Nano Structured Materials-Synthesis, Properties, Self Assembly and Applications
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Module - 4
Lecture - 31
Photocatalysis – III

Welcome to the course on nano structured materials; synthesis, properties, self assembly and applications. We are in the module four of this course and we are we are working on photocatalysis right now and we have two lectures on photocatalysis and today is the third lecture on photo catalysis and this is also the lecture three of module four. So, in photocatalysis in the previous lectures, we looked at the basic ideas of catalysis in the presence of light and how UV light and visible light catalyst catalyze reactions through the generation on of electrons and holes.

Two important criteria are the electron and holes should be generated efficiently and the second thing is the electron and hole should be separated from each other. So, that they do not recombine and release a photon. So, this recombination has to be prevented and this charge separation is an important part in the design of new materials, which will allow for enhanced efficiency of the photocatalyst.

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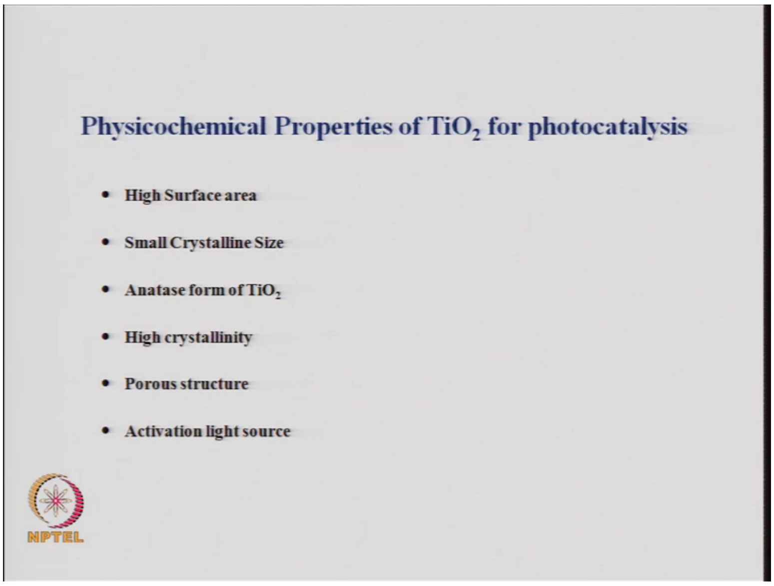

Physicochemical Properties of TiO_2 for photocatalysis

- High Surface area
- Small Crystalline Size
- Anatase form of TiO_2
- High crystallinity
- Porous structure
- Activation light source

Now, the Photocatalysis as we see you can have high surface area, small crystalline size the specially we are discussing for titanium dioxide and in this case the anatase form of titanium dioxide is very important. There are three forms of titanium dioxide; the rutile form is the high temperature form whereas the anatase form is the low temperature form and we require the anatase form for high photocatalytic activity. So, the anatase form is very important then T i O 2 photocatalyst can be prepared with high crystallinity; it can be prepared with high porosity. So, porous structure of titanium can be prevented and the activation through a light source is possible in T i O 2.

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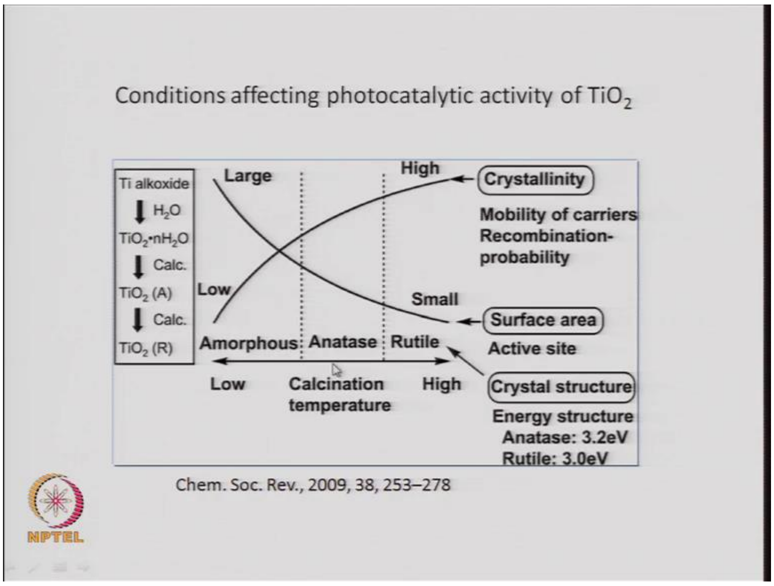

Conditions affecting photocatalytic activity of TiO_2

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Let us look at the conditions affecting the photocatalytic activity of T i O 2. Now, T i O 2 is normally prepared through an alkoxide through solution methods. We start from a titanium alkoxide and typically we take titanium isopropoxide and when you hydrolyze it with water, you get this kind of hydrates at low temperature. Then, when you heat it further you calcine it; you get the anatase form of T i O 2, if you heat is further that is you further calcine you get the rutile form of T i O 2. Now, if you look at the properties if you have at low temperature, you normally have the amorphous form and at low temperature you have low a very low surface area; in this case you have a large when you have large crystallinity especially like in rutile.

So, if you have the surface area, which is low and you may have very large surface area both are possible; the activity goes down if the surface area goes down. So, the activity will be large when the surface area is very high and the activity will become small when the surface area is small. In crystallinity, if you have very high crystallinity, then which you get at high temperatures and in the rutile form; you will get this high crystallinity. In the anatase form, somewhere in the middle you have reasonable crystallinity and reasonable surface area whereas, in the rutile form you have high crystallinity and small surface area. The difference between the rutile and anatase in the band gap anatase and the band gap of 3.2 electron volts and rutile has the band gap of 3 electron volts.

So, if you decrease this surface area the number of active sites also decreases. So, what you want is very a balance between crystallinity and surface area and that you achieve in the middle. Because, if you have very amorphous type of T i O 2, which you will get in the initial stages of the hydrate formation. Then, your active sides will be low although you having a high surface area because of poor crystallinity. So, it is good to work in this region, where you have the anatase form of T i O 2. Now, T i O 2 is a very efficient photocatalyst, but you need ultra violet radiation UV light. Normally, we would like to use visible light and to use the solar spectrum; we would like to use the visible light and the material should be active under visible light; visible light is in the lower energy region compared to UV light.

So, visible light active photocatalyst is really needed for practical applications and will be economical, if we have efficient visible light catalyst. So, how do we modify the normal T i O 2, which is a UV light photocatalyst to make it into a visible light photocatalyst? That can be done by doping T i O 2 with different materials like non-metals, transition metals or organic dyes. All of them can modify the behavior of T i O 2 with respect to the incoming radiation. And all of them you have to choose appropriately the type of non-metal or transition metal or organic dye to control the band gap of T i O 2 or effectively generate electron and hole pairs by using visible light instead of ultra violet light.

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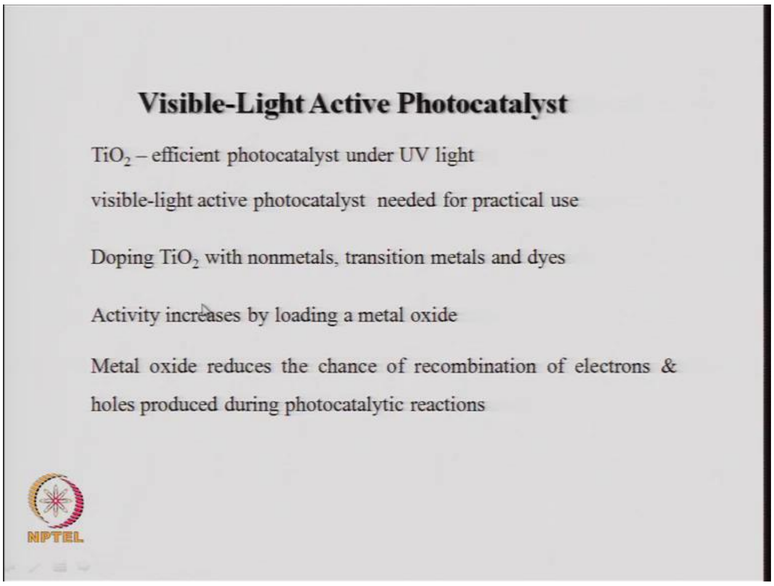

Visible-Light Active Photocatalyst

TiO_2 – efficient photocatalyst under UV light

visible-light active photocatalyst needed for practical use

Doping TiO_2 with nonmetals, transition metals and dyes

Activity increases by loading a metal oxide

Metal oxide reduces the chance of recombination of electrons & holes produced during photocatalytic reactions

You can also increase the activity of the catalyst by loading a metal oxide and we will see examples of these; the metal oxide typically reduces the chance of recombination of the electrons and holes, which are produced during the photocatalytic reactions. So, hence there are several ways by which people are trying to use dopants to modify the band gap or to effectively create electrons and holes in the using visible light. Because T i O 2 is available in large amounts in the earth and T i O 2 is environmental friendly. So, it is a very challenging problem and important problem to convert T i O 2 of visible light photocatalyst instead of a UV photocatalyst.

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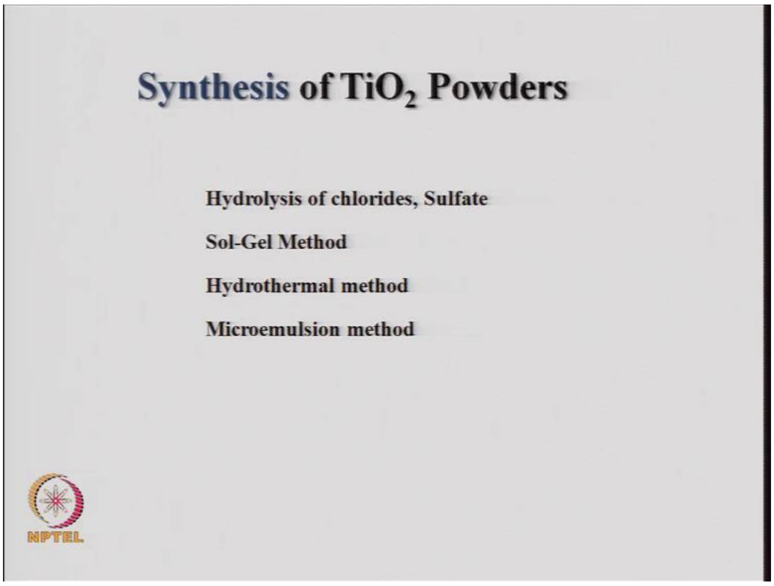

Synthesis of TiO_2 Powders

Hydrolysis of chlorides, Sulfate

Sol-Gel Method

Hydrothermal method

Microemulsion method

Now, how do you make titanium dioxide? If you have to make it in the lab titanium dioxide is of course, available in nature also, but you want to make titanium dioxide in the lab or in industry in bulk quantities. So, how do you make titanium dioxide, which is active and hence you want to make anatase form of titanium dioxide. So, people have found several methods like the hydrolysis of chlorides of sulfates of titanium salts and they have used the Sol-Gel method, which is a very popular method.

We have discussed in our earlier lectures or they have used the hydrothermal method, where you use teflon or steel containers to create a pressure in either aqueous medium or using a solvent, and some pressure is created at the action occurs under pressure at temperatures around 100 to 200 or 250 degree centigrade or may be sometimes up to three hundred or three fifty degree centigrade.

There is another method, which is microemulsion method where you use titanium salts and appropriate surfactants to make microemulsion, where you can make nano-reactors using this microemulsion, which are present in solution depending on the type of surfactant and solvent even control the size of the nanoreactors. Then, you can do reactions using the titanium salts and hydrolyze them within the nanoreactors to give you nanoparticles of T i O 2, which are of the anatase form after certain calcination step. So, people can have used all these methods to make titanium oxide, nano powders in large amounts and in the anatase form.

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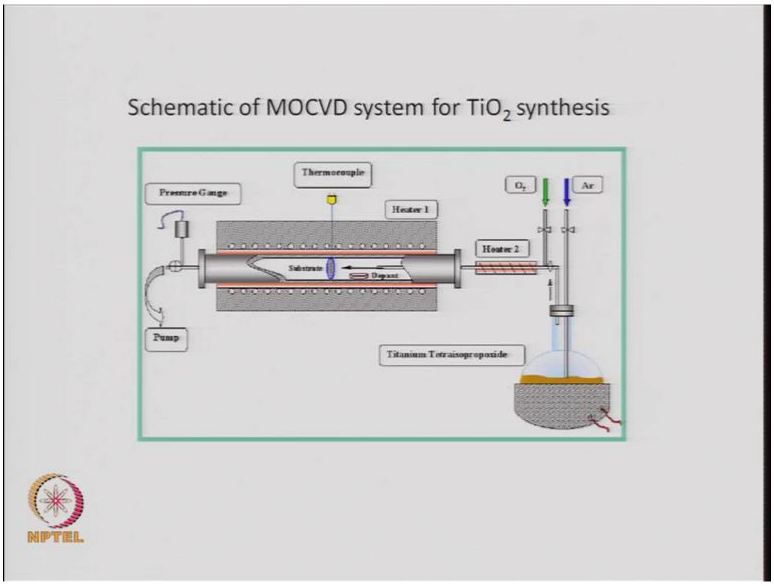

Schematic of MOCVD system for TiO_2 synthesis

Now, this is another technique by which T i O 2 can be synthesized, this is the metal organic chemical vapor deposition or MOCVD in general as it is told, where you have your material, which can be titanium isopropoxide as discussed earlier. So, it is an alkoxide of titanium and that passes through a heater and there are several other heaters and temperature sensors in the furnace. So, there is a furnace through which this titanium isopropoxide is passed in the presence of oxygen and organ. Then, at this temperature which you can control the titanium isopropoxide can be calcined over a substrate and T i O 2 is generated on top of a substrate and if you want some metals to be doped metal oxides to be doped.

Then you put this metal oxide or a metal as a dopant here and the temperature should be sufficient to volatilize, this dopant and then the dopant mixes with the incoming stream of the titanium isopropoxide and forms T i O 2 on this substrate along with the metal or metal oxide dopant. This kind of system can generate large amount of very high quality films of T i O 2 on the surface of appropriately chosen substrates. Substrates can vary from silicon to glass to cords and variety of substrates, you can choose depending on what is your application of this photocatalyst.

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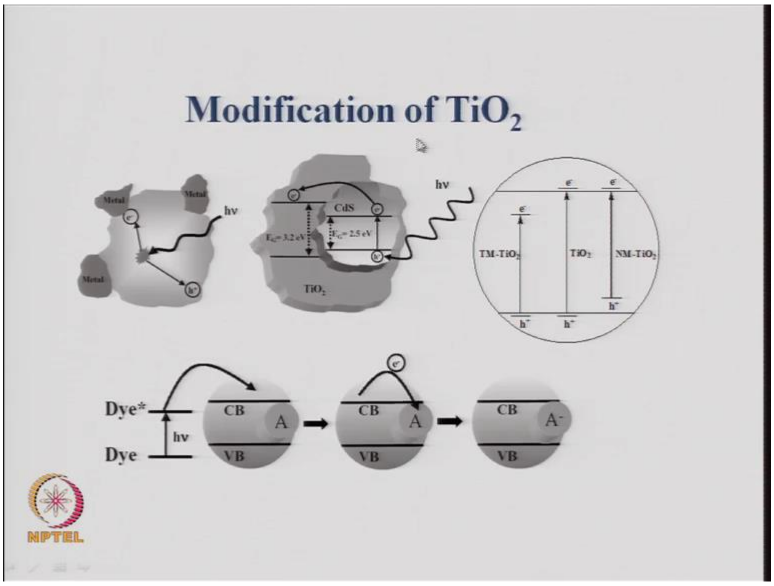
Modification of TiO_2

Now so how do we modify T i O 2? Because we just discussed that we want to modify T i O 2, which is a visible light UV light catalyst in general, but we want to use visible light. So, how do we modify this T i O 2 by doping metals metal oxides and what happens when you doped metal and metal oxides to the band gap or to the valence band levels or to the conduction band levels? So, this is kind of graphic to show you that when the photons fall on the photocatalyst, which has got some metal particles on top. So, it is a metal doped T i O 2. So, we have modified T i O 2 with the metal the metal particles are here and this is the titanium dioxide particle and when light falls on this particle T i O 2; then electrons and holes are generated now, the electrons if they can migrate to the surface and meets the metal; the metal is an efficient conductor.

So, this will take away this electron quickly and so the electron this electron, which is produced here, is separated from the hole and that is what is one of the important points how to separate electron and hole. Because of this metal dopant the electron has this tendency to go to the metal and the metal is the good conductor and then it moving to the electron. So, the electron and hole are separated. So, both the properties generation of electron and hole pair and transport of electron and hole away from each other such that they do not recombine both then can be met, which makes then this material this metal doped T i O 2 will be good for photocatalyst.

Now, you can also dope a semiconductor. So, cadmium sulfide is a semiconductor and this is your original T i O 2 particle. So, assume that you have cadmium sulfide particle doped it doped in T i O 2. Now, T i O 2 has band gap 3.2 electron volts and this is the balanced band and this is the conduction band level of T i O 2, whereas cadmium sulfide has a smaller band gap of 2.5 electron volts. So, in it can take lower energy and create electron hole pair. So, cadmium sulfide can be triggered to generate electrons and holes with lower energy of 2.5 electron volt whereas, T i O 2 will require 3.2 electron volts. So, lower energy if you give you can still generate electron and hole because of the presence of cadmium sulfide. Then, this electron can migrate to the conduction band of the T i O 2 and the hole this hole is generated in the cadmium sulfide.

So, when the light fall on cadmium sulfide the electron is goes to the conduction band and the electron is transferred to the T i O 2. So, the electron and hole are separated now on two different particles. The hole is retained on the cadmium sulfide and the electron goes to the T i O 2. Now this is a metal doped T i O 2; this was semiconductor doped T i O 2 and then you can have an organic dye doped T i O 2. So, if an organic dye is doped in T i O 2, then what happens is this energy level of the energy gap the organic dye to create an electron when light falls is suppose it is in the visible. Then, this electron goes to the excited state of the dye; the dye is now in the excited state. Then, the electron from the conduction levels or the higher orbital is transferred to the conduction band of T i O 2.

Then, you can have some acceptor molecules, which will take over these electrons. So, the from the conduction band of the T i O 2 the electron can be accepted by say an acceptor and that acceptor will get reduced. So, A will get reduced to A minus because the electron will be transferred from the conduction band of T i O 2 to the acceptor. So, three particular cases we looked at modification of T i O 2; metal doped modification of T i O 2; semiconductor doped modification of T i O 2 and then organic dye doped T i O 2. On dye sensitized solar cells is a very important area, in which you are using a dye to start this mechanism of electron being generated and then electron hole being separated.

So, if you look at the band diagrams you can create different types of levels. So, suppose this is the original levels; this is the conduction bands of T i O 2 and this is the balanced band of T i O 2. When you are doping transition metals it is possible to have chosen a transition metal, such that you now have levels, which are lower than the conduction band of T i O 2. So, the electron will be here because is lower in the energy than this and you can have a hole in the lower energy level or you can have a non-metal doping T i O 2. Then, you have an energy level, which is higher than the balanced band of T i O 2. So, this is the balanced band of T i O 2.

So, in higher than the balanced band of T i O 2 and the electron this energy may be closed to the conduction band of T i O 2. So, either you can lower the conduction band or you can increase the energy of the balanced band electrons or hole valance band hole. So, the hole will be here and the electron is here. So, these are two modifications to the bare T i O 2, which is shown here. So, this is also possible and this is also possible. So, this kind of changes in the band diagram by doping is called generally, bang gaped engineering.

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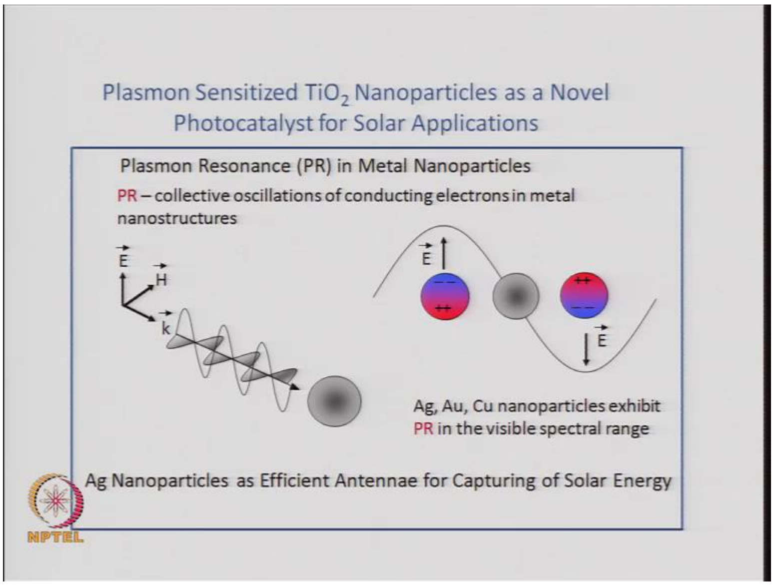

Plasmon Sensitized TiO_2 Nanoparticles as a Novel Photocatalyst for Solar Applications

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

Ag Nanoparticles as Efficient Antennae for Capturing of Solar Energy

You can also sensitized or increase the efficiency of titanium dioxide nanoparticles by using metal particles through their Plasmon resonance. Now, we all know when we have metal nanoparticles the conduction electrons of the metal nanoparticles can have collective oscillations. Now, these collective oscillations of the conduction electrons can sensitize the T i O 2 nanoparticles and this has been observed for silver, gold, copper nanoparticles, where they exhibit Plasmon resonance in the visible range. So, you shine light in the visible and the conduction electrons of the metal nanoparticles like silver or gold then get excited.

You have this collective oscillations and then this excitation acts like an antennae. The metal particles acts as an antennae, because this collective oscillation is generated by trapping a visible light energy or the solar energy and then it can enhance the catalysis of T i O 2. Once the silver nanoparticle, which is doped on top of T i O 2 acting as an antennae catches the visible light radiation and then it can create electrons and holes in the T i O 2 to which it is connected.

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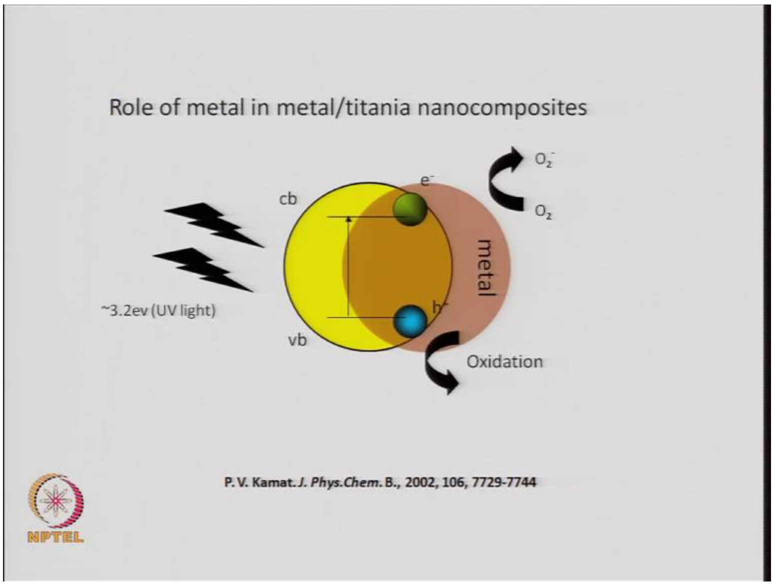

Role of metal in metal/titania nanocomposites

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

So, this is what is shown here. So, you have this metal particle and you have the T i O 2. So, this is the connection band of T i O 2 these are valence band of T i O 2. Now, what can happen is if you use the UV light, then you can excide this. So, you can create electron here and hole here in the T i O 2 and when you create electrons here. Then another property of the metal is that it can quickly take away the electron and then it can reduce any species; for example, oxide can oxygen gas can be reduced to this kind of super oxide ion. Now, this reduction is possible, because the electron generated in the conduction band of titanium T i O 2 is quickly transfer to the metal and the metal then electrons in the conduction band; in the metal can get will reduce this oxygen and the hole, which is in the valance band can be used to oxidize some species.

So, this is another possibility were you using UV light, but the metal is enhancing the application of the electron and the hole that is the reducing and the oxidizing capabilities are enhanced by the presence of the metal. In the previous case, these surfaces Plasmon are basically acting as an antenna to trap energy in the visible specter range. Then, it helps in the sensitization of the nanoparticles. In this case you are not using the visible light you are using UV light, but you are efficiently removing the electron and hole because of the conduction properties of the metal and the metal then can quickly reduce some molecule which may be oxygen and give you this super oxide ion.

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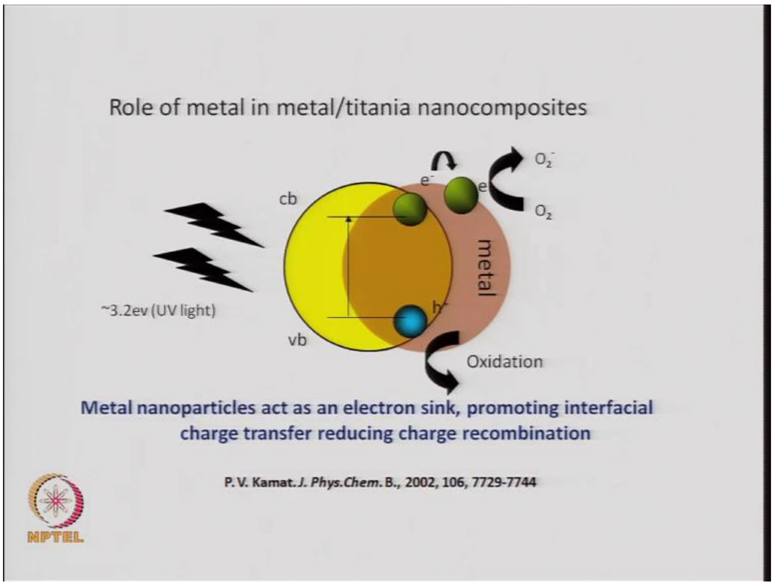

Role of metal in metal/titania nanocomposites

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

Now, you can have so here the metal act nanoparticle act as on electron sink as I mention earlier and it promotes interfacial charge transfer. Basically, it reduces the probability that the electron created in the conduction band of T i O 2 will interact with the hole on T i O 2, because the electron is been removed from there. So, they metal is acting as an electron sink.

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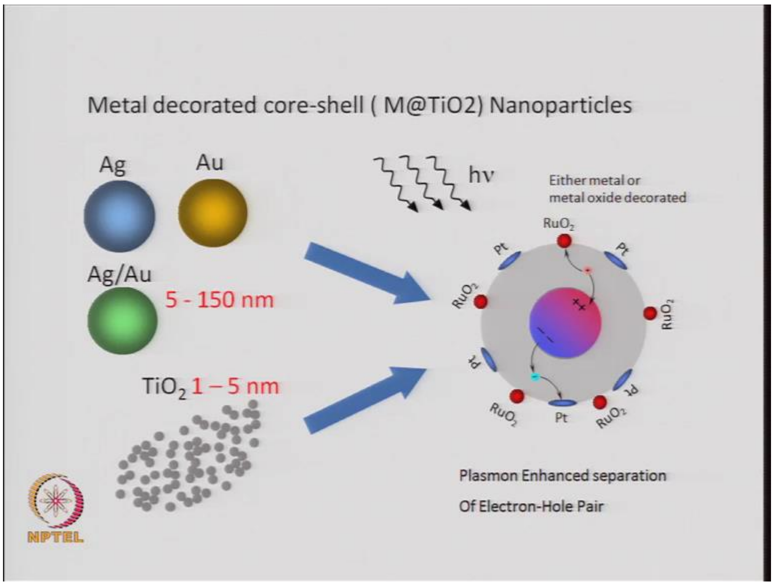

Metal decorated core-shell (M@TiO2) Nanoparticles

Plasmon Enhanced separation
Of Electron-Hole Pair

Now, you can also more complex nanostructure, where can have metal decorated on core shell nanostructure. So, core shell nanoparticles we know that there is one particle and it is covered by something else. So, the particle inside is the core and the material, which is covered outside is the shell. So, here you can have metals like silver, gold or alloys like silver, gold or copper, nickel or you can make large number of alloy of varies sizes between five to hundred fifty nanometers. Then, you take this metal particle inside and on the outside of this gray part; you put your titanium and there are methods by which you can make this shell out of pure titanium oxide.

So, the smaller particle the better you will have higher catalytic property the efficiency will high. So, if you have small particles of T i O 2 and you make a shell around the metal nanoparticles, then you will get a structure of this. So, that will be core shell nanoparticle, but in this case it is metal decorated core shell; that means, on top of the T i O 2 you again have either some metal or metal oxide. So, either some metal or metal oxide you can choose one of them or depending on that you will have now Plasmon enhanced separation of electron hole pair.

So, this metal nanoparticle will be activated by the light and you will have this Plasmon surface Plasmon because of the oscillation of the conduction electrons that will couple to the T i O 2 and then you will get electron and holes. If you have a particle like a metal like platinum, then the electron will get quickly separated on to the platinum and then the hole will reside in the core and the electron will move to the surface. So, you have effectively separated the hole and electron if you use an oxide like ruthenium oxide; then it does not take up the electron like platinum does, but it will remove the hole. So, then the electron will remain in the core and the hole will go to the surface.

So, depending on whether you have put platinum or you have put ruthenium dioxide on the surface of the T i O 2, you can have the hole on the T i O 2 R U O 2 surface. So, hole will be re moved from the metal or if you put metal particles like platinum on the surface of the T i O 2. Then, electron can be removed more effectively and then the holes remain inside the core of the core shell nanoparticle. So, this is a very efficient an interesting design of core shell metal oxide nanostructures, where you have a three materials designed. You have an inner core, which is made of a metal nanoparticle like silver, gold, platinum or something and then you have a shell of titanium dioxide on top of that.

You have some decoration of small particles of either metal and metal or metal oxide and these particles on the surface, which decorate the surface of T i O 2 act as a sink for either the electron or the hole. So, as we discussed if it is platinum particles on the surface; it will act as a sink for electrons and then the hole are inside the core and the electron is on the surface. So, that charge is separated. So, the efficiency of photocatalyst is enhance the opposite is the hole goes to the surface and the electron stays in the core that is possible if you use ruthenium dioxide as particles decorating on the surface. Now, if you have metal particles covered with T i O 2 covered with S I O 2, then the visible light will not active.

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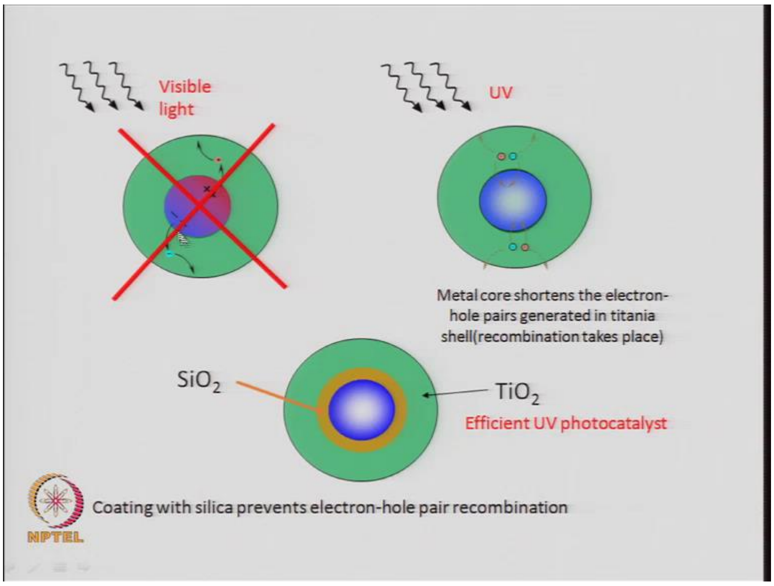

Metal core shortens the electron-hole pairs generated in titania shell(recombination takes place)

Efficient UV photocatalyst

Coating with silica prevents electron-hole pair recombination

Because T i O 2 will not activate the electron will not generate electron or holes because of band gap T i O 2 is 3.2 electrons volts and the visible light is insufficient in energy to create electrons and holes. So, this is not possible; however, if you shine UV light and you have the metal and you have T i O 2 then you can have electrons and holes, but the metal core shortens the electron hole pair. So, you recombine and hence you do not get charge separation easily. So, this is not going to a very efficient photocatalyst although you will generate electron and hole, but the life time of the electron and hole will be very small and they will quickly recombine.

So, this is also not a good situation; now the third situation is that you have a metal particle inside then you prove put a layer of something like silica this brown part. Then, on top of that you put titanium and titanium is an efficient UV photocatalyst and this titanium, which creates electron and holes the because of the silica coating the electron, which goes towards the metal will not be recombining with the hole. So, electron hole recombination will be prevented by the presence of intermediate thin layer of silica. So, this is another design of core shell structures, where you may titanium to be active in the UV efficiently; off course still it is not active with the visible with this configuration.

But it is active in the UV and the efficiency is high, by putting a silica layer in between the metal core and the outside titanium, which will actually create electron hole spear when UV light shines on it. So, these are three models, one model not effective in visible light; second model not effective in visible light and also not effective efficiently in UV light and this is a model which is not effective in visible light, but very catalyst in UV light.

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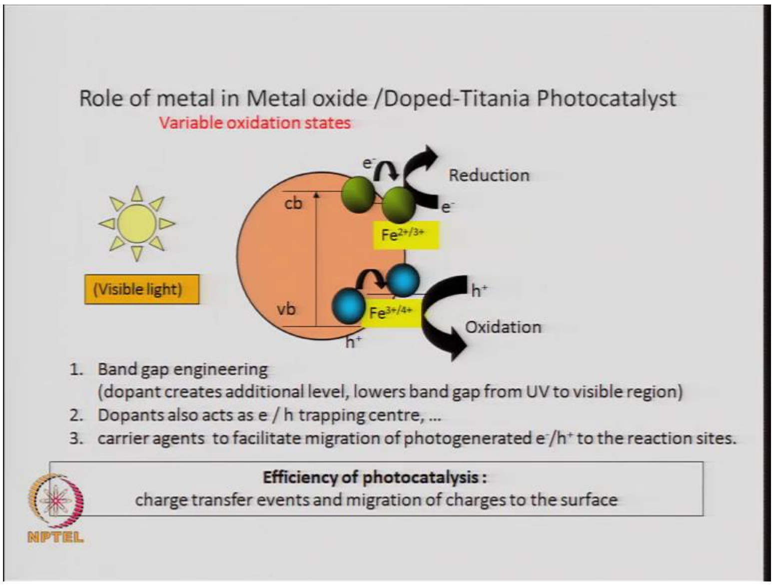

Role of metal in Metal oxide /Doped-Titania Photocatalyst

Variable oxidation states

1. Band gap engineering
   (dopant creates additional level, lowers band gap from UV to visible region)
2. Dopants also acts as e / h trapping centre, ...
3. carrier agents to facilitate migration of photogenerated e^-/h^+ to the reaction sites.

Efficiency of photocatalysis :
charge transfer events and migration of charges to the surface

Now, if what is the role of the metal oxide, you can though metals we studied have different role and we looked at several cases of metal doping. How it can remove the electron if it outside and what it does if it is in the core. Now, look at metal oxide and choose metal, which can have variable oxidation stretch. Now these can lot of all transition well oxide show variable oxidation states; for example, iron shows oxidation states of two plus three plus some time four plus and in extreme cases even six plus. So, can have iron at with varies oxidation states. Similarly, you can also have cobalt with 2 plus 3 plus or vanadium 4 plus 5 plus, etcetera.

So, if you choose a metal oxide, which can show variable oxidation states and dope it with titanium T i O 2; then it can be a very good photocatalysis in the visible rate. So, how does that happen? You have again the large spear showing you T i O 2 particle and the band gap of T i O 2 this is a conduction band and valance band. Now, you have doped this titanium dioxide with metal oxide in a metal oxide that you are chosen is iron oxide. So, iron oxide will have possibilities of being in iron two plus three plus three plus four plus and so if you have these kinds of oxides on the top of the surface.

So, then what can happen? So, if you have electron and hole generation even with less energy you can create these levels were electron in the conduction band can go to the iron three plus and iron three plus will get converted to iron two plus. So, you start with F e 3 situations iron is three plus, but iron three plus, when it gains an electrons becomes iron two plus and if you have an electron, which is coming you can do this reduction. Now, if you have iron three plus here. So, if you have a hole iron three plus will get converted to iron four plus. So, in the presence of electron iron two plus iron three plus will get converted to iron four plus.

So, both are possible of the variable oxidation state of iron and the dopant also creates addition level. So, these levels are created additional levels. So, although T i O 2 has this band gap, but the actual band gap will be due to the smaller intermediate levels, which are introduce by the metal oxide dopant. Then, this gap is lower in energy then this gap and if falls in the visible light region then it will become a visible light photocatalyst. So, this kind of band gap engineering when creates the doped ends create additional level and lowers band gap from ultraviolet to the visible region. And hence this catalyst becomes active in the visible region. So, here important thing is you chosen a metal oxide with variable oxidation states.

So, now the doped end also acts as an electron hole trapping center; because here you can see this acts as an electron trap. Because it is removing electrons from here and this way you if you can choose some other material it can act as a hole trap right. So, you can have doped ends, which not only lowers the band gap from UV to visible. But they are also acting as electron hole trapping center, finally they are also can be acting as electron hole center. Finally, they also can be used as carrier agents to facilitate migration of electrons and holes to the reaction sides.

So, wherever reaction is occurring because of the presence of theses metal oxides on the surface they act as good carrier agents because they help in the migration of the photo generated electrons and holes. Though so two things are important as usual charge transfer events how the electron hole are created and then migration of this charges to the surface; both this effect and enhance the efficiency of the photocatalyst.

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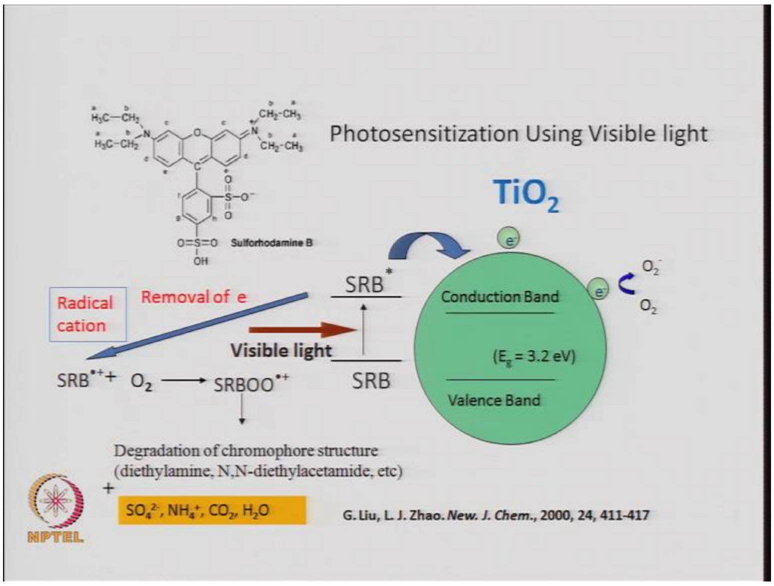

Photosensitization Using Visible light

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

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

Now, this is a case where it is photosensitization using UV visible light. So, how you are going to use this visible light using a dye, which is acts as photosensitizer; so in the previous case you brought down the band gap by adding metal oxide as dope ends and then visible light became useful to make it act as a photocatalyst. So, T i O 2 with the iron oxide dopant became a photocatalyst UV. But here you are not using metal oxide you are using a dye, which is organic compound. So, see this large molecules with the aromatic rings and some pendent substituent; you can see that this dye, which is sulforhodamine B.

This particular dye can be used to sensitize T i O 2 because the energy levels of the sulforhodamine dye is a in the region of the visible light. So, using the energy levels of the dye of the sulforhodamine B; you can excite the sulforhodamine B you using visible light such that the electron goes to a excited state and this SRB excited is the excited molecule and then the electron in this state can be transfer to the conduction band of the T i O 2. So, the visible light is a basically taken up by the dye the sulforhodamine B dye here and electron gets excited and in the excited state the sulforhodamine B, then transfers an electron to the conduction band width, which it has an interfere. So, the dye is doped into the T i O 2.

So, this electron is transferred to the conduction band and then that electron can be further used for reduction. So, it is then acting as a catalyst because it will do this reduction reaction and some molecule is there which can pick up an electron then that will get reduced. So, what happens to these molecules after it loses this electron; the sulforhodamine B excited molecule it loses an electron it becomes a radical cation. So, after removal of the electron the electron goes to the titanium dioxide and then the sulforhodamine B becomes radical cation and then it react with oxygen further. Then that forms another radical cation and which finally, decomposes to form smaller molecule.

So, this organic structure gets decomposed. So, that is also a catalytic reaction; that means you are trying to remove and organic dye you are the broken the organic dye by exiting the organic dye with visible light. This photo degradation of the organic dye through are radical cation in the presence of oxygen can be seen and final degradation products of this chromophore; chromophore is something, which can give out light. So, because it florescence sulforhodamine B is has a property of fluorescence and so it is called a chromophore and is an organic compound. So, here we are more interested in seeing that how titanium was photosensitized using visible light and the dye breaks down and gives some rise to some product plus may be some ions like sulfate ion ammonium ion and gases like carbon dioxide, water vapor and this electron of titanium is also used for reduction.

So, this is a case of how organic dyes having a particular difference in the energy levels and the ground states and excited state can be used in conjunction with T i O 2 to act as visible light photocatalyst. So, important thing very important thing is that this energy gap should be such that it can be this molecule can be excited with visible radiation. Then, only you can get this SRB star, which means the excited sulforhodamine b is the ground state of sulforhodamine B is excited state of sulforhodamine B and from the excited state electron transfer to conduction band T i O 2. Then, it becomes radical cation and further under goes degradation in the presence of oxygen.

This electron can be used for reduction of some other species. So, this was another case. So, we studied cases of metal doped titanium, core shell titanium decorated with metals then core shell titanium with an interfacial layer in between; how it can become efficient UV photocatalyst. Then, we added metal oxides where the metal has variable oxidation states and how that can enable titanium to be visible light photocatalyst and this was a dye sensitization. So, the dye an organic dye is used, which has particular energy levels can accept visible light and it is visible light photocatalysis that can be observe using sulforhodamine B as an example and the electron in T i O 2 further reduce other agents.

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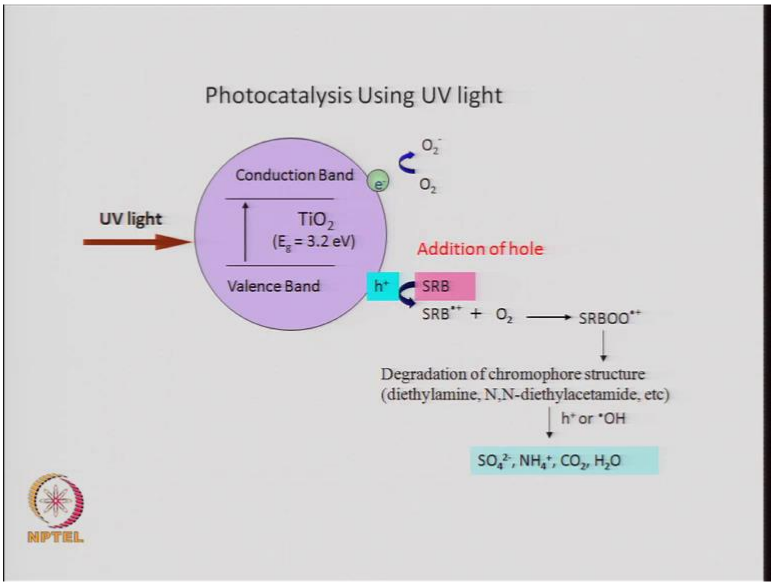

Photocatalysis Using UV light

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

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

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

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

Now, another property the previous one we photosensitized using visible light. Now, let us look at another problem, where we can do photocatalysis using a UV light and with the dye, but this is another mechanism. So, under UV light under UV light the energy will be observed now with T i O 2; in the presence visible light T i O 2 cannot accept the radiation because of the lower energy; but the sulforhodamine B accept the radiation. In this case, the UV region the high higher energy light is being accepted by the T i O 2 nanoparticles because it matches the energy.

So, 3.2 electron volts is in the ultraviolet and so you will have electron generated in the conduction band and holes in the valance band. So, these electrons can then reduce oxygen and this hole can then act on the dye. So, here we are looking at addition of a hole on the dye to create again a radical cation of sulforhodamine B. This has been is simple from here what we are studied in the previous slide that the radical cation then acts with oxygen to give you another radical cation and that breaks down to give you small molecules like diethylamine N-N dimethylacetamide etcetera. Then in the presence of holes are hydroxyl radicals, it gets converted to this simple molecules or ions.

So, as in the previous case the radical cation of sulforhodamine B is formed by the removal of electrons from excited state of sulforhodamine B and you get the radical cation; the same radical cation in this case you obtain not by removal electrons, but by addition of hole. So, two different processes one acting in the presence of UV light and one acting in the presence of ultraviolet light, in the presence of sulforhodamine as a dye or an organic reagent. How the same product of the dye occurs can be understood? Because in this although the mechanism is the different in this case the sulforhodamine B degrades through the addition of a hole and in the previous the sulforhodamine degrades by removal of electron.

Then goes oxidation and then degradation so two different things using similar materials TiO2 and sulforhodamine B as the organic dye, but the different mechanism of degradation of the dye is the due to the different energy that you are supplying in one case you are supplying visible light. In the other case you are supplying ultraviolet light. Hence, the mechanism changes and the degradation happens due to electron in one case that loss of electrons in one case whereas, in the other case it is addition of holes, but both cases lead to the radical cation sulforhodamine B and then further reduction further degradation in the presence of oxygen.

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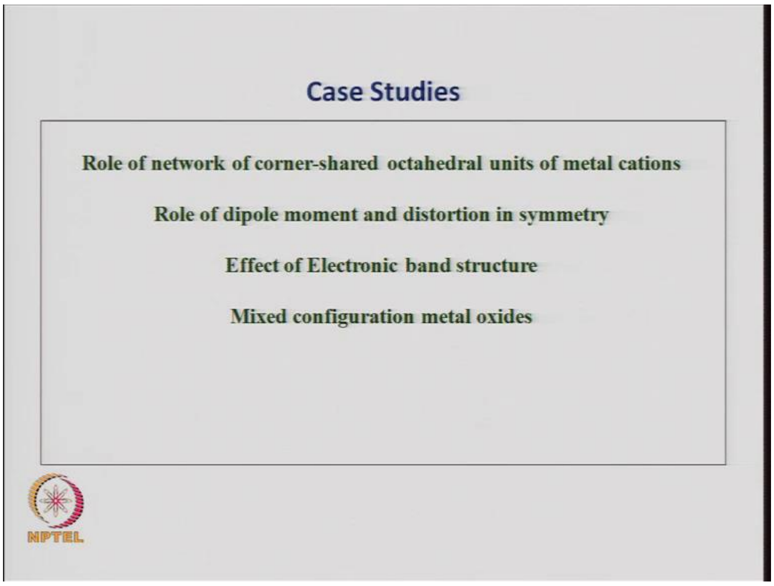

Case Studies

Role of network of corner-shared octahedral units of metal cations

Role of dipole moment and distortion in symmetry

Effect of Electronic band structure

Mixed configuration metal oxides

Now, let us look at few other case studies, where we will see what is the role of network of corner-shared octahedral units of metal cations? So, will see when you use metal oxides other than T i O 2; these are not T i O 2 these are other oxides; why they are photocatalyst in certain cases especially, when you have corner shared octahedral, it shows high photocatalytic efficiency. Then, what is the role of the dipole moment and distortion in symmetry? How it effect the photocatalytic properties?

Then, effect of electronic band structure hence the overlap of the orbitals of the metal oxides if there is good overlapping the bands will become broad and things will be different. So, effect of overlapping of orbitals varying to changes in the electronic band structure. Then, what happens when you have mixed configuration of metal oxides? So, will look at some of the case is, which have the different properties.

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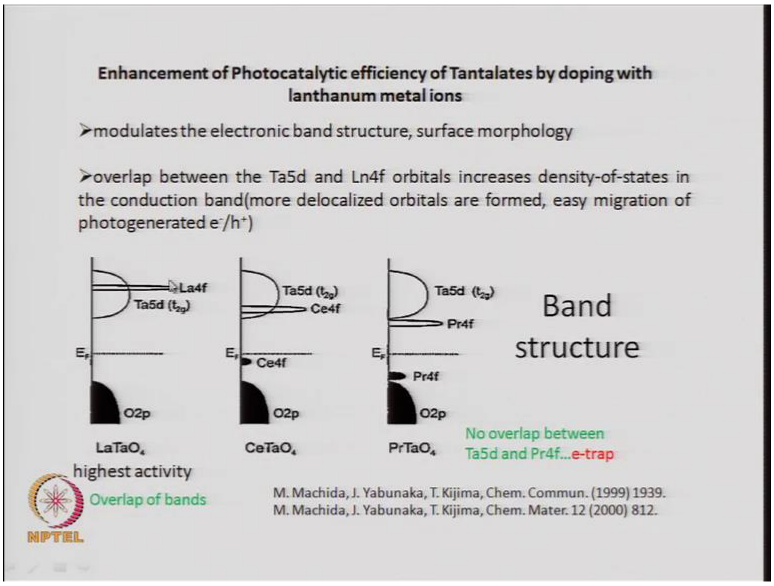

Enhancement of Photocatalytic efficiency of Tantalates by doping with lanthanum metal ions

- modulates the electronic band structure, surface morphology
- overlap between the Ta5d and Ln4f orbitals increases density-of-states in the conduction band(more delocalized orbitals are formed, easy migration of photogenerated e^-/h^+)

Band structure

highest activity

Overlap of bands

No overlap between Ta5d and Pr4f...e-trap

M. Machida, J. Yabunaka, T. Kijima, Chem. Commun. (1999) 1939.
M. Machida, J. Yabunaka, T. Kijima, Chem. Mater. 12 (2000) 812.

So, in this particular case this is the basically you are looking at how the overlap of metal particle metal and the oxygen their orbitals overlap and if it is good overlap or bad overlap what happens to the photocatalytic properties. So, these are not T i O 2; now we are discussing other oxides say, this is a tantalum based oxide and it can be having a third element also. So, there is some rarer tantalite or barium dependent tantalum oxide etcetera. This is rarer tantalite L a T a O 4 in which case you have an orbital of tantalum 5 d band of tantalum 5 d all the orbital 5 d overlap to form a band of tantalum 5 d, which looks like this and is the energy scale and this is an oxide.

So, will have oxygen levels and the oxygen levels are here much below the tantalum 5 d levels, which means this band has been formed from the 5 d orbitals of tantalum and this band has been formed the 2 p orbitals of the oxygen. Now, when you have lanthanum also lanthanum appears to have very sharp band or narrow band it is called a narrow band. Because the width of the band is very broad here in tantalum were compare to that this is very narrow is almost like a discrete energy orbital.

Now, the energy of the lanthanum 4 f orbital, which is a very narrow band is lying somewhere in between within the energy levels possible for the tantalum 5 d band. When such things happen; that the orbital energies are similar then there is good overlap of bands. So, there is an excellent overlap of the lanthanum 4 f and tantalum 5 d bands and good overlap of these bands increases the activity of the catalysis and that is overlap of that is the case shown here were the highest activities reported, because it has overlap of the lanthanum n tantalum orbitals and bands.

Now, here you see that this narrow band is shifted down. This is a case of cerium and so it will have moderate efficiency, whereas in this case were the praseodymium compound. The narrow band of corresponding to the praseodymium 4 f orbitals is much lower and has no overlap between the tantalum 5 d orbitals, which are contained in this band with the praseodymium 4 f orbitals. So, there is hardly any overlap and if it there is no overlap then this acts as an electron trap; once electron comes it stays here and so it can as an electron trap especially, in the 4 f orbitals of praseodymium, since it is a narrow band the wider the band there is more delocalization. The narrower the band then it is complete localization and very little electronic movements. So, it acts like an electron trap.

So, from the band structure these kind of diagrams are called band structure diagram and give you a lot of idea about the possibility of the movement of electrons the conductivity of electrons through electrons and the band gaps and difference. What will be the optical band gap? All these you can understand while looking at the detail band structure for these oxides. So, one thing is clear that better the overlap of the orbitals higher is the activity and poorer is overlap over orbitals or bands then the activity will be very low and the electron will be trap and the electron will not be able to reduce anything because it is trapper there.

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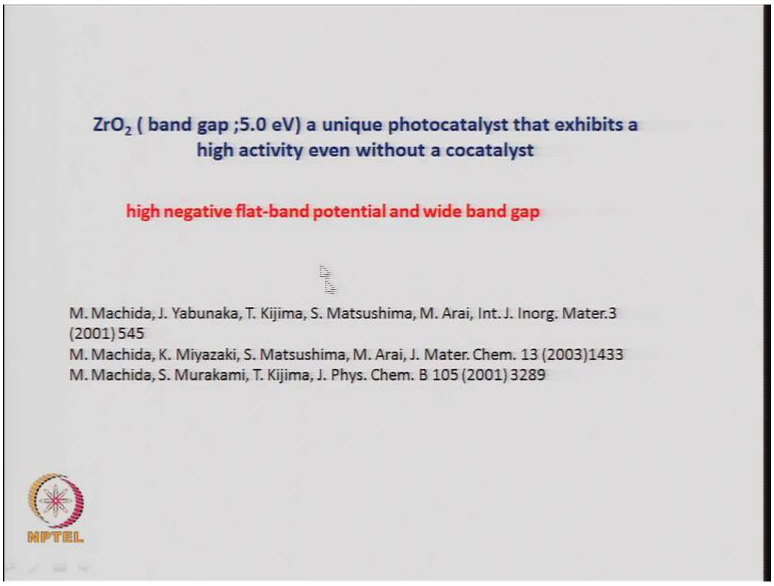

ZrO_2 (band gap ;5.0 eV) a unique photocatalyst that exhibits a high activity even without a cocatalyst

high negative flat-band potential and wide band gap

M. Machida, J. Yabunaka, T. Kijima, S. Matsushima, M. Arai, Int. J. Inorg. Mater.3 (2001) 545
M. Machida, K. Miyazaki, S. Matsushima, M. Arai, J. Mater. Chem. 13 (2003)1433
M. Machida, S. Murakami, T. Kijima, J. Phys. Chem. B 105 (2001) 3289

Now, also possible that you can have a high activity without cocatalyst a cocatalyst sometimes added, which help in reducing the band gap or helps in effective electron transfer or hole transfer. Now, zirconia has a band gap of 5 electron volts and it is a unique photocatalyst that shows a very high activity and the reason of this is it has a high negative flat band potential. So, if you are flat band potential is very high; then it should be negative the high negative flat band potential will lead to very good photocatalysis. So, this is an example zirconia is an example of that.

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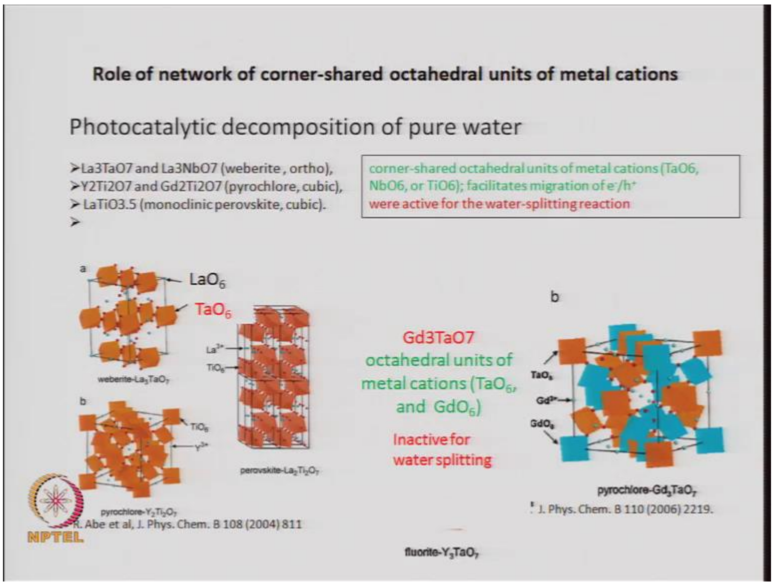

Role of network of corner-shared octahedral units of metal cations

Photocatalytic decomposition of pure water

- ➢ La_3TaO_7 and La_3NbO_7 (weberite, ortho),
- ➢ $Y_2Ti_2O_7$ and $Gd_2Ti_2O_7$ (pyrochlore, cubic),
- ➢ $LaTiO_{3.5}$ (monoclinic perovskite, cubic).
- ➢

corner-shared octahedral units of metal cations (TaO_6, NbO_6, or TiO_6); facilitates migration of e^-/h^+ were active for the water-splitting reaction

Gd3TaO7 octahedral units of metal cations (TaO_6, and GdO_6)

Inactive for water splitting

R. Abe et al, J. Phys. Chem. B 108 (2004) 811

J. Phys. Chem. B 110 (2006) 2219.

Another very important thing is, corner sharing octahedral unit. So, many many structures are known were the metal oxygen is bounds are within an octahedra. These octahedra are corner shard of edge shared or phase shared. Now the most important and large number of compounds are known were there are corner shared octahedral units of the metal cation. So, if is a tantalite you have T a O 6 octahedra. So, niobate you have niobium o 6 octahedra and these niobium o 6 octahedra or tantalum o 6 octahedra are corner shared. Now, if they are corner shared then it appears that the activity is very high; because this corner shared octahedral as shown here will help in a migration of electrons and holes.

This will be this has been shown to be very good photocatalyst for water splitting reaction and the reason is a tantalum oxide is a highly connected corner shared octahedral unit, whereas the rarer the lanthanum also has an octahedral. But it is not connected to the tantalum octahedra; in such cases the photocatalysis is very high. There is another example were you have two types of octahedra; tantalum oxide and another rarer oxide. But when there are two type of octahedral and they get interconnected, then the activity for the photocatalysis decreases.

So, what it means is you need one this tantalum oxide or niobium oxide, whichever is going to act as the main site for photocatalysis should have corner connectivity of octahedra and it should not be interfere by some other octahedra say of a rarer. So, if it is unhindered then the activity is very high if it hindered by other octahedra, then it becomes inactive. So, this is very important the role of corner shared octahedral unit and the presence of linear chains of this octahedra is very important.

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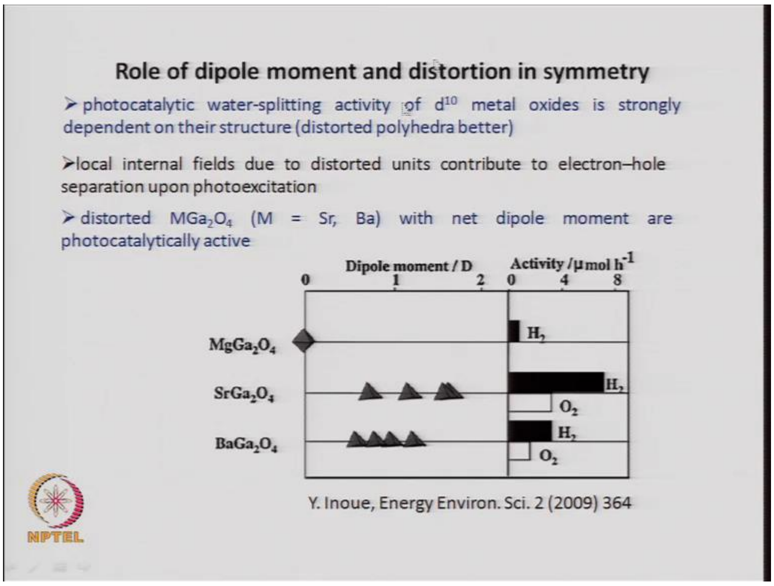

Role of dipole moment and distortion in symmetry

- photocatalytic water-splitting activity of d^{10} metal oxides is strongly dependent on their structure (distorted polyhedra better)
- local internal fields due to distorted units contribute to electron–hole separation upon photoexcitation
- distorted MGa_2O_4 (M = Sr, Ba) with net dipole moment are photocatalytically active

Y. Inoue, Energy Environ. Sci. 2 (2009) 364

If you have distortion in octahedra and if you have dipole moment, then what the effect on the water splitting photocatalysis activity? Now, the activity for the d 10 metal oxides is strongly dependent on the distortion on their structure. You can see that whenever you have distortion then you will have local internal feels, which will contribute to electron hole separation on photo excitation. Now, if you have distorted gallium oxide like this, which have a net dipole moment they were found to be photo catalytic activity.

So, dipole moment will be generated as cause of distortion. So, whenever you distortion you have high dipole moment; this is zero dipole moment very low activity; the high dipole moment and this is high activity. So, distortion high dipole moment high and so it will lead to higher activity.

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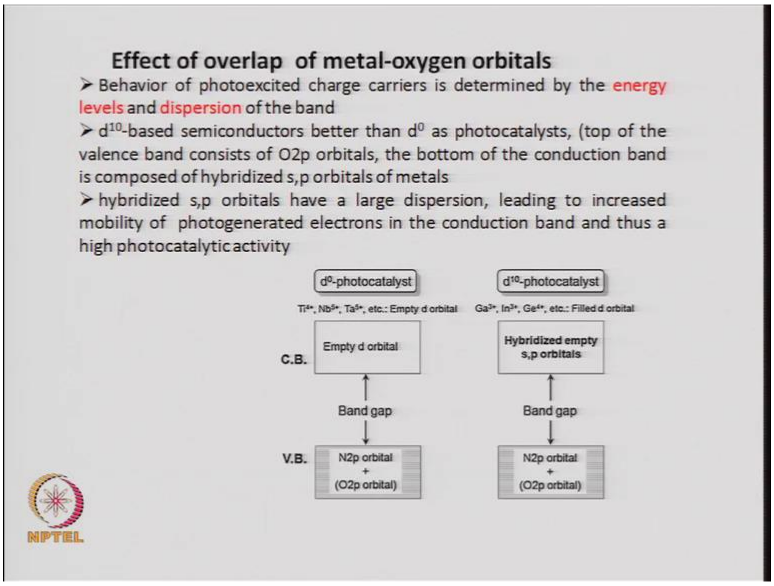

Effect of overlap of metal-oxygen orbitals

- Behavior of photoexcited charge carriers is determined by the energy levels and dispersion of the band
- d^{10}-based semiconductors better than d^0 as photocatalysts, (top of the valence band consists of O2p orbitals, the bottom of the conduction band is composed of hybridized s,p orbitals of metals
- hybridized s,p orbitals have a large dispersion, leading to increased mobility of photogenerated electrons in the conduction band and thus a high photocatalytic activity

So, there is another case. How you increase the activity by better overlap of metal oxide orbitals? You can increase the band width by having good hybridization or overlap of metal oxygen orbitals; that will also give you increased mobility of the photo generated electrons in the conduction band and lead to high photocatalytic activity.

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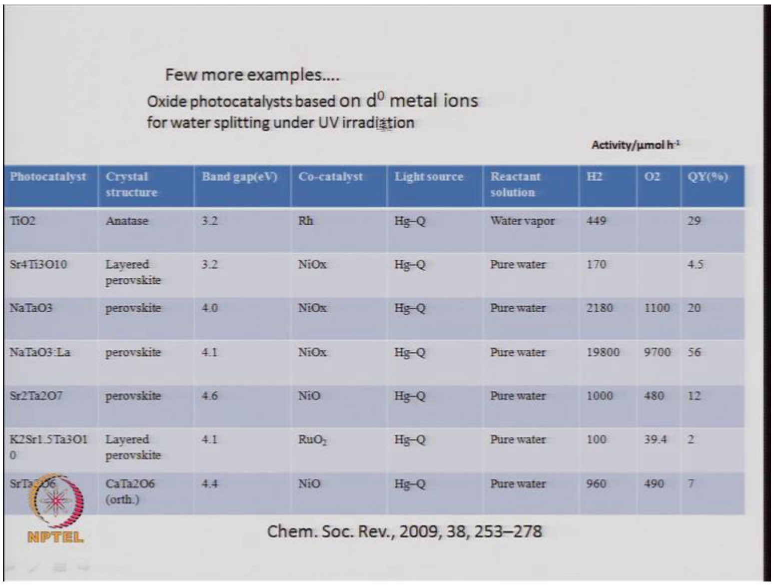

Few more examples....

Oxide photocatalysts based on d^0 metal ions for water splitting under UV irradiation

						Activity/μmol h⁻¹		
Photocatalyst	Crystal structure	Band gap(eV)	Co-catalyst	Light source	Reactant solution	H2	O2	QY(%)
TiO2	Anatase	3.2	Rh	Hg–Q	Water vapor	449		29
Sr4Ti3O10	Layered perovskite	3.2	NiOx	Hg–Q	Pure water	170		4.5
NaTaO3	perovskite	4.0	NiOx	Hg–Q	Pure water	2180	1100	20
NaTaO3:La	perovskite	4.1	NiOx	Hg–Q	Pure water	19800	9700	56
Sr2Ta2O7	perovskite	4.6	NiO	Hg–Q	Pure water	1000	480	12
K2Sr1.5Ta3O10	Layered perovskite	4.1	RuO_2	Hg–Q	Pure water	100	39.4	2
SrTa[illegible]O6	CaTa2O6 (orth.)	4.4	NiO	Hg–Q	Pure water	960	490	7

Chem. Soc. Rev., 2009, 38, 253–278

So, these are some of the examples of oxide based on d 0 metal ions. So, you can see titanium anatase and very good photocatalyst, you can see lanthanum doped sodium tantalite where you have T a o 6 octahedra, and these are linear and shows very high efficiency. So, with these examples I will come to the conclusion of this lecture today and then we will have our continuation of this lecture in our next class.

Thank you very much.