Plasmon Sensitized TiO_2 Nanoparticles as a Novel Photocatalyst for Solar Applications

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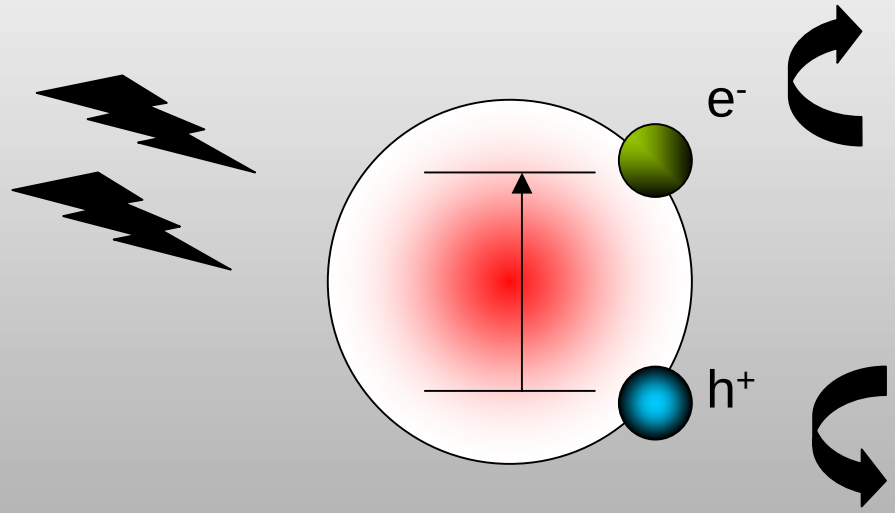

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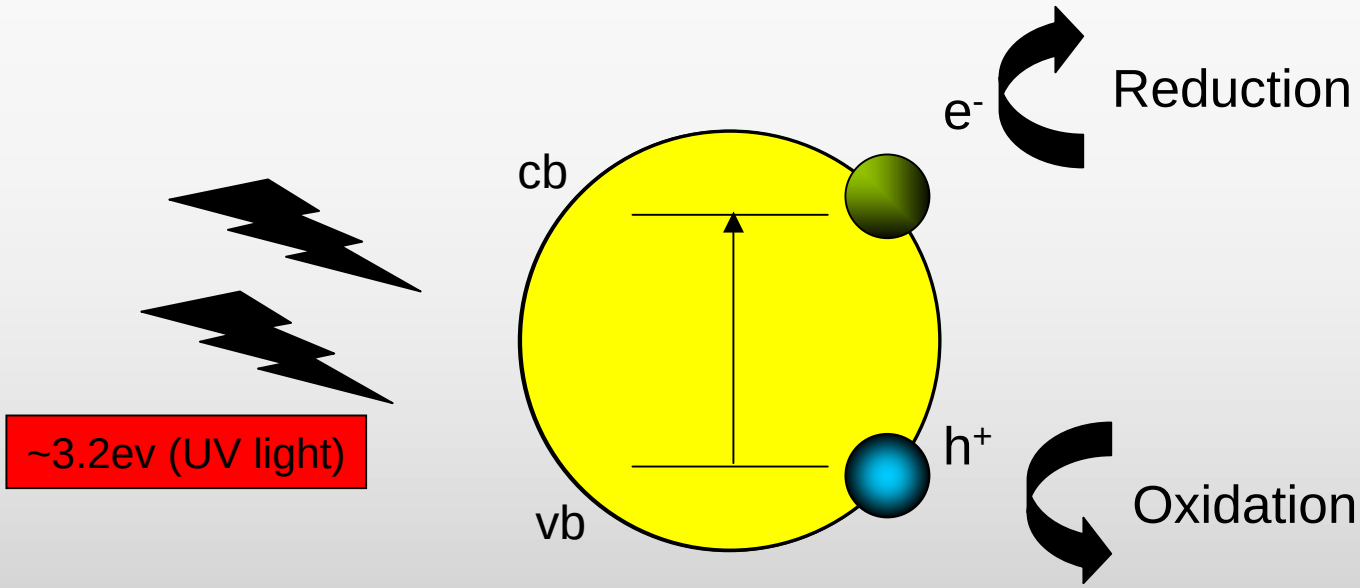
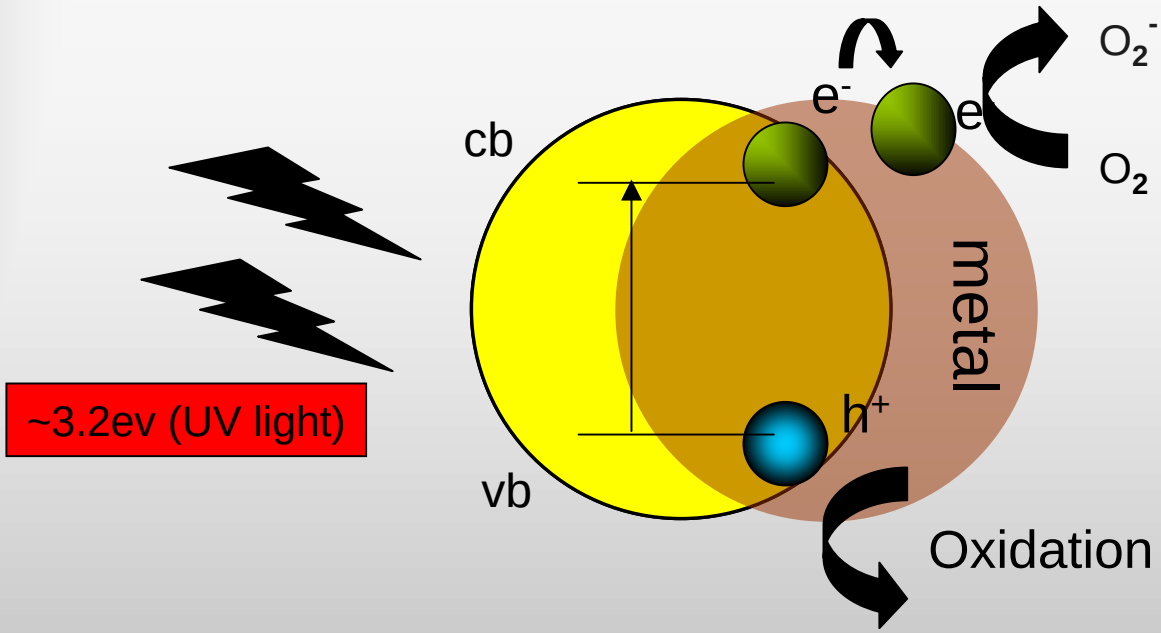
Titania Photocatalyst



Electron-Hole recombination is on the order of < 30ps, hence efficiency is low (< 5%).

Efficiency of photocatalysis depends on how well one can prevent this charge recombination

Role of metal in metal/titania nanocomposites



Metal nanoparticles act as an electron sink, promoting interfacial charge transfer reducing charge recombination

P. V. Kamat. *J. Phys.Chem*. B., 2002, 106, 7729-7744

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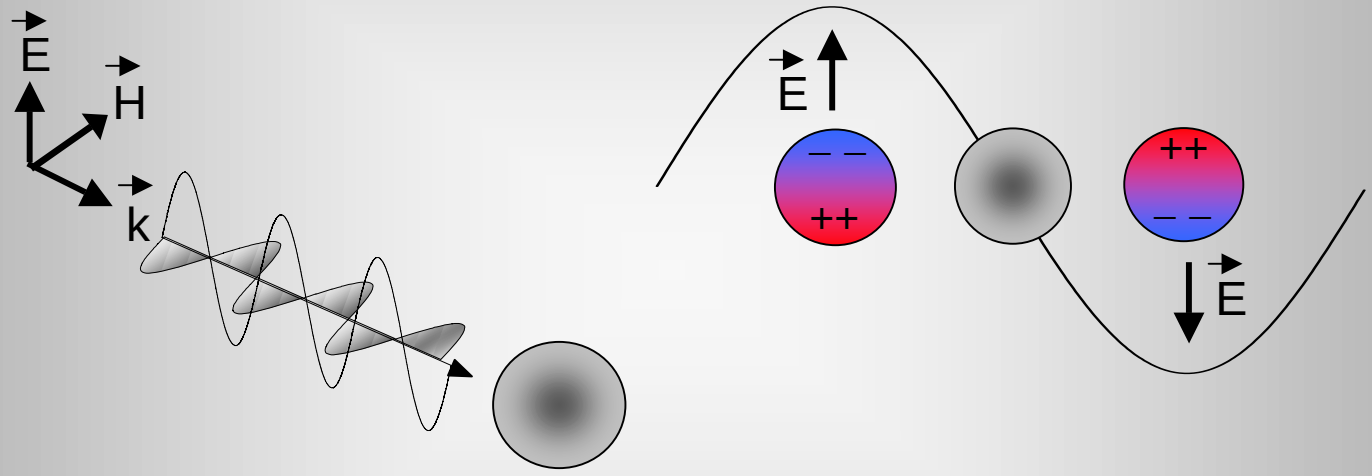
Plasmon Resonance (PR) in Metal Nanoparticles

PR – collective oscillations of conducting electrons in metal nanostructures



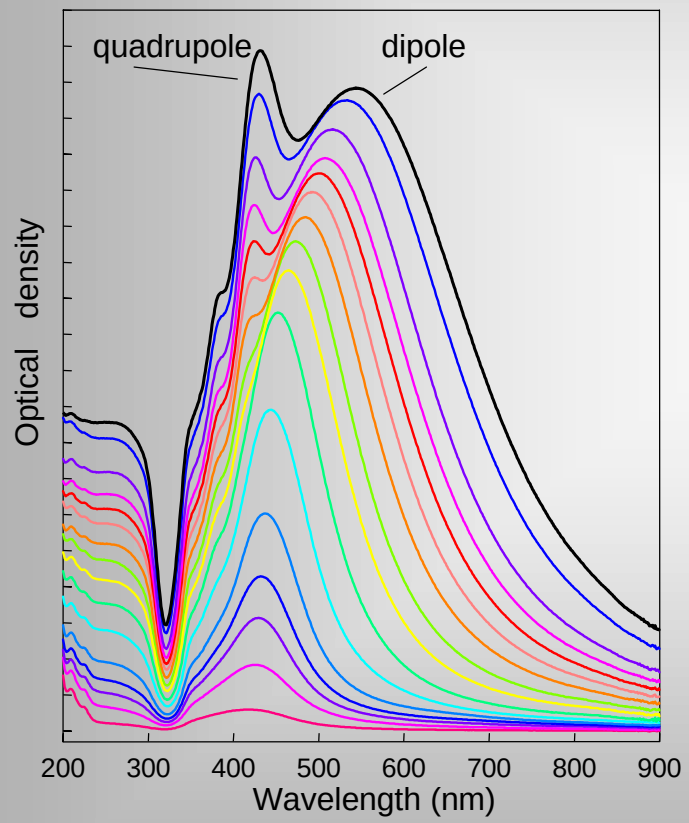
Ag, Au, Cu nanoparticles exhibit PR in the visible spectral range

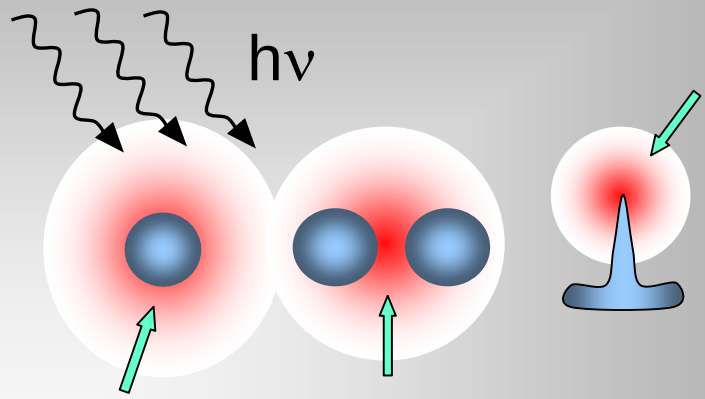
$$\omega_p = (ne^2/\varepsilon_0 m_e)^{1/2}$$

$$\varepsilon_{metal}(\omega_p) = 0$$

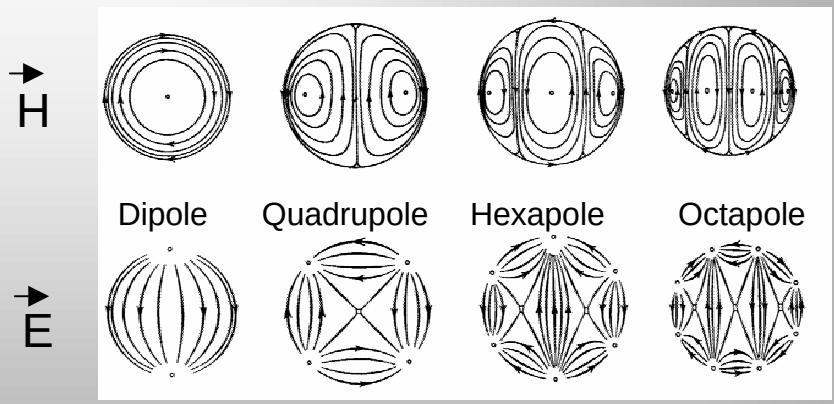
Optical Properties of Silver Nanoparticles

Extinction Spectra of Ag Nanoparticles
as a Function of Size

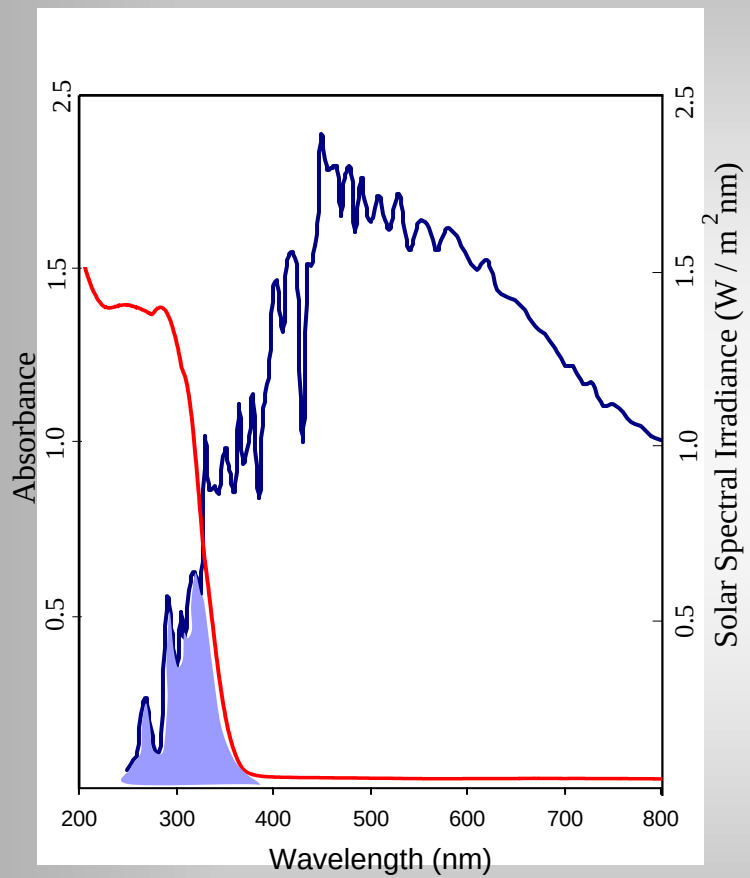


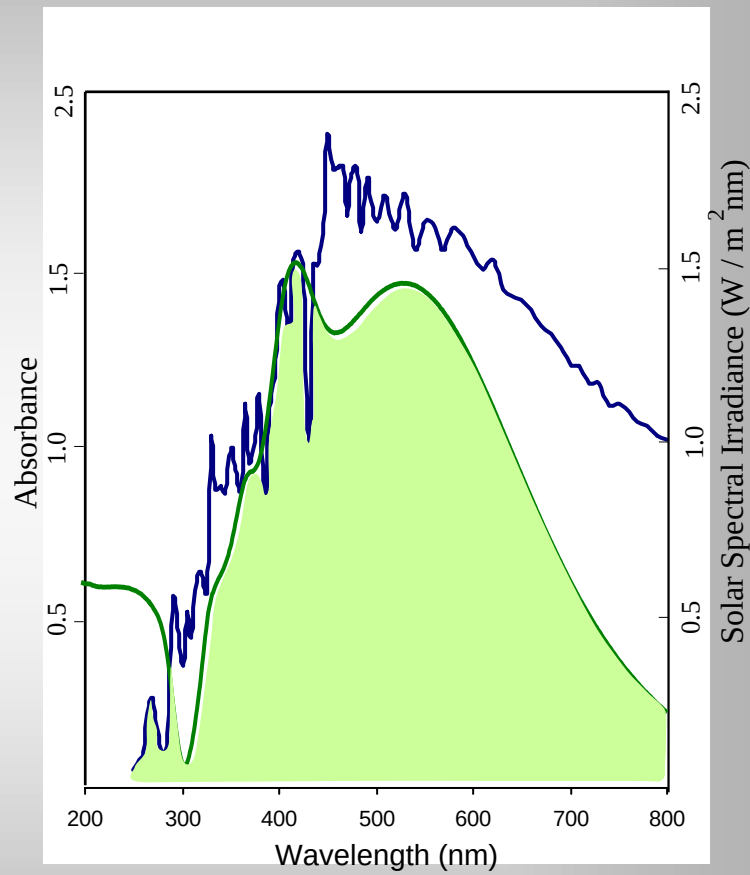


Local Field is Enhanced
Several Orders of Magnitude!



Ag Nanoparticles as Efficient Antennae for Capturing of Solar Energy





Solar Spectrum is from J.H.Seinfeld and S.N.Pandis"Atmospheric Chemistry and Physics" John Wiley &Sons, Inc. New York, Chichester, Brisbane, Singapore, Toronto (1998)

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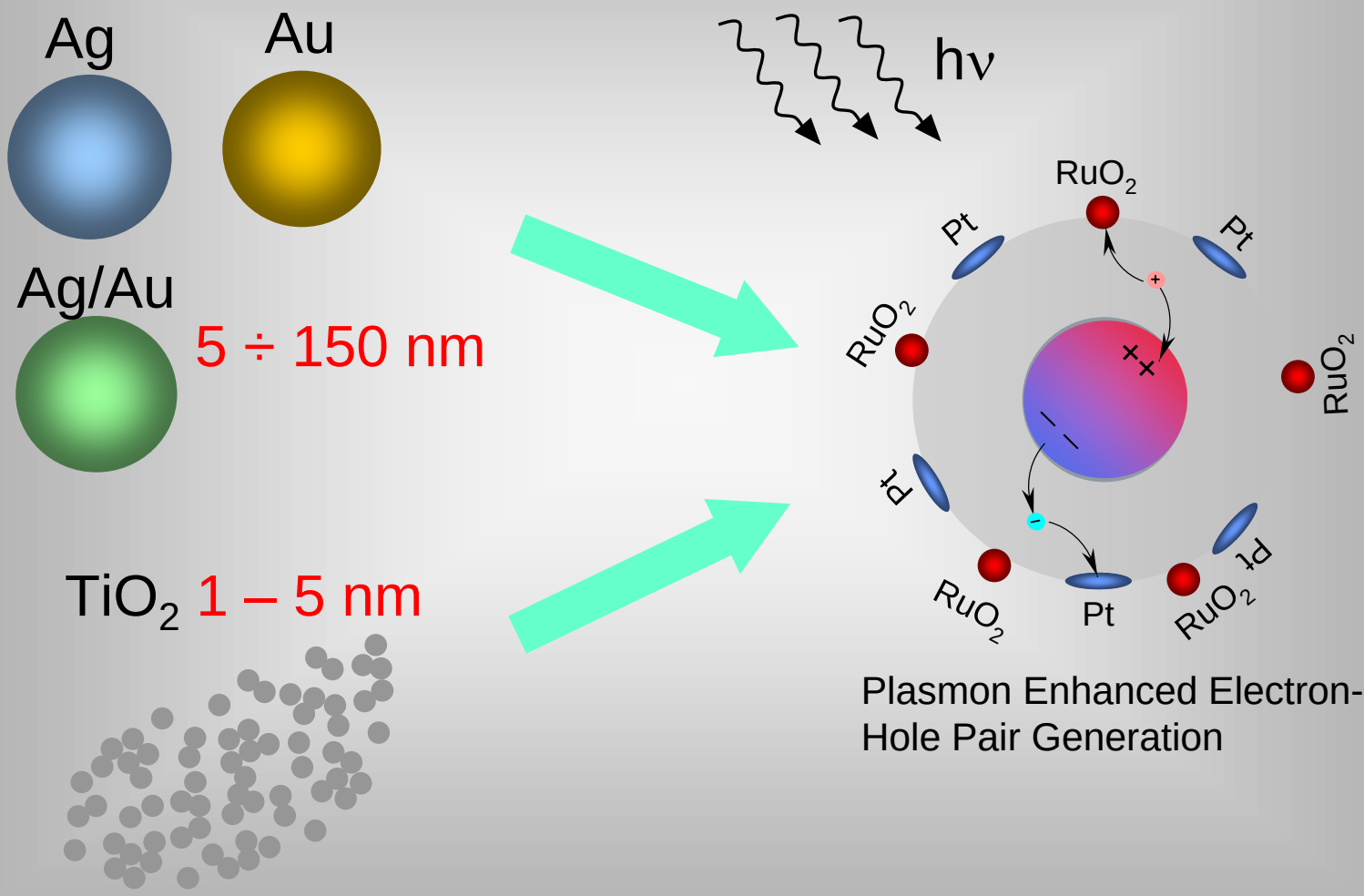
Titania Coated Metal Nanoparticles



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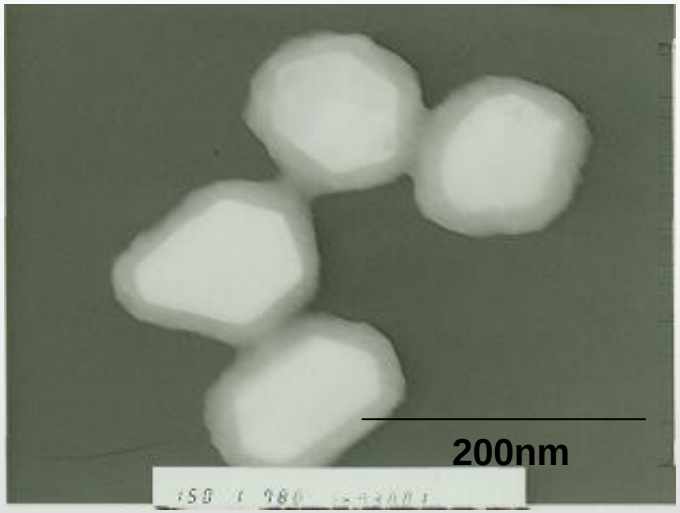
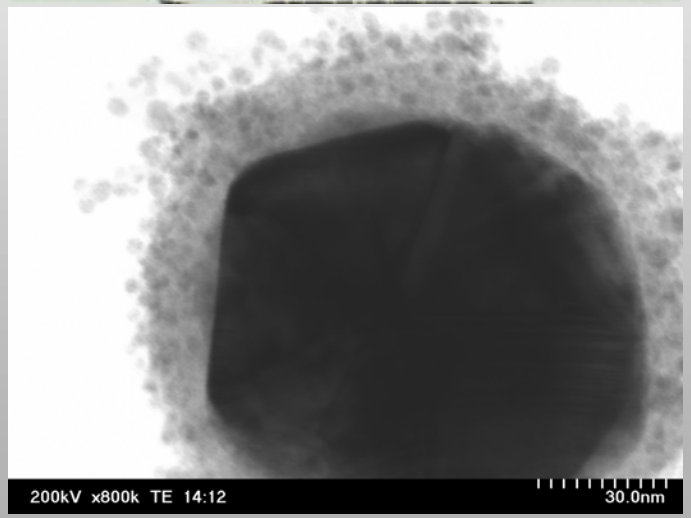
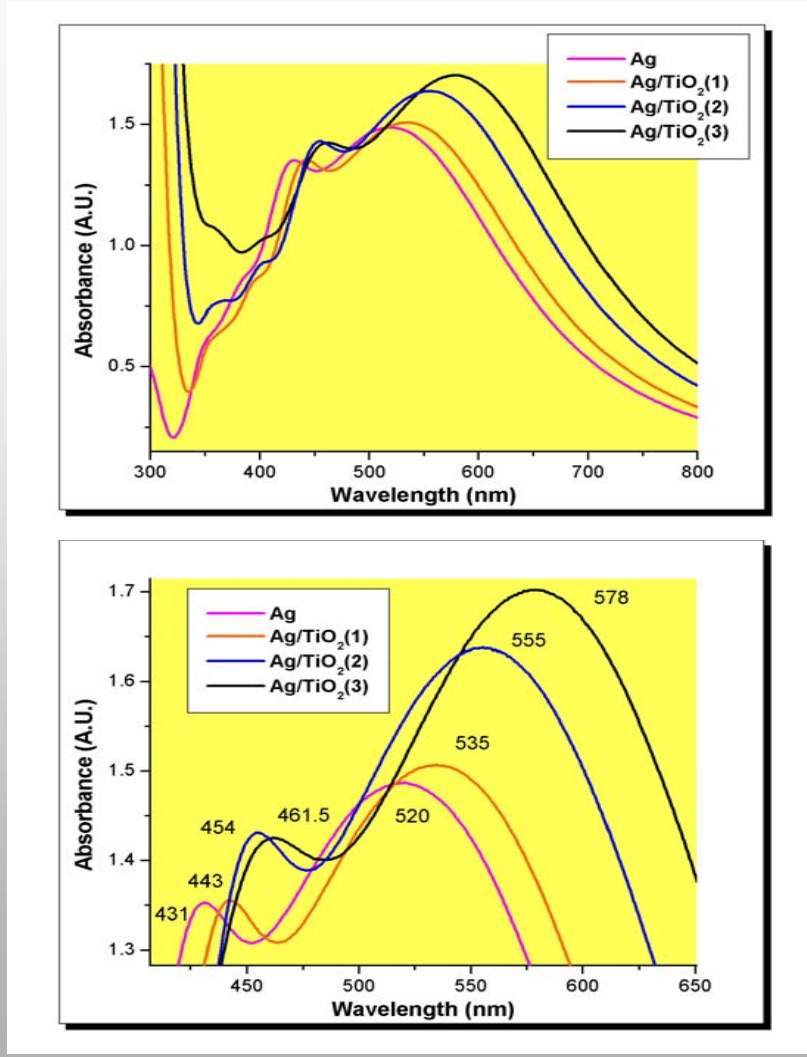
Titania coated Silver Nanoparticles







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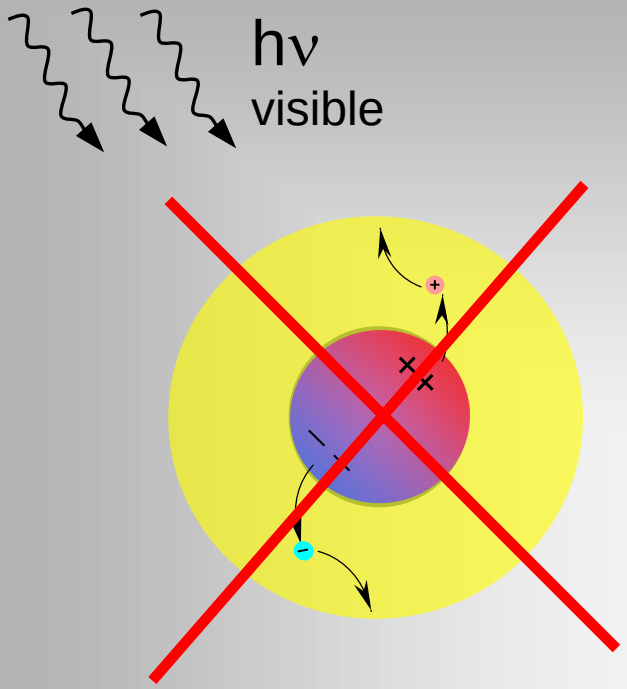

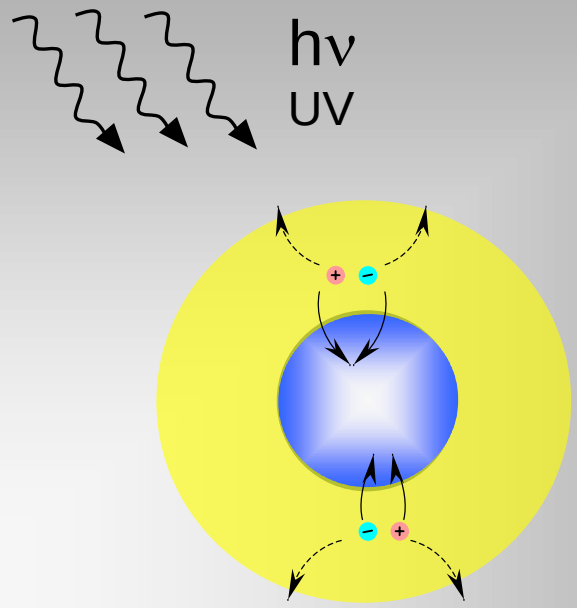

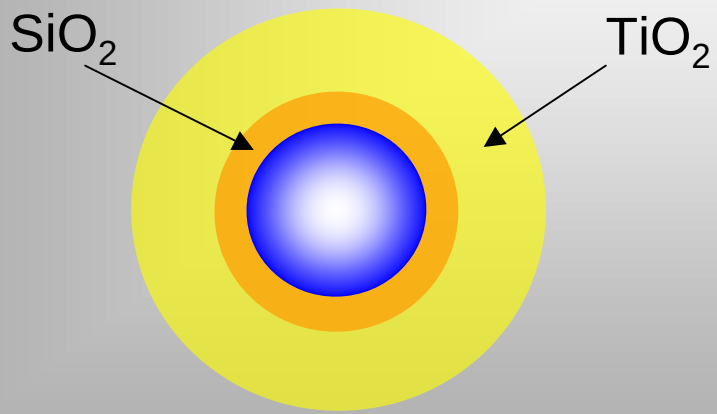

Metal core shortens the electron-hole pairs generated in titania shell

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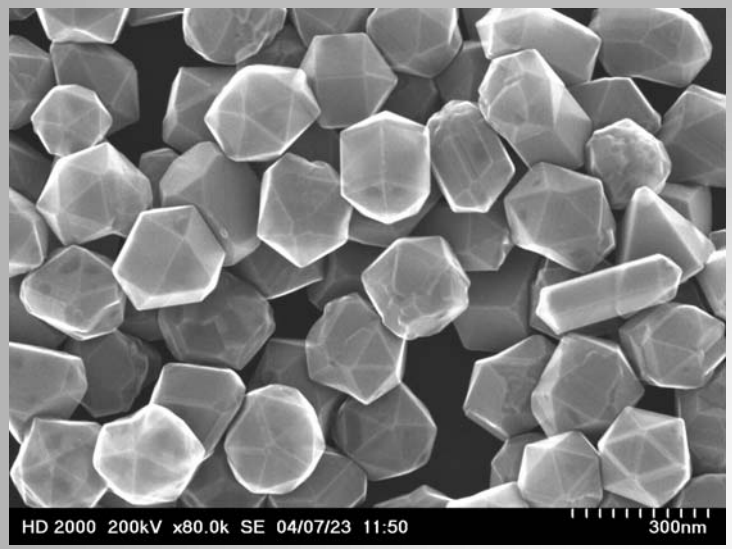
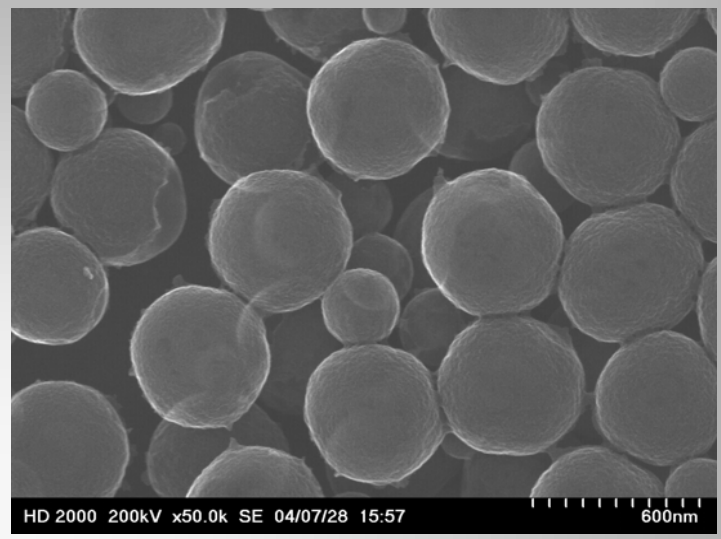
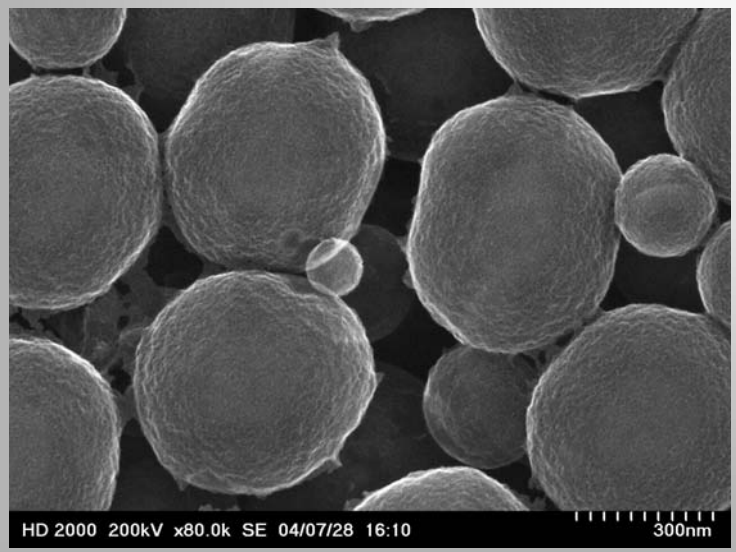
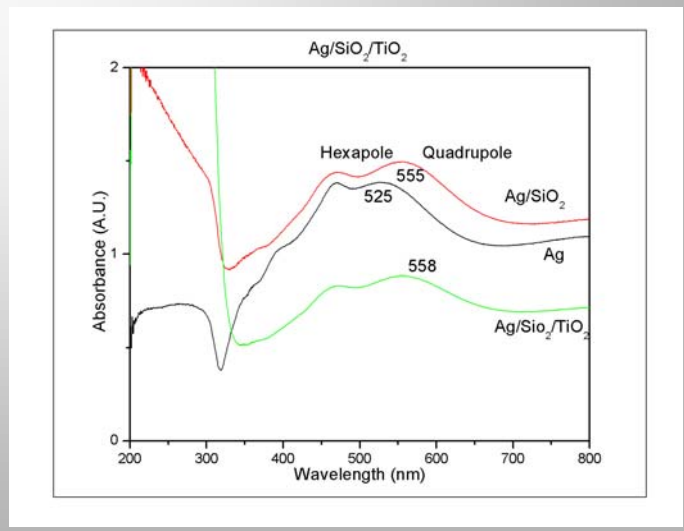
Ag core SiO_2/TiO_2 Nanoparticles









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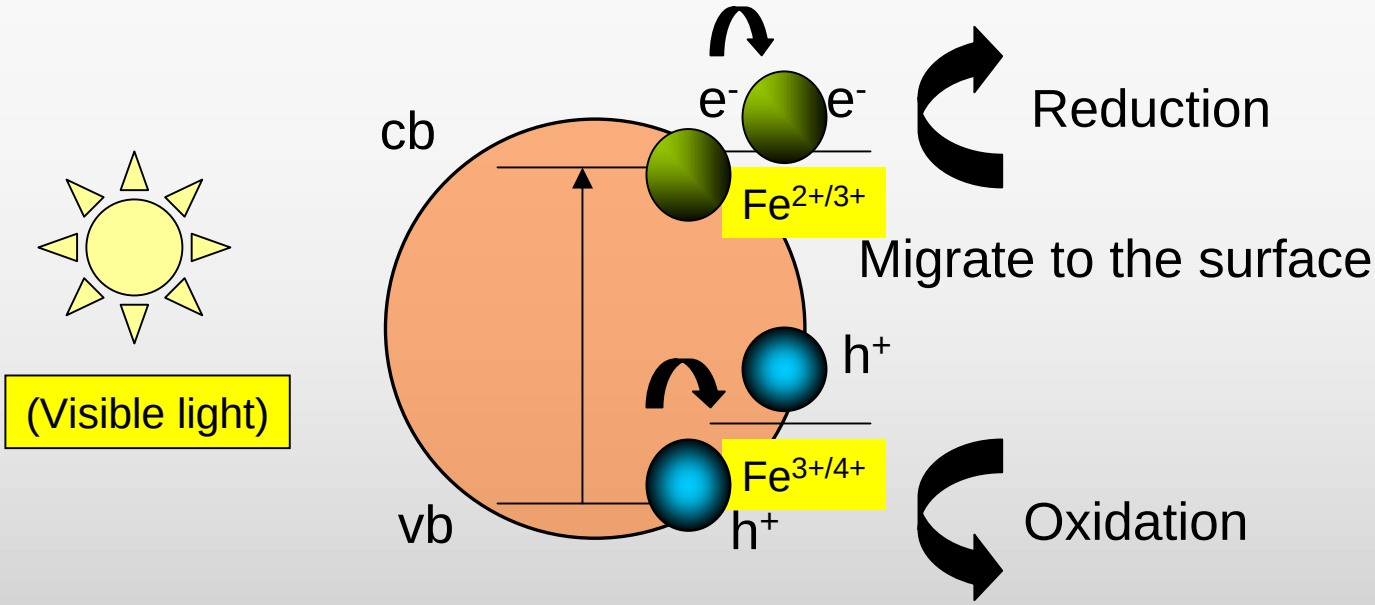
Metal Ion Doped-Titania Photocatalyst

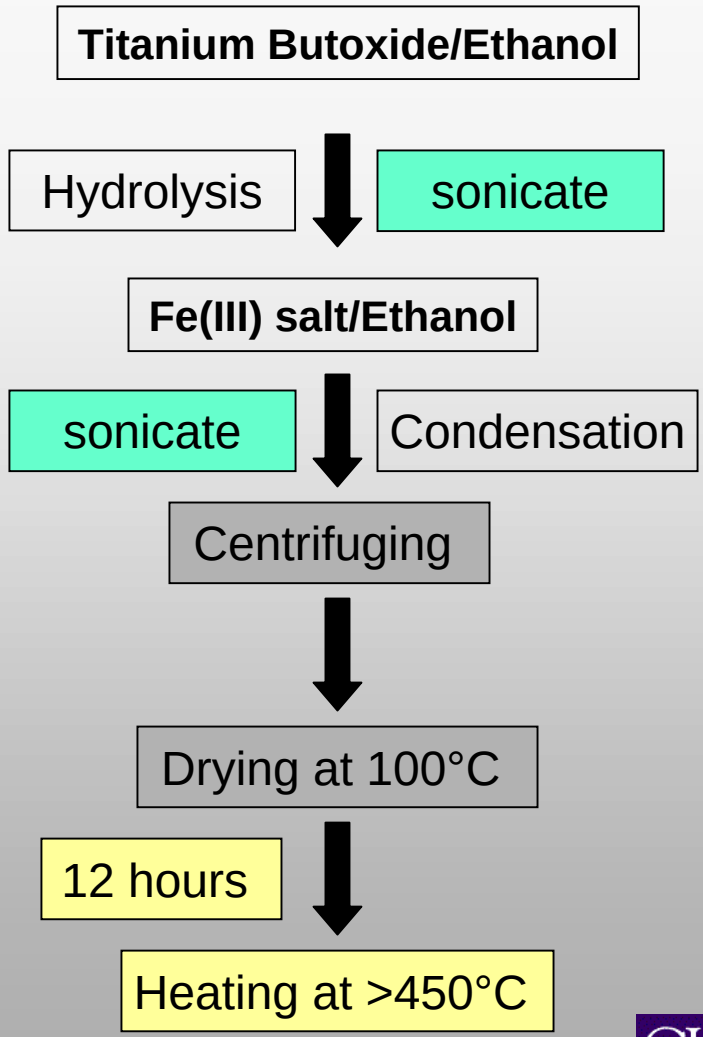


Dopants influences intrinsic properties of titania resulting in lowering the band gap and shifting light absorption into visible spectral range

Dopants should be both good electron and hole traps

Efficiency of photocatalysis depends on various charge transfer events and migration of charges to the surface

Synthesis of Fe^{3+}-doped TiO_2



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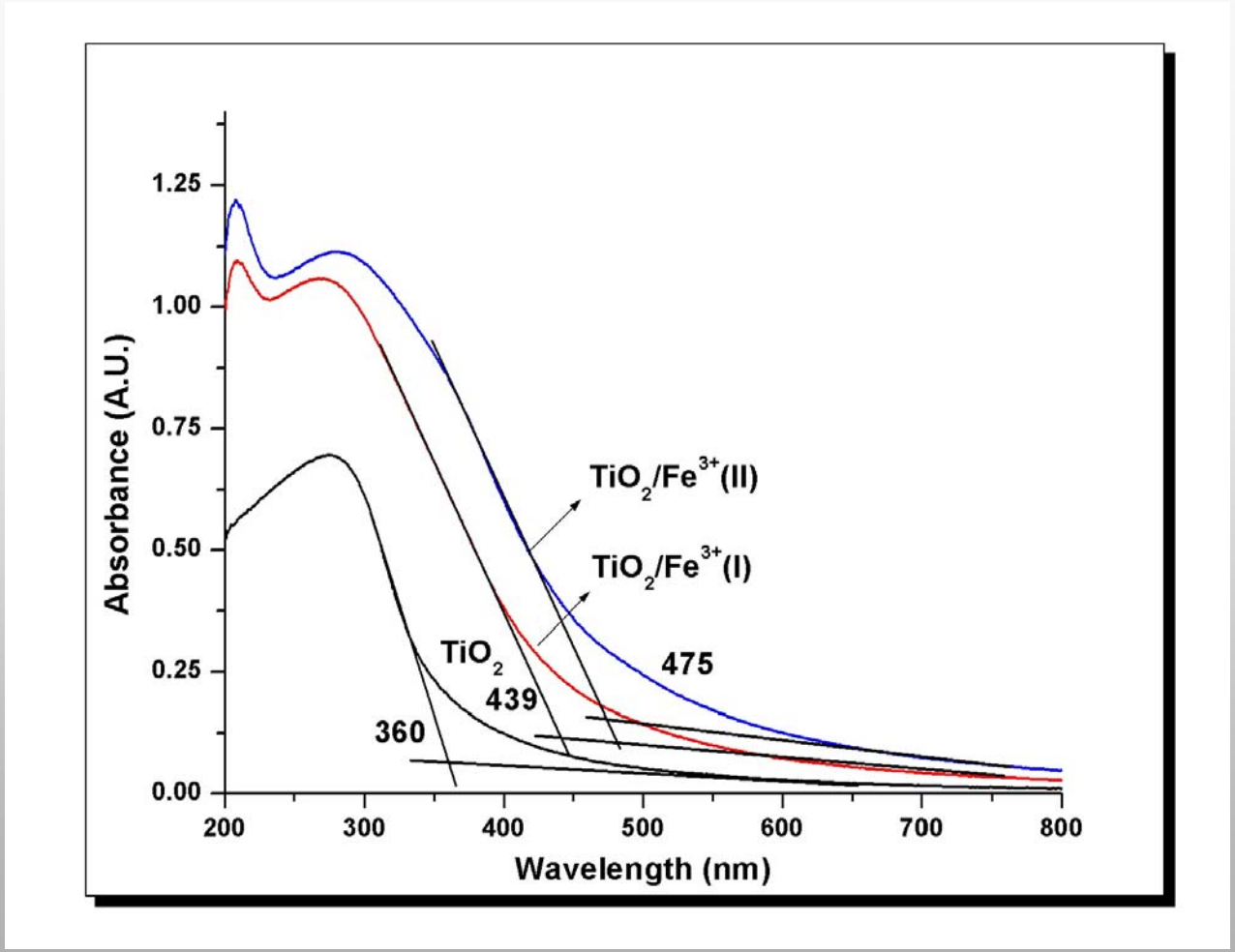
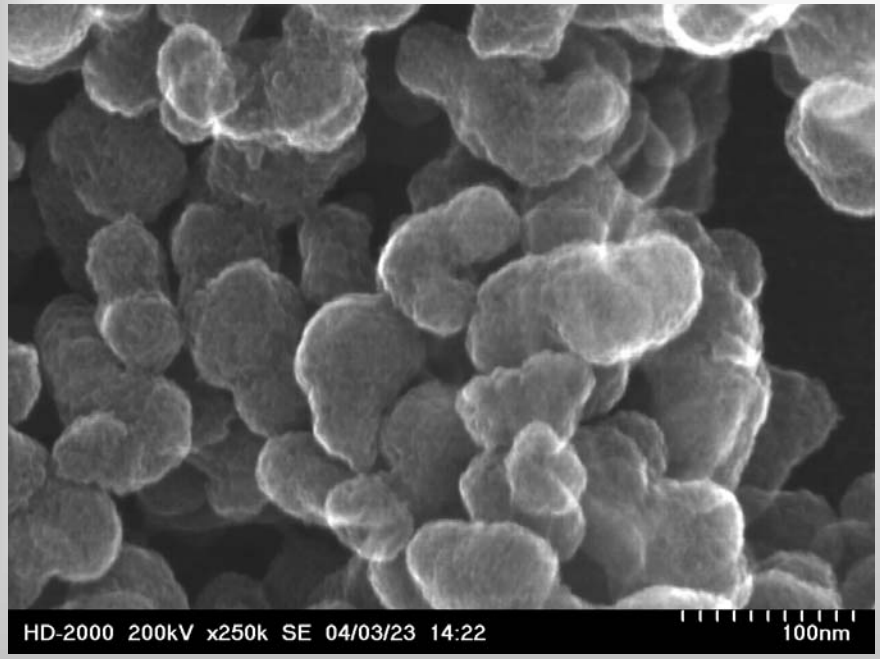
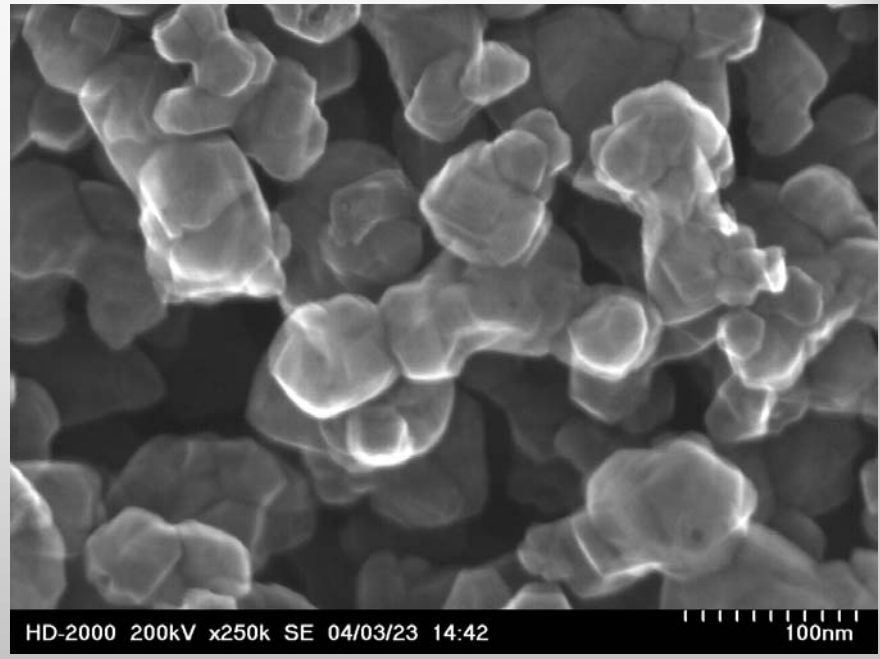
UV-Vis Absorption Spectra of Fe^{3+}-doped TiO_2 : Effect of Fe^{3+} concentration



Electron Microscopy



TiO_2 as prepared (amorphous)



TiO_2 after heat treatment (crystalline)

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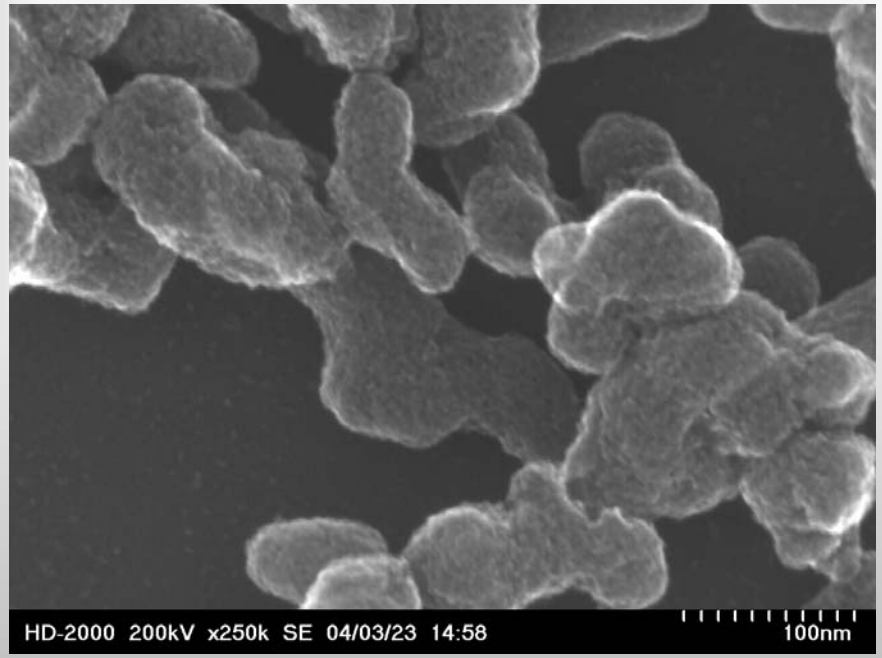
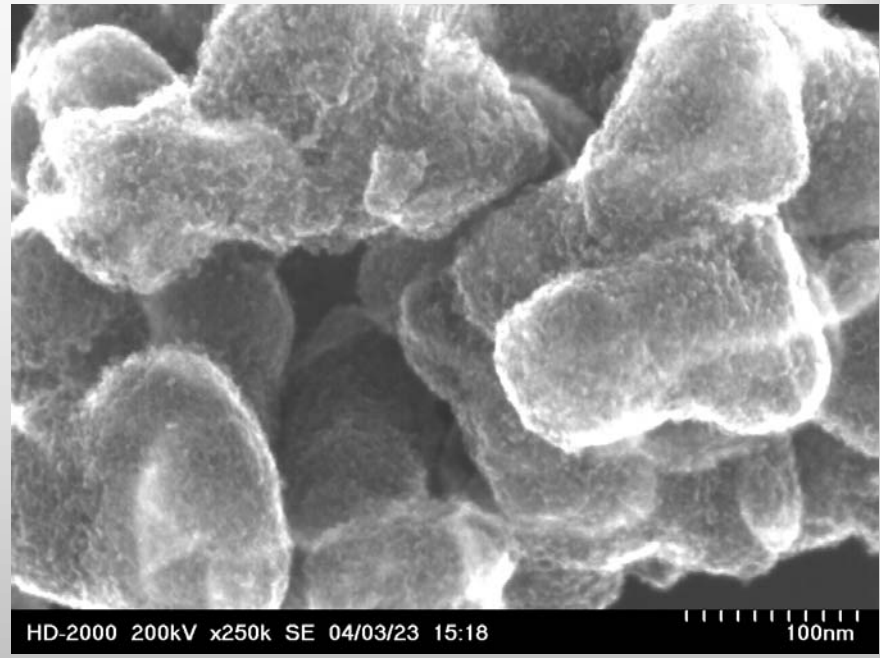
Electron Microscopy



Fe^{3+}/TiO_2 as prepared (amorphous)



Fe^{3+}/TiO_2 after heat treatment (semi-crystalline)

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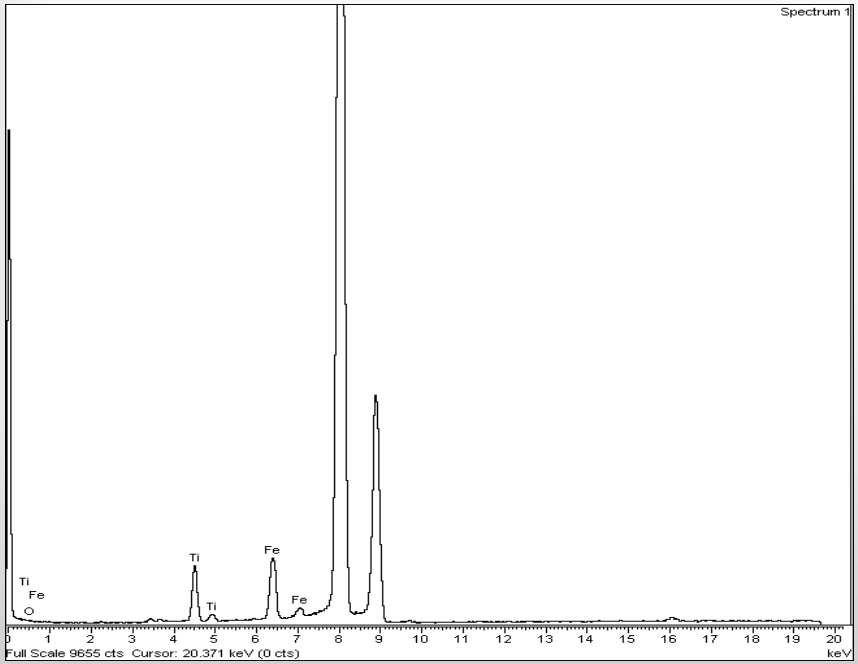
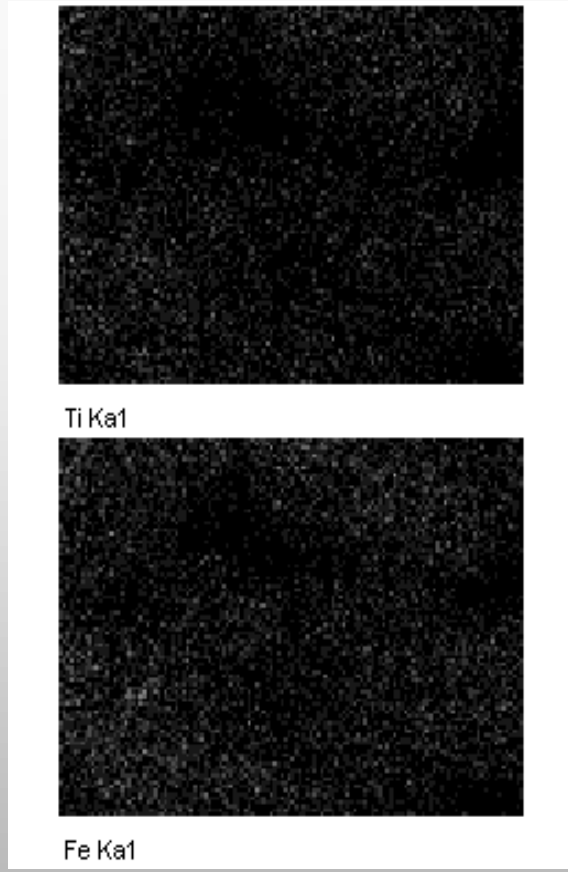
EDX spectra and Mapping of Fe^{3+}-doped TiO_2



EDX spectra shows the presence of iron at >8 atomic % which arises from both surface and bulk Fe^{3+} sites



EDX mapping studies indicate the uniform dispersion of iron within the TiO_2 matrix

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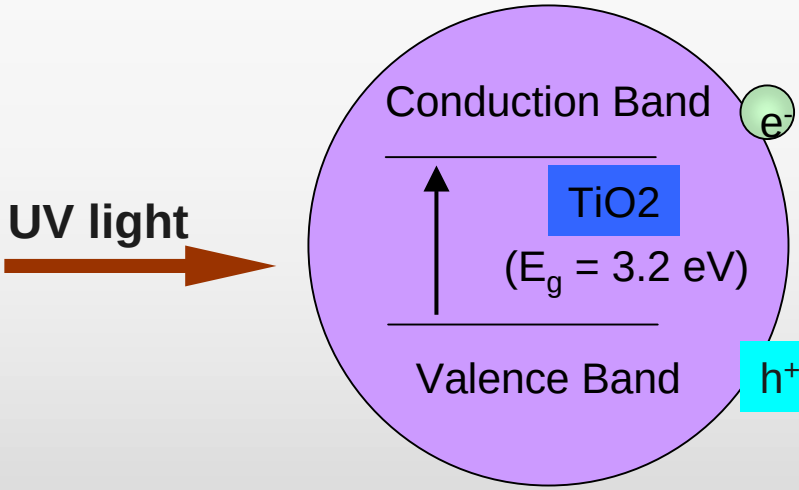
Photocatalysis Using UV light

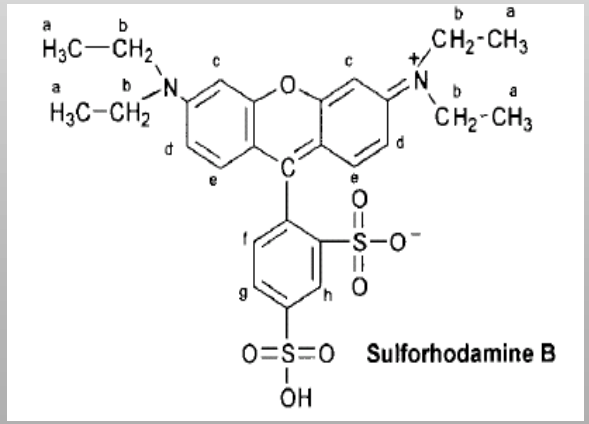


$SRB^{\bullet+} + O_2 \longrightarrow SRBOO^{\bullet+}$

Degradation of chromophore structure
(diethylamine, N,N-diethylacetamide, etc)

h^+ or $^{\bullet}OH$

SO_4^{2-}, NH_4^+, CO_2, H_2O



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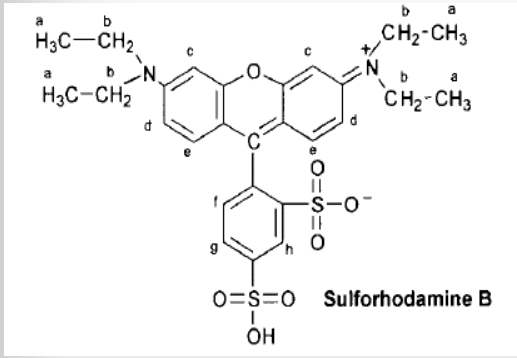
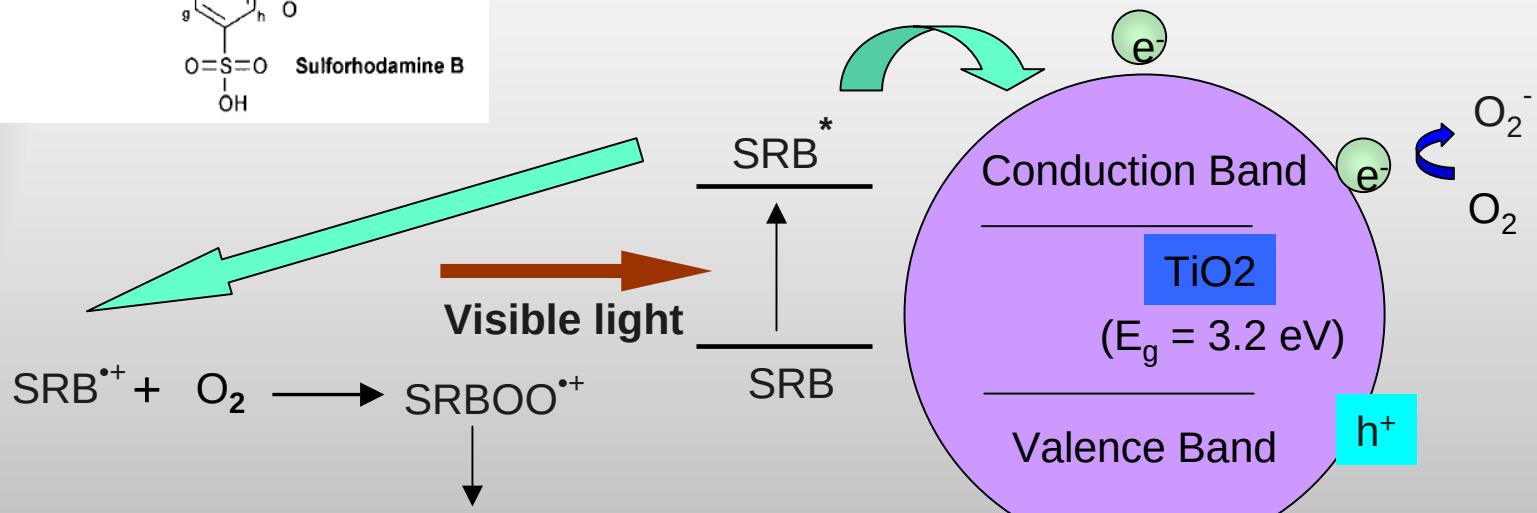
Photosensitization Using Visible light





Degradation of chromophore structure
(diethylamine, N,N-diethylacetamide, etc)

\+ SO_4^{2-}, NH_4^+, CO_2, H_2O

G. Liu, L. J. Zhao. *New. J. Chem.*, 2000, 24, 411-417

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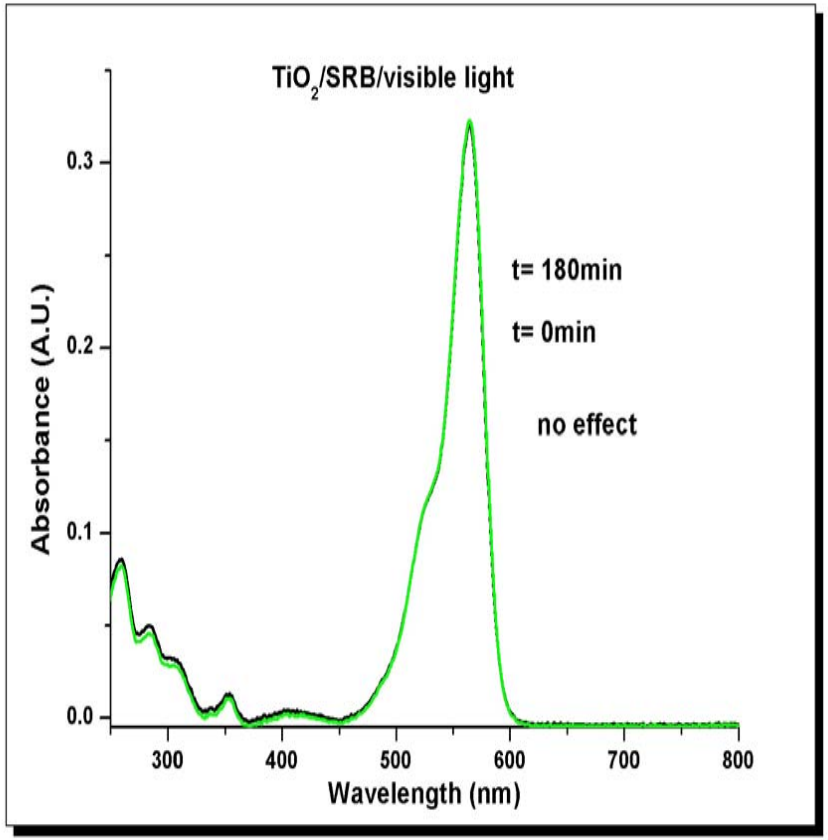
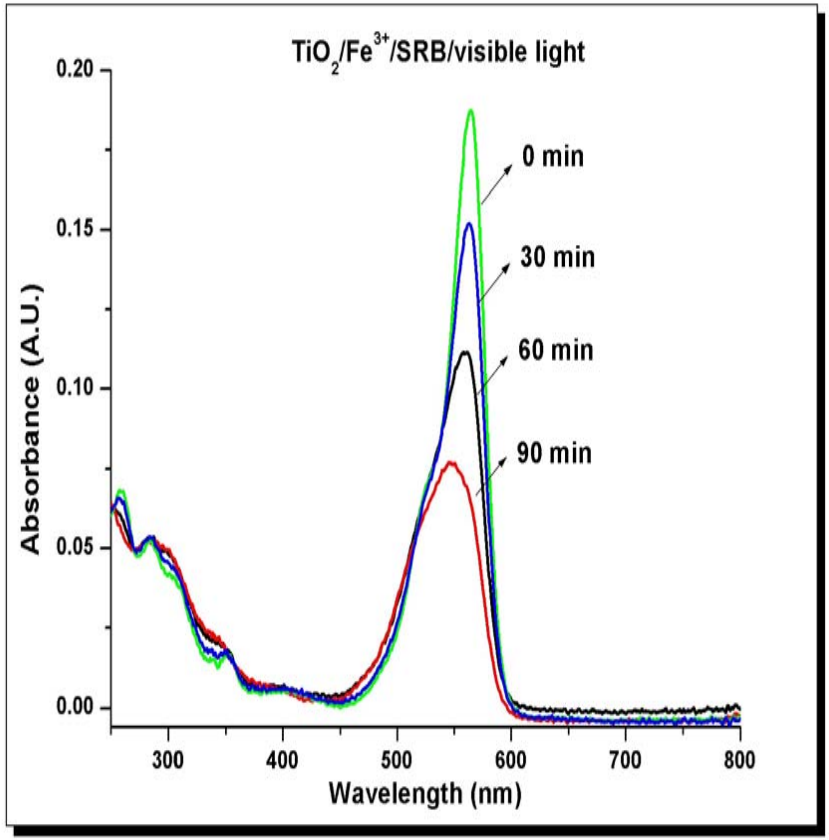
Photocatalysis Experiments





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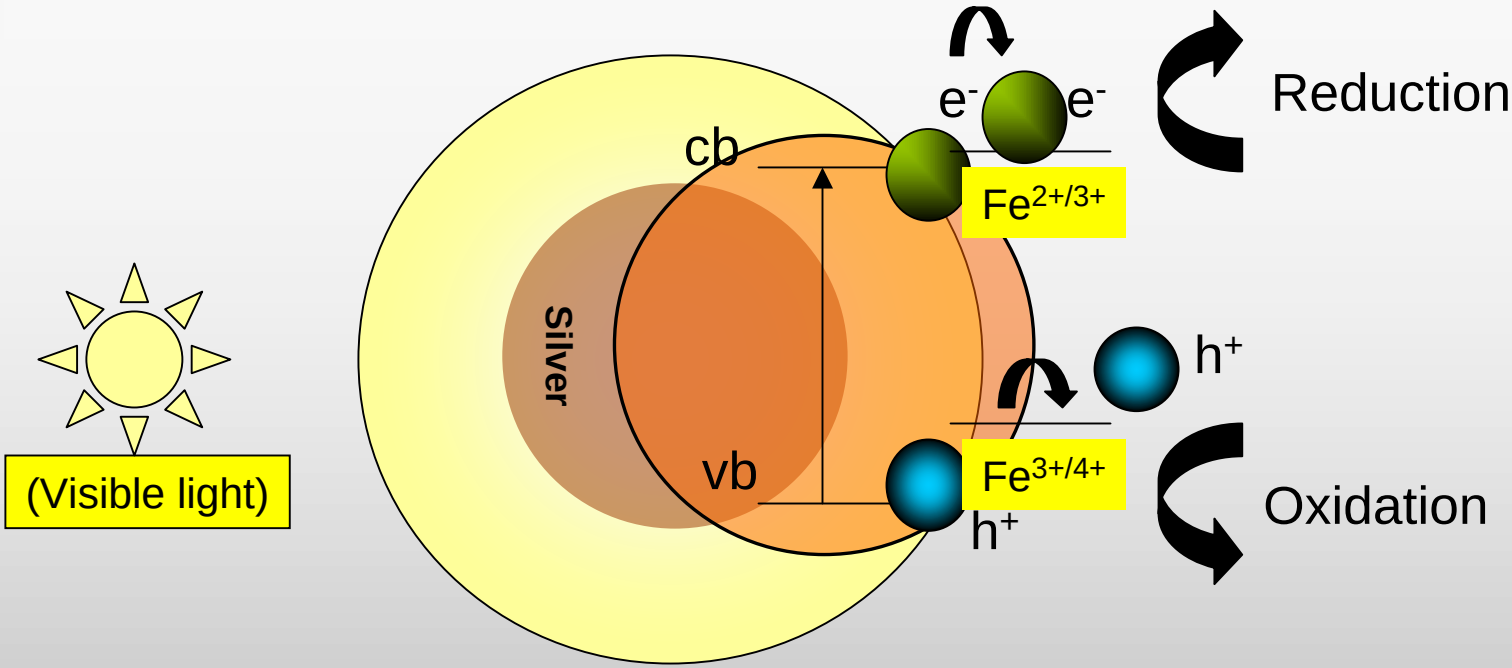
Role of metal in Metal/Doped-Titania Photocatalyst



At the plasmon resonance frequency there would be efficient resonance light absorption.

Band-gap excitation wavelength should reasonably match silver plasmon resonance frequency

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Conclusions

Titania coated silver nanoparticles were synthesized using sol-gel technique.

Fe^{3+}- doped Titania that is sensitive to visible light was synthesized.

From the degradation of sulforhodamine dye experiments true doping effect was observed in the Fe^{3+}- doped Titania photocatalyst

Efforts are underway to coat silver nanoparticles with Fe^{3+}- doped Titania .

Photocatalytic activity of Fe^{3+}- doped Titania and silver coated with Fe^{3+}- doped Titania will be compared.

Current Member of the Group

David Evanoff, Katrina Daniels,

Amar Kumbhar, Steve Hunson,

Mark Kinnan, Sravanti Ambati,

Kenia Parga