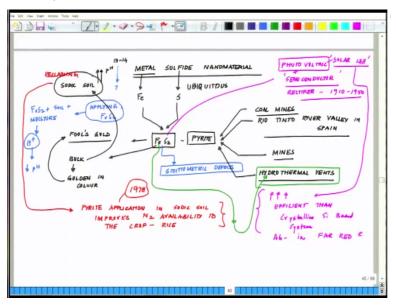
### Nanotechnology in Agriculture Prof. Mainak Das Biological Sciences and Bioengineering and Design Programme Indian Institute of Technology-Kanpur

## Lecture-18 Iron Pyrite and Seed Pre-treatment

Welcome back to the course on nanotechnology and its role in agriculture, so the previous class we started with iron pyrite and we talked about the different role of iron pyrite for last 100 years or little more than 100 years and if you recollect.

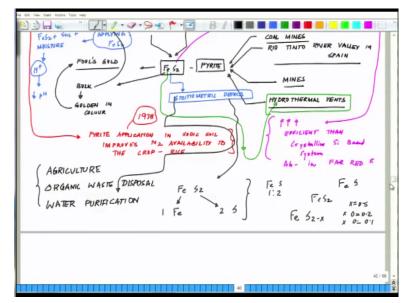
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So, we talked about the ubiquitousness of iron pyrite, so it is kind of available most of the places and it has been used for or in the attempts are being made to use it as a photovoltaic material and in India it has been largely used during 1970s, 75, 78 to reclaim sodic soil or other alkaline soil because once it is gets into the soil in bulk amount it make the soil pH like lower, so from an alkaline soil you can bring in down to a neutral pH by adding iron pyrite.

And it has been observe in such soil it has been let to a more nitrogen absorption by the crops, especially by the rice crops okay. Whereas when it has been used directly into normal soil it has actually made soil acidic. So, I has to really handle for any kind of for reclamation it has to be handled with extreme care okay, apart from it, it has been observe that these kind of a material

has something called stoichiometric defect what is the stoichiometric defect is that is where we ended in last class.



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So, this is where we are going to talk about a stoichiometric defect, so whenever we talk about FeS2 the assumption or understanding is that there is 1 atom of Fe, and 2 atoms of sulfur. Now in real life that is brought what happens what essentially happens is out of say 10 million molecules of FeS2. The surface durably molecules which or maybe slightly into the core there will be molecule which does not balanced it out like all the time the ratio 1:2 of iron to sulfur is not maintained.

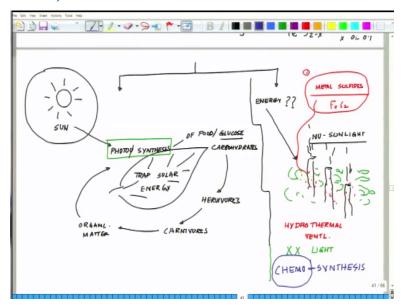
There are molecules which may not have 1 sulfur maybe instead of FeS2 in the cluster they will be some FeS. So likewise it has been observed that the final ratio what it turn out be 2-X and this X could be 0.5, 0.2 or it could be 0.1 whatever you know that is the material. The point is not that every iron atom has bonded to 2 sulfur. There will be iron atom which maybe divide of it and these kind of defects are called stoichiometric defect.

And stoichiometric defect plays a critical role in the surface property of these molecules. And this is what is very very critical for you to understand that iron pyrite comes with set of stoichiometric defect and that is why lot of it is application in electronics kind of got hampered because of it. But there is a positive sight to it and will come later into that what is the positive sight of having stoichiometric defect.

And stoichiometric defect cold be utilized for multitude of applications in agriculture, organic waste disposal and maybe even in water purification this may come pretty handy especially when you have to remove organic residues. But at this stage just understand the fundamental concept of stoichiometric defect.

And this is stoichiometric defect could be exploited at the nano level at a much more easier or with lot of more ease. Now previous class I talked about the presence of iron pyrite in the hydrothermal vents. So, hydrothermal vents, so as of now talk while talking about hydrothermal vent if we understand there are 2 ways life has formed.

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The original understanding was that life has evolved on the floor of earth in the ocean from the water and the process which has govern much of it is sun. The energy the major source of energy sun and living system in the form of plants have trap solar energy in the form of photosynthesis, photo means light and synthesis of food using light energy synthesis of food or in other words synthesis of glucose molecule okay.

So, solar energy driven synthesis of food by the plants or carbohydrates and these carbohydrates are the plants are consumed by herbivores, herbivores consumed by carnivores or omnivores and then again they become part of the organic matter and the simple cycle continued what we call as food chain okay. Now the first the only thing which is known about formation of life in terms of survival of life in terms of photosynthesis.

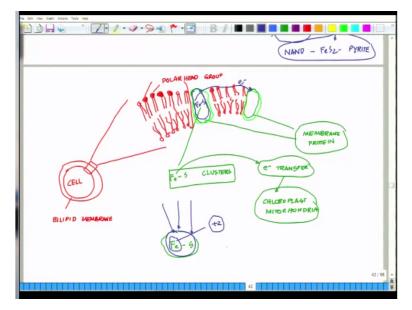
But the storyline changed some I would say 30, 40 years back almost 4 decades back now during 19 late 70s it was observed deep inside the ocean fairly deep in different Atlantic and Pacific rims as these diverse were going down almost close to the float or sea floor. They observe something which they observe lot of smoke coming out from deep inside the ocean and this is where there is absolutely no sunlight.

And around these smokers they name this is smokers are white and black smokers, around these smoking chimneys in and around it was filled with something strange life forms. And these were growing, these were bubbling all over the place very very strange life forms another question which absolutely boggled a scientist is what is the source of energy, energy source. Because all our textbooks up to that point was relying on the fact that sun is the only source of energy okay.

But then this is a very different situation here there is no sun, no sun rays really can penetrate through this yet this place is filled with life. So, who is giving energy to them and it look this whole area is rich in different kind of transition metal, metal sulfides. And the one which is in such amount is pyrite, so these pyrite the source of energy or is it playing a critical role. So stoichiometric defect the first fact I gave you.

The second fact what I am holding out here after telling you is the metal sulfides in hydrothermal vents okay, we will pull all these threads together soon. So the third in the same line I am going to put across is.

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If you look at the cell membrane all of we have seen the cell membrane any cell membrane plant cell membrane, animal cell membrane we will observe something very interesting. If these are the lipid bi-layers which is forming the cell membrane then you will see lot of proteins which are present there like this, several proteins. So just to give you idea okay, so this is what you are looking at, this is a cell and the box is the one which I am amplifying out here.

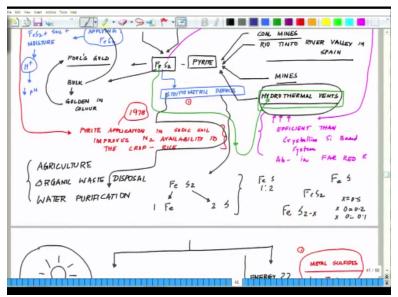
And this is the bilipid membrane here is the magnification of bilipid membrane with polar head groups and polar head groups are here also in both inside and outside. And with a hydrophobic tail and here you are having these area of membrane protein which are setting there. There could be channels, there could be pore and series of them are there especially in the chloroplast, mitochondria.

And they in their membrane which are also lipid bilayer membrane, there are lot of iron sulfur clusters. As if and these iron sulfur cluster are involved in electron transfer whether it is mitochondria, whether it is in chloroplast or it is mitochondria. Now if you look at it, it seems like life has evolved around iron and sulfur. In the most strange places if you look at it hydrothermal vent which is one of the most strange place where life has evolved.

And there was a name which was given to the life form which evolves there which is not dependent on light. So, independent of light there is no light and these kind of life forms which

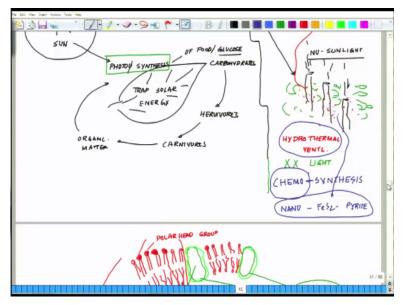
evolve there is called the process is called chemo-synthesis or the energy called life form to survive is derive from some kind of a chemical, some kind of a breaking of the chemical okay.





So, clue number 1 what I gave you is stoichiometric defect 1.

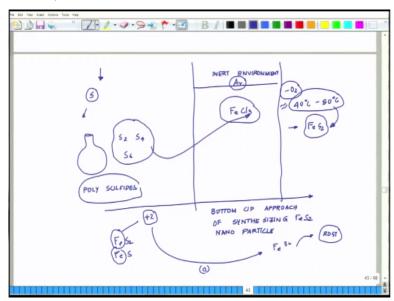
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Second the life form in the hydrothermal vents tune and this part is filled with they appears to what you observed here as I told you is nano FeS2 or nano pyrite okay. And the third thing is most of our current date cells have lot of this iron sulfur clusters which are involved in short and long range electron transport. Now the remark we are making looks like iron sulfur complexes or iron sulfur compounds plays a critical role in our day today life.

Now getting in spite by this during 2010, 2011 we attempted a very simple experiments and that is what we are going to share now. So natural pyrite comes the bulk natural pyrites comes with the contaminants of lot of different other atoms because it has profound binding with the sulfur atoms and you will see cadmium, arsenic and all these kind of impurities. So, what we did we synthesize nano pyrites.

So, how we synthesize as I told you there were 3 things which you would follow, we will talk about the synthesis, we will talk about characterization and in that process we will figure out what is the shape and the dynamics of the molecule.



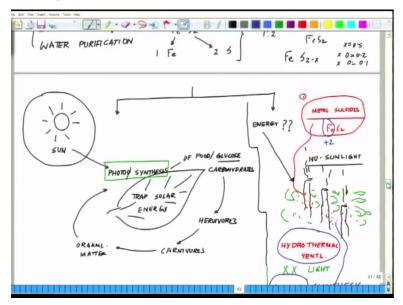
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So, we synthesize nano pyrite by a simple way may it poly sulfur and will I will give you the references in 1 tube we made a lot of poly sulfur molecule, poly sulfur means S2, S4, S6 likewise okay. It is a mixture which is called polysulfide, made a lot of polysulfides in 1 vessel and in the other vessel we have iron salt to react and this reaction happen in an inert environment where we allow poly sulfide to react with iron salt okay.

And this is one of the process of bottom up approach of synthesizing FeS2 nanoparticles and in an inert environment organized environment this reaction happen. The reason to have an organized environment is otherwise iron will get oxidized to Fe3 state. So when we talk about FeS2 or FeS these are the moieties where iron is in oxidation state of +2. Otherwise if you in any iron compounds the floor of earth they all are oxidized to Fe2 to Fe3 in the presence of oxygen.

And what we call as which relates to the formation of rusting. So, here we are having certain iron on the rust of earth or in the earth floor which remain which maintain their oxidation state in 2. And same here most of the iron sulfur cluster or all iron sulfur clusters iron is in an oxidation state of +2, they are in the ferrous state.

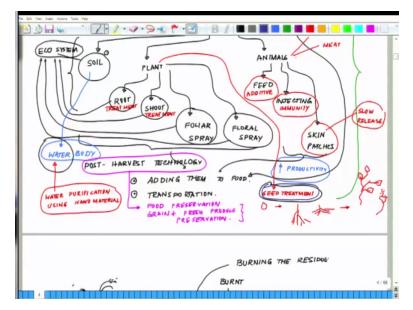
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Same out here iron is in oxidation state of +2 with it is hydro thermal vent okay. Now we I will provide the detail layout of how we made the iron sulfide. So, but this is the overall synthesis of iron sulfide by end bottom of approach where in a small round bottom flask you created an organized environment, you created and –oxygen environment and at moderately low temperature of around 40 degree centigrade to 80 degree centigrade you synthesize iron sulfide.

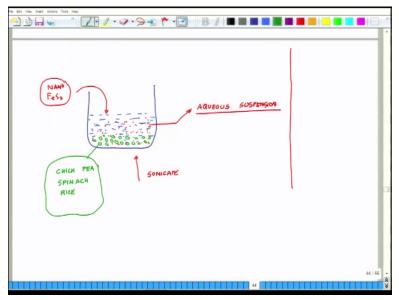
Next what we try, we thought that could this agent be used as a seed stimulant because if iron sulfur has been involved in the evolution of all the survival of life could it do some very interesting stuff to the seeds, it is a very out of box and just let us give it a shot. So, what we did is instead of because this was clear that you cannot really apply this to the field because it may lead to acidity and all sorts of other problem.

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But seed treatment if you recollect in the very beginning when you started of yes seed treatment or seed pretreatment agent. So, this is where we are starting to do a seed pretreatment.

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So, what you do you take a vessel you have all your seeds here and you put water and then and on that you add a finite amount of FeS2 nano FeS2, nano FeS2 does not dissolve in water. So, what it form is an aqueous suspension, so what will you see is if you really sonicated it a whole lot you will see suspensions sizes may even go for the smaller but there will be suspensions all over the place. And to start off with some of our initial experiments where with chick pea, spinach, rice to see what is the effect of nano FeS2 as a seed treatment agent. So, we will continue the story from here what we observe and what is the research which have undergone since we say 2011 till 2018 when I am delivering this course on different crops are effect of a nanomaterial as a seed priming or as a seed treatment agent, thank you.