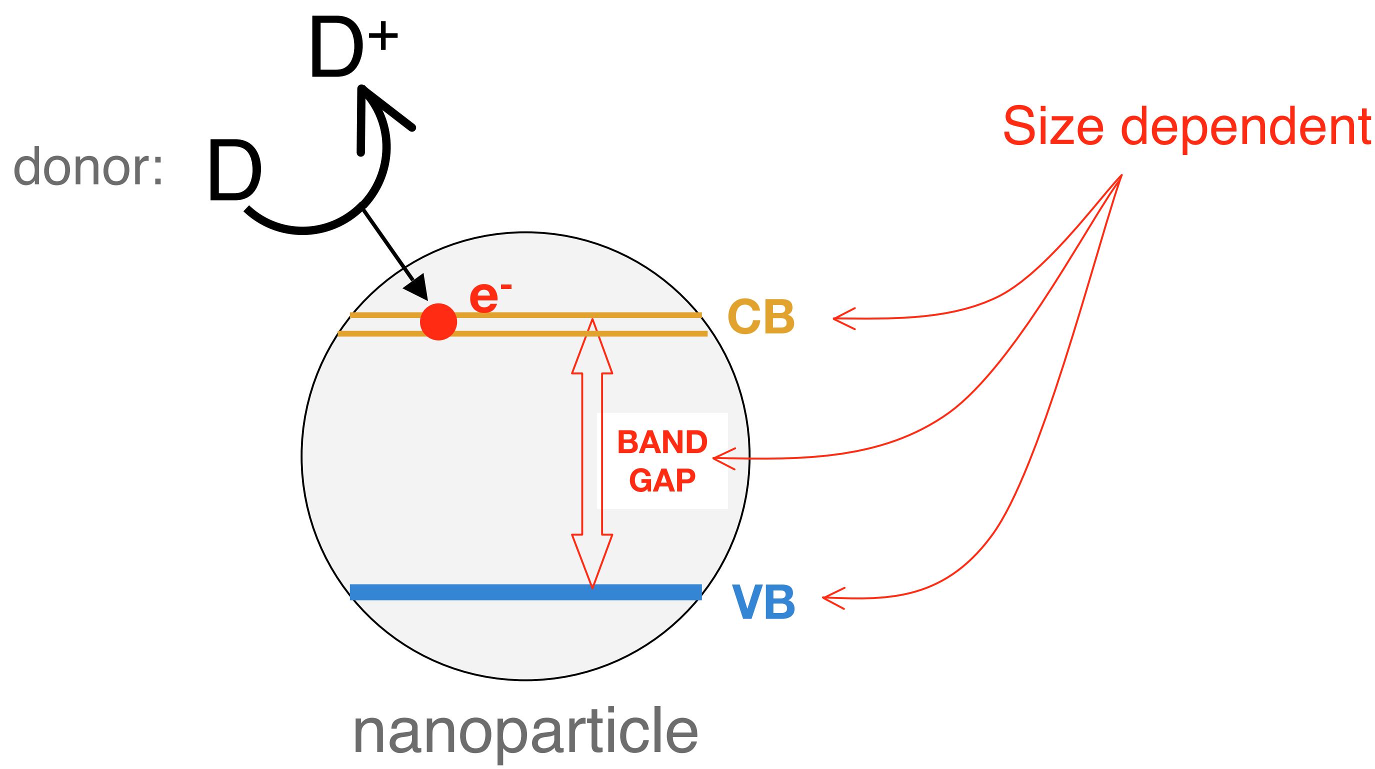
VB and CB energy positions are size dependent

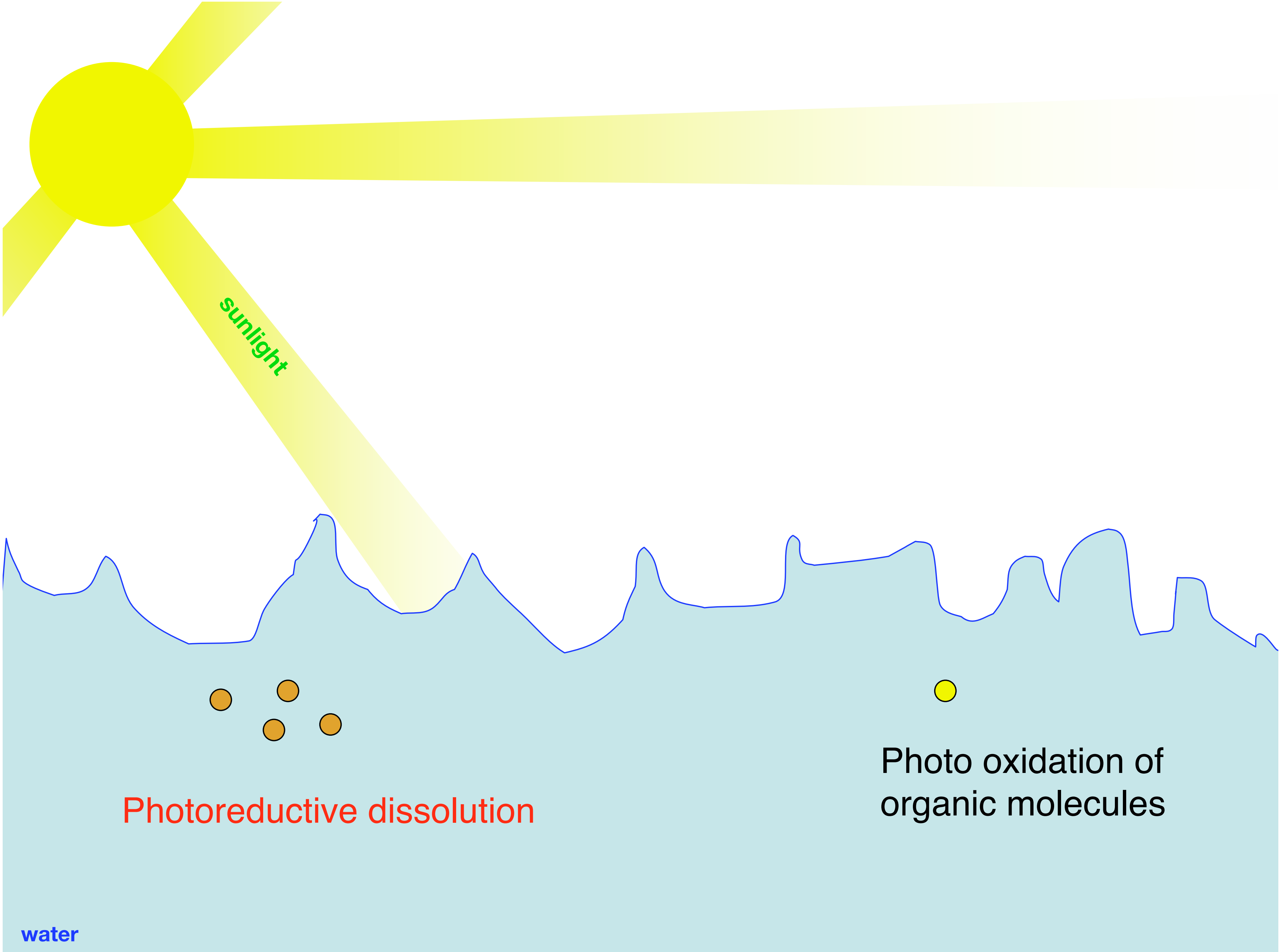


Lüning et al.,
Solid State Commun. **112**, 5 (1999)

See Gilbert & Banfield chapter

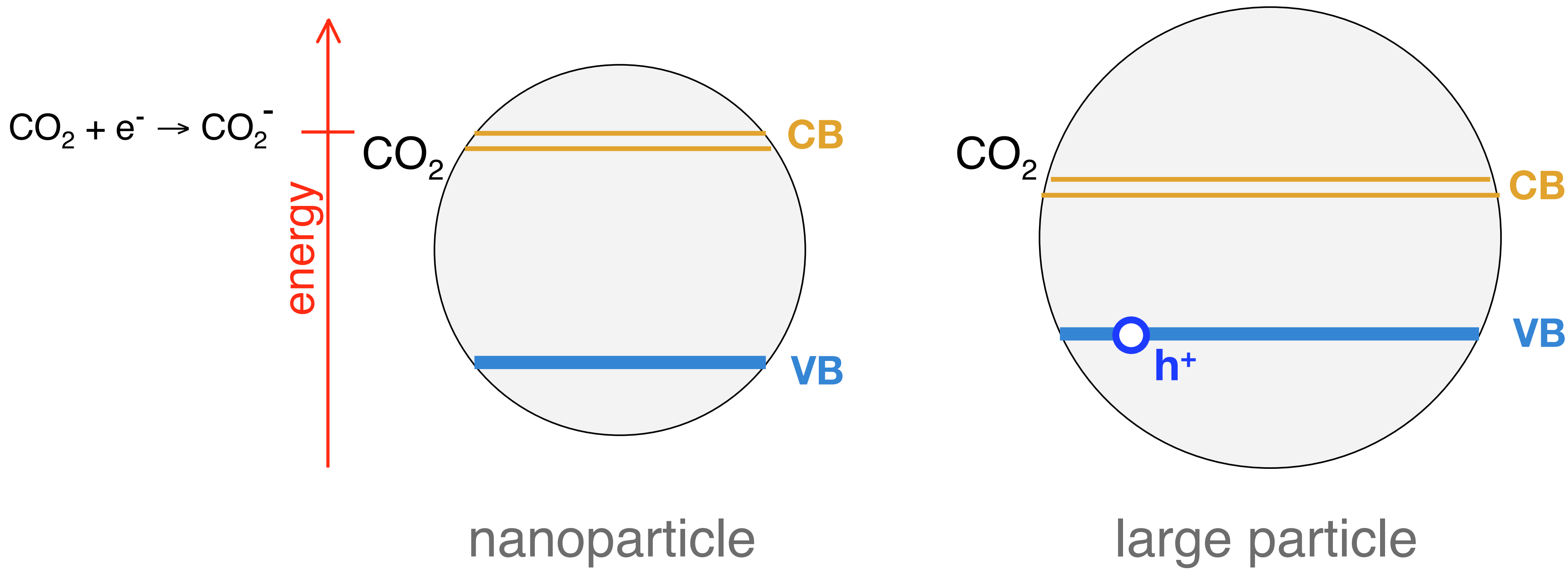
Redox reactivity of semiconductor nanoparticles




sunlight
Photoreductive dissolution
Photo oxidation of
organic molecules
water

Photoredox reactions of semiconductor nanoparticles

CO_2 **photoreduction** mechanisms on ZnS, CdS etc



Photoredox reactions of semiconductor nanoparticles

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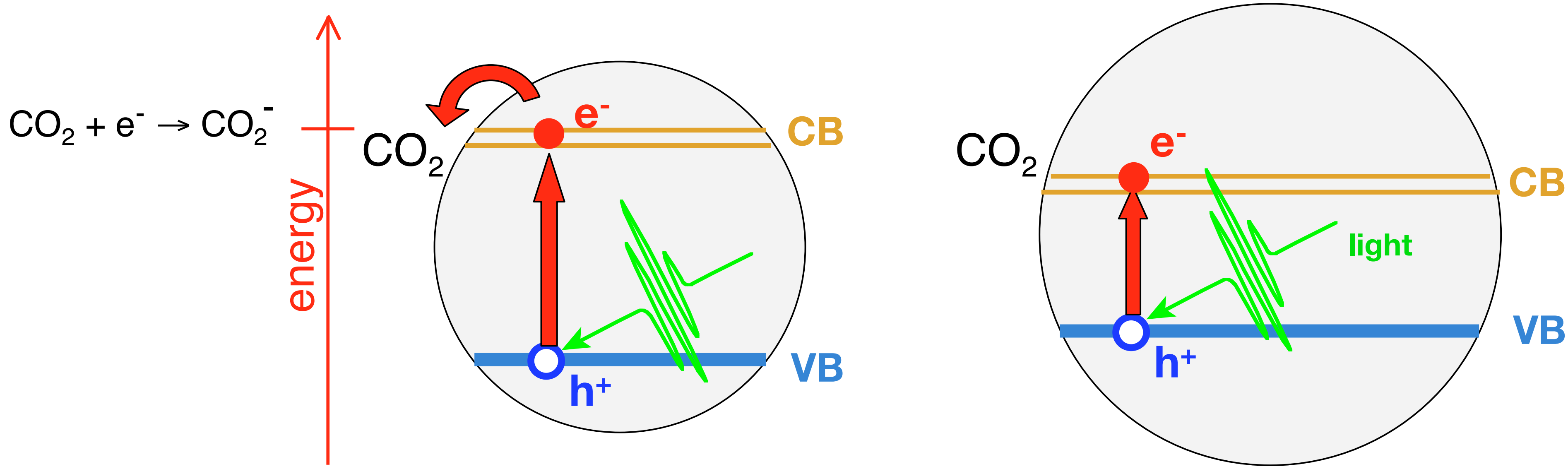
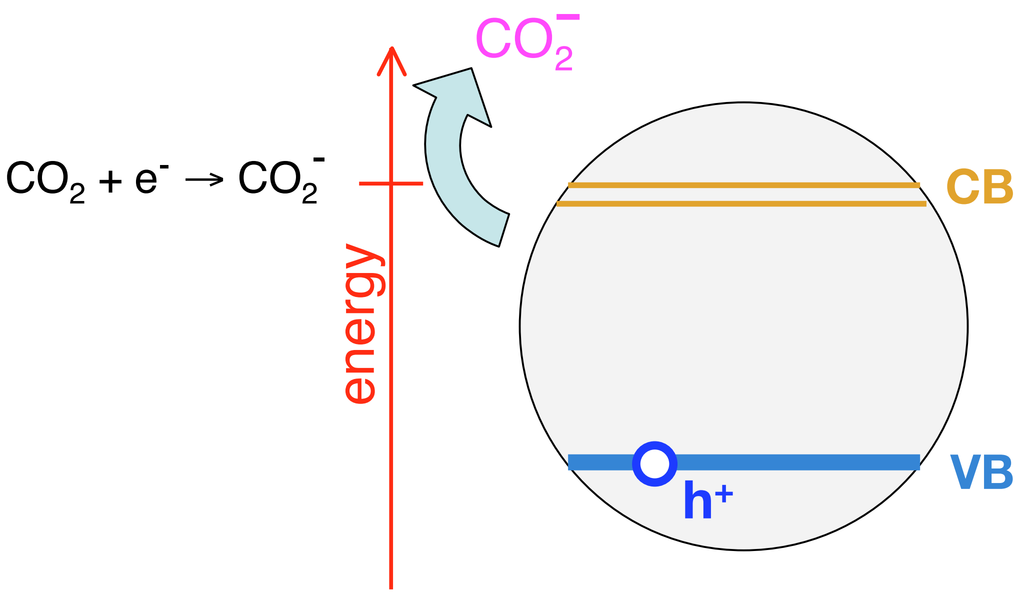
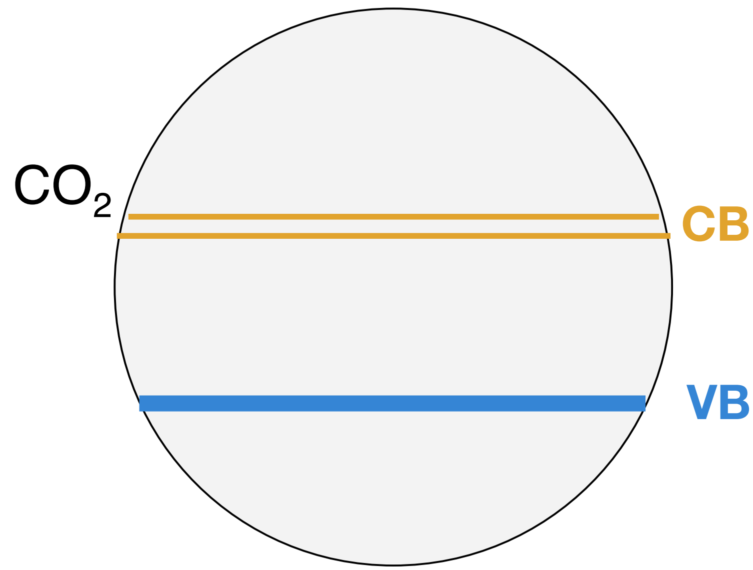


Photoredox reactions of semiconductor nanoparticles

CO_2 **photoreduction** mechanisms on ZnS, CdS etc



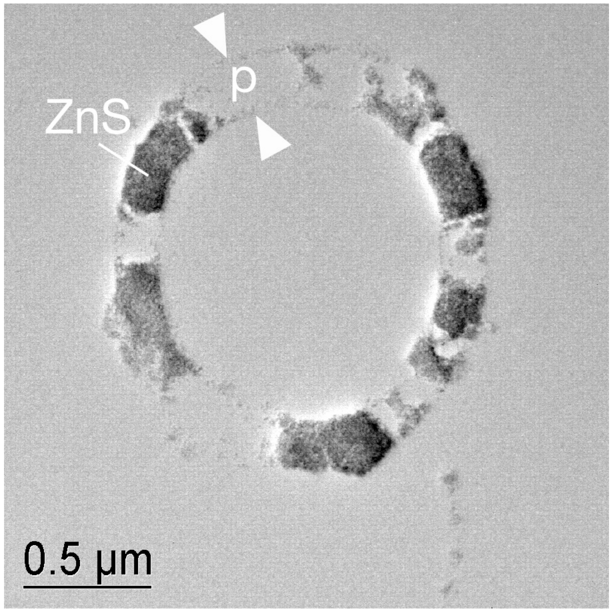
Diameter < $d_{critical}$:
CB electrons sufficiently reducing



Diameter > $d_{critical}$:
CB electron cannot reduce CO_2

Photoredox reactions of semiconductor nanoparticles

Photochemical reactions at nanoparticle surfaces
can create cytotoxic radicals



TEM image courtesy of Ken Williams

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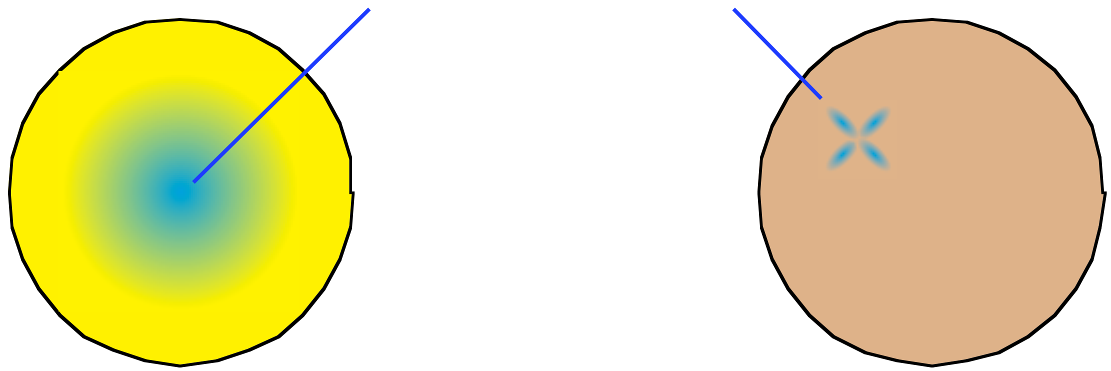
Electronic structure of oxide nanoparticles

Size effects likely to be smaller in materials with partially filled *d*-states

conduction electron wavefunction *



delocalized electron semiconductor

e.g. sulfides

itinerant electron semiconductor

e.g. Mn, Fe oxides

** artist's view*

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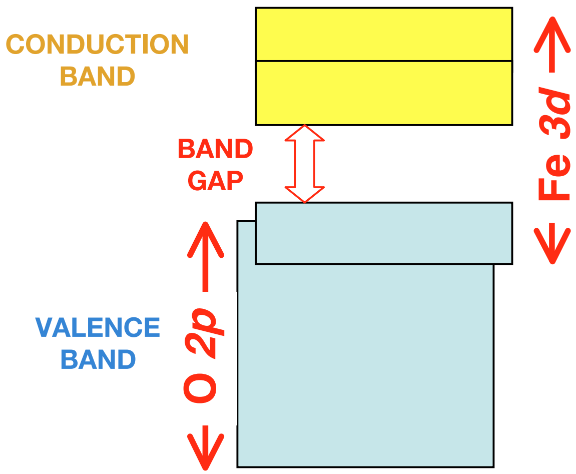
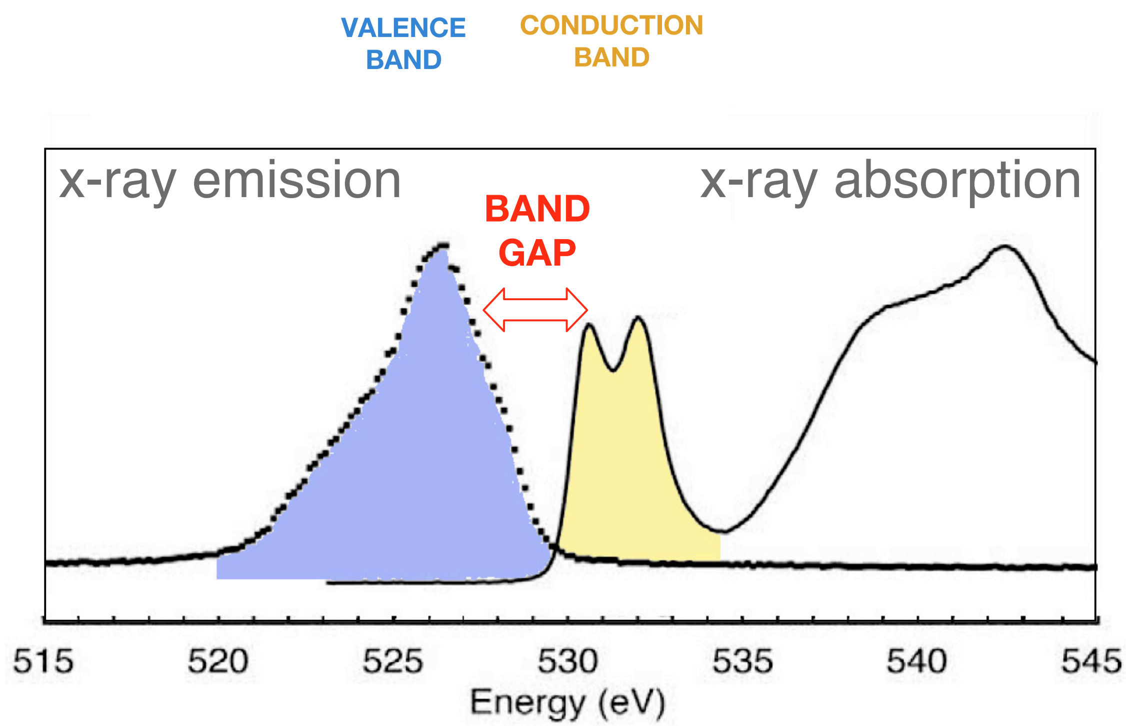
Electronic structure of hematite α-Fe_2O_3

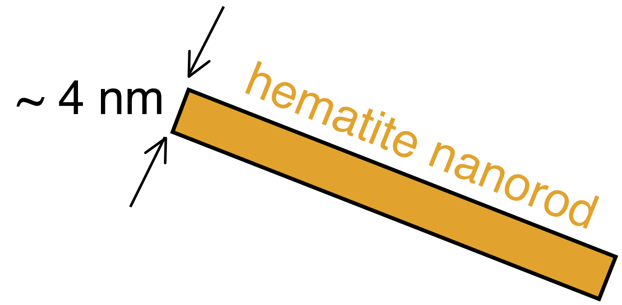
Bulk band gap ≈ **2.2 eV**



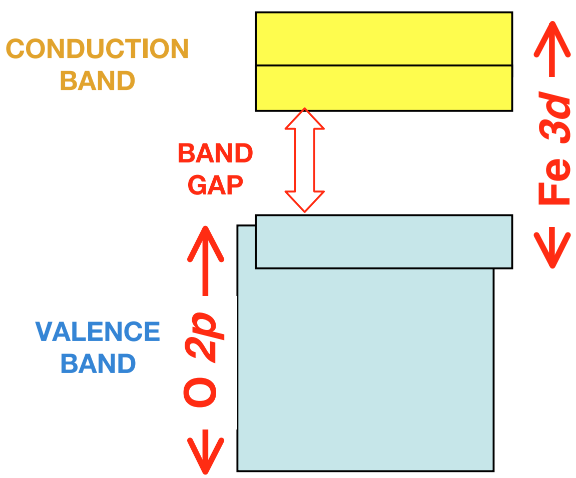


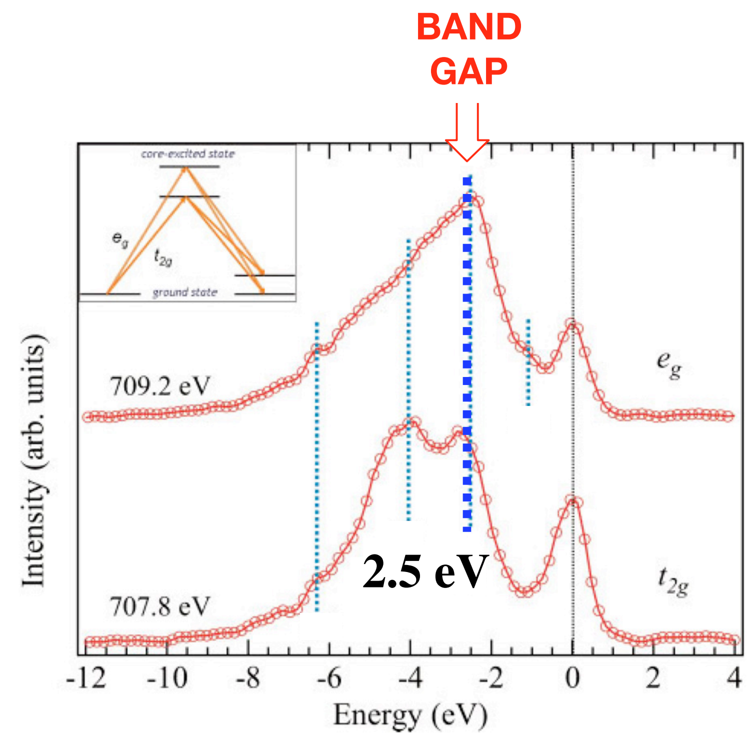
Sherman,
Geochem. Cosmochem. Acta **69**, 3249 (2005)

Electronic structure of hematite nanorods



Nanorod band gap ≈ **2.5 eV**

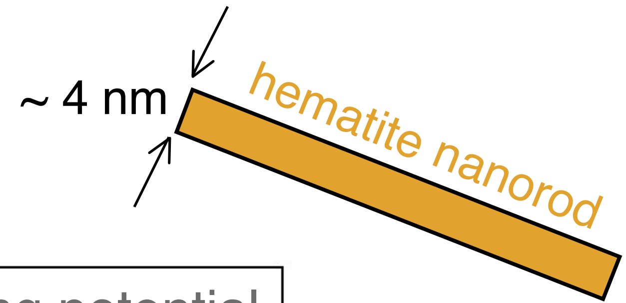




resonant
x-ray emission

Vayssieres et al,
Adv. Mater. **17**, 2320 (2005)

Electronic structure of hematite nanorods



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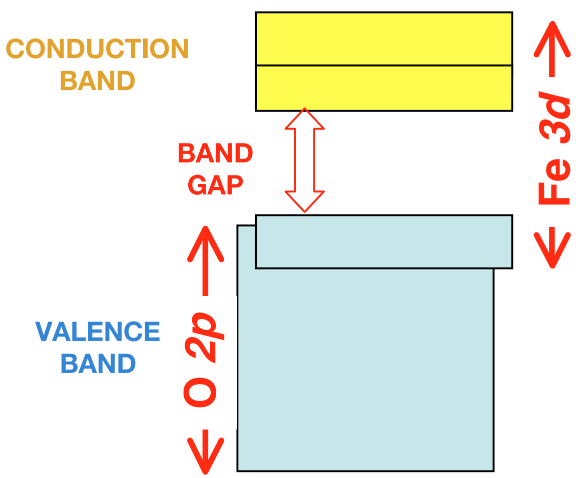

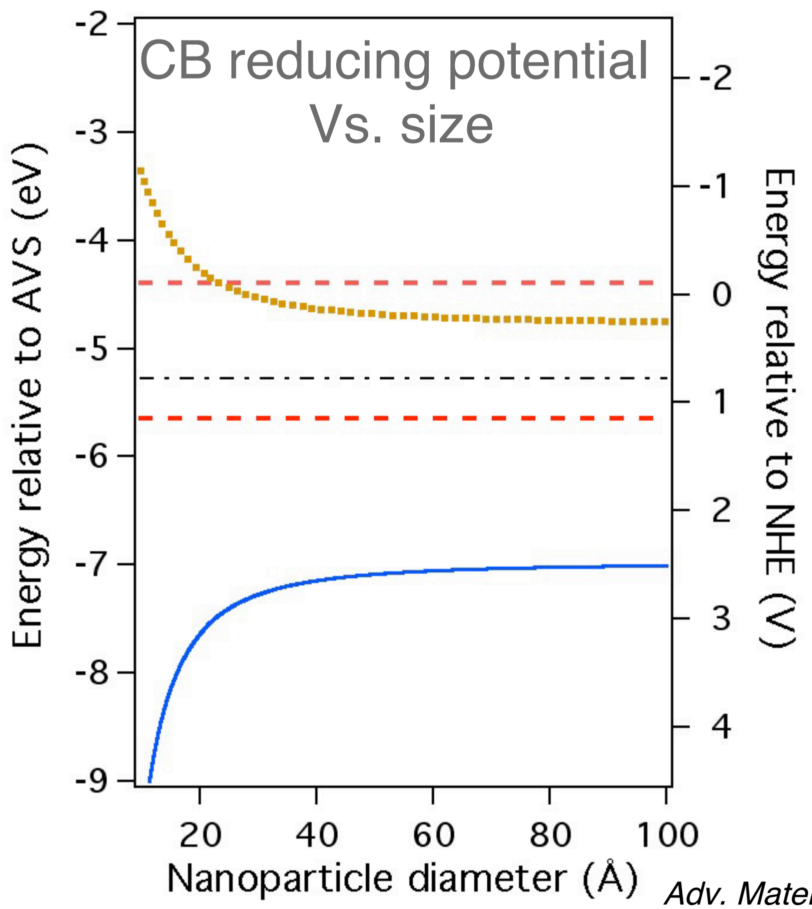

$H^+ + e^- \rightarrow \frac{1}{2} H_2$

CB

$\alpha\text{-}Fe_2O_3/Fe^{2+}$ (aq)

$\frac{1}{2} O_2 + H^+ + 2e^- \rightarrow OH^-$

VB

Vayssieres et al, *Adv. Mater.* **17**, 2320 (2005)

Electronic structure of hematite nanorods

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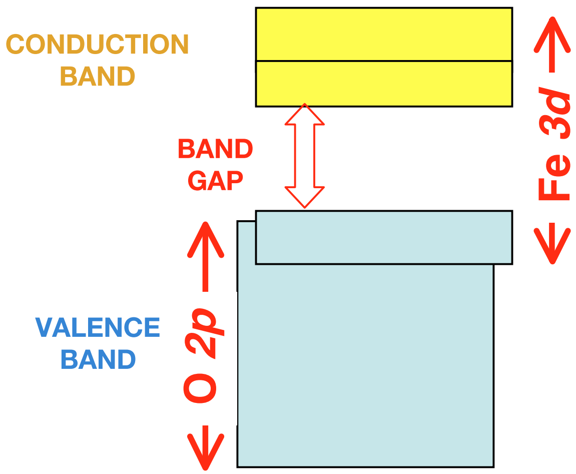


Implications:

Nanoscale hematite and other iron oxide materials may differ in their intrinsic reactivity relative to the bulk

Additional factors for the reactivity of nanoparticles

Small particle size not the only factor affecting reactivity

Surface structure

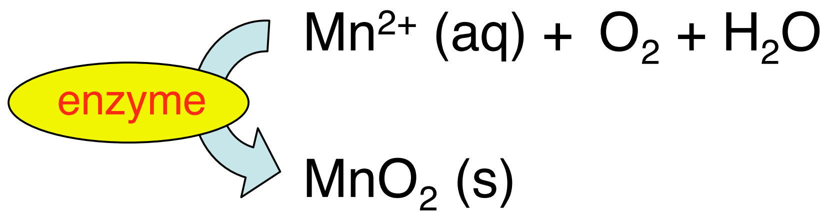
Chemically bound adsorbates

Impurities

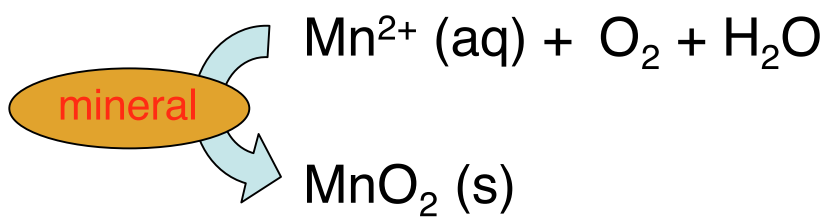
Surface reactivity of hematite nanoparticles

Catalysis of Mn oxidation

biological



abiotic



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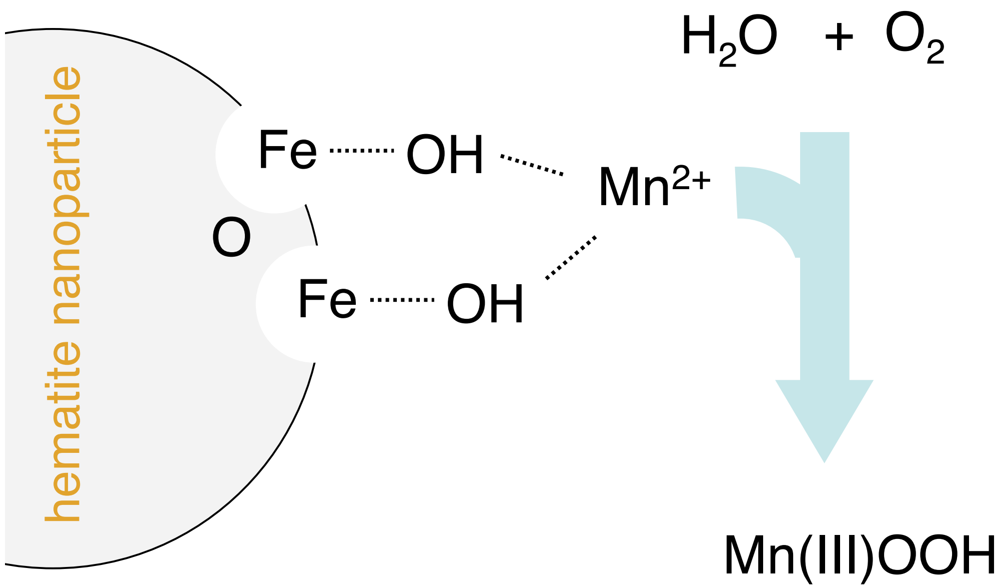
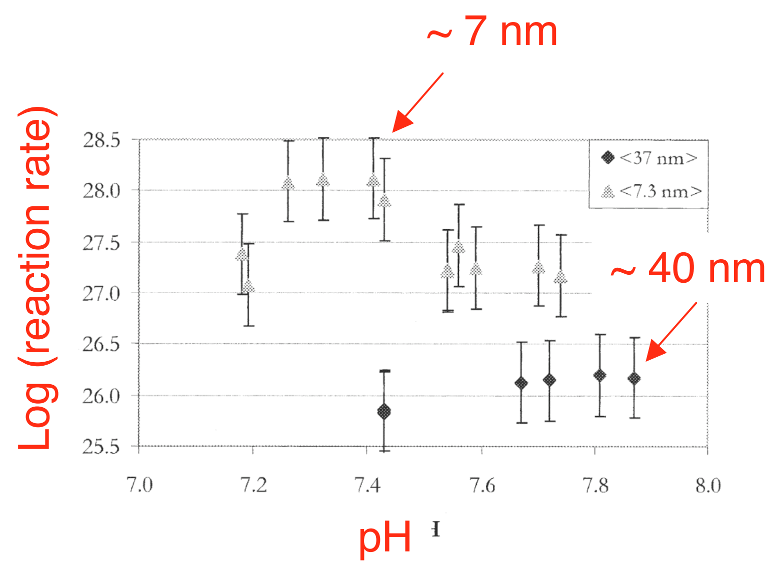
UNIVERSITY OF CALIFORNIA, BERKELEY

Surface reactivity of hematite nanoparticles

Hematite nanoparticle surfaces catalyze the oxidation of Mn^{2+} ~ 10x faster than bulk mineral





Madden & Hochella,
Geochem. Cosmochem. Acta **69**, 389 (2005)

Surface reactivity of hematite nanoparticles

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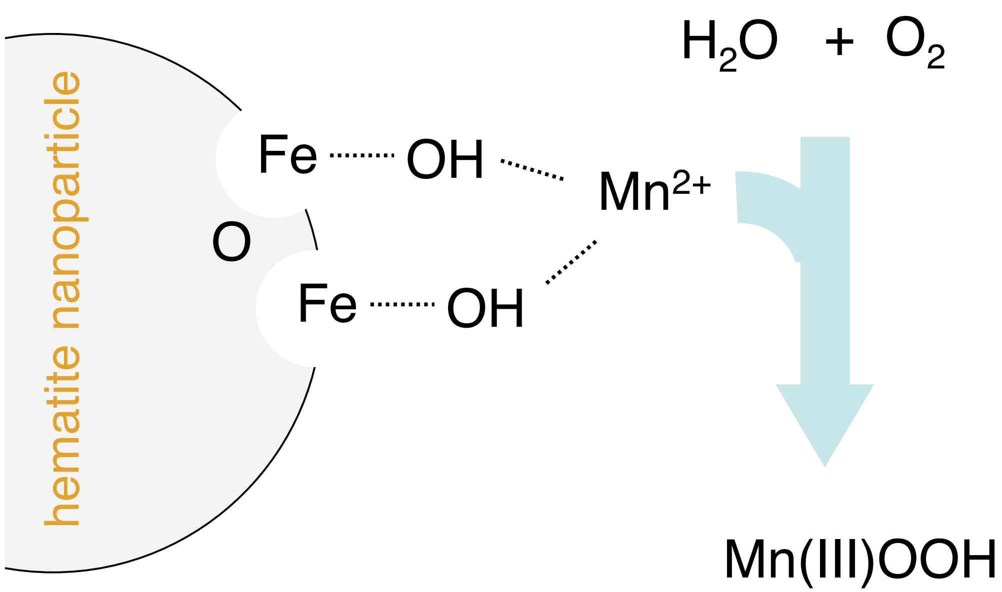
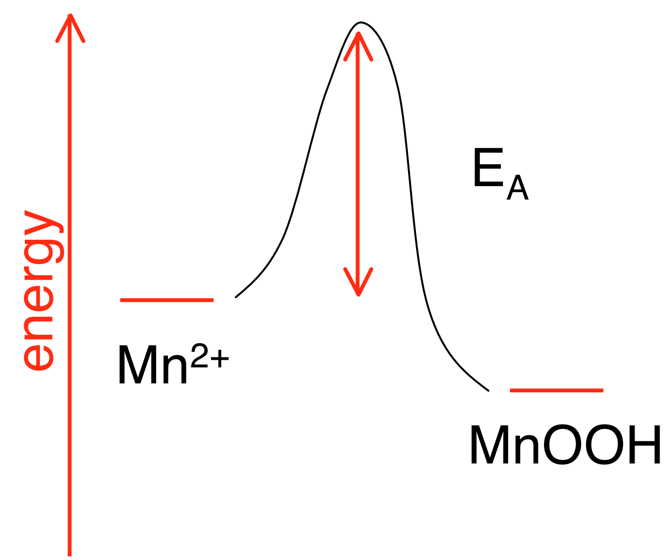
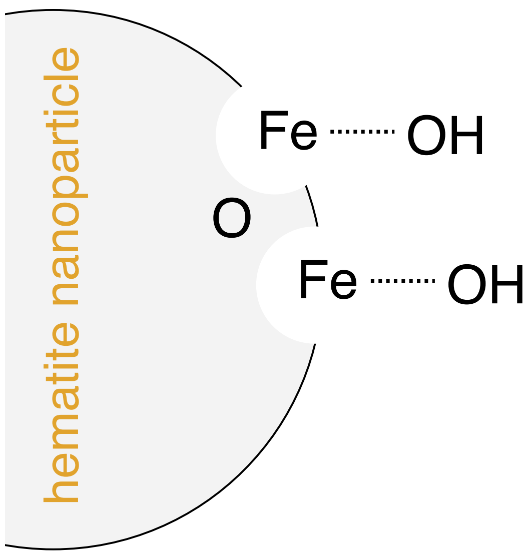




Madden & Hochella,
Geochem. Cosmochem. Acta **69**, 389 (2005)

Surface reactivity of hematite nanoparticles

Implication: Modified sites for binding of aqueous ions and charge-transfer molecules

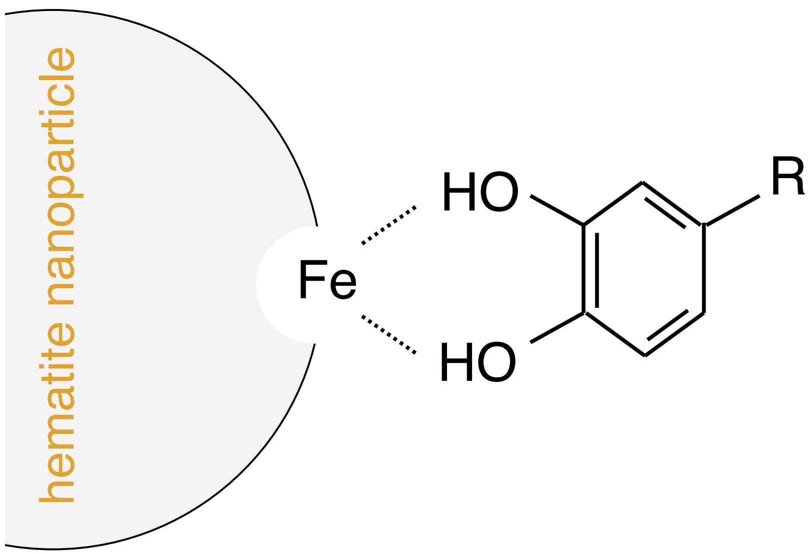


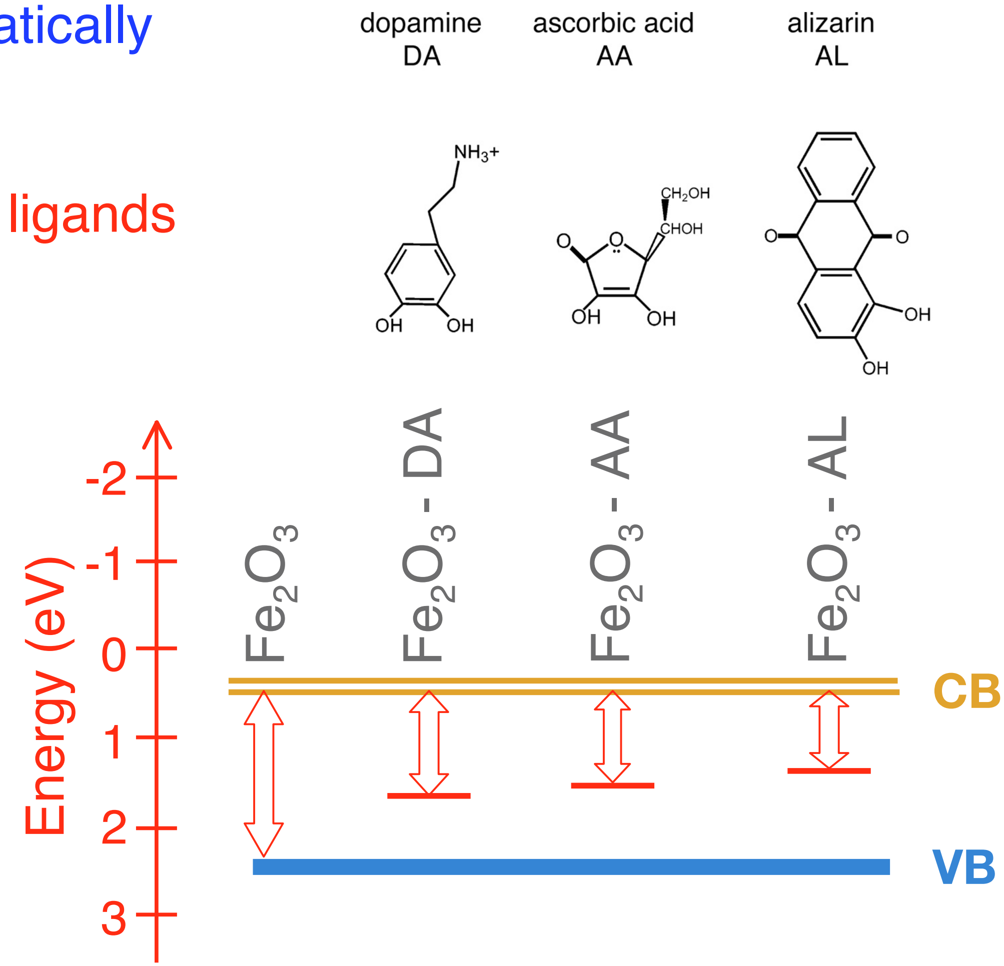
Biomolecular interactions with hematite nanoparticles

Organic adsorbates can dramatically change effective band gap

⇒ nanoparticle + organic ligands

= new material





Rajh et al.,
J. Phys. Chem B **106**, 10543 (2002)

Conclusions
… and areas for further work

- Nanoparticles are reactive components of biogeochemical systems

- Mineral nanoparticles can exhibit intrinsically modified reactivity

- Nanoparticle-ligand interactions very significant

Conclusions
… and areas for further work

- Nanoparticles are reactive components of biogeochemical systems
  - Roles in geochemical cycling to be elucidated

- Mineral nanoparticles can exhibit intrinsically modified reactivity
  - Oxide nanoparticles poorly understood

- Nanoparticle-ligand interactions very significant
  - Structural and chemical implications of ligand binding

Acknowledgments

Y. Suzuki, C. Chan, J. Moreau & K.H. Williams for TEM micrographs

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