

# Chapter 5 Computational design of catalytic materials

- An introduction to catalysis and surface chemistry
- *d*-Band theory of catalysis
- **Photocatalysis and plasmon-enhanced catalysis**

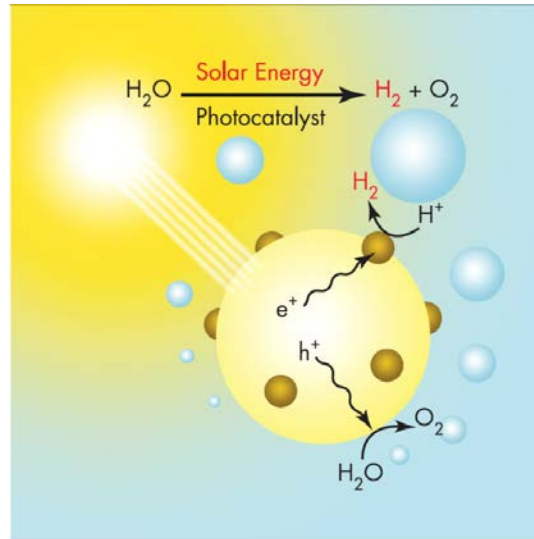
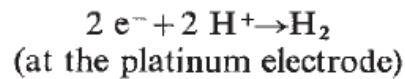
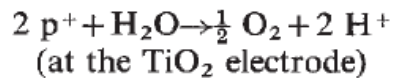
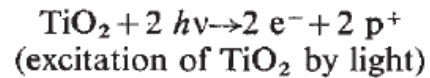
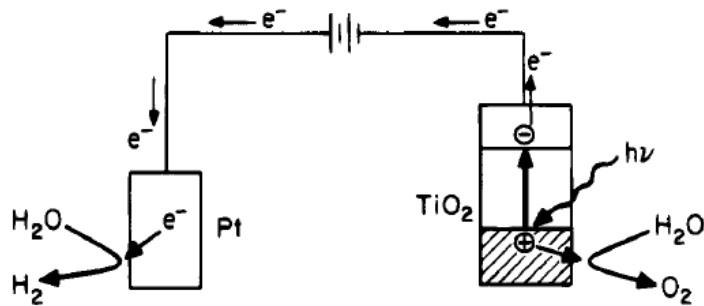
# Photocatalysis and plasmon-enhanced catalysis

- Fundamental Issues of Photocatalysis
- Fundamentals & Challenges of Photocatalysis---  
Real space imaging of photocatalytic water splitting
- Plasmon-Enhanced Photocatalysis

# Important Photocatalytic Processes

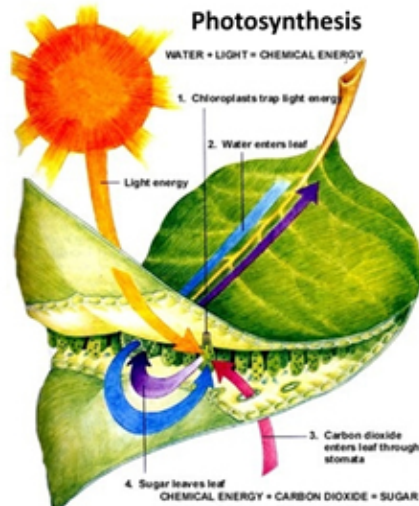
- Photodecomposition of water
- Photocatalytic formation of fuel
- Photocatalysis in pollution abatement

# Photocatalytic water splitting & fuel production

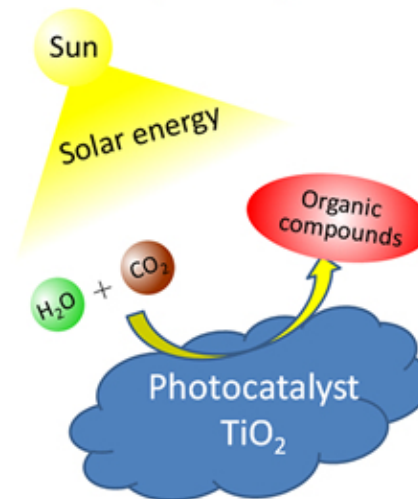


A. Fujishima, K. Honda, *Nature* **238**, 37 (1972).

## Natural photosynthesis



## Artificial photosynthesis



# Hydrogen Production Technologies

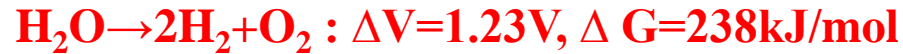
Various methods and technologies have been developed and a few of them have already been practiced. These technologies can be broadly classified as:

- **Thermo-chemical routes for hydrogen production**
- **Electrolytic generation of hydrogen**
- **Photolytic means of hydrogen formation**
- **Biochemical pathways for hydrogen evolution and**
- **Chemical (steam ) reformation of naphtha**

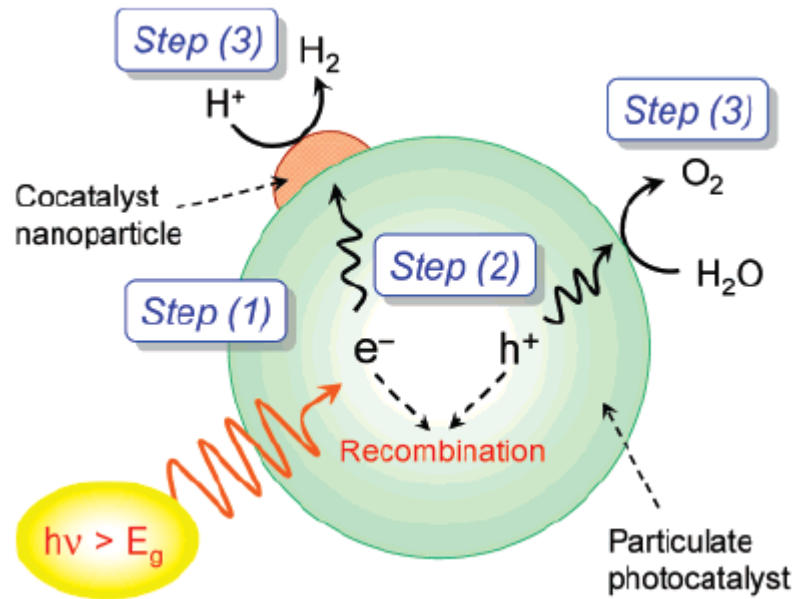
# Photoelectrolysis of Water: Holy Grail of Electrochemistry

The discovery of photo-electrolysis of water directly into oxygen at a n-TiO<sub>2</sub> electrode and hydrogen at a Pt electrode by the illumination of UV light is attributed to Fujishima and Honda though photo catalysis by ZnO and TiO<sub>2</sub> has been reported much earlier by Markham in 1955.

# Process on the Photoexcited Semiconductor Surfaces and Bulk



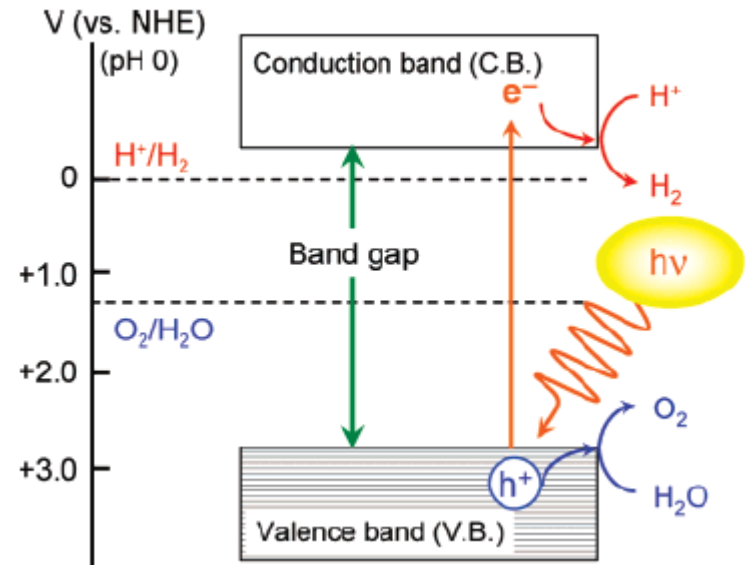
- **Step 1:** Photon with energy above 1.23eV ( $\lambda < \sim 1000$  nm) is absorbed.
- **Step 2:** Photoexcited electrons and holes **separate and migrate** to surface.
- **Step 3:** Adsorbed species (water) is reduced and oxidized by the electrons and holes.



Only when three steps are simultaneously completed photocatalytic activities can be obtained. Thus, suitable bulk and surface properties, and energy structure are required for photocatalysts.

# Photocatalyst Material Requirements

- **Band Gap:** Band gap  $>1.23\text{eV}$  and sufficiently small to make efficient use of solar spectrum ( $\sim <3\text{eV}$ ). For the concern of thermodynamics, the band edges of the electrode must straddle the redox of water.
- **High Crystallinity:** is needed to yield an efficient charge transfer to the surface of the semiconductor, because defects act as recombination sites.
- **Long Term Stability:** Charge transfer used for water splitting reaction and not for corrosion.



The reducing power depends on the conduction band minimum (CBM) energy. The closer the CBM energy to the vacuum level, the stronger the reducing power is. On the other hand, the oxidizing power is measured by the valence band maximum (VBM) energy. The lower the VBM energy, the higher the oxidizing power.



# Why Semiconductor?

## Metals

No band gap

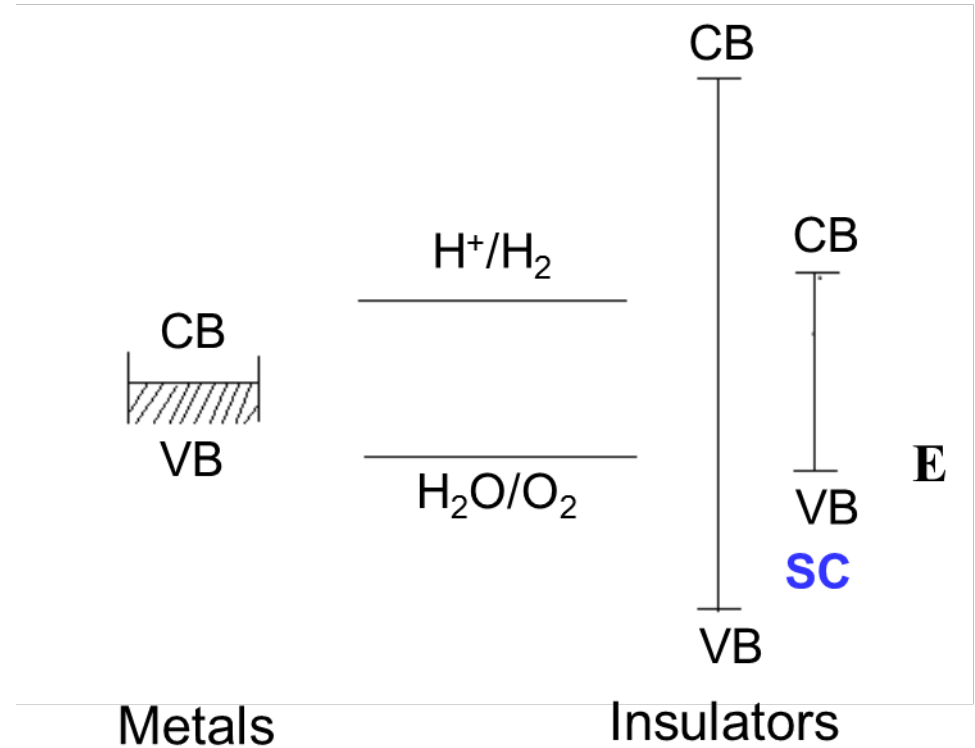
Only reduction or oxidation

Depends on the band position

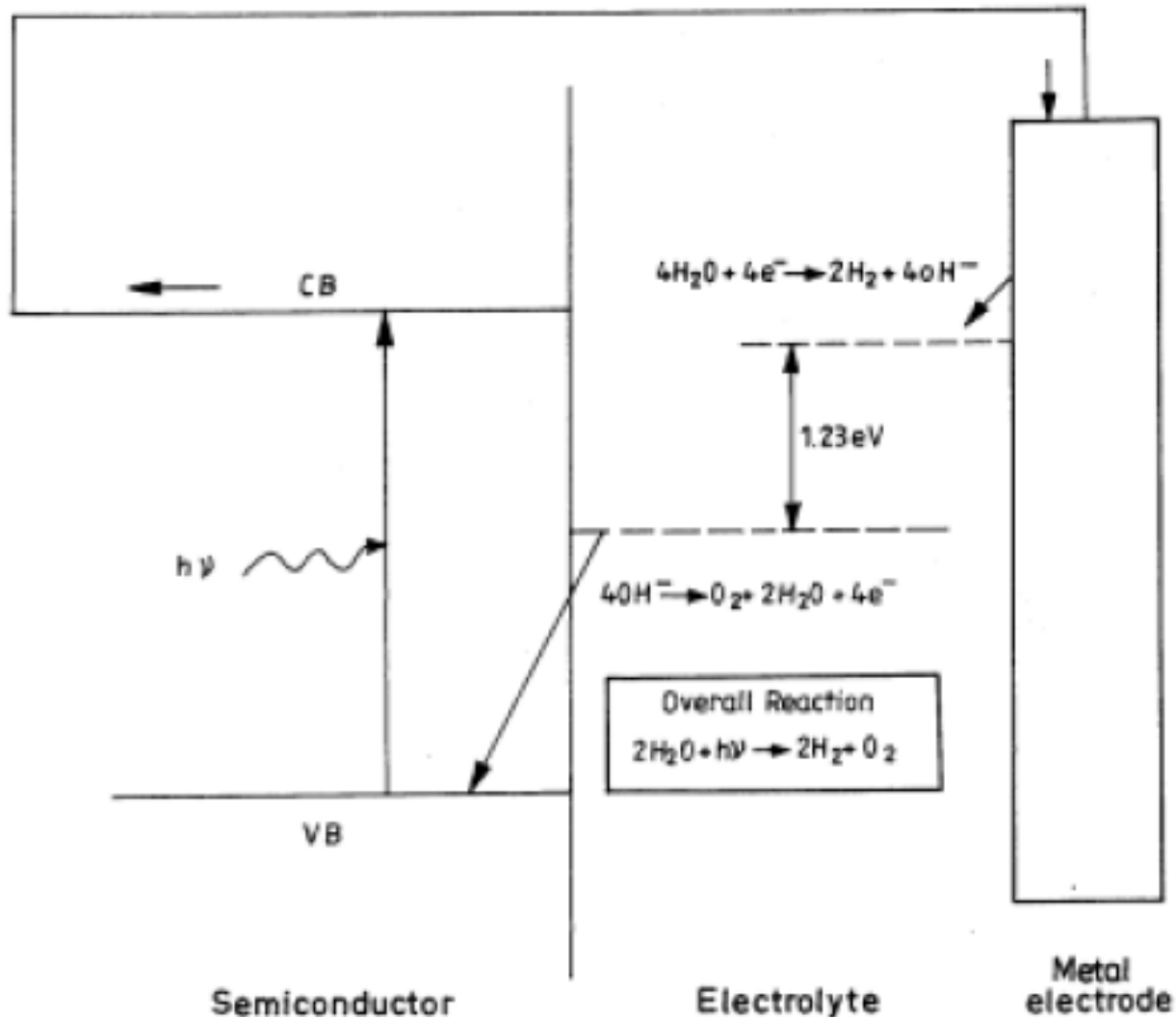
## Insulators

High band gap

High energy requirement



# Typical Cell Structure for the Photocatalytic Water Splitting



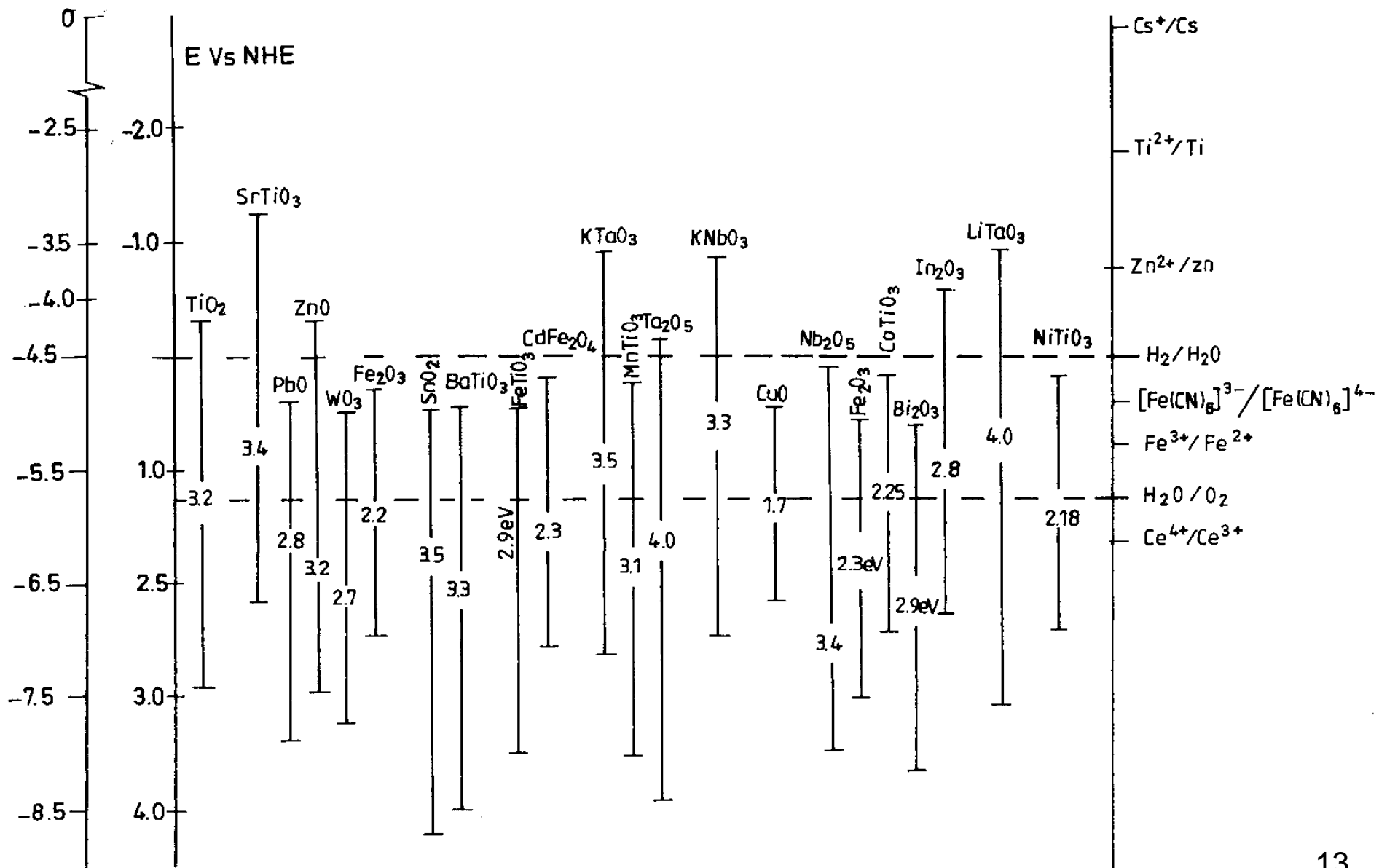
# Material Design for Photocatalysis

- ❖ should have high quantum yield of photoexcited carrier generation
- ❖ should have high charge transfer efficiency
- ❖ high forward catalyst activity and turnover number
- ❖ without deterioration of the material stability

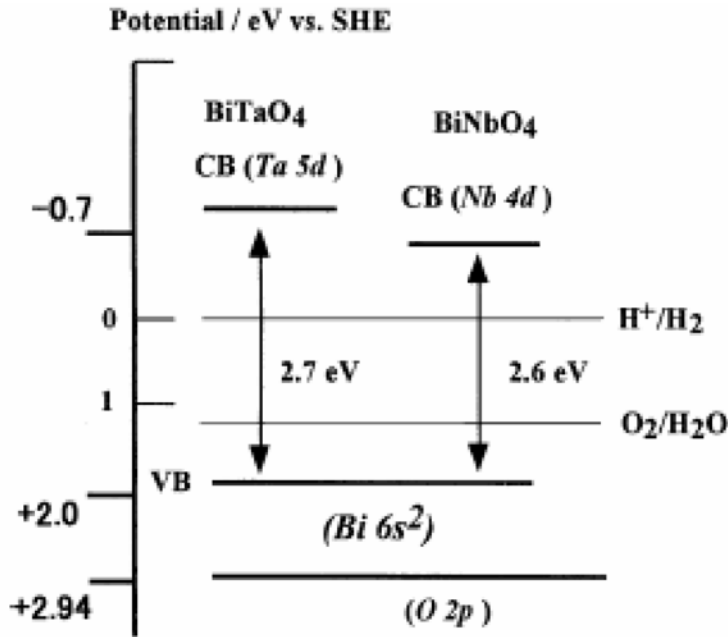
# **Bandgap Engineering for Efficient Water Photocatalysts**

- Efficient utilization of solar radiation
- Thermodynamics requires the band edges of the electrode to straddle the specific redox reaction.

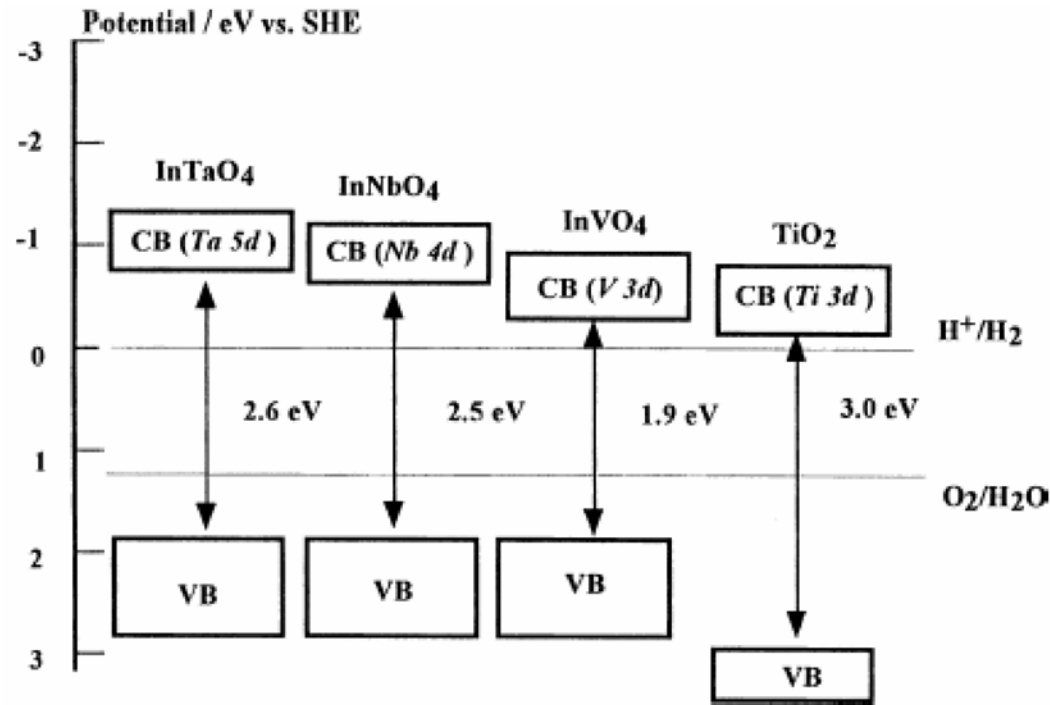
# Positions of bands of semiconductors relative to the standard potentials of several redox couples



# Bandgap Engineering for Improving the Utilization of Solar Radiation



The bandgap changes because the filled 6s<sup>2</sup> band of Bismuth lies on top of the 2p band of oxygen. This way the bandgap can be decreased.

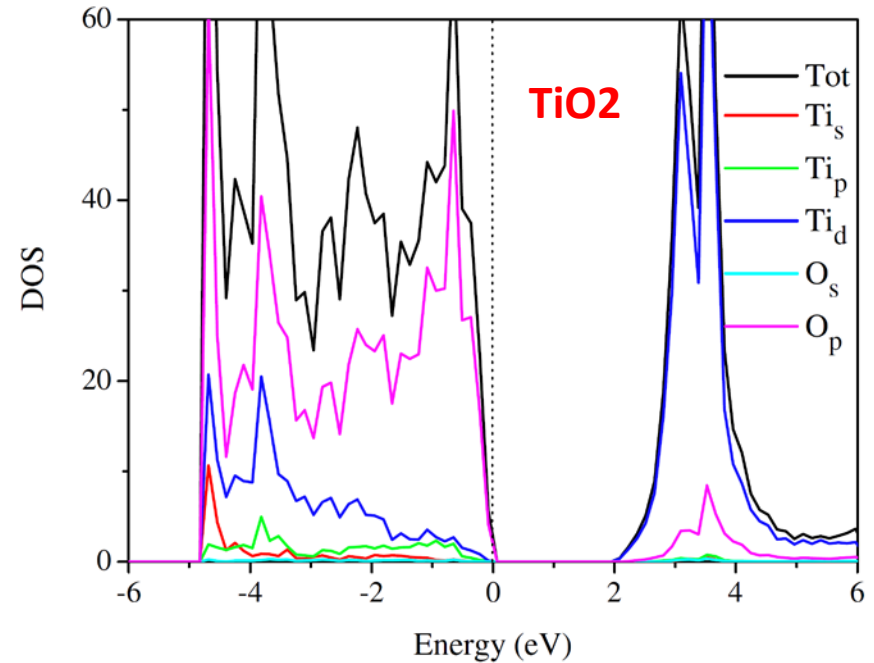
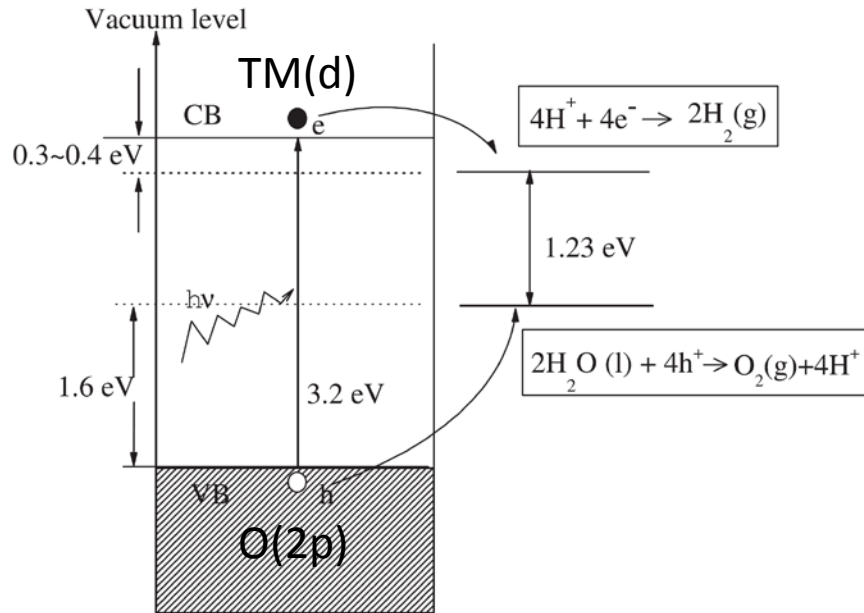


An addition of a co-metal, Indium, raises the VBM, whereas the CBM is shifted down from 5d, 4d to 3d, because TM with a higher atomic number has a higher valence shell.

# Doping for Improving the Utilization of Solar Radiation

To improve the photoelectrochemical activity of a semiconductor (e.g., TiO<sub>2</sub>) for hydrogen production through water splitting, the band edges of the semiconductor should be tailored to match with visible light absorption and the hydrogen or oxygen production levels.

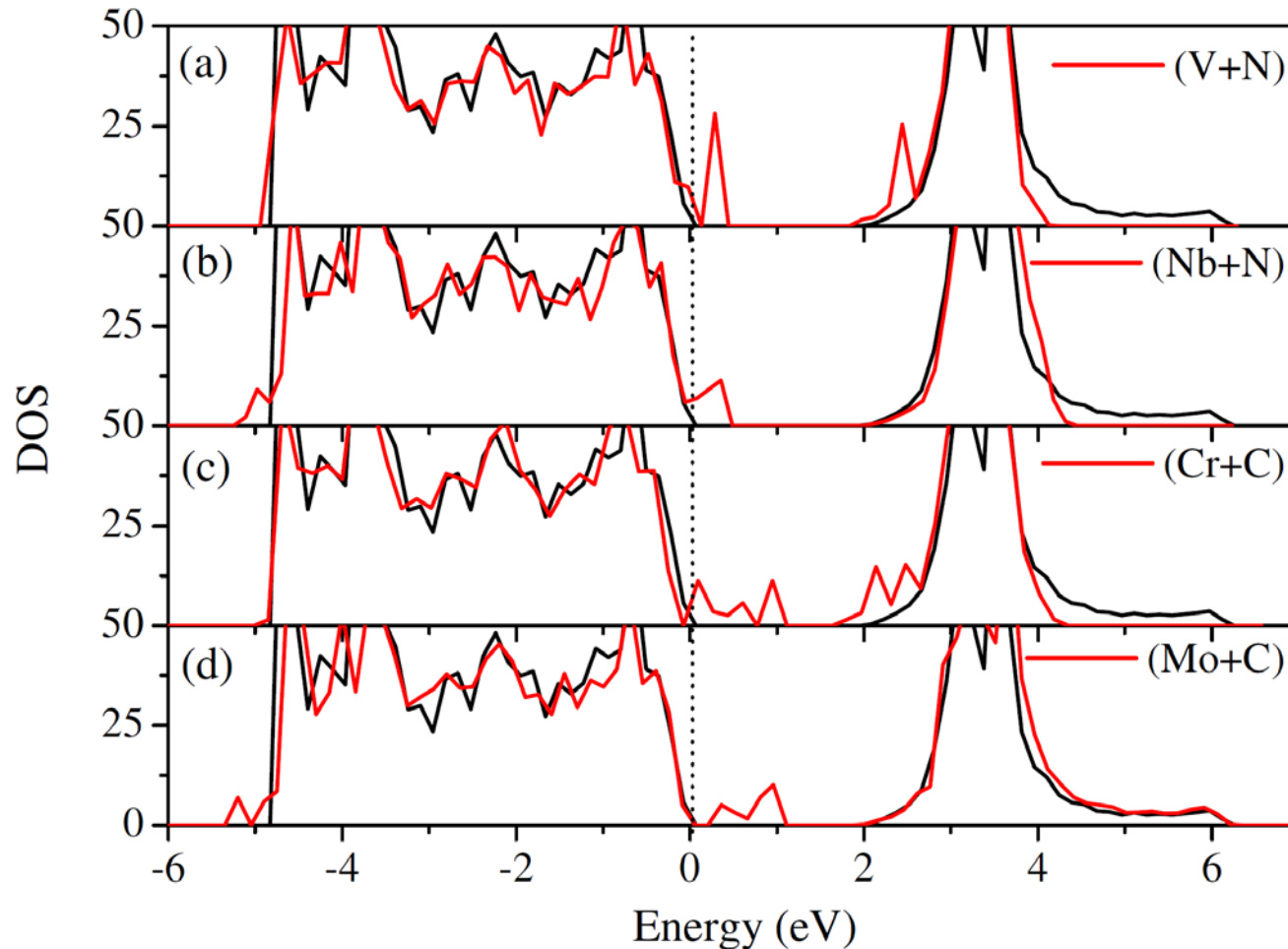
To modify the band structure through doping, we first need to know the atomic wave function characters of the band-edge states.



To modify the VBM of TiO<sub>2</sub>, we should choose dopants with different atomic *p* orbital energy than O, whereas to modify the CBM, we should choose dopants with different atomic *d* orbital energies than Ti.

# Improved the Utilization of Solar Radiation via Doping

**Passivated codoping in TiO<sub>2</sub>:** such as  $Mo_{Ti} + C_O$



TiO<sub>2</sub>:(Mo+C) has the highest figure of merit for PEC water splitting, because not only does it reduce the band gap by about 1.1 eV, it also causes very small perturbation on the position of the conduction band edge. Passive codoping does not produce partially occupied impurity bands that can facilitate the formation of recombination centers.



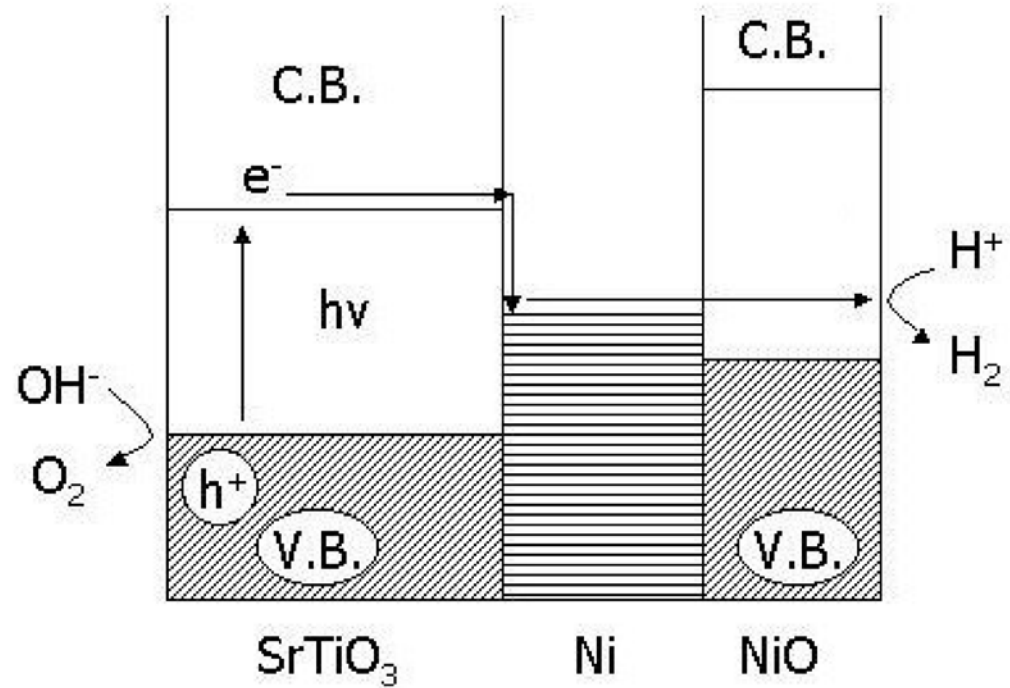
# **Bandgap Engineering for Efficient Water Photocatalysts**

- Improve charge transfer
- high catalyst activity of the redox reaction

# Improve Charge Transfer via Heterojunction:

## Nickel(II) Oxide (NiO)

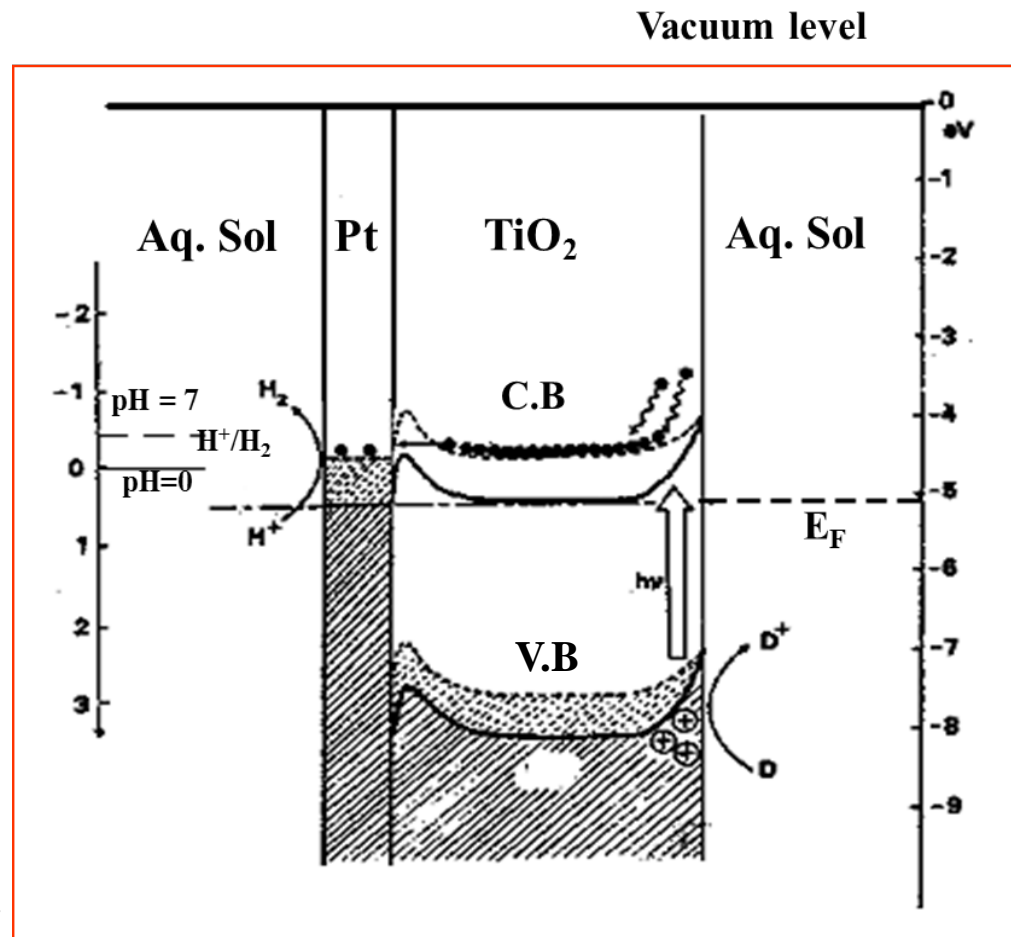
❖ Water splitting is enhanced by the addition of nickel oxide onto the surface. Hydrogen gas is formed on the nickel oxide surface and the oxygen is released from the photocatalyst surface.



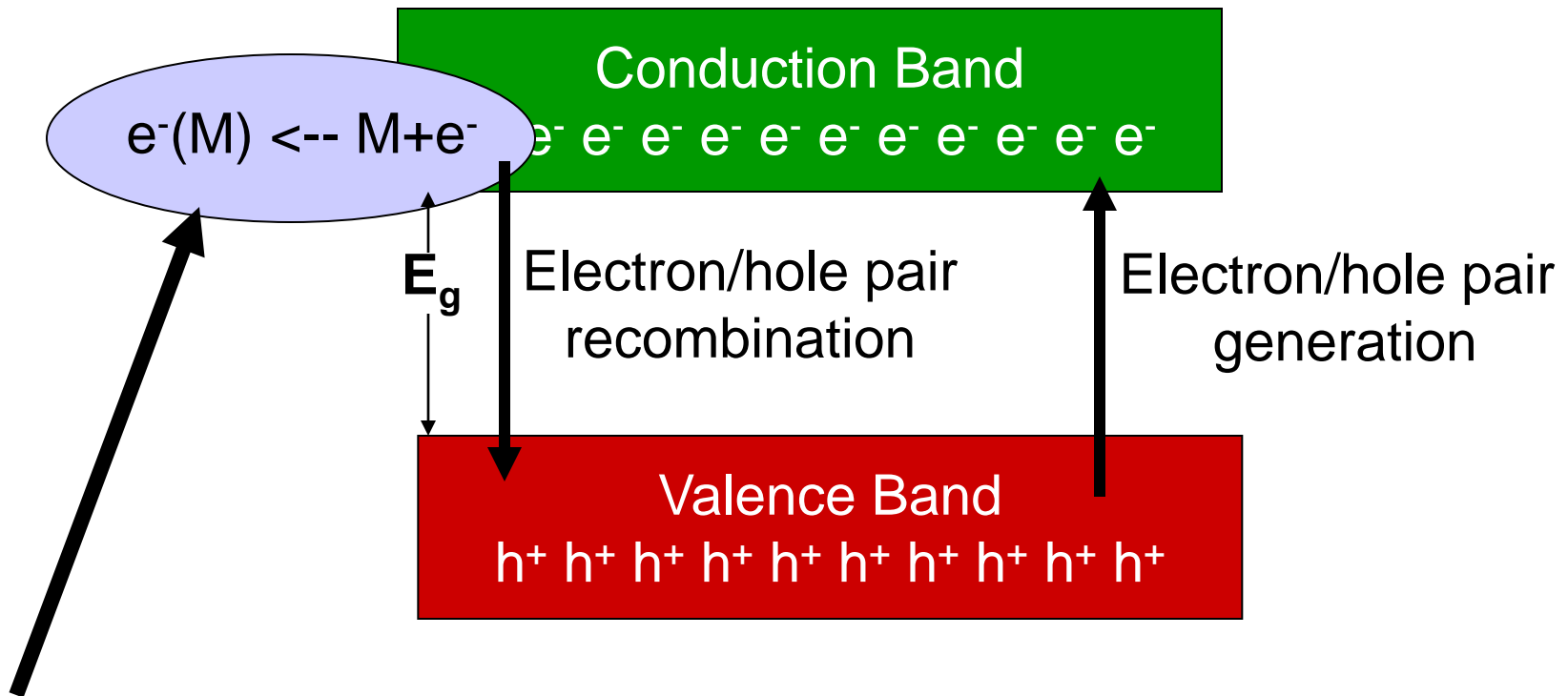
# Improve Charge Transfer via Heterojunction: Pt/TiO<sub>2</sub> INTERFACE

Platinum is a metal and therefore the electrons generated in the photocatalyst are transferred to the surface via conduction through the platinum. But platinum can catalyze both the forgoing and the reverse reaction. Hydrogen that is produced will immediately react with oxygen to water. This problem can be solved by adding iodine to the reaction mixture.

- ❖ Electrons are transferred to metal surface
- ❖ Reduction of H<sup>+</sup> ions takes place at the metal surface
- ❖ The holes move into the other side of semiconductor
- ❖ The oxidation takes place at the semiconductor surface



# Recombination Reduction by Metal Doping

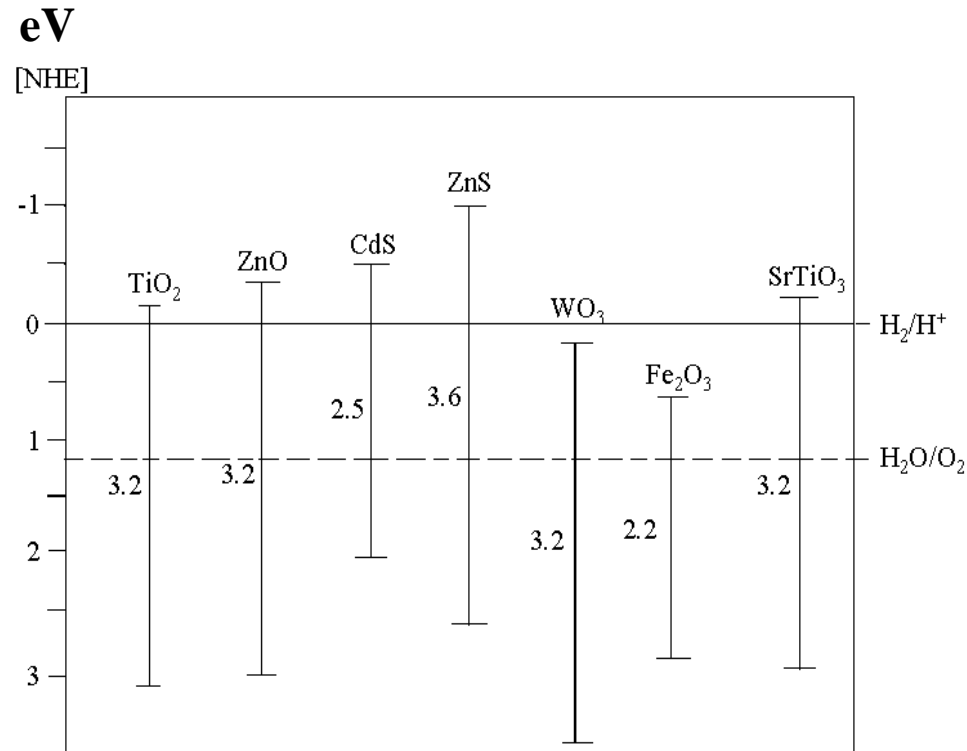


Metallic promoter attracts electrons from  $\text{TiO}_2$  conduction band and slows recombination reaction

# Advantages from Semiconductor Nanoparticles

- high surface area
- good morphology (reduced recombination) and short migration distance of photoexcited carriers
- presence of active surface states
- band gap tunability

**CdS** –has appropriate positions of the VB & CB edge for the hydrogen production.  $S^{2-}$  in CdS is oxidized by photo-generated holes. However, it can be a good photocatalyst under visible light irradiation if a hole scavenger exists.



Relationship between band structure of semiconductor and redox potentials of water splitting

# Photocatalysis and plasmon-enhanced catalysis

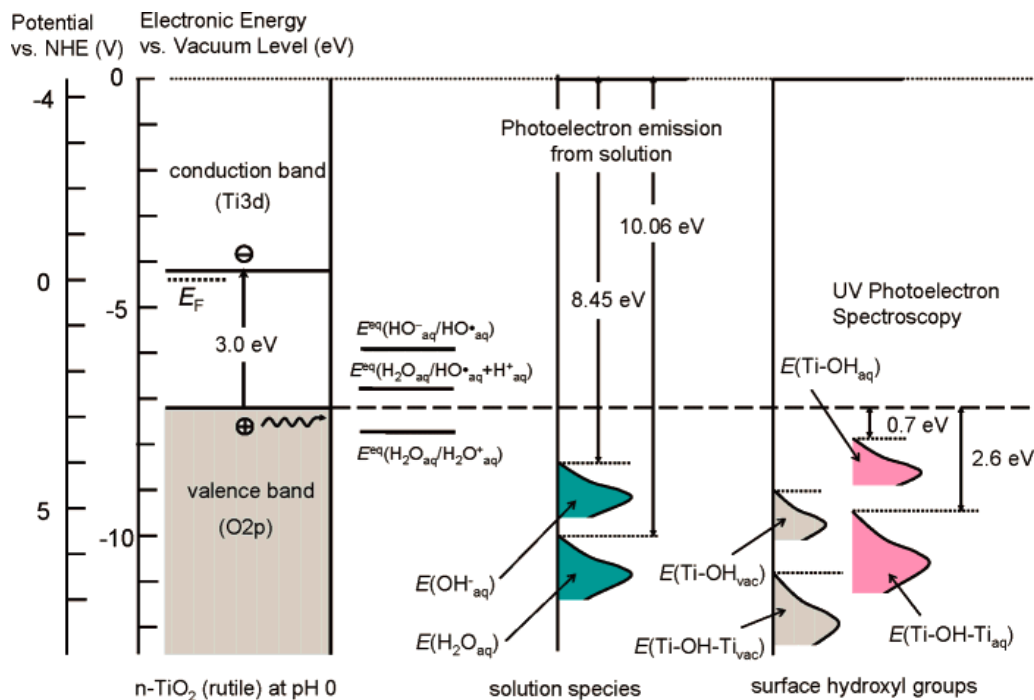
- Fundamental Issues of Photocatalysis
- **Fundamentals & Challenges of Photocatalysis**
  - Real space imaging of photo-catalyzed water splitting
- Plasmon-Enhanced Photocatalysis

# Fundamental issues:

- What are the specific reaction sites for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on  $\text{TiO}_2$  ?
- What is the initial reaction step for water splitting ?  
How does it happen ? **Photocatalytic or not?**
- What is the reduction process for  $\text{CO}_2$  ? How can the electron attachment be reached?
- Some related issues: adsorption and reaction of  $\text{O}_2$  ,  $\text{CO}$ , methanol...

**Can we atomically resolve these reduction processes ?**

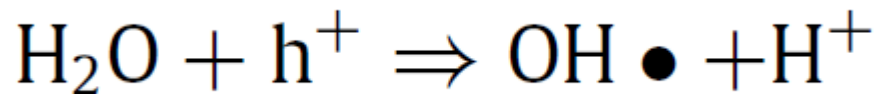
# Pictures from ground state electronic structures of H<sub>2</sub>O



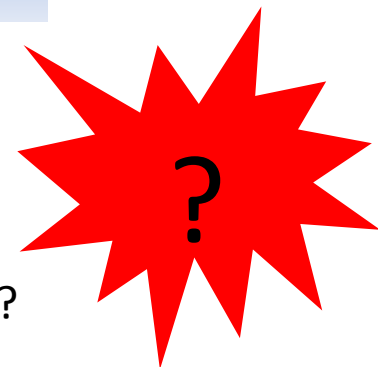
A. Imanishi et al., J. Am. Chem. Soc. 2007, 129, 11569-11578

## Energy mismatch between TiO<sub>2</sub> and H<sub>2</sub>O

Under  
Debate



What is the initial reaction step: oxidation by holes?





# Observation of Photocatalytic Dissociation of Water on Terminal Ti Sites of $\text{TiO}_2(110)\text{-}1\times 1$ Surface

Shijing Tan, Hao Feng, Yongfei Ji, Yang Wang, Jin Zhao, Aidi Zhao, Bing  
Wang,\*

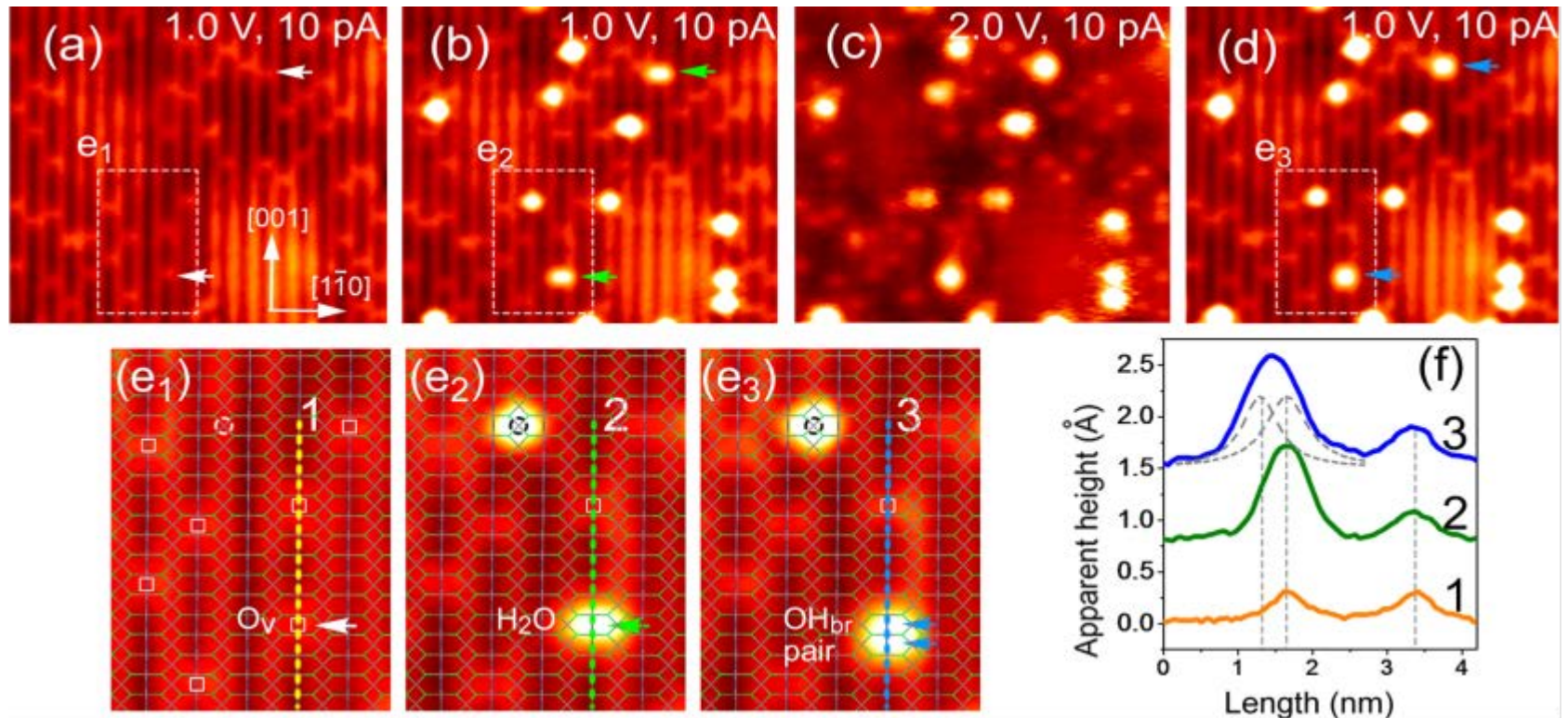
Yi Luo, Jinlong Yang, and J. G. Hou\*

*Hefei National Laboratory for Physical Sciences at the Microscale,  
University of Science and  
Technology of China, Hefei, Anhui 230026, P.R. China*

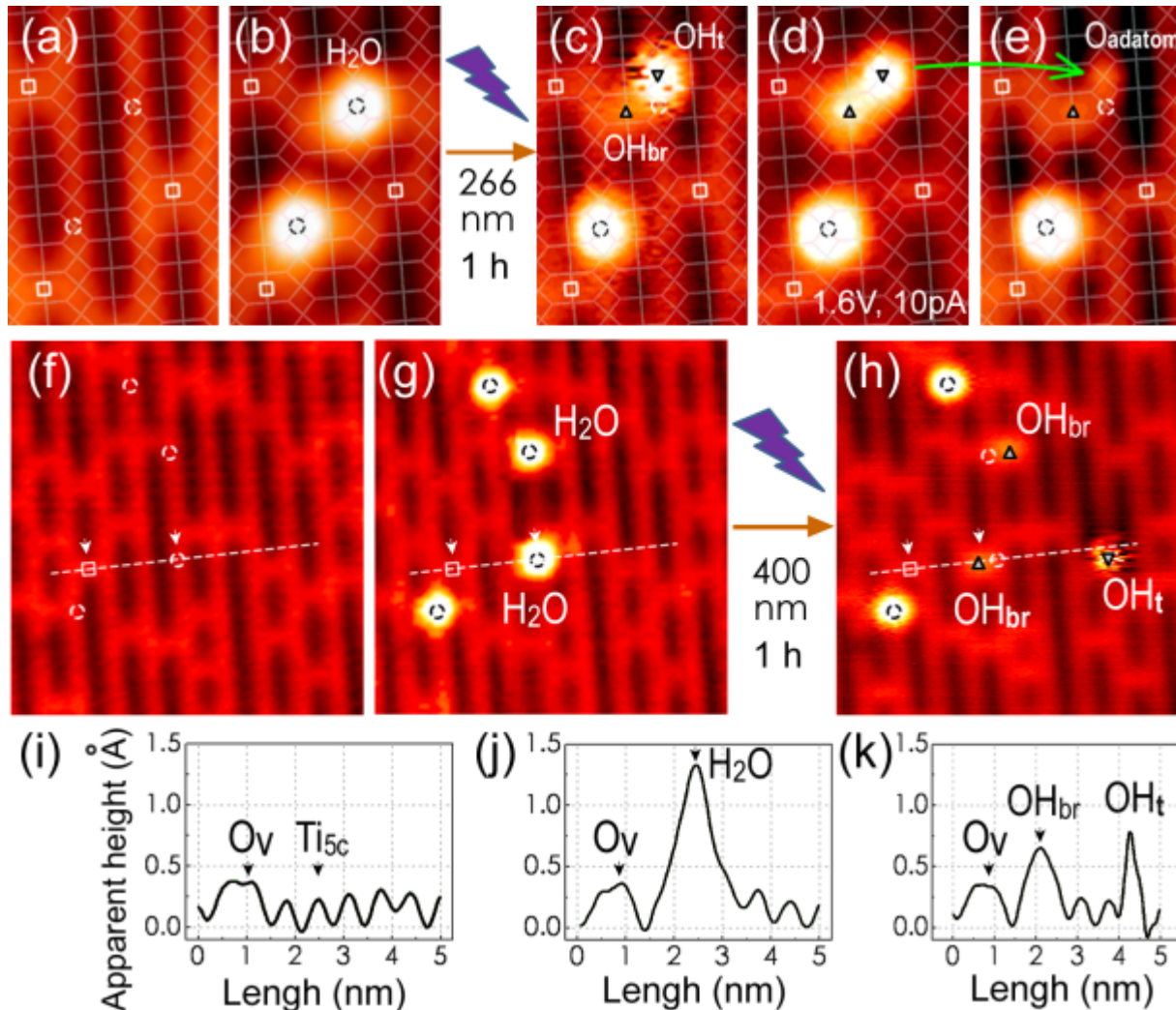
*Submitted to JACS*

# STM Images before and after water adsorption

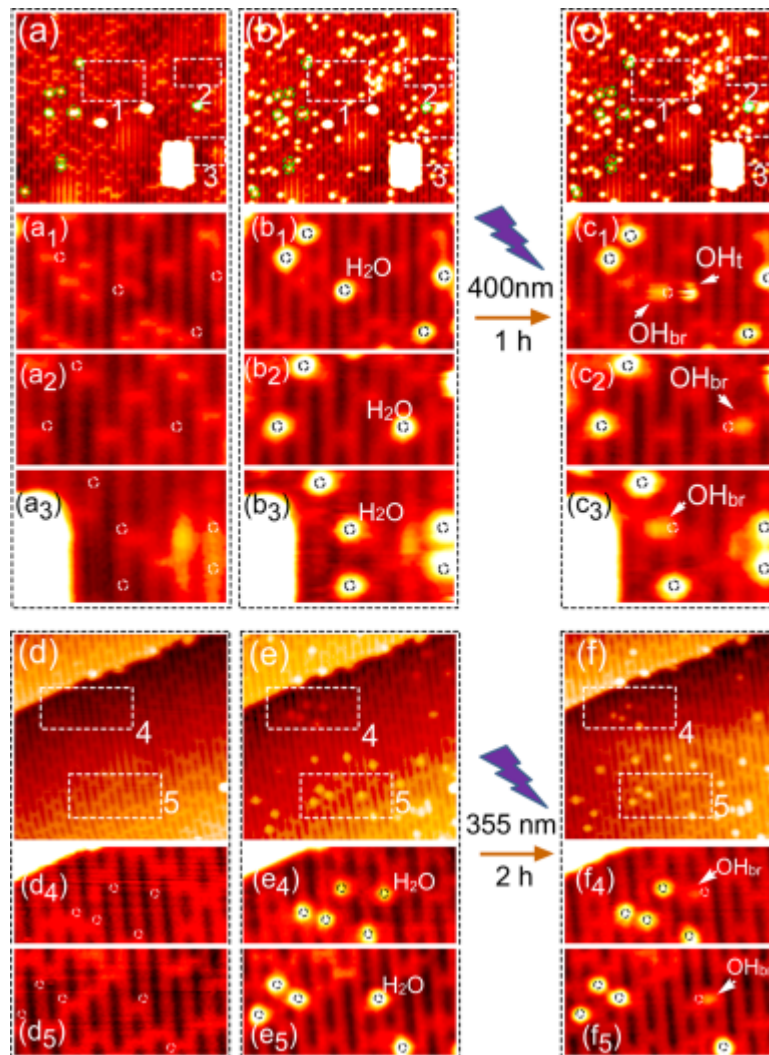
Concentration of surface hydroxyl groups may affect photocatalytic activity.



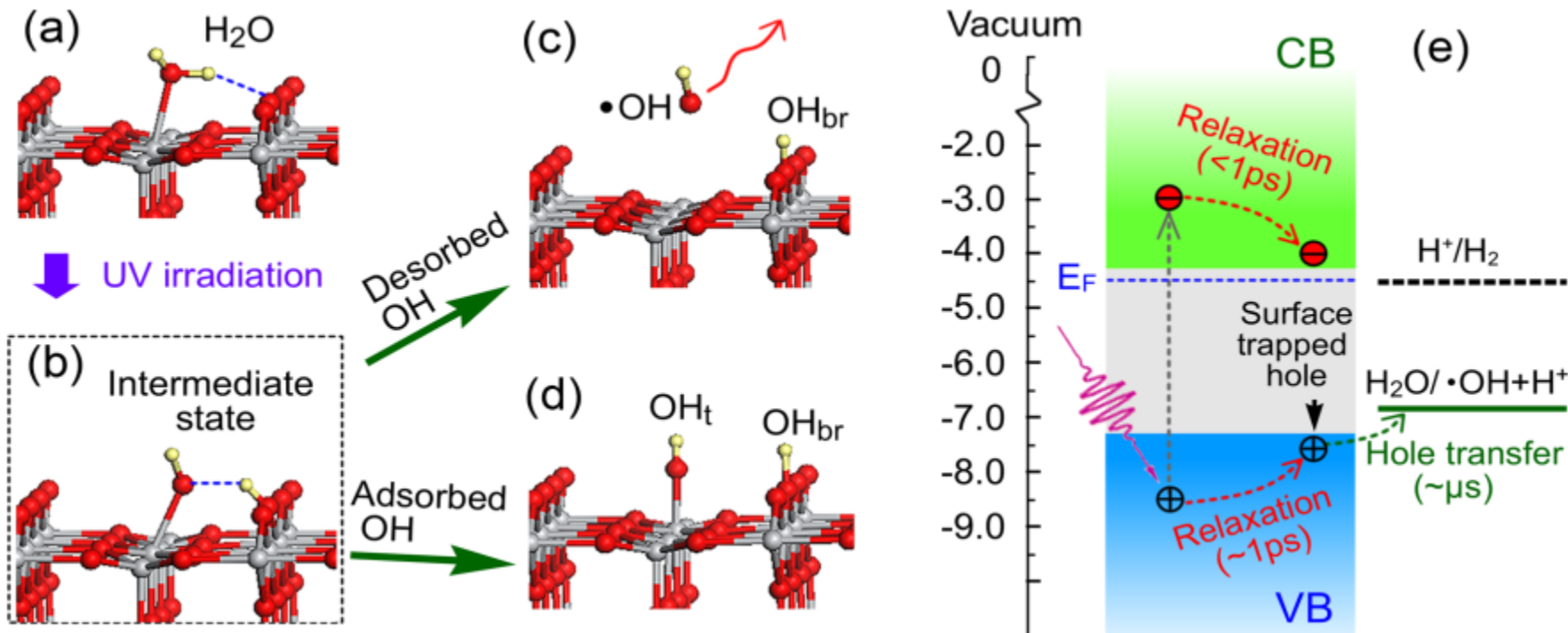
# STM Images before and after water adsorption & Dissociation



# STM Images before and after water adsorption, Dissociation & Light Illumination



# DFT Modeling

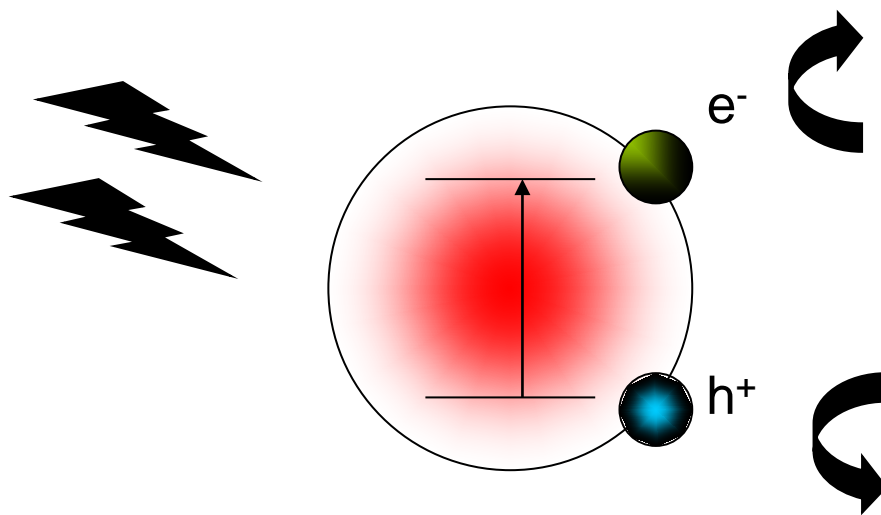


Two surface sites play an important role in the adsorption process, namely the five-fold coordinated titanium site and the bridging oxygen site. The oxygen of a water molecule is pulled towards the five-fold coordinated titanium site. One of the hydrogen atoms is directed to the bridging oxygen via hydrogen bonding, which becomes increasingly stronger and eventually the water molecule dissociates into a hydroxyl anion and a proton, that coordinates to the the bridging oxygen.

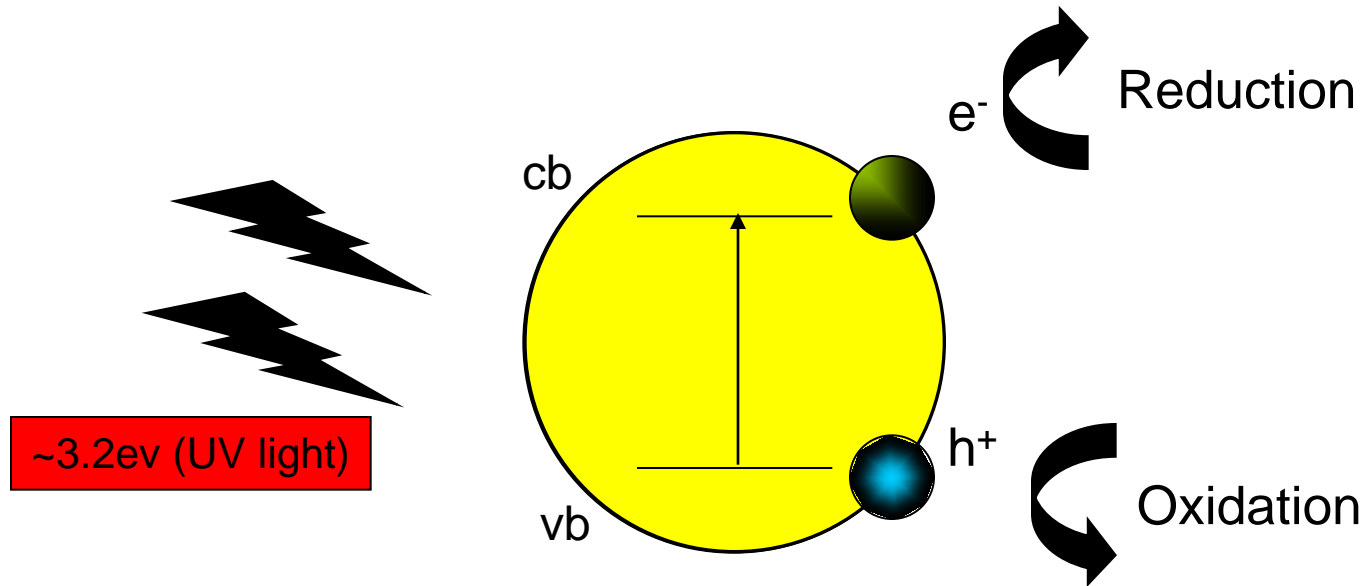
# Plasmon Sensitized TiO<sub>2</sub> Nanoparticles as a Novel Photocatalyst for Solar Applications

George Chumanov

Department of Chemistry, Clemson University, Clemson, SC 29634



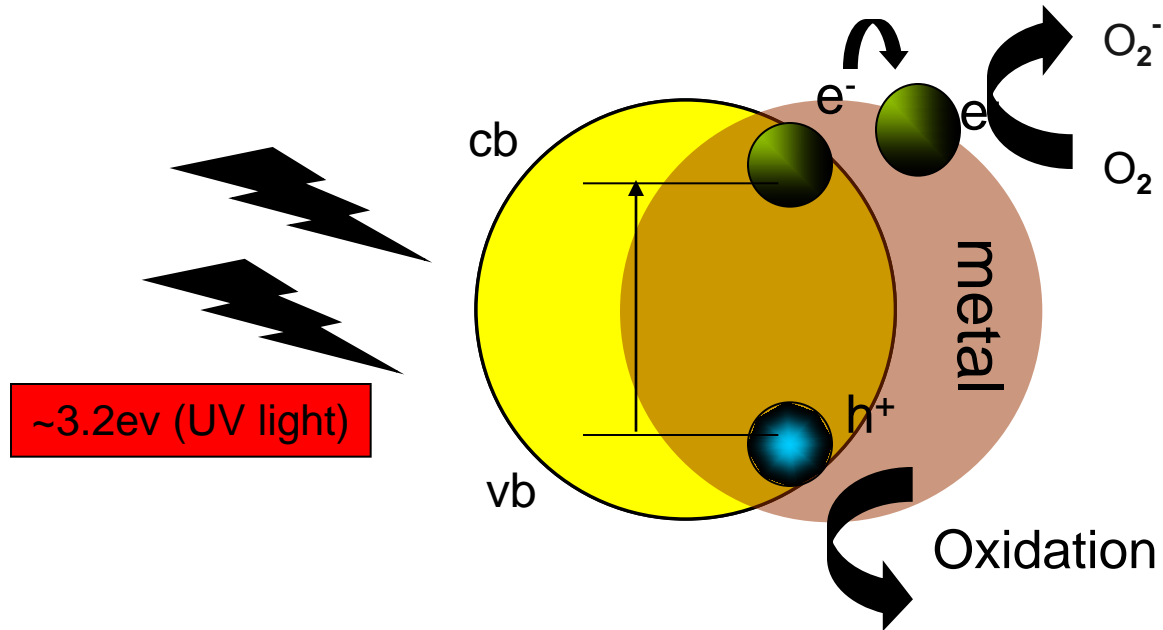
# Titania Photocatalyst



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

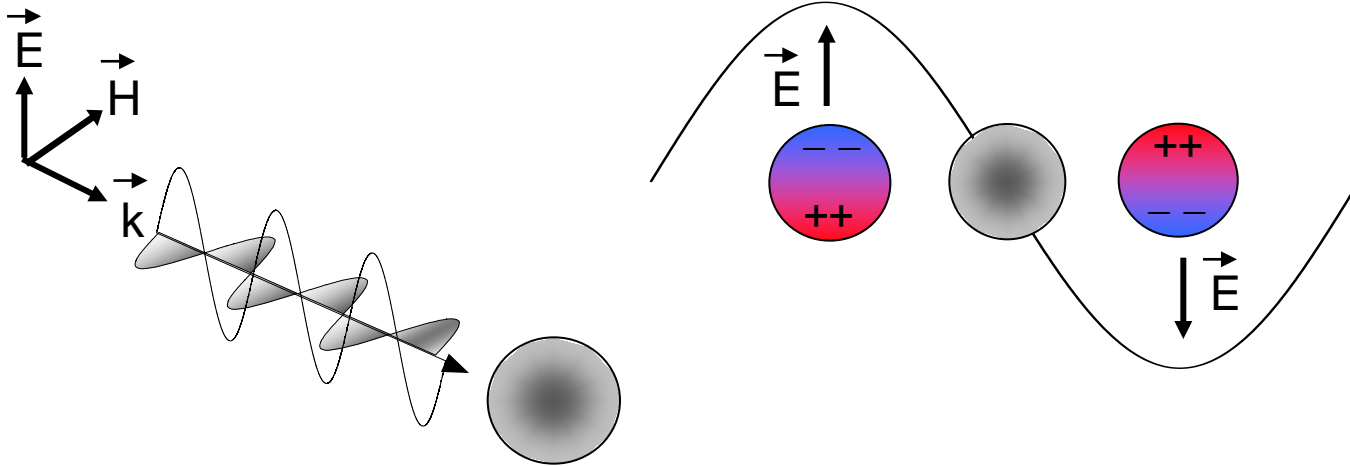


Metal nanoparticles act as an electron sink, promoting interfacial charge transfer reducing charge recombination



# Plasmon Resonance (PR) in Metal Nanoparticles

**PR** – collective oscillations of conducting electrons in metal nanostructures



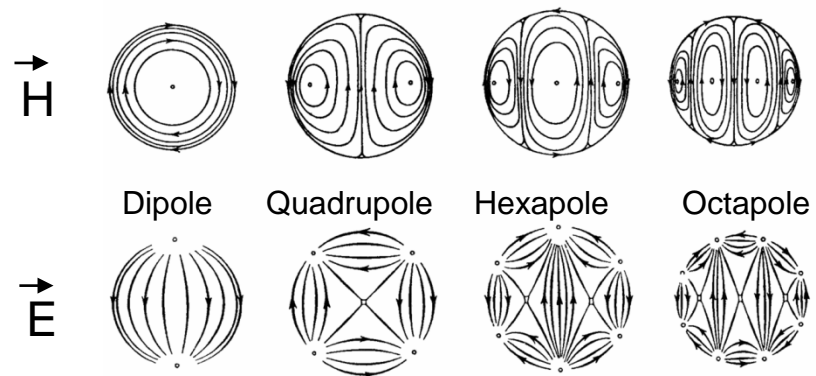
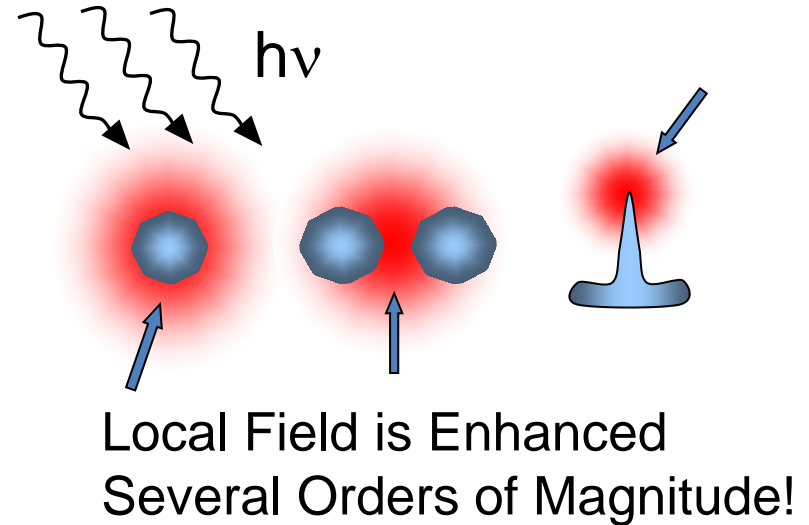
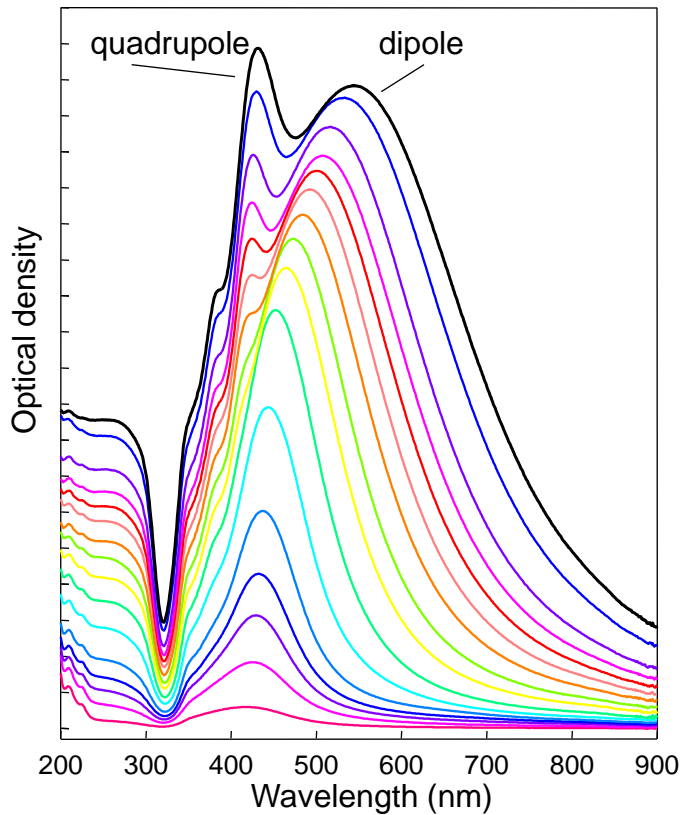
Ag, Au, Cu nanoparticles exhibit **PR** in the visible spectral range

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

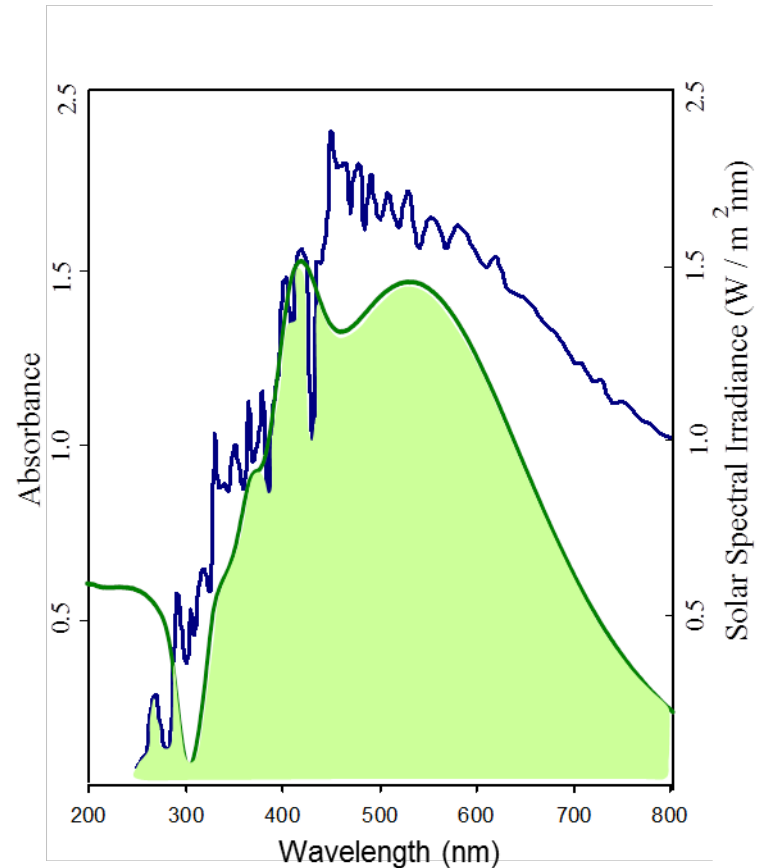
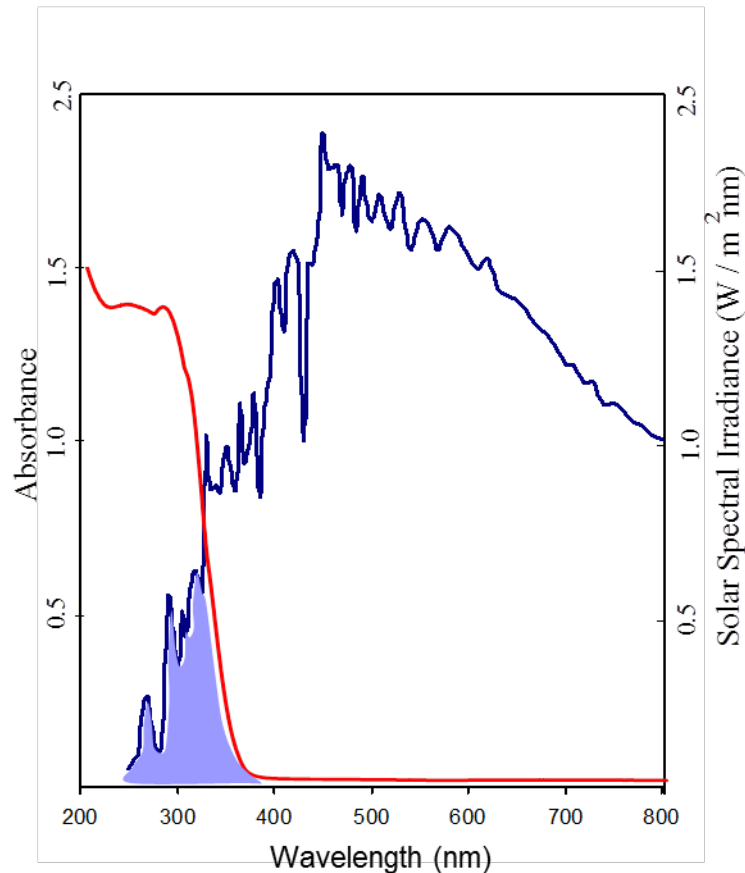
$$\epsilon_{\text{metal}}(\omega_p) = 0$$

# Optical Properties of Silver Nanoparticles

Extinction Spectra of Ag Nanoparticles  
as a Function of Size

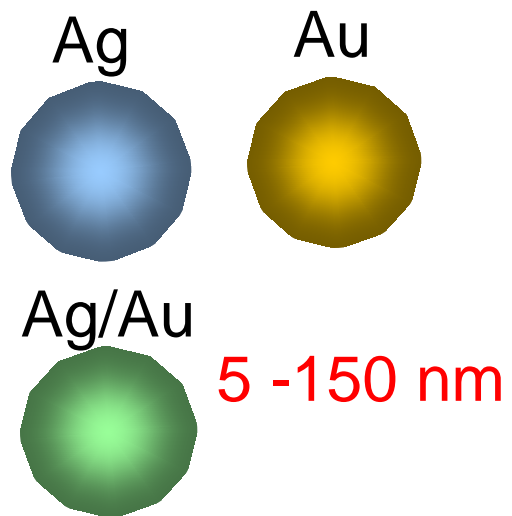


# Ag Nanoparticles as Efficient Antennae for Capturing of Solar Energy

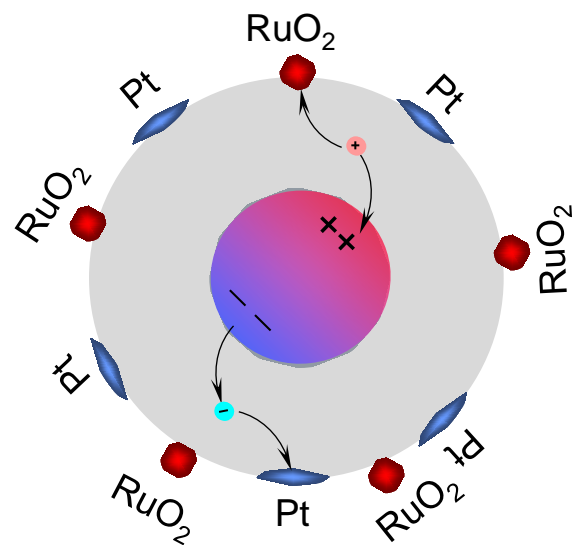
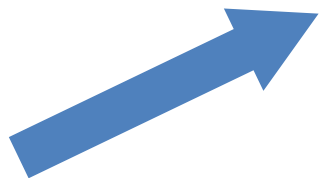
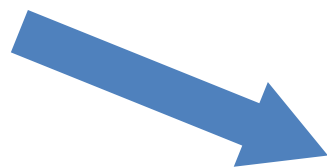
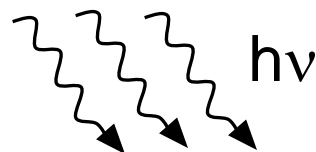
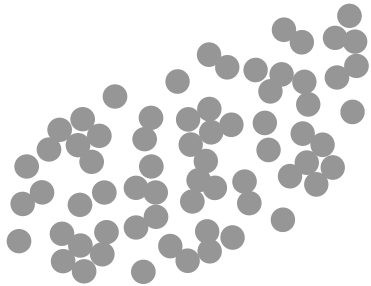


Solar Spectrum is from J.H.Seinfeld and S.N.Pandis" Atmospheric Chemistry and Physics" John Wiley & Sons, Inc. New York, Chichester, Brisbane, Singapore, Toronto (1998)

# Titania Coated Metal Nanoparticles

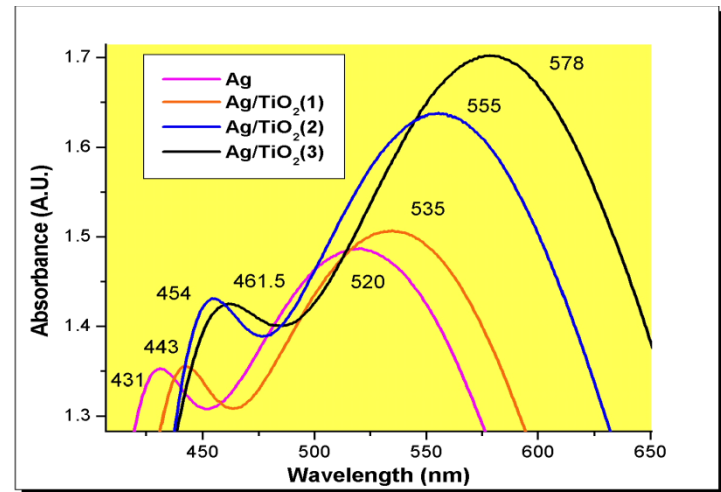
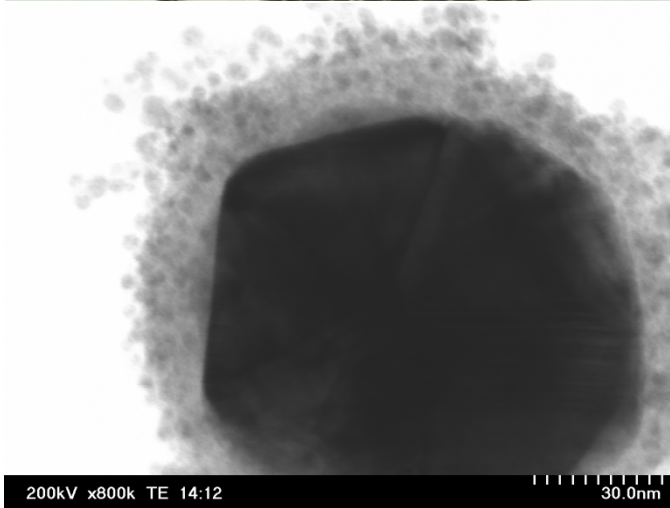
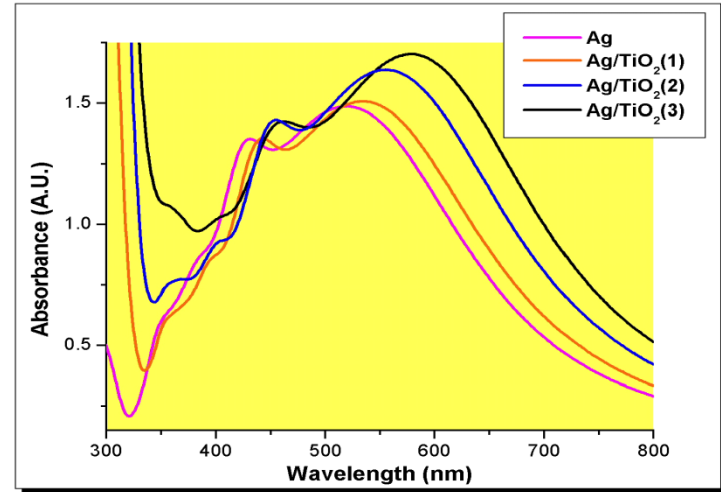
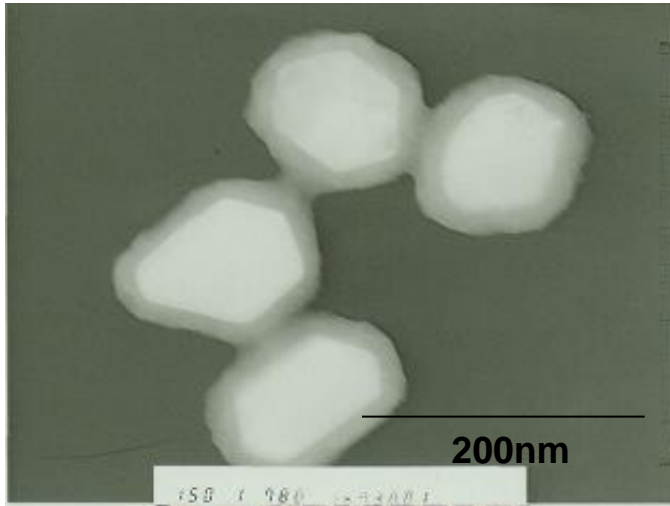


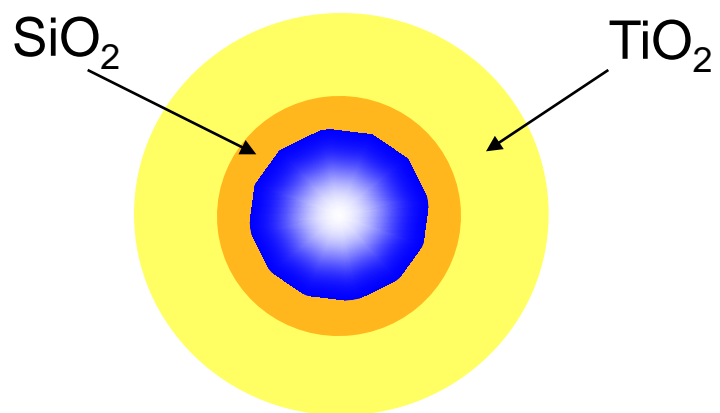
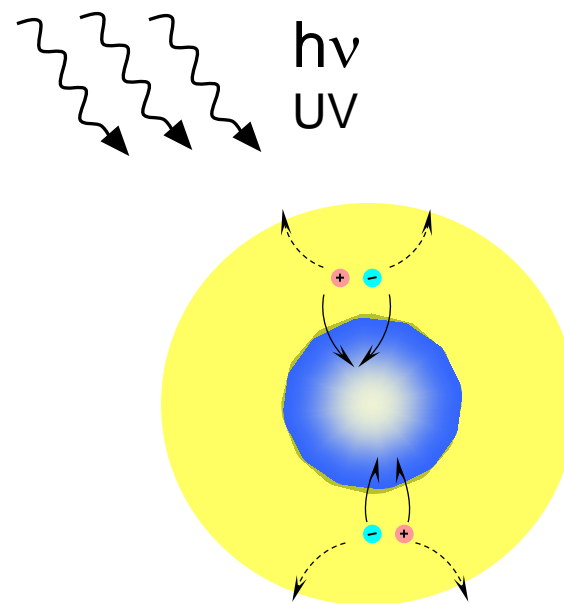
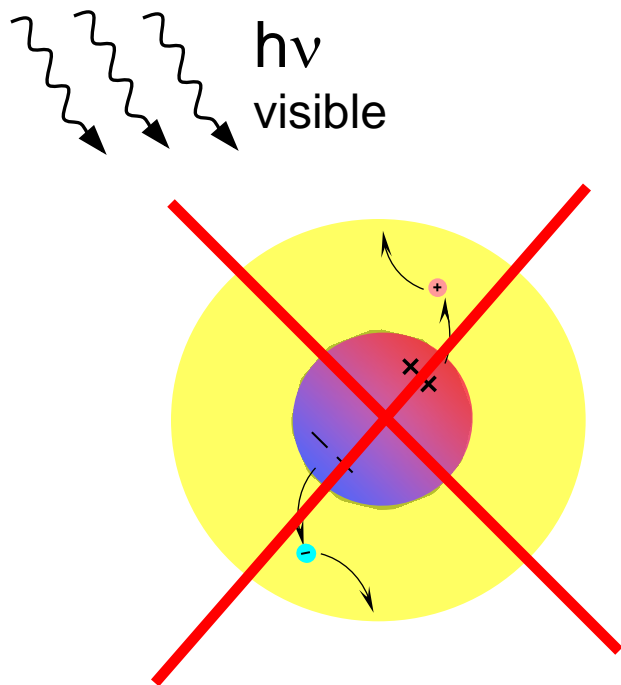
TiO<sub>2</sub> 1 - 5 nm



Plasmon Enhanced Electron-Hole Pair Generation

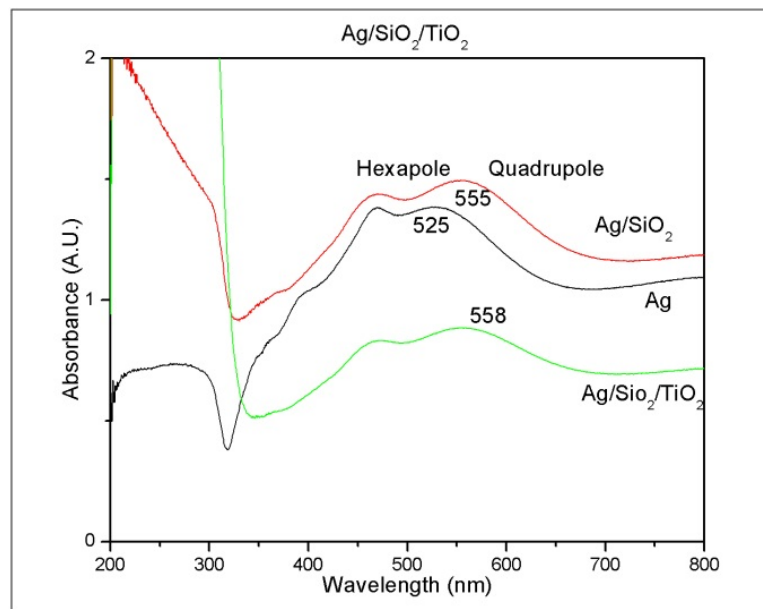
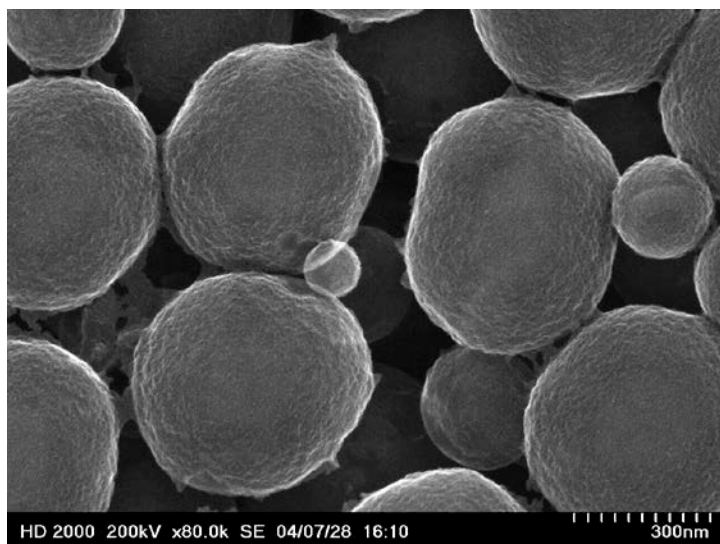
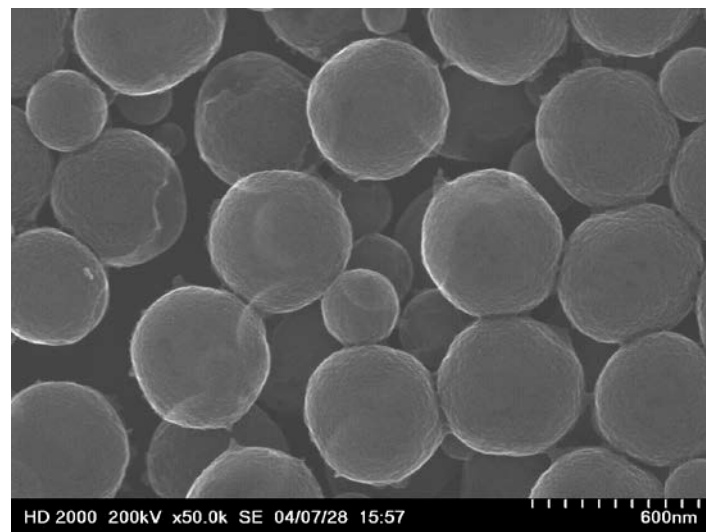
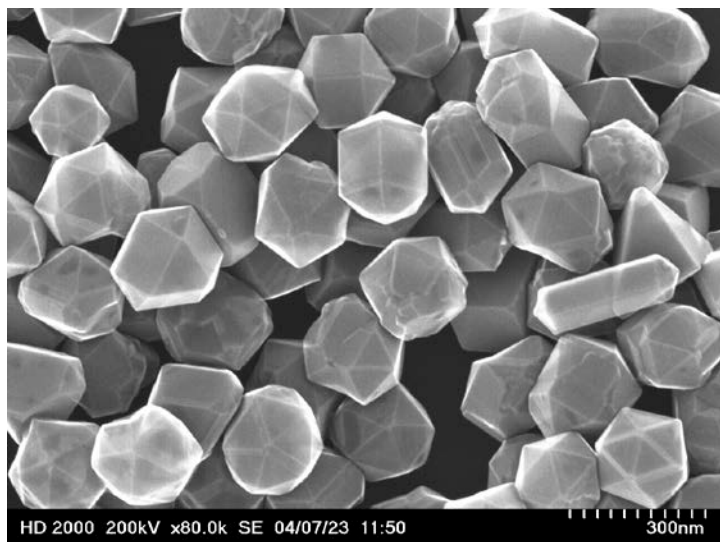
# Titania coated Silver Nanoparticles



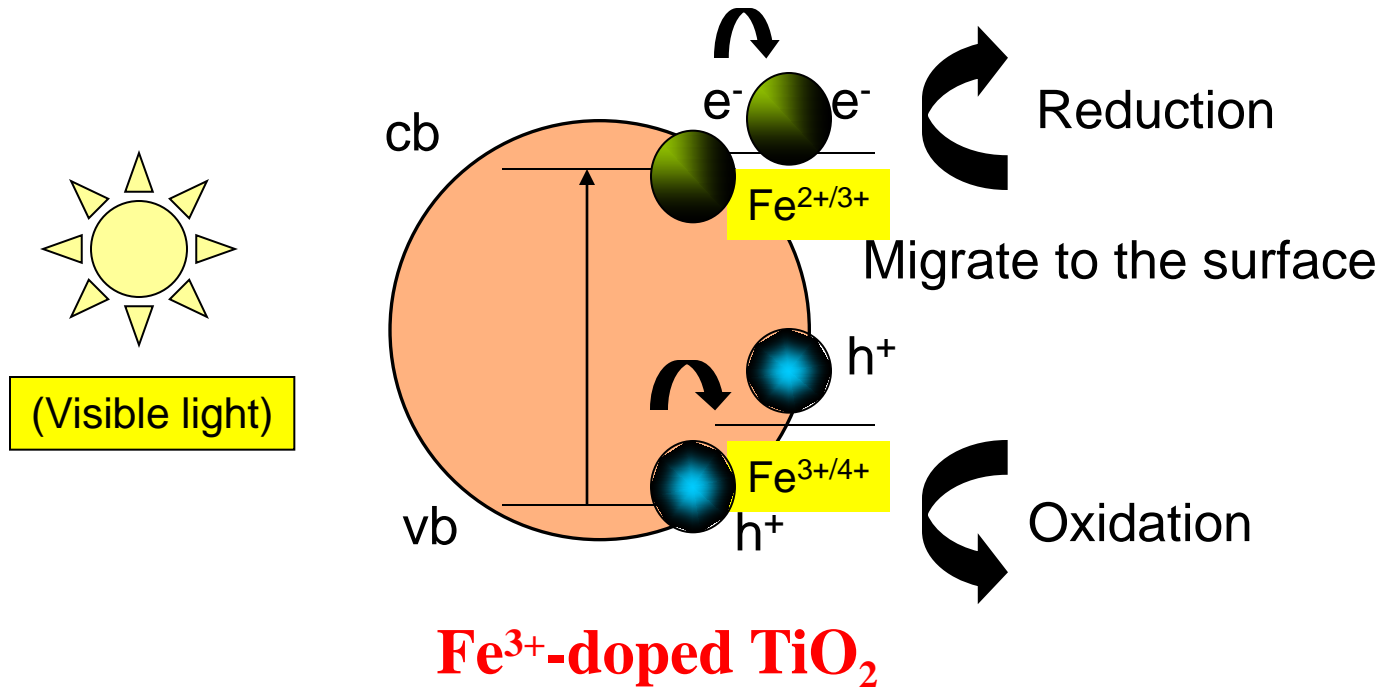


Metal core shortens the  
electron-hole pairs  
generated in titania shell

# Ag core SiO<sub>2</sub>/TiO<sub>2</sub> Nanoparticles



# Metal Ion Doped-Titania Photocatalyst



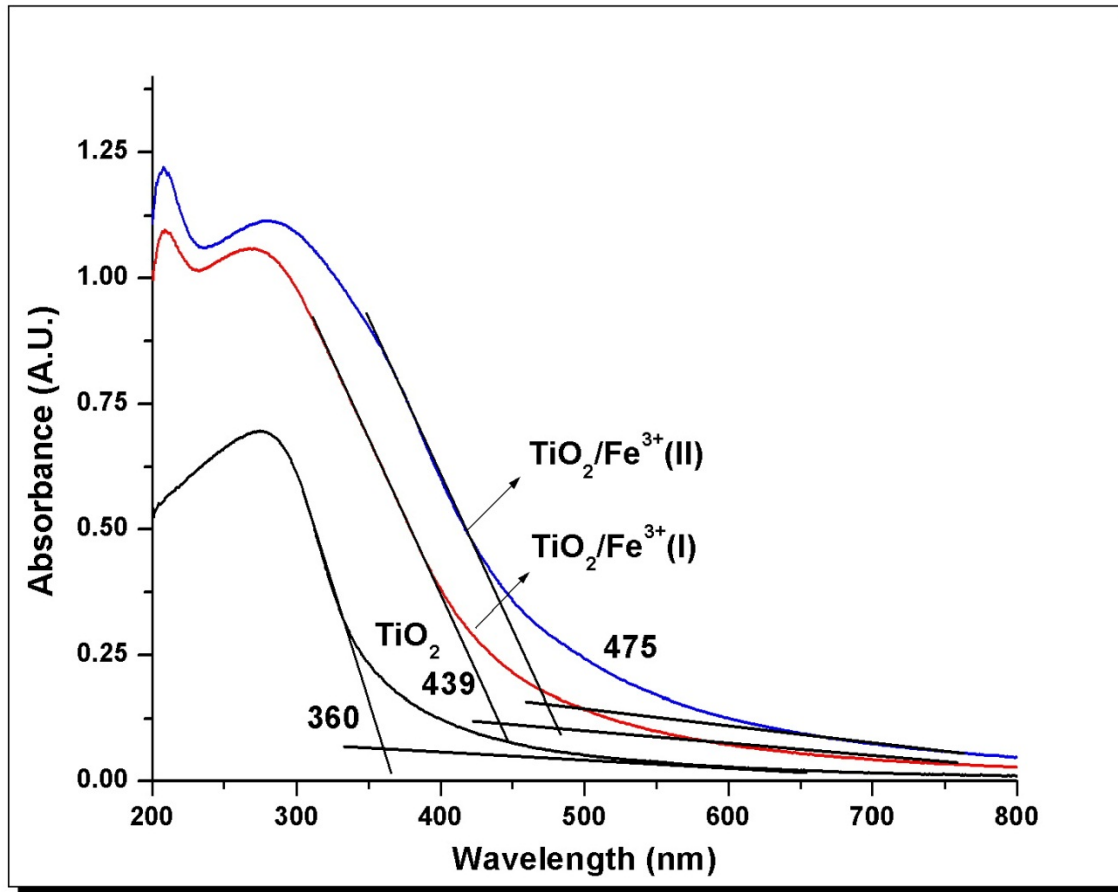
Dopants influences intrinsic properties of titania resulting in lowering the band gap and shifting light absorption into visible spectral range

Dopants should be both good electron and hole traps

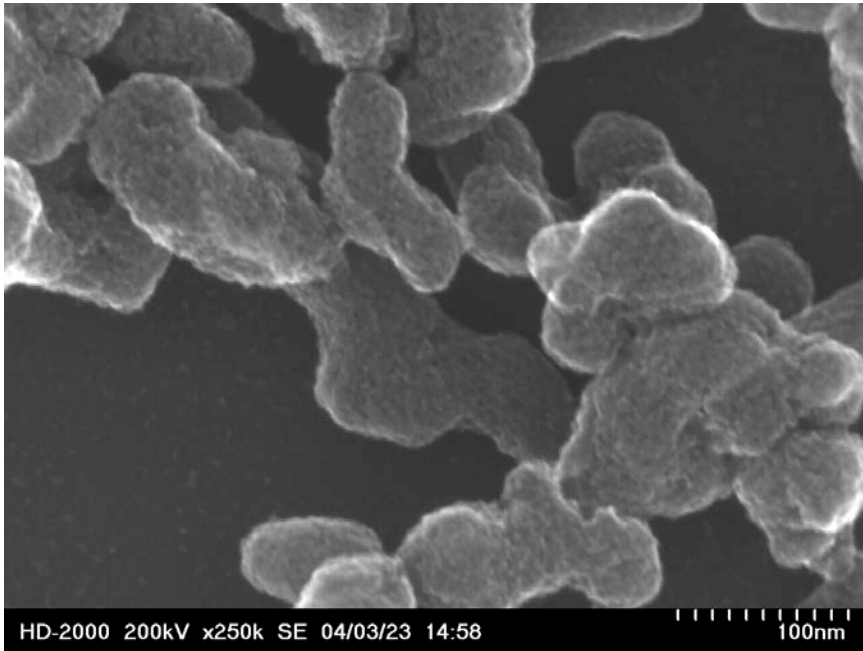
Efficiency of photocatalysis depends on various charge transfer events and migration of charges to the surface



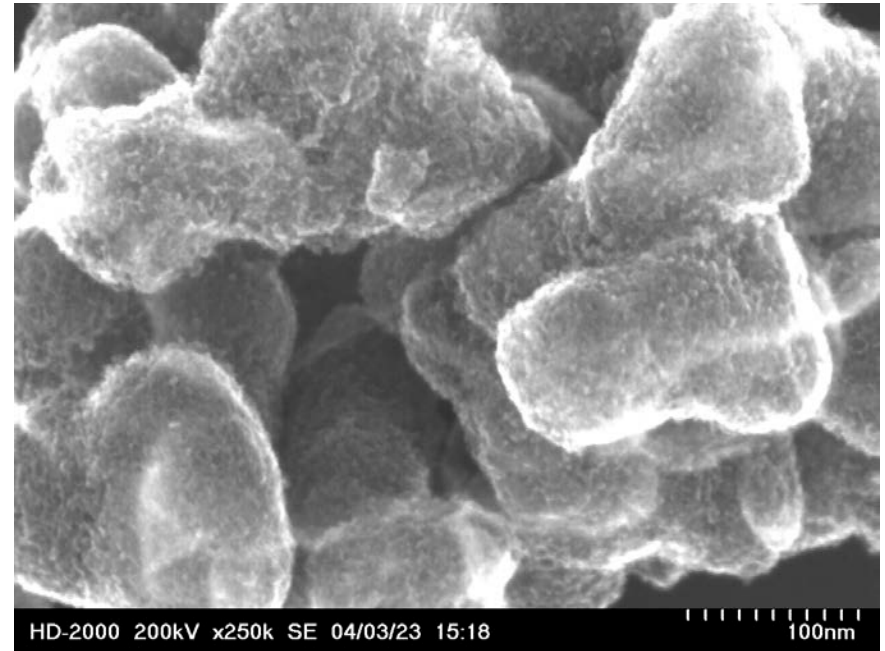
# UV-Vis Absorption Spectra of Fe<sup>3+</sup>-doped TiO<sub>2</sub> : Effect of Fe<sup>3+</sup> concentration



# Electron Microscopy

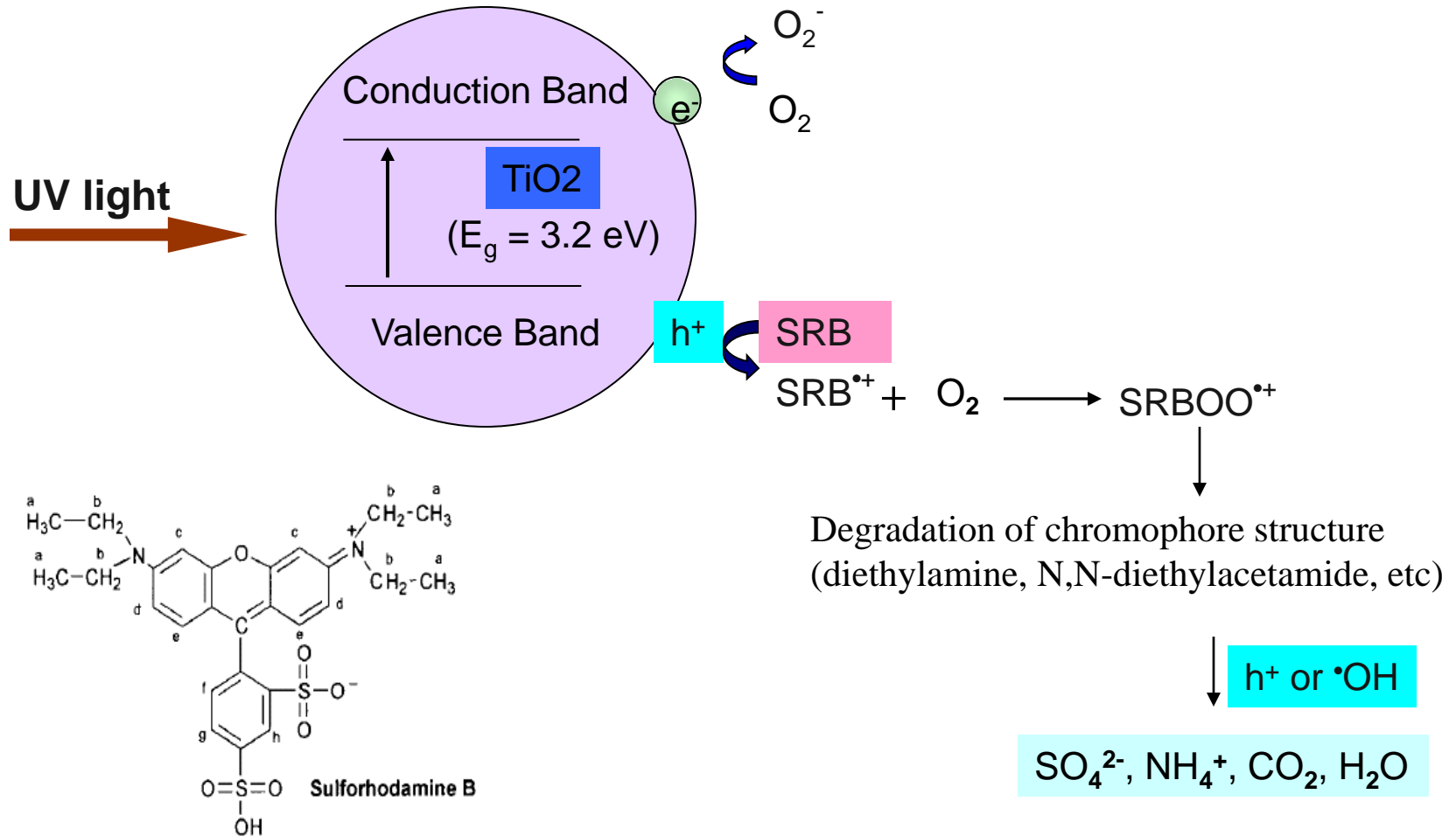


Fe<sup>3+</sup>/TiO<sub>2</sub> as prepared (amorphous)

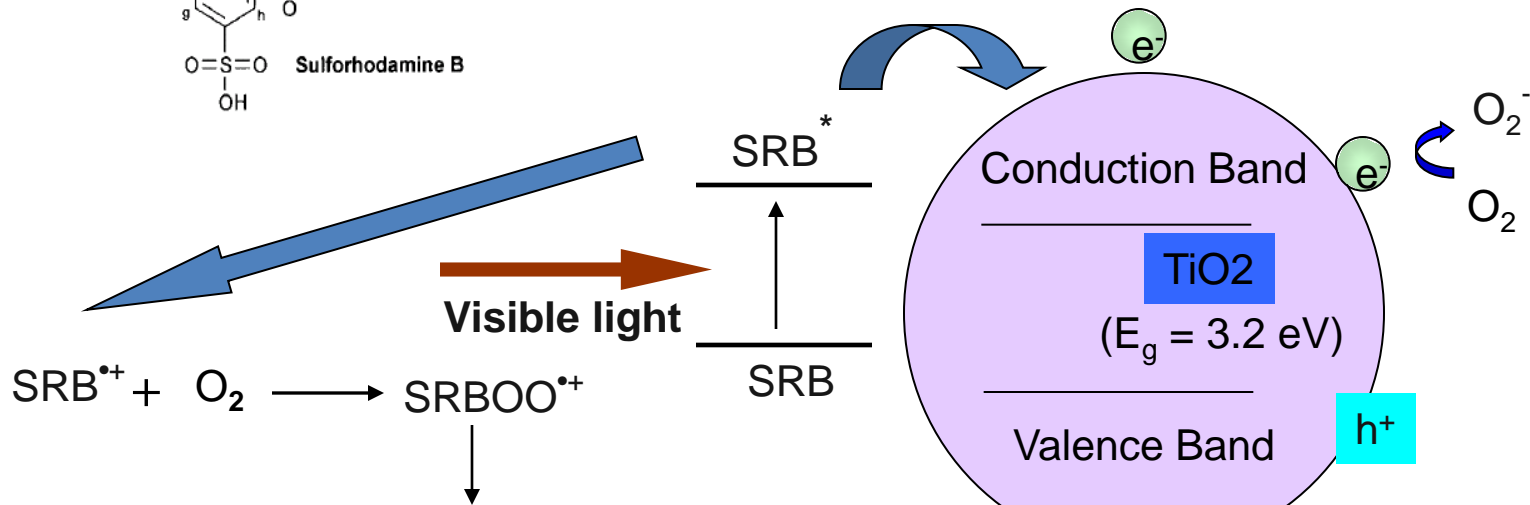
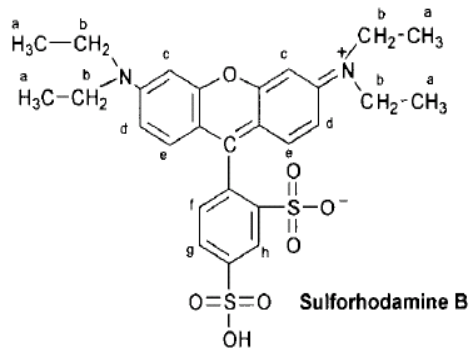


Fe<sup>3+</sup>/TiO<sub>2</sub> after heat treatment (semi-crystalline)

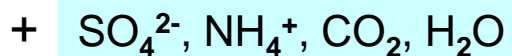
# Photocatalysis Using UV light



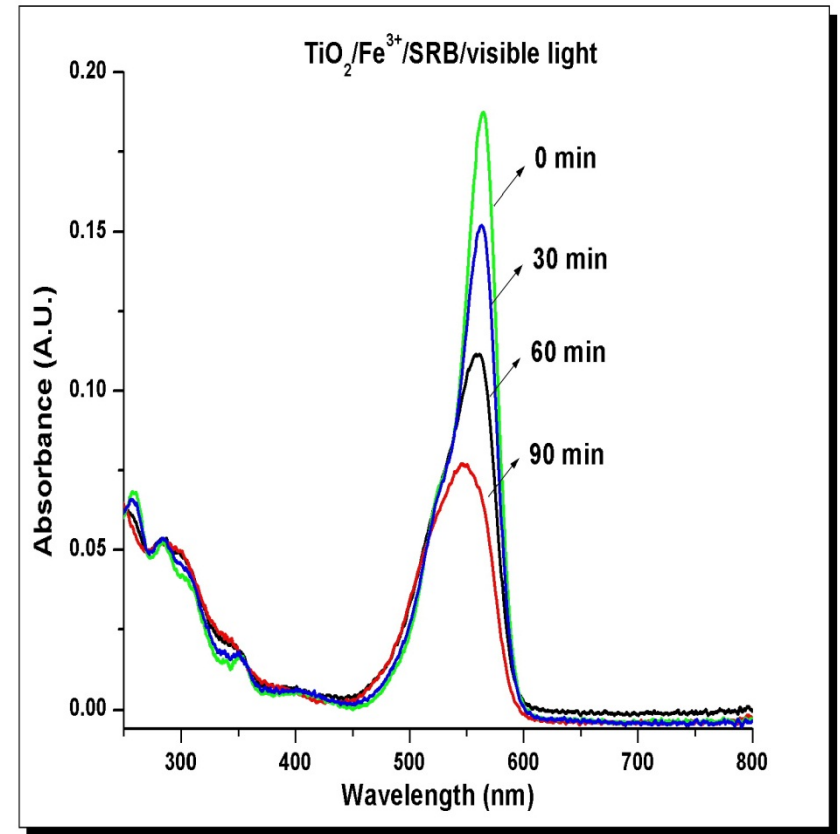
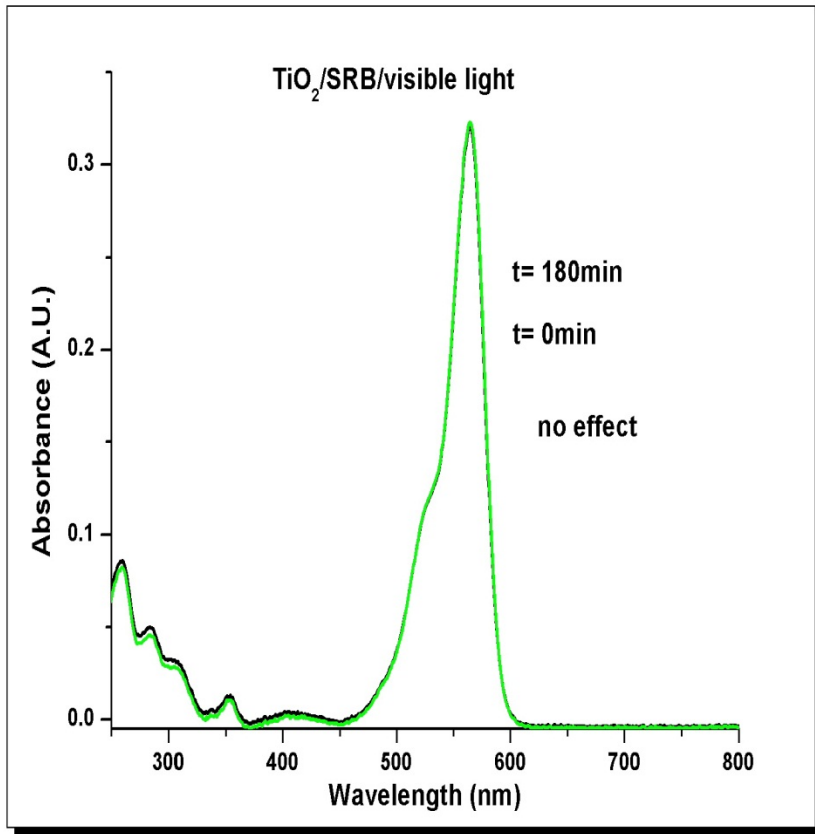
# Photosensitization Using Visible light



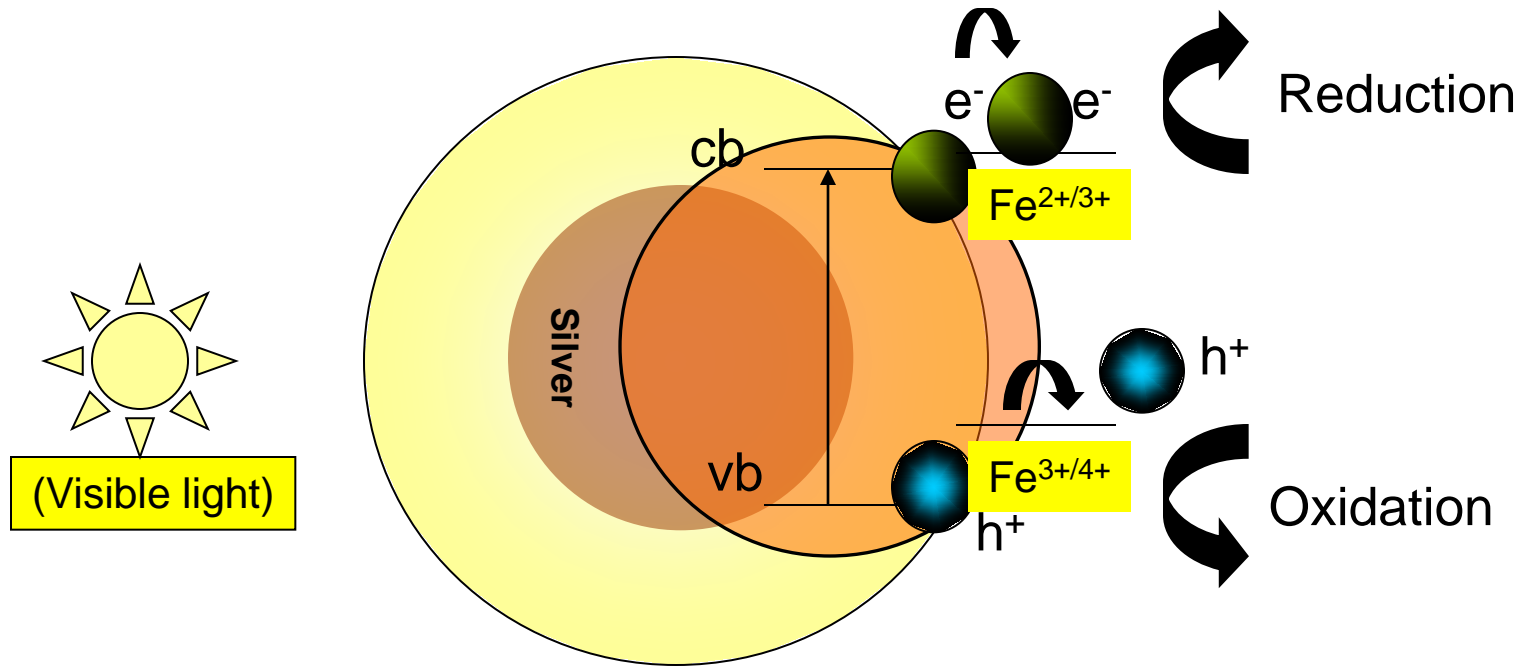
Degradation of chromophore structure  
(diethylamine, N,N-diethylacetamide, etc)



# 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.

Fe<sup>3+</sup>- 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<sup>3+</sup>- doped Titania photocatalyst

Efforts are underway to coat silver nanoparticles with Fe<sup>3+</sup>- doped Titania .

Photocatalytic activity of Fe<sup>3+</sup>- doped Titania and silver coated with Fe<sup>3+</sup>- doped Titania will be compared.