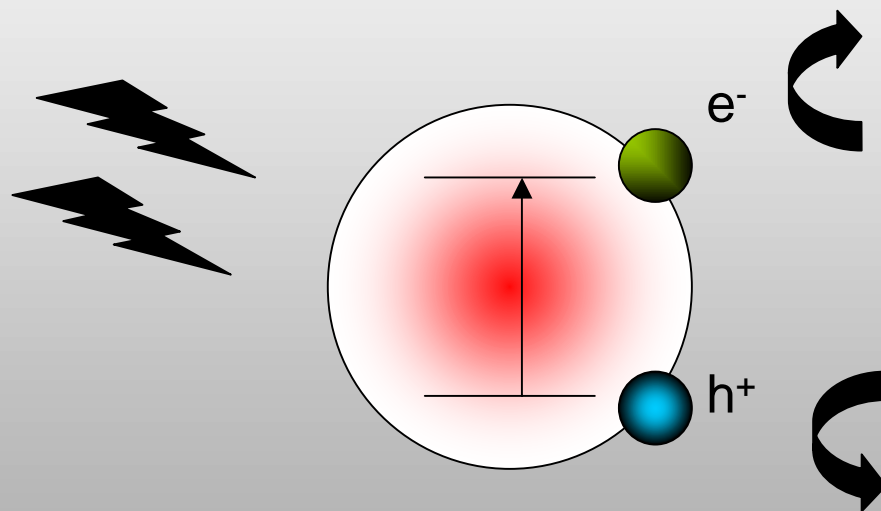


US EPA ARCHIVE DOCUMENT

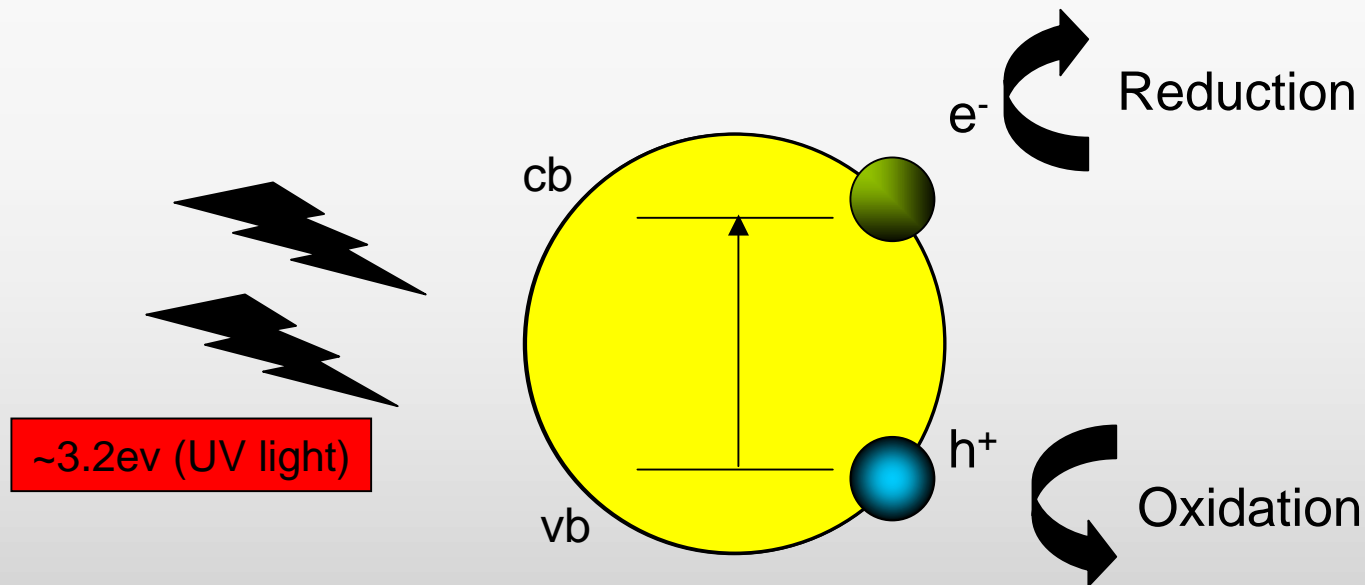
Plasmon Sensitized TiO₂ Nanoparticles as a Novel Photocatalyst for Solar Applications

George Chumanov

Department of Chemistry, Clemson University, Clemson, SC 29634



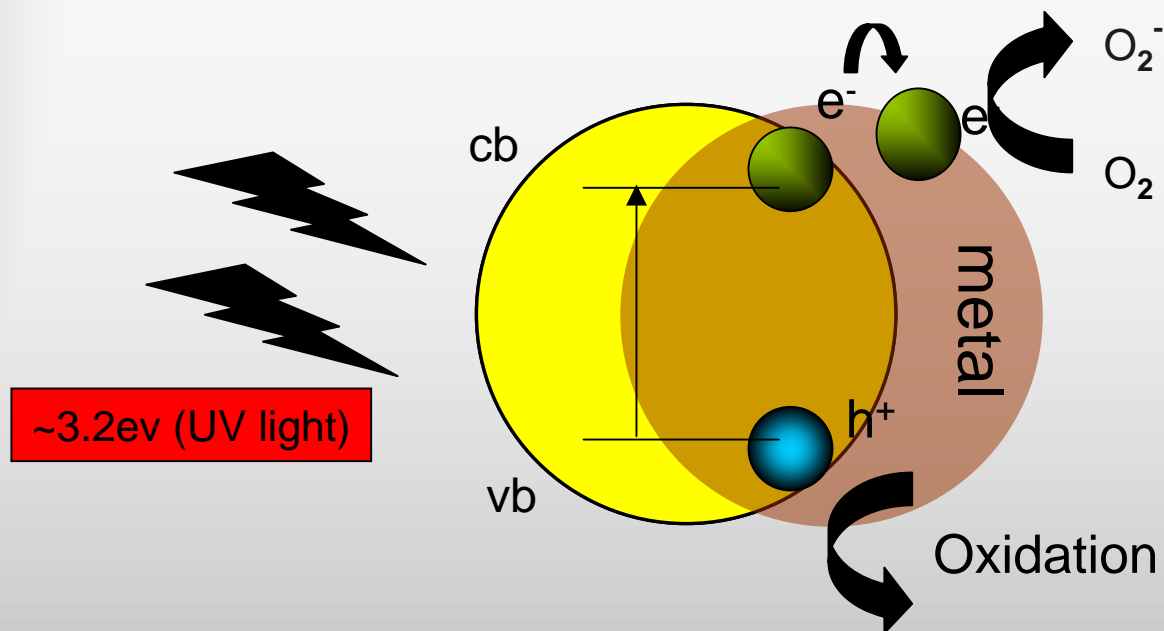
Titania Photocatalyst



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

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

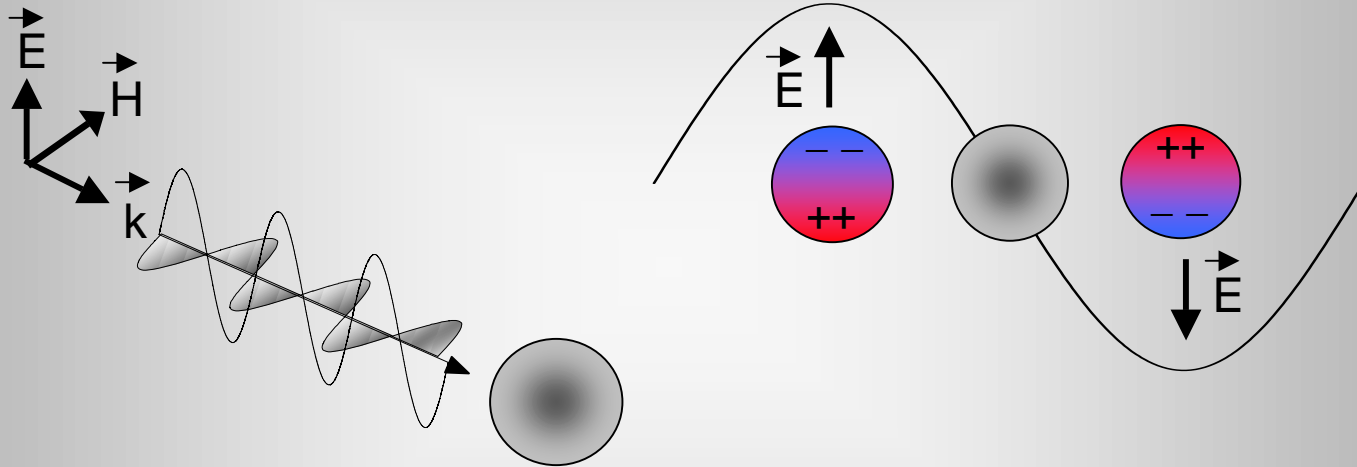
Role of metal in metal/titania nanocomposites



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

Plasmon Resonance (PR) in Metal Nanoparticles

PR – collective oscillations of conducting electrons in metal nanostructures



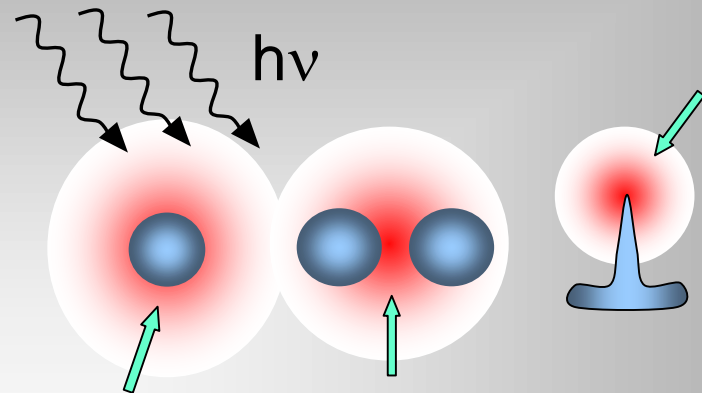
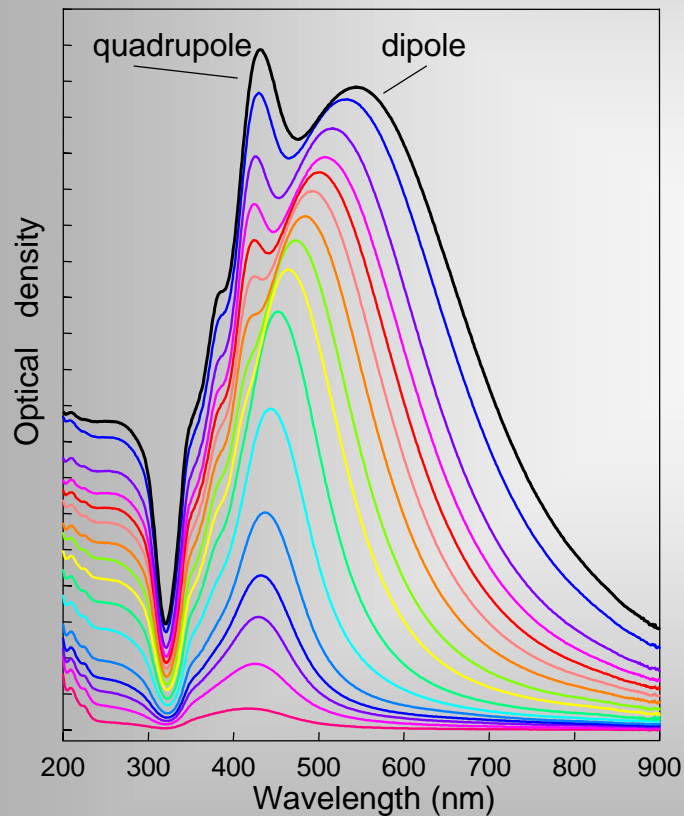
Ag, Au, Cu nanoparticles exhibit **PR** in the visible spectral range

$$\omega_p = (ne^2/\epsilon_0 m_e)^{1/2}$$

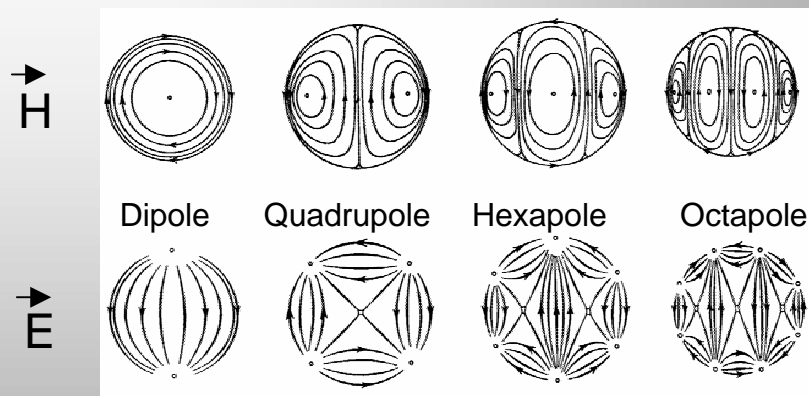
$$\epsilon_{\text{metal}}(\omega_p) = 0$$

Optical Properties of Silver Nanoparticles

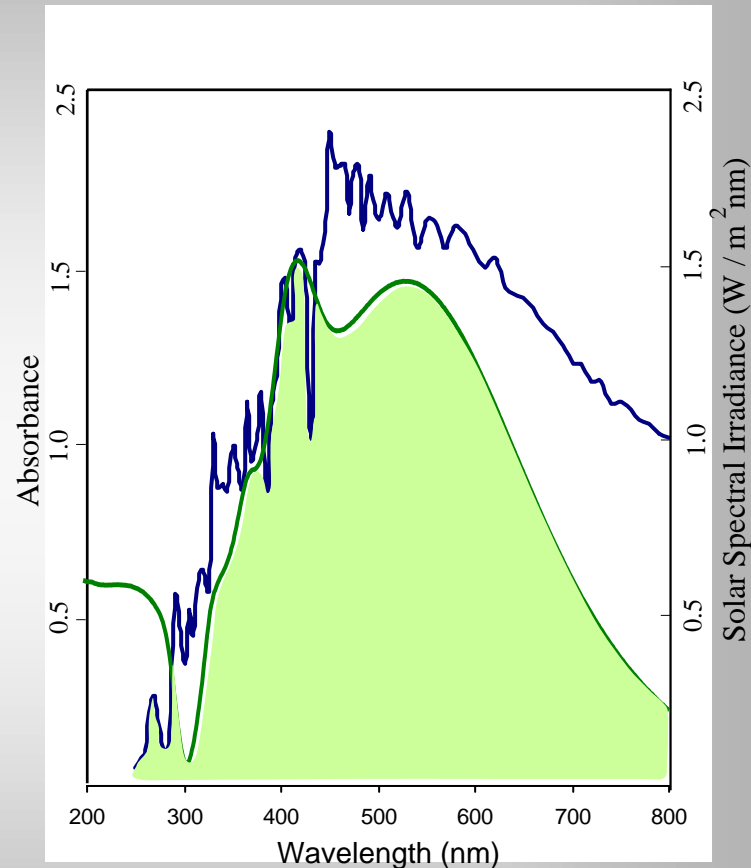
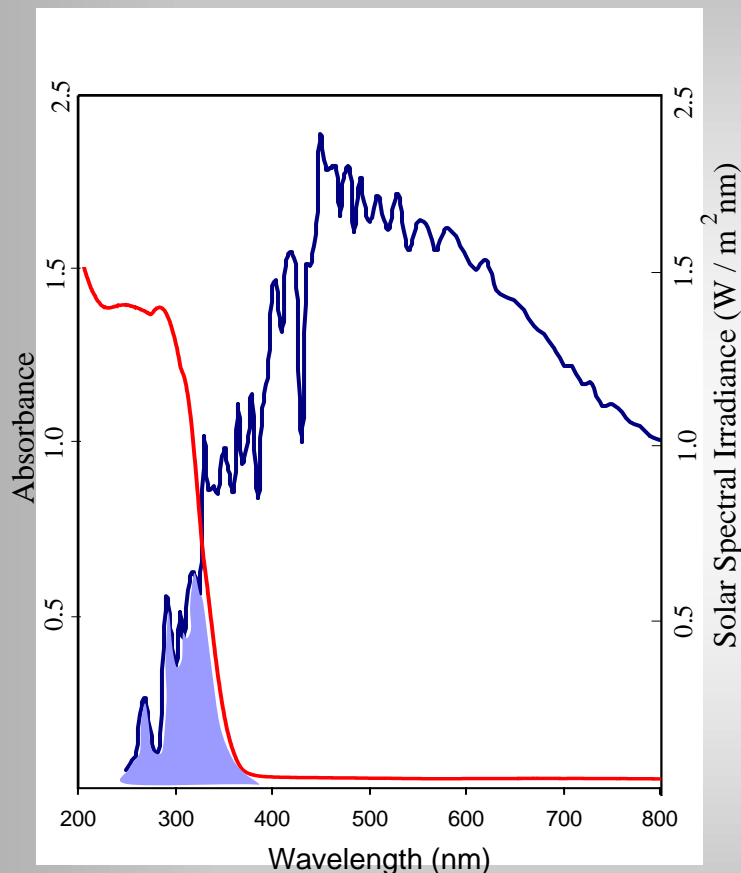
Extinction Spectra of Ag Nanoparticles as a Function of Size



Local Field is Enhanced
Several Orders of Magnitude!

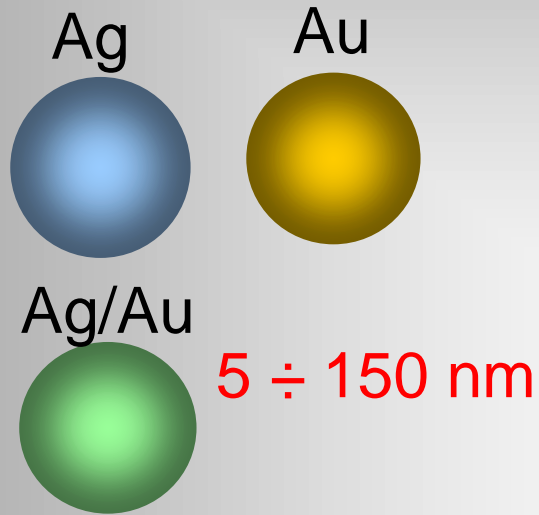


Ag Nanoparticles as Efficient Antennae for Capturing of Solar Energy

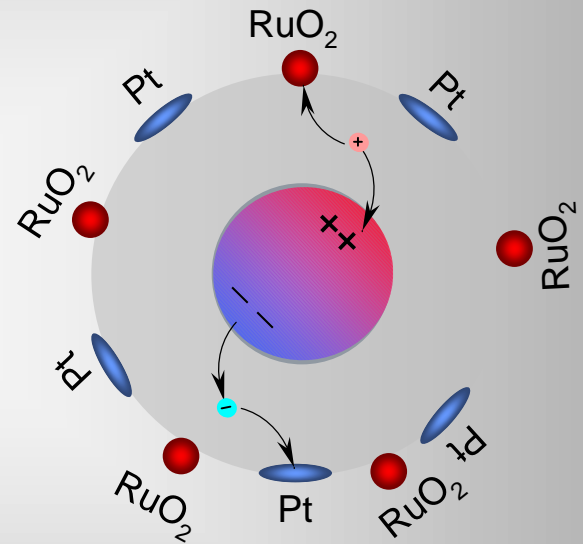
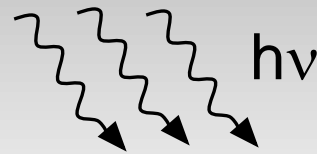
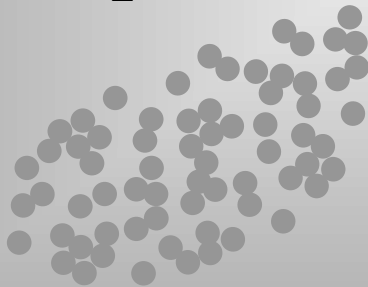


Solar Spectrum is from J.H.Seinfeld and S.N.Pandis "Atmospheric Chemistry and Physics" John Wiley & Sons, Inc. New York, Chichester, Brisbane, Singapore, Toronto (1998)

Titania Coated Metal Nanoparticles

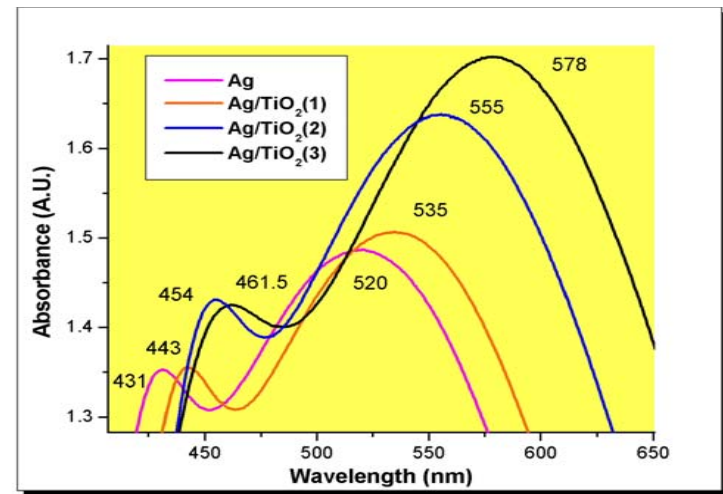
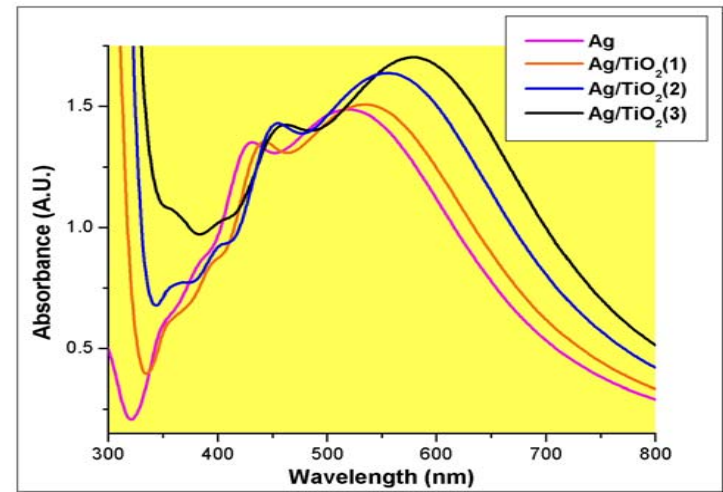
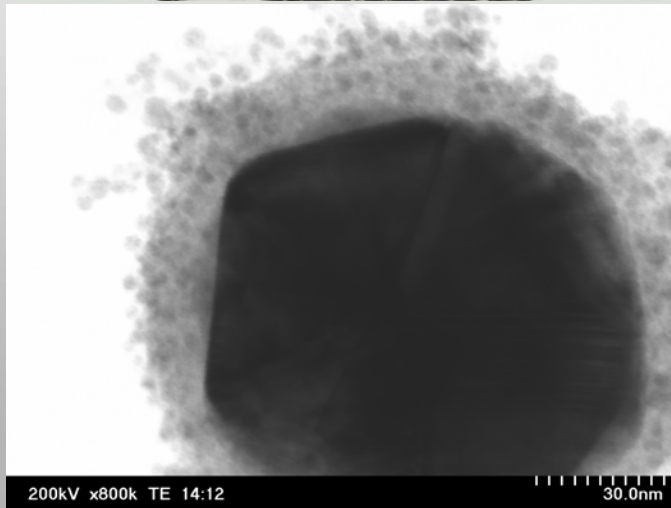
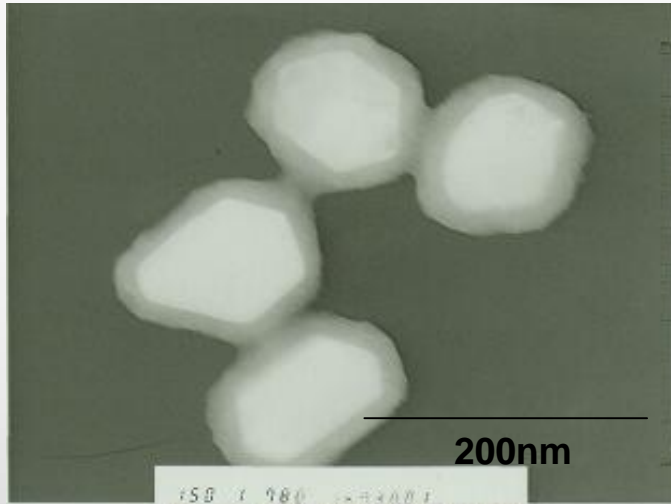


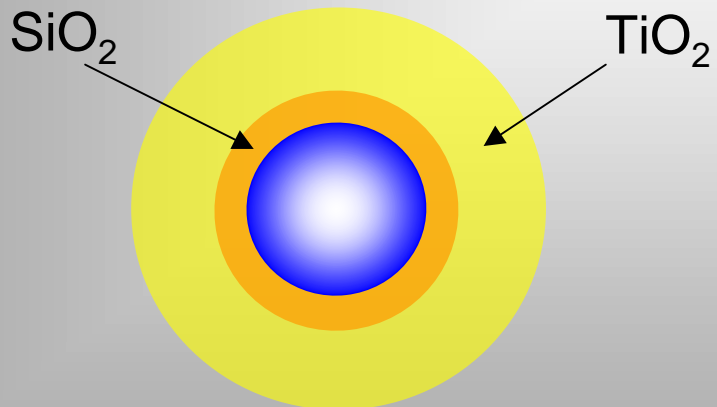
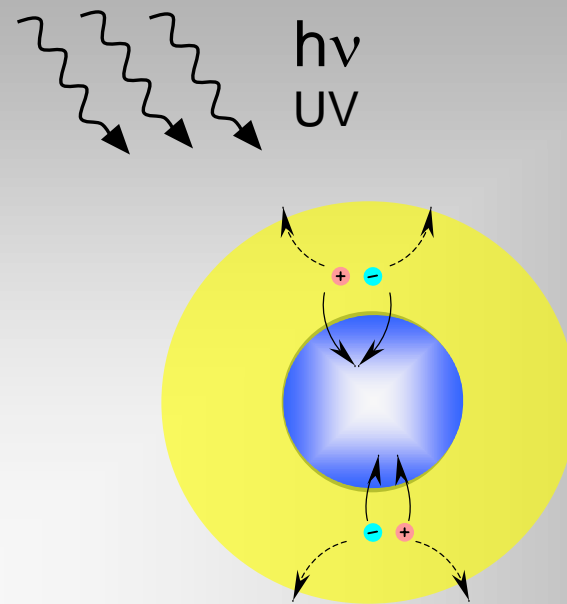
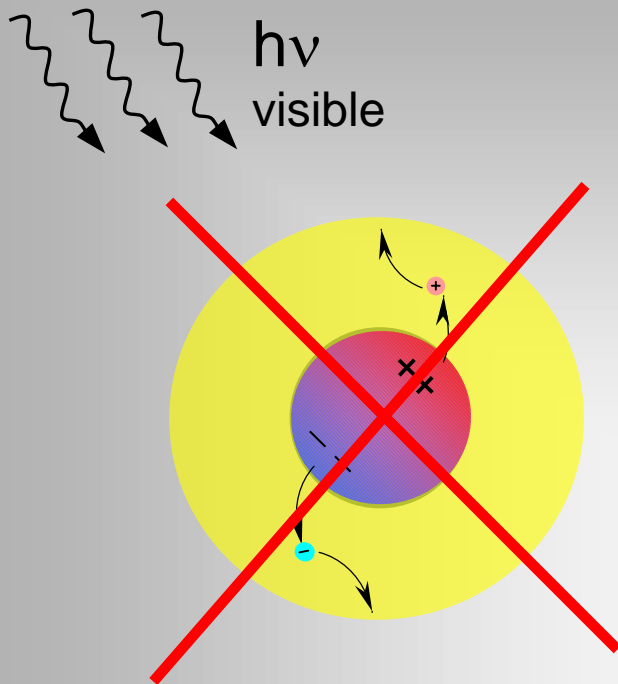
TiO₂ 1 – 5 nm



Plasmon Enhanced Electron-Hole Pair Generation

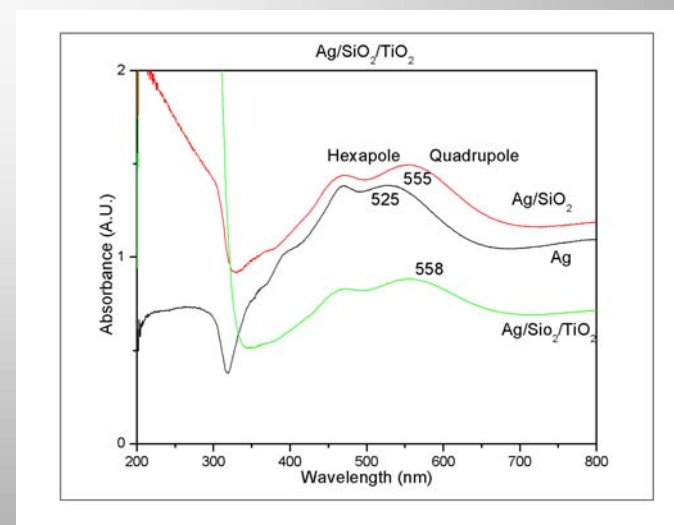
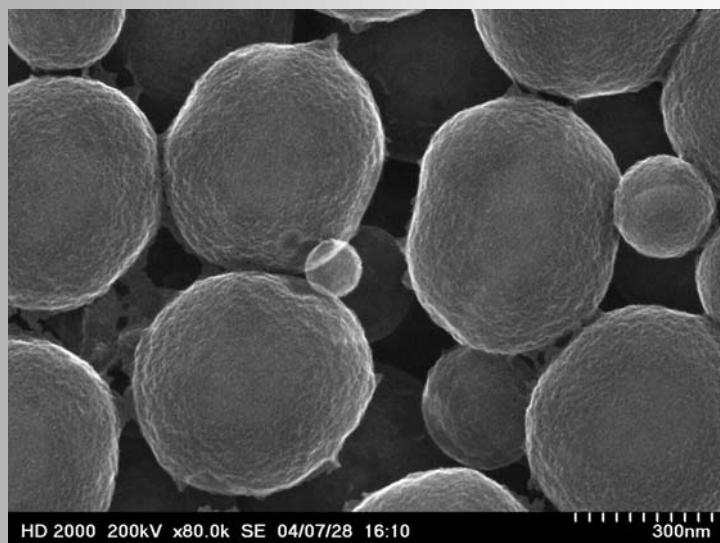
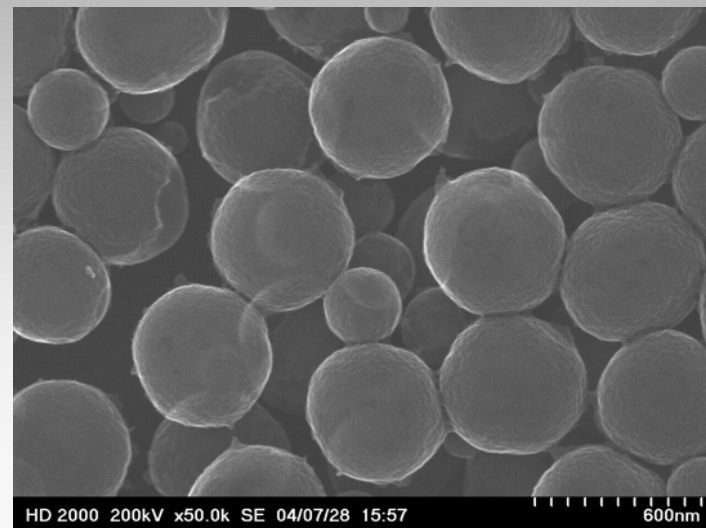
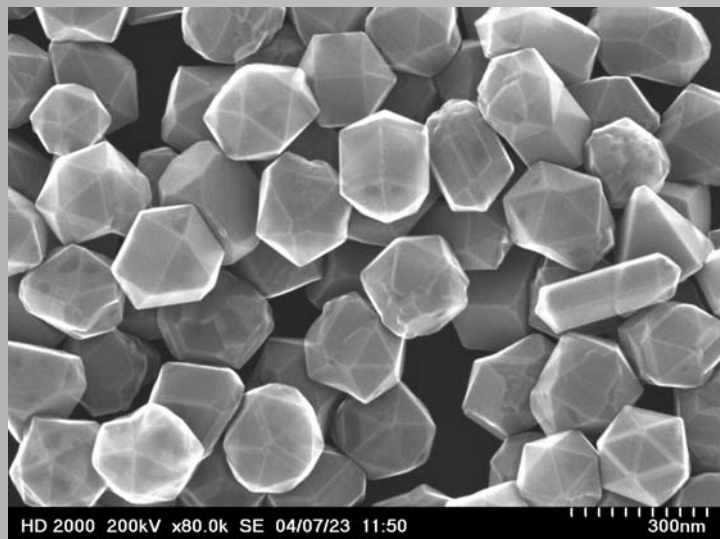
Titania coated Silver Nanoparticles



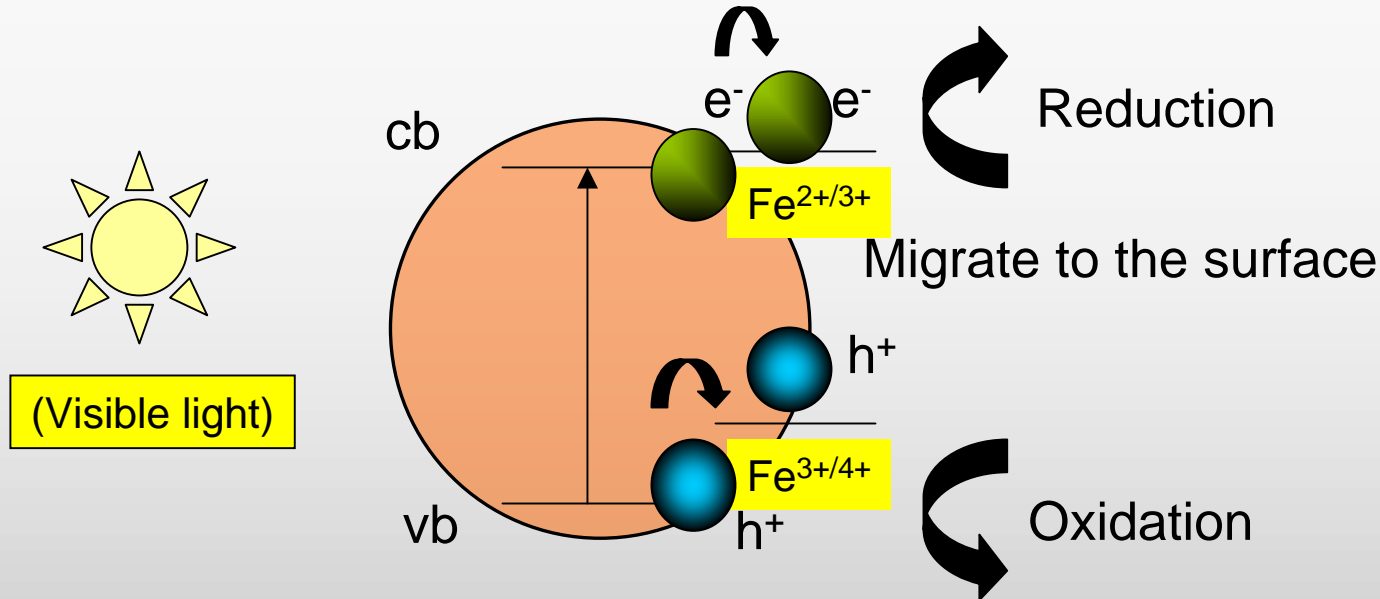


Metal core shortens the electron-hole pairs generated in titania shell

Ag core SiO₂/TiO₂ Nanoparticles



Metal Ion Doped-Titania Photocatalyst

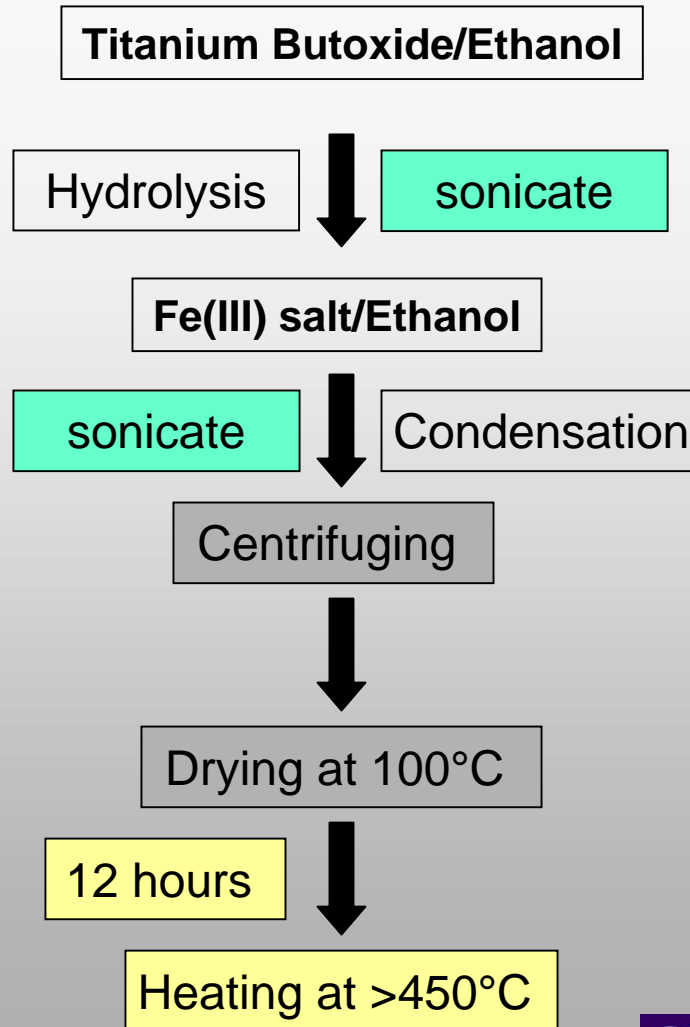


Dopants influence the intrinsic properties of titania, resulting in lowering the band gap and shifting light absorption into the visible spectral range.

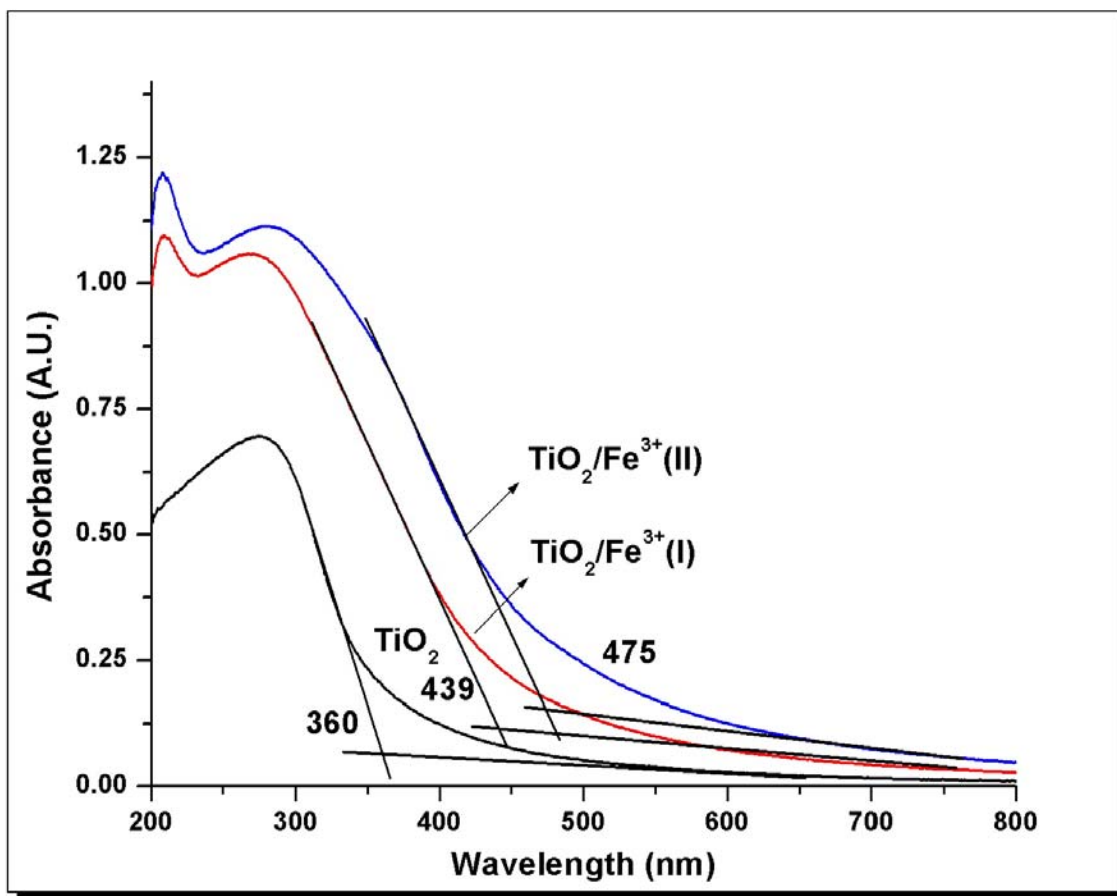
Dopants should be both good electron and hole traps.

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

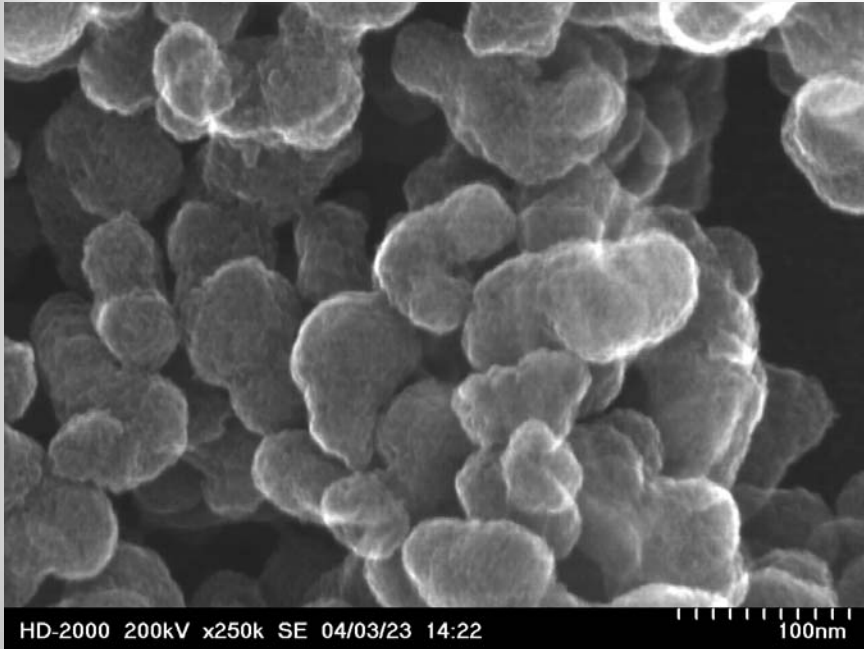
Synthesis of Fe³⁺-doped TiO₂



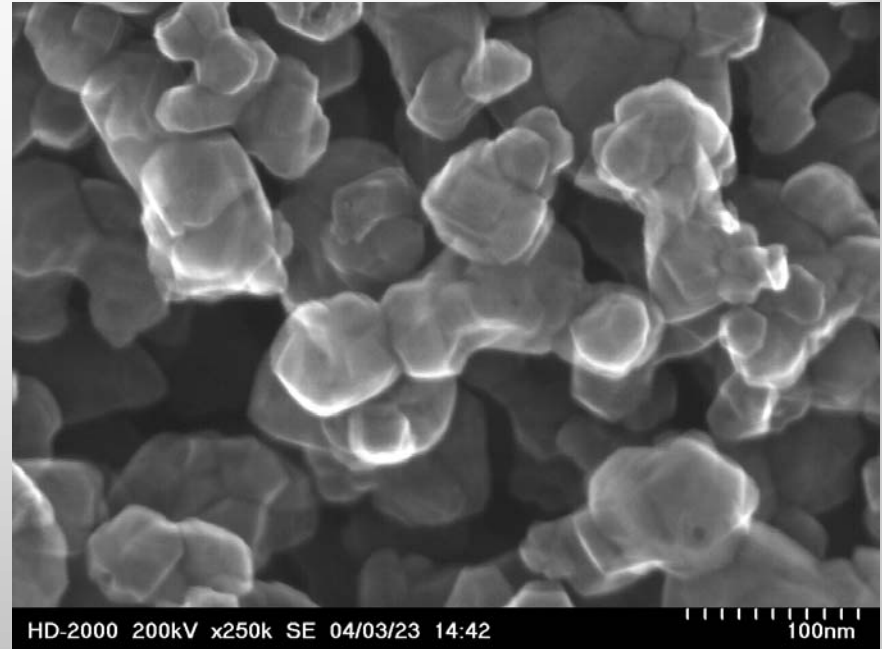
UV-Vis Absorption Spectra of Fe³⁺-doped TiO₂ : Effect of Fe³⁺ concentration



Electron Microscopy

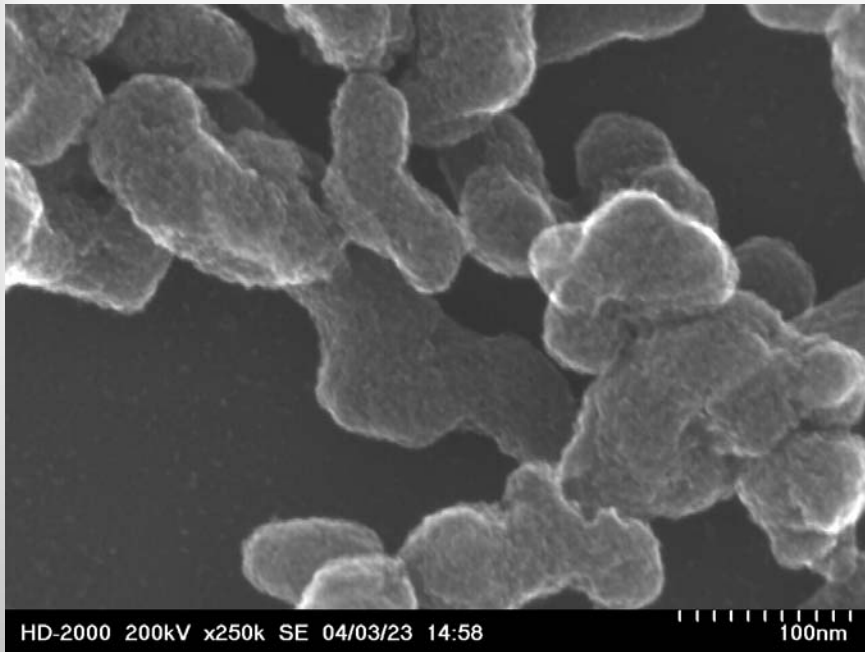


TiO₂ as prepared (amorphous)



TiO₂ after heat treatment (crystalline)

Electron Microscopy

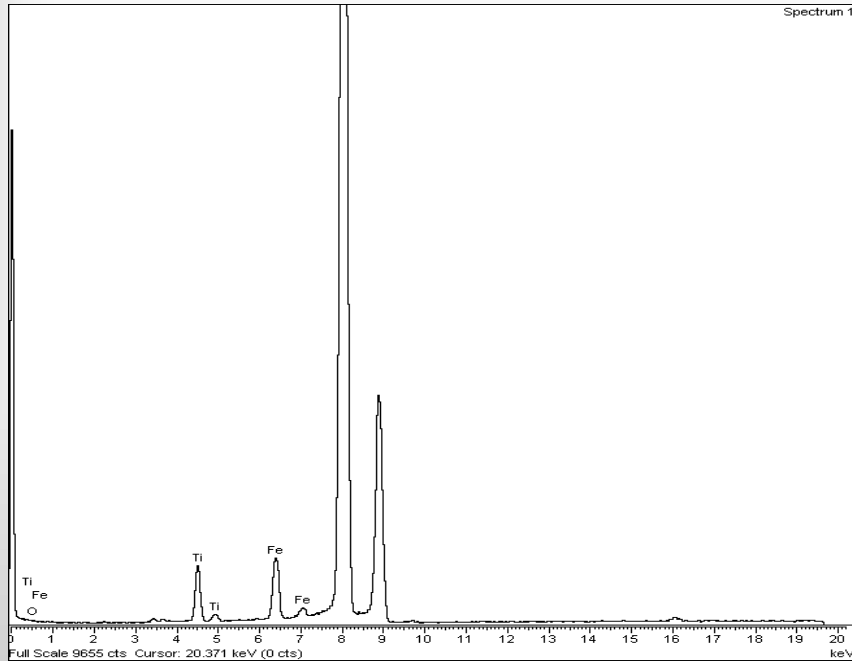


Fe³⁺/TiO₂ as prepared (amorphous)



Fe³⁺/TiO₂ after heat treatment (semi-crystalline)

EDX spectra and Mapping of Fe³⁺-doped TiO₂



EDX spectra shows the presence of iron at >8 atomic % which arises from both surface and bulk Fe³⁺ sites



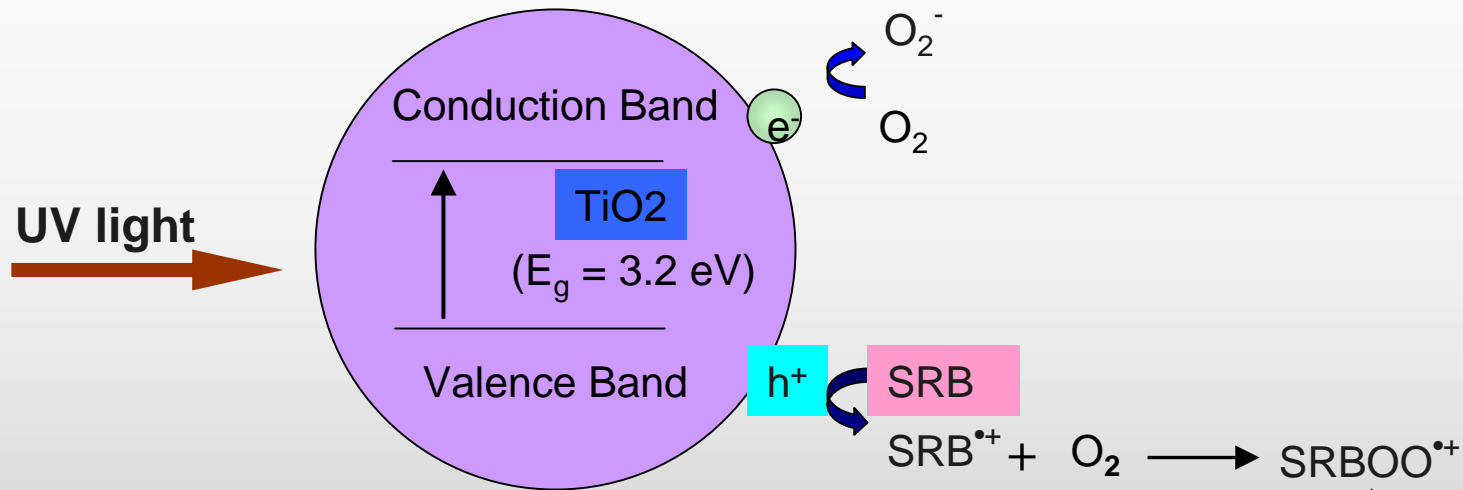
Ti Kα1



Fe Kα1

EDX mapping studies indicate the uniform dispersion of iron within the TiO₂ matrix

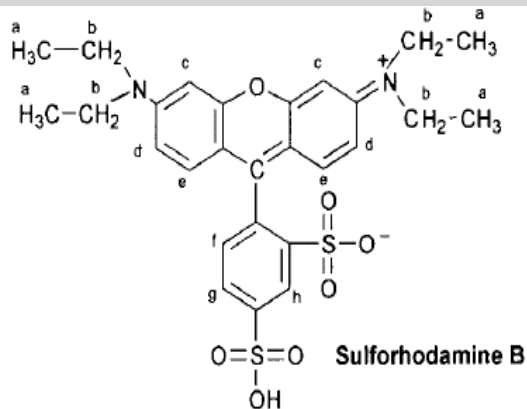
Photocatalysis Using UV light



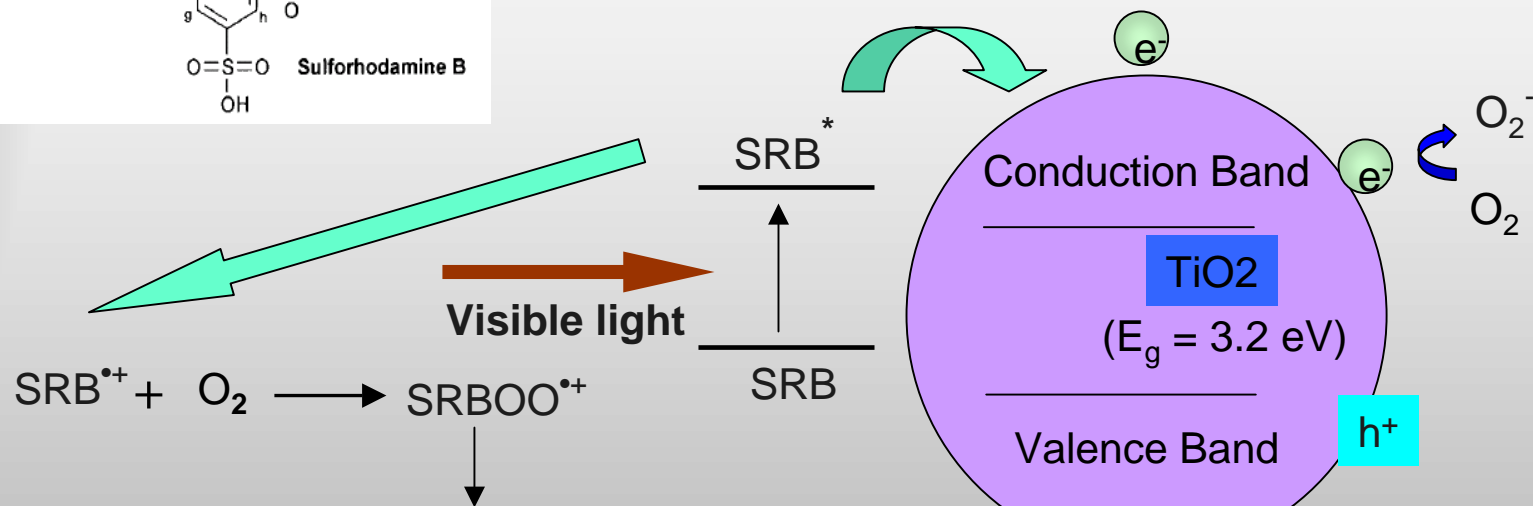
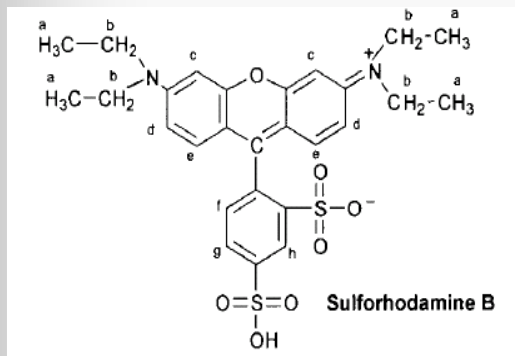
Degradation of chromophore structure
(diethylamine, N,N-diethylacetamide, etc)

h^+ or $\bullet OH$

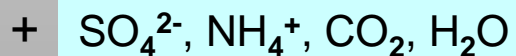
$SO_4^{2-}, NH_4^+, CO_2, H_2O$



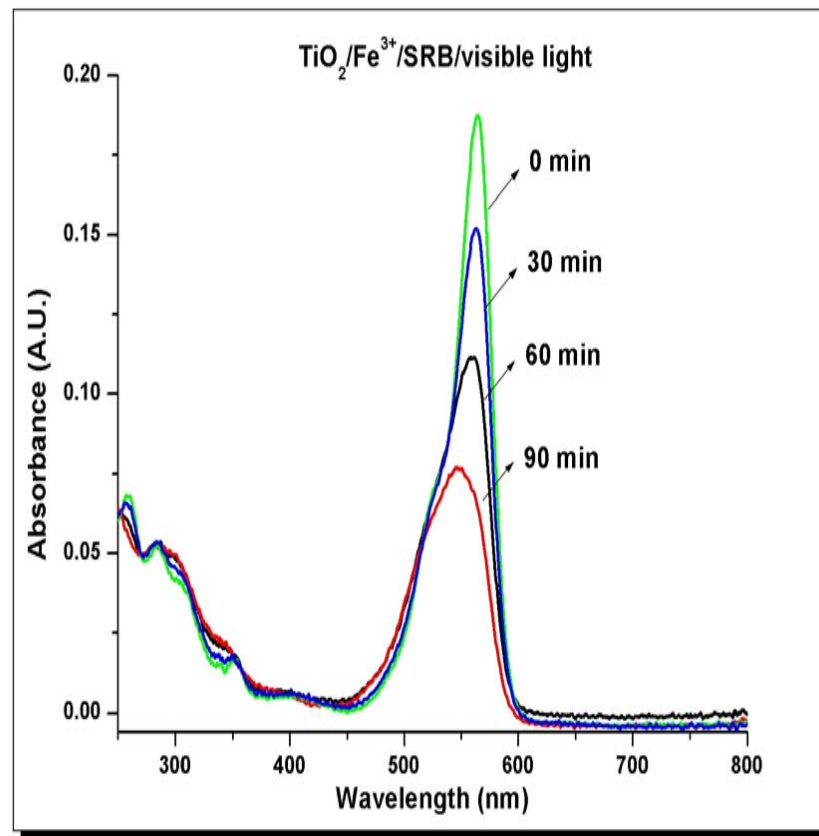
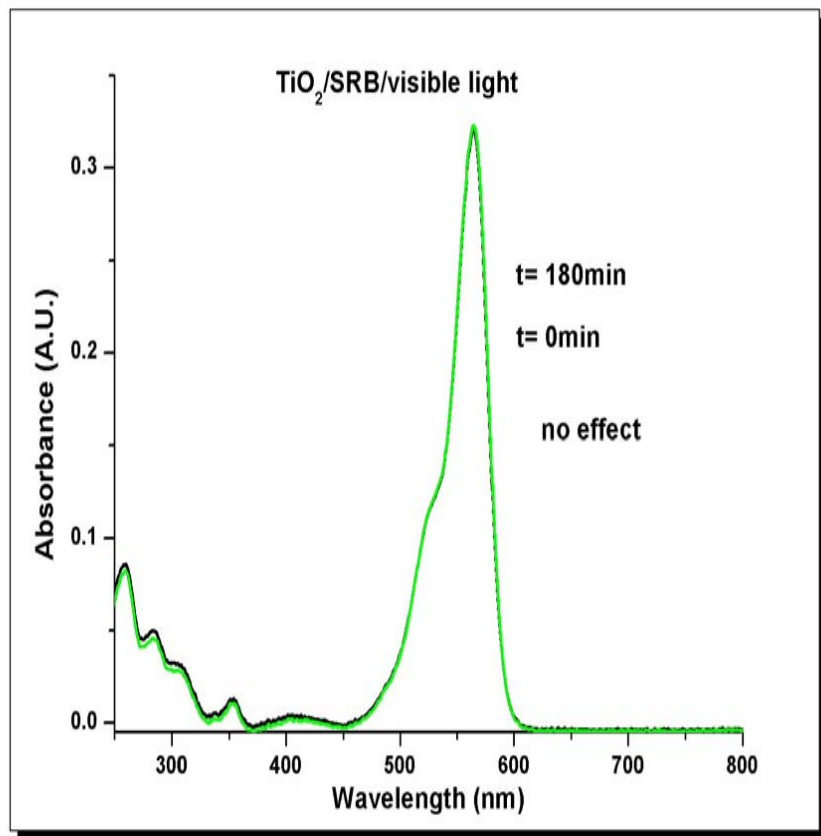
Photosensitization Using Visible light



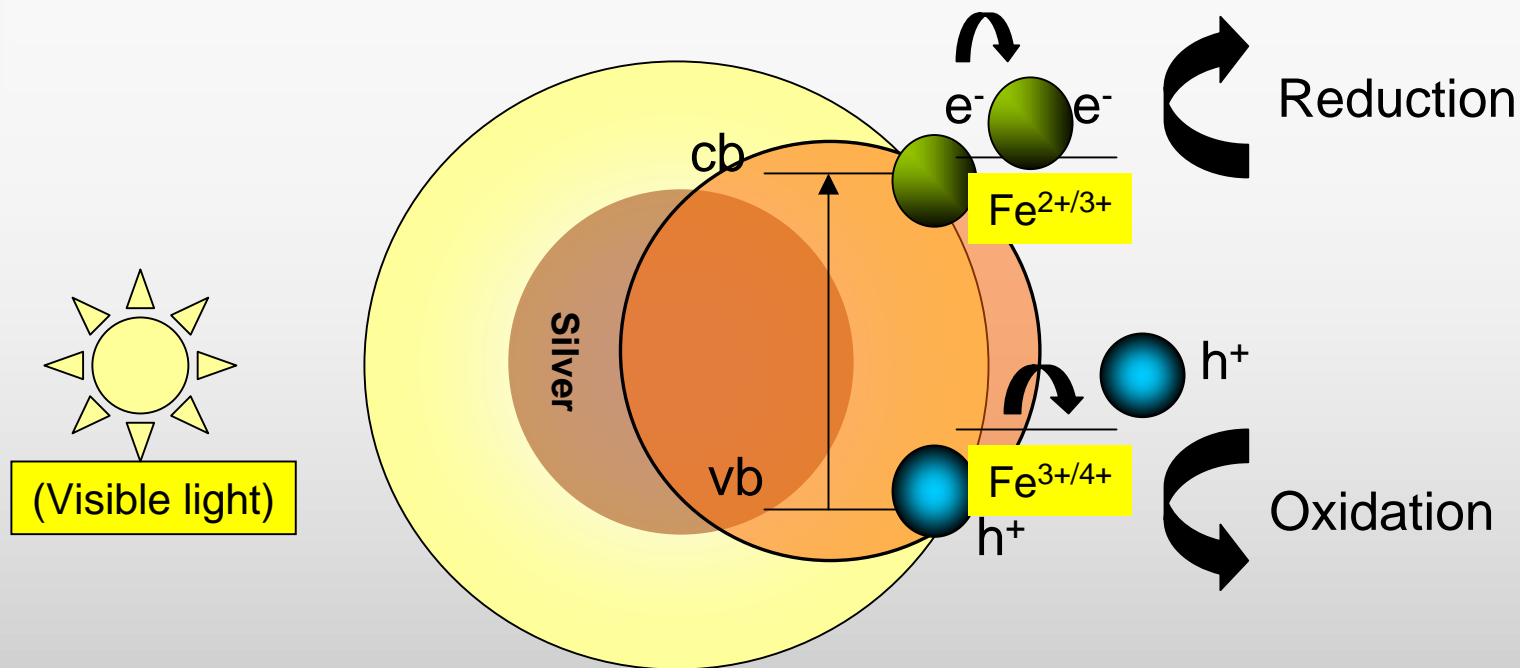
Degradation of chromophore structure
(diethylamine, N,N-diethylacetamide, etc)



Photocatalysis Experiments



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

Conclusions

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

Fe³⁺- doped Titania that is sensitive to visible light was synthesized.

From the degradation of sulforhodamine dye experiments true doping effect was observed in the Fe³⁺- doped Titania photocatalyst

Efforts are underway to coat silver nanoparticles with Fe³⁺- doped Titania .

Photocatalytic activity of Fe³⁺- doped Titania and silver coated with Fe³⁺- doped Titania will be compared.

Current Member of the Group

David Evanoff, Katrina Daniels,
Amar Kumbhar, Steve Hunson,
Mark Kinnan, Sravanti Ambati,
Kenia Parga

