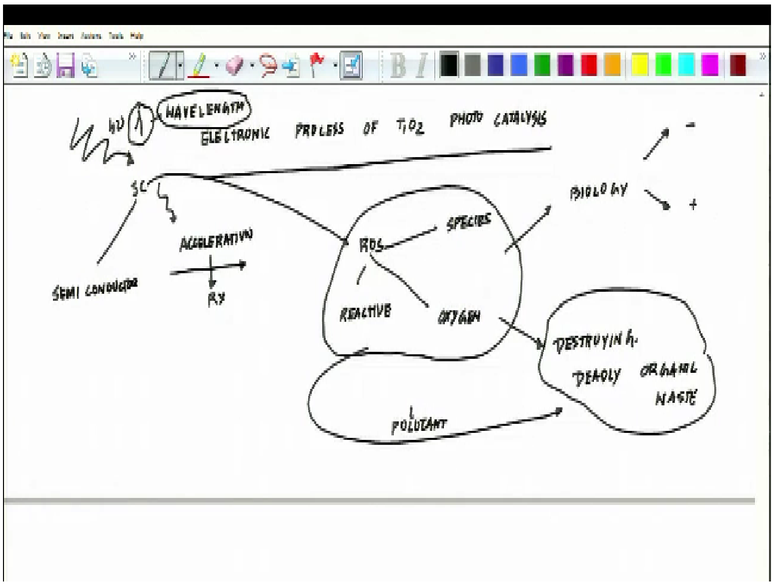
Nanotechnology in Agriculture
Prof. Mainak Das
Biological Sciences and Bioengineering and Design Programme
Indian Institute of Technology-Kanpur

Lecture-39
Case study of Titanium Di Oxide-Part-II

Welcome back to the lecture series in application of nanotechnology in agriculture. So today we are talking about one of the case studies in last couple of classes of titanium di oxide, we have already seen it has agricultural applications, now you are observing that the same material is having applications in diverse areas including electronics, photo electrochemical cell, splitting of water in a photo electrochemical cell by virtue of which it can be used for purification of water.

Production of hydrogen as a fuel it is having amazing anti-fogging and self-cleaning property because when for excited its hydrophilicity become marvellous it can self-clean itself and the light falls on it. So it could be used as the coating material for vehicles and then we observe that this can be used as desensitized solar cells. So let us look at little bit now about the electronics which are involved in it.

(Refer Slide Time: 01:25)



We will be talking about now electronic processes of titanium dioxide photo catalysis, electronic this will be brief electronic process of titanium dioxide, photo catalysis ok. Now we need to talk about this photo catalysis is widely used to describe the process in which acceleration of a reaction occurs there is an acceleration, so there is a reaction happening and this reaction is getting accelerated when a material usually a semiconductor interacts with light of sufficient energy of a certain wavelength.

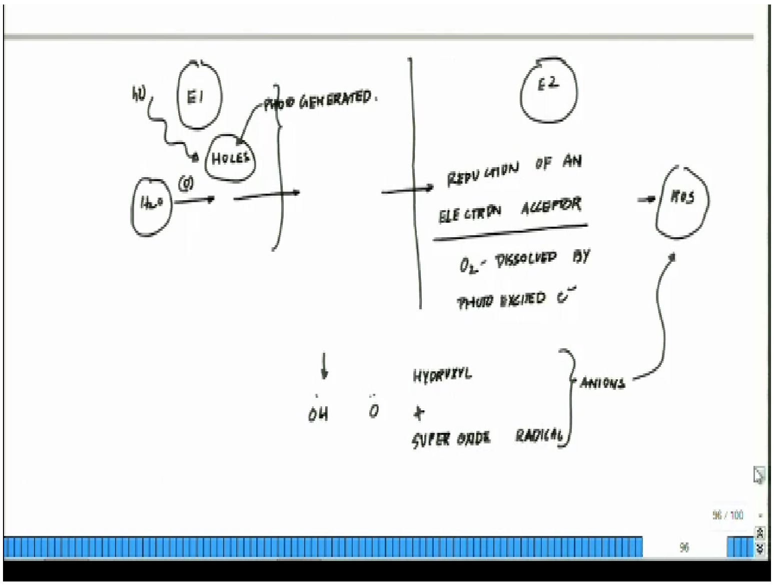
So basically there is a semiconductor, this was your semiconductor, so the semiconductor is interacting with light of certain wavelength or multiple wavelength ok, is interacting with multiple or specific wavelength, while it attract with the light, interact with light of sufficient energy to produce reactive oxygen species are ROS, so this semiconductor is producing ROS reactive oxygen.

And you all are well versed with ROS, we have talked about CeO2 cerium oxide with scavenger ROS. Now we are talking about a material which generates ROS, having just give you little bit of overview of this concept, when you talk about ROS here, so as I told you ROS is a double edged sword, at one hand it could lead to inflammation and diseases and other hand in human body itself ROS could be used by the immune cells to fight against microbes.

But then there is another aspect of ROS, so what we have learnt in biology is it could have detrimental effect and or it could have it could have negative, it could have positive, but in industry section ROD could be used for destroying deadly organic waste. So this ROS on a different fragment could be used for a totally different purpose ok. Now coming back to the mechanism what you are talking about which can led to the photo catalytic transformation of a pollutant.

So this ROS is basically here we are talk about that whole pollutant disposal aspects of it, it must be noted that during the photo catalytic reaction at least 2 even must occur ok, and this part is the extraction important there need for 2 events which must occur simultaneously in order for a successful production of ROS species to occur.

(Refer Slide Time: 05:23)

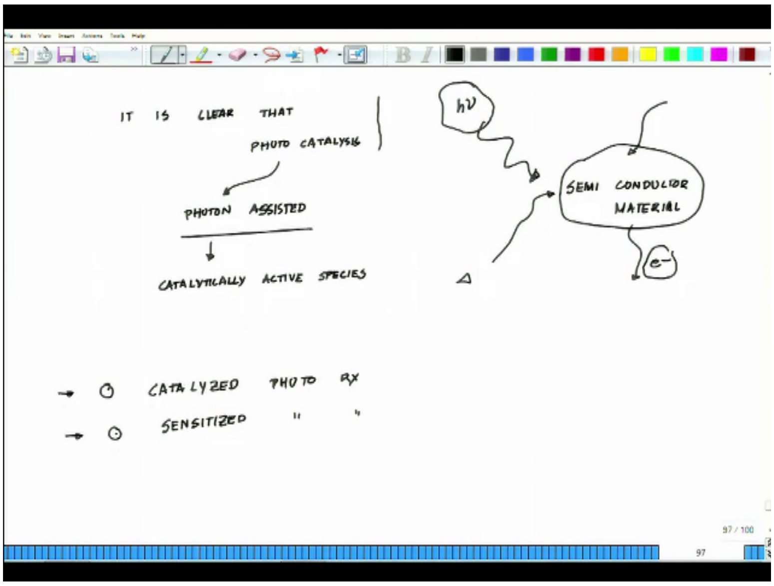


What are those events E1 and E2 ok, for successful production of ROS which is reactive oxygen species. So that 2 critical events involves where water which is absorbed in the material has to get oxidized and the event 2 which will I be talking now. So the first event which needed to happen out here is this is the event 1 where water is coming and what it is doing is that oxidation of the dissociative adsorb H2O.

This is the dissociative adsorb H2O by photo generated holes. So these are the photo generated holes, so these photo generated holes exactly leads to oxidation of the water and the second even involve reduction of an electron acceptor which is typically dissolved oxygen, reduction of an electronic acceptor and within this case is oxygen which is the dissolved oxygen ok.

So it is the dissolved oxygen by photo excited electrons ok**.** These reaction led to the formation of hydroxyl this whole thing leads to the formation of hydroxyl and superoxide radical anion hydroxyl and superoxide, so hydroxyl and superoxide radical anions which is essential is your reactive oxygen species, it is clear that photo catalysis implies photon assisted generation of catalytically active species rather than the action of light as a catalyst in a reaction ok.

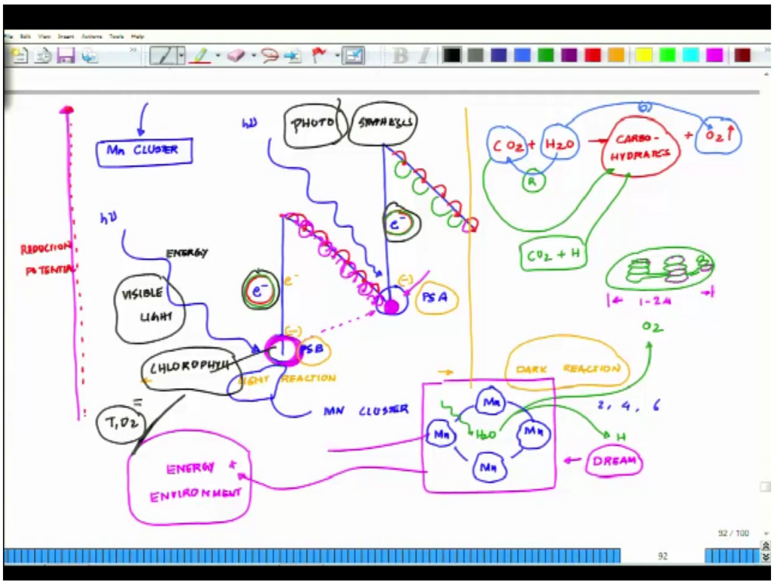
(Refer Slide Time: 08:36)



So this part is important to understand it is clear that when you talk about photo catalysis implies photon assistant, this whole thing is photon assisted, so photon assisted generation of catalytically active species, so you are generating catalytically active species ok. So this catalytically active species are basically photon generate, so rather than action of light as catalyst in a reaction.

So essentially what is to be highlighted is that light is only providing sufficient energy one should realise light is just that mild energy which is needed. So you have this light coming on a semiconductor material and semiconductor material is ejecting out an electron. So light is just providing that assistance, so it could be provided by something else also, in order for that it may be heat also.

(Refer Slide Time: 10:25)



It could be something else also ok, but the semiconductor materials means that small amount of energy to ensure that it generates an electron, why this is important if you look at it and if you go back to when I was talking about photosynthesis exactly the same thing, is visible light which is providing the energy to happen and why it is call photosynthesis is that. This is driven in terms of it is assisted by light.

And (()) (10:47) it could be any light ok photosynthesis, it is the life which is helping for providing the sufficient energy for the synthesis of the carbohydrate molecules exactly same way just imagine in the centre instead of chlorophyll which is nature's molecule for generation of photo excited electrons. So these are those photo excited electron. Now just equated with TiO2. So in other word then chlorophyll is also a semiconductor material ok.

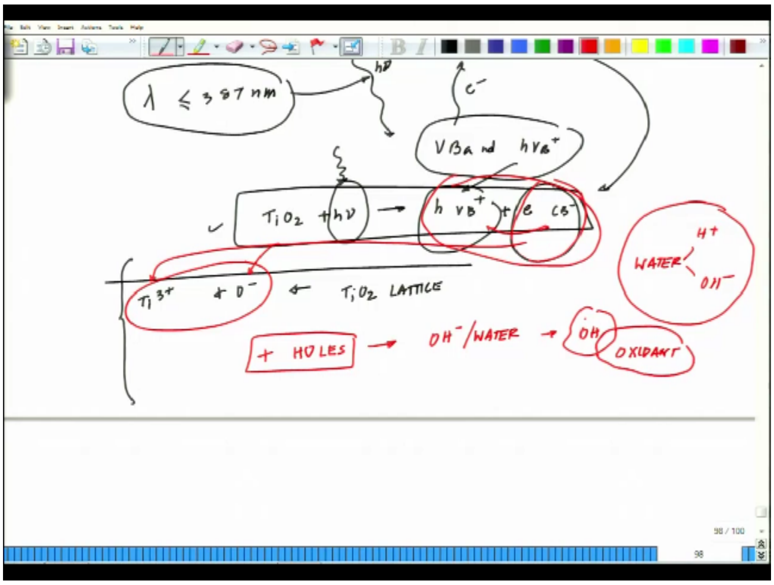
And it has certain light where it generates an electron. So this is that similarity I am trying to draw and in result is fairly the same ok, so and that reactive oxygen species are the reactive electron is out here, that electron which is photo excited. Now if the initial photo excitation process occurs in an adsorbent molecule which then interacts with the ground state of the catalyst substrate.

The process is referred to as catalyst photo reaction, if on the other hand the initial photos excitation takes place in the catalyst substrate and the photo excited catalyst that interacts with the ground state adsorbent molecule. The process is called sensitized photo reaction. So there are 2 concept catalyse photo reaction and sensitized photo reaction. This catalyse if you wanted to going depth these are the terminologies you have to understand.

Catalysed photo reaction and sensitized photo reaction. These are the 2 concept when we talk about these kind of materials ok, catalyse photo reaction, if on the other hand the initial photo excitation takes place in the catalyst substrate and the photo excited catalyse then interacts with the ground state adsorbent molecule the processes a sensitize photo reaction and in most cases heterogeneous photo catalysis refers to semiconductor photo catalysis or semiconductor sensitize photo reaction ok.

So in photo catalysis if you look about it light of energy greater than the band gap of semiconductor. This part is extremely important light having an energy greater than the band gap of a semiconductor.

(Refer Slide Time: 13:19)



So in titanium oxide if you remember when we talk about retile, we talk about it is a band gap of 3 to 3.2, it has 3 polymorphs and they vary from 3 to 3.2 electron volts ok. So the light energy what has to be provided in photo catalysis light of energy greater than the band gap of a semiconductor. So the light energy h mu has to be greater has been light energy has to be greater than 3 to 3.2 electron volt ok.

In case of anatase Tio2 the band gap is 3.2 electron volt, therefore UV light of wavelength around 387 nanometer is required. This has more energy than 3.2, the adsorption of the photon excites an electron to the conduction band ok, the adsorption of the photon, so you have the semiconductor material which is getting wavelength from in that case that case what will happen to repeat it.

In the case of anatase TiO2 the band gap is 3.2 therefore you needed a UV wavelength of 387 nanometer, the absorption of a photon excites an electron to the conduction band which is e CB which is the conduction band electron now generating a positive hole in the valence band ok, in the valance band hvB because valence band is losing an electron therefore this becomes a positive.

So now we have TiO2+h mu is generating a hVB, this is the valance band, this is the one and + an electron eCB ok. So this is in the conduction band and this in the valence band ok. The charge carriers can be trapped, now this part is extremely important to understand the charge carriers can be trapped as Ti3+ and O defects site in TiO2 lattice. So titanium has this defect site. So as remember when we talked about iron pyrite I told you that iron pyrite has been stoichiometric defects.

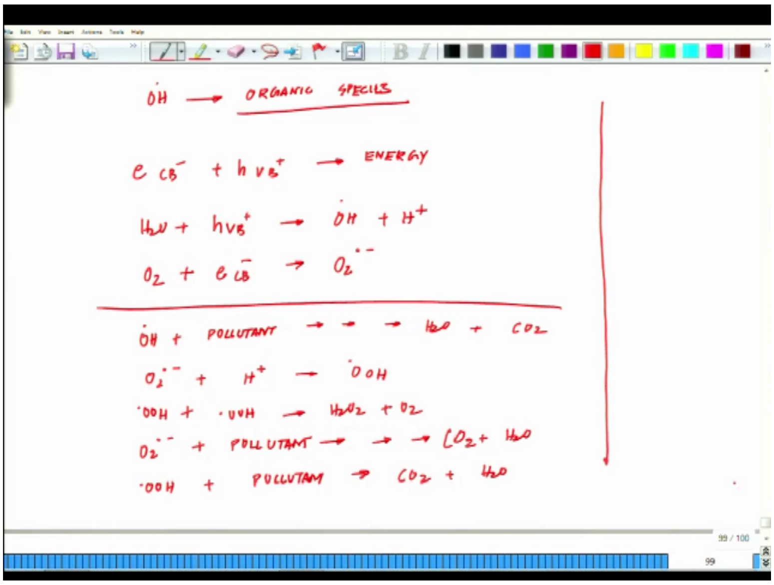
So much of these molecules come with a series of isometric defects such a defects which could be identified by using x-ray photoelectron spectroscopy and very interestingly these defects could be utilised for its application. So defect is in a sense give the material positive layer in terms of its utility, usability and translatability ok. So coming back where I was so I told you that TiO2+ water+ sorry + light is generating combination electron and hole ok.

And the charge carriers can be trapped as Ti3+ and O- defect site in the TiO2 lattice or they can recombine dissipating the energy and this is another problem that they could even recombine electron and whole can recombine and they can dissipate the energy. So you have to prevent the recombination alternatively the charge carriers can migrate to the catalyst surface and initiate redox reaction with adsorbent ok.

Now this is what you are asking for alternative labour charge carriers can migrate so you have the charge carriers. So these are the charge carriers what you are having, so these charge carriers are adsorb, charge carriers can be trapped into Ti3+ or O- sites or charge carrier may recombine and dissipate the energy. Now what will happen alternatively the charge carriers can migrate to the catalyst surface.

And initiate redox reaction with adsorbent ok and adsorb has water ok, positive holes can oxidised OH- or water at the surface ok. So positive holes can oxidise OH- of water or water because when we talk about water we are talking about H+ and OH- ok. So now this OH- is transform to produce OH radical which is hydroxyl radical, we talked about it just few minutes back which are extremely powerful oxidant.

(Refer Slide Time: 18:55)

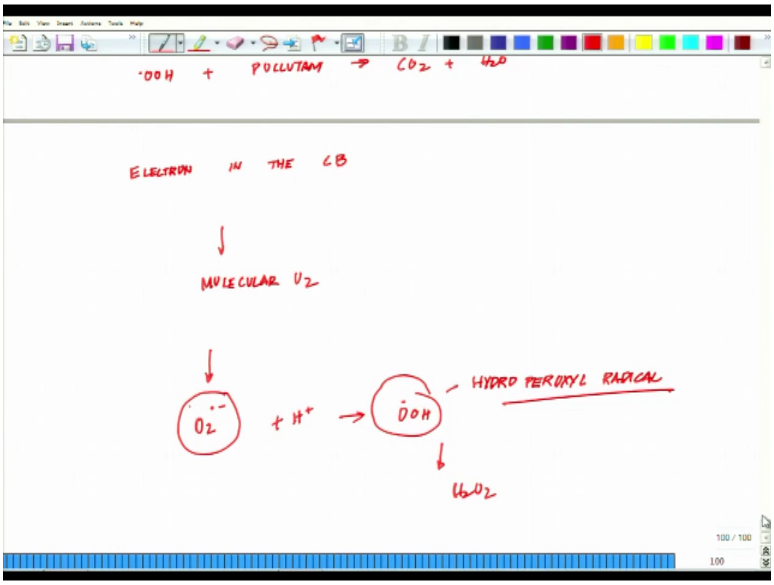


So this was one powerful oxidant because we are generating ROS reactive oxygen species. Similarly the hydroxyl radical can subsequently be oxidized OH could subsequently be oxidized ok, because can subsequently oxidized the organic species. So this is when you talk about the organic pollutants or any other stuff oxidized organic species with mineralization producing mineral salt like Ceo2 and water ok.

So now if I so this is that reactive oxygen species what we are creating eCB- in the conduction band +H vB+ which is in the valence band you have the energy and H_2O+h in the valence band is generating OH.+ a proton which you could see as a H^+ are there. Now on the other hand the next set of reaction vary of oxygen+eCB conduction band generate another free radical or another reactive oxygen species.

Now here is next reaction where you are having OH dot+the pollutant is generating H_2O+CO_2 and the other reaction could be O_2.- +H^+ generating OOH or OOH+another OOH it could create hydrogen peroxide. This will remind you of the role of pyrite while generates trace amount of this O_2.- + a pollutant. This is where you are destroying the extremely harmful organic waste H+pollutant generating CO_2+H_2O.

(Refer Slide Time: 21:48)



And if you look at it there is series of reactions which are happening here and these are and these are just a handful of them. So electron in the conduction band can be rapidly trap by the molecular oxygen, so electron in the conduction band could be rapidly trap by the molecular oxygen adsorb on the titanium particles which is reduced to form superoxide radical which is O2.- ok.

And that may further react with H+ to generate hydroperoxyl radical. This is called hydroperoxyl radical and further electrochemical reduction yields H2O2 as I showed you in the reaction ok. These reactive oxygen species may also contribute to the oxidative pathway such as degradation of pollutant ok. So to realise that same titanium dioxide which has agricultural role has now showing tremendous promise in photo electrochemical cell. So I am closing here, in the next class will little bit further before closing down, thank you.