

Selection of Nanomaterials for Energy Harvesting and Storage Applications
Prof. Kaushik Pal
Department of Mechanical and Industrial Engineering
Indian Institute of Technology, Roorkee

Lecture – 07
H₂ Production from Thermochemical Process

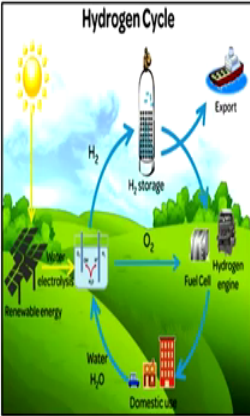
Hello my friends. Today, we are going to discuss our new chapter is on Hydrogen Production from Thermochemical Process. So, basically in this particular lecture or maybe in this particular couple of lecture series basically we are dealing with that whatever the wastage of the energy basically we are getting or maybe we are doing this like that sun or maybe the tidal or maybe the wind. So, basically that whole energy we are unable to utilize. So, some portions it is utilizing for the mankind for our day to day life, but some energy we are wasting.

So, if we will be able to capture those wasted energy and then that can be used for the future energy generations. So, basically as we know that fossil fuels or maybe some kind of petroleum products are going to be finished maybe within couple of years or maybe within a decade. So, basically then we have to move to some kind of unconventional or maybe non-conventional energy sources is a in terms of may be the solar energy, in terms of some kind of fuel cells. So, basically now the scientists are tending to work on those kind of materials to generate some kind of non-conventional energy sources. So, which we can utilized in near future.

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Introduction:

- With increasing concern regarding climate change, pollution and energy security related to the decreasing availability of fossil fuels, the search for clean and renewable energy sources has become one of the greatest challenges for the sustainable development of society.
- Core to this development is the need for advanced energy conversion systems such as water electrolysis, fuel cells and metal-air batteries.
- Hydrogen has highest energy content per unit of mass of any chemical fuel and can be substituted hydrocarbon in a broad range of application.
- Its burning process is non polluting.



The diagram, titled "Hydrogen Cycle", illustrates the process of hydrogen production, storage, and use. It starts with "Renewable energy" (represented by a sun and solar panels) and "Water" being used in "electrolysis" to produce "H₂" and "O₂". The "H₂" is then stored in "H₂ storage" (represented by a tank). From storage, it can be "Exported" (shown by a ship) or used in a "Fuel Cell engine" (shown by a car). The "Fuel Cell engine" produces "Domestic use" (represented by a house) and "Water H₂O", which is then recycled back to "electrolysis".

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So, basically this kind of advanced energy conversion systems such as water electrolysis, as I told already fuel cells and metal ion batteries or maybe metal IR batteries. So, this kind of new technology are coming into the picture.

So, basically in this particular topic we are going to discuss about the hydrogen energy. So, basically hydrogen has the highest energy content per unit of mass of any chemical fuel and can be substituted the hydrocarbon in a broad range of applications. Its burning process is non-polluting. So, hydrogen, so if you go for any kind of petrol any kind of diesel gasoline, so if we burn, they will generate the toxic gas in terms of carbon dioxide or maybe the carbon monoxide. But if we burned the hydrogen it will not generate any kind of toxic gases which can be harmful to the environment. So, production of the hydrogen and storing of hydrogen is the great challenge nowadays to the scientist.

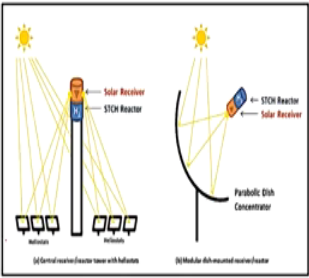
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Thermochemical water splitting:

- Thermochemical water splitting uses high temperatures—from concentrated solar power or from the waste heat of nuclear power reactions—and chemical reactions to produce hydrogen and oxygen from water.
- This is a long-term technology pathway, with potentially low or no greenhouse gas emissions.

HOW DOES IT WORK?:

- Thermochemical water splitting processes use high-temperature heat (500 – 2000 °C) to drive a series of chemical reactions that produce hydrogen.
- The chemicals used in the process are reused within each cycle, creating a closed loop that consumes only water and produces hydrogen and oxygen.



The diagram shows two solar reactor configurations. (a) Central receiver reactor tower with heliostats: A central tower (receiver) is surrounded by a field of heliostats (mirrors) that reflect sunlight onto the receiver. (b) Modular dish-mounted receiver reactor: A parabolic dish concentrator is mounted on a receiver, which is positioned to focus sunlight onto a reactor located at the focal point of the dish.

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So, basically how we can produce? So, there are some methods. So, in one of the methods is known as the thermochemical water splitting. So, thermochemical water splitting from the name itself you can understand say suppose I am having that water which is nothing, but the H_2O . And if I will be able to break H plus O H minus then H that can be useful in the near future itself. So, thermochemical water splitting uses high temperatures from concentrated solar power or from the waste heat of nuclear power reactions and chemical reactions to produce the hydrogen and oxygen from the, this is the main and this is the main, so from the water itself.

This is a long term technology pathway which potentially low or no greenhouse gas emissions. As I told already it is not going to generate any kind of toxic gases which can be harmful to the human being. How does it work? Thermochemical water splitting process use high temperature heats from 500 to 2000 degree centigrade to derive a series of chemical reactions that produce the hydrogen. The chemical used in this process are re used within each cycle creating a closed loop that consumes only water and produces the hydrogen and oxygen.

So, simple, what we are trying to do? We are trying to break the water molecules over there. So, in this particular case there are two types, you can see that one is called the central receiver reactor tower with heliostats another one is that modular dismantled receiver or maybe the reactor. So, in this particular case what we are doing? The

sunlights are coming, then we are concentrating the whole sunlight into the solar receiver, it is generating the high temperature over there due to that the water splitting into two halves, one is the hydrogen, another one is in the oxygen.

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Example of solar thermochemical cycle:

- Scheme of a two-step solar thermochemical cycle based on metal oxide redox reactions.
- Here, M_xO_y denotes a metal oxide, and M the corresponding metal or lower-valence metal oxide.
- In the first, endothermic solar step, M_xO_y is thermally dissociated into the metal or lower-valence metal oxide M and oxygen.
- Concentrated solar radiation is the energy source for the required high-temperature process heat.
- In the second, exothermic non solar step, M reacts with water to produce hydrogen.
- The resulting metal oxide is then recycled back to the first step.

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So, example of solar thermochemical cycle; so, scheme of a two step solar thermochemical cycle based on metal oxide redox reactions. So, basically, the reactions by which we are breaking it into the hydrogen and oxygen is known as the metal oxide redox reactions. Here, M_xO_y denotes a metal oxide and M the corresponding metal or lower-valence metal oxide. In the first, endothermic solar step M_xO_y is thermally dissociated into the metal or lower valence metal oxide M and oxygen. So, basically it is a two step process, one is the endothermic process, another one is the exothermic process.

Then the concentrated solar radiations is the energy source for the required high temperature process heat. In the second, exothermic non-solar step m reacts with water to produce the hydrogen. So, first case it is producing the oxygen and the second case it is producing the hydrogen. The resulting metal oxide is then recycle back to the first step itself. So, in this particular case what happened? We are having that concentrated solar energy, in this particular case it is coming to the solar reactor where as I told already it is producing the oxygen. And then that M is again reacting with the water itself the water we are injecting in this from particular point and it is generating the hydrogen. After that

again this $M \times O$ is going into the first case. So, that is the recycle process is going on in which we are getting oxygen and hydrogen separately in two different equations, one is the endothermic reactions, another one is the exothermic reactions.

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Sulfur – Iodine thermochemical water splitting:

- Thermochemical water-splitting is the conversion of water into hydrogen and oxygen by a series of thermally driven chemical reactions
- Thermochemical water-splitting (S-I cycle):

$$\begin{array}{c}
 H_2SO_4 \rightarrow \frac{1}{2}O_2 + SO_2 + H_2O \quad (>800^\circ C) \\
 H_2SO_4 + 2HI \leftarrow I_2 + SO_2 + 2H_2O \quad (<120^\circ C) \\
 2HI \rightarrow I_2 + H_2 \quad (>300^\circ C) \\
 \hline
 H_2O \rightarrow H_2 + \frac{1}{2}O_2
 \end{array}$$

- With a suitable catalyst, the high temperature decomposition of sulfuric acid achieves 10% conversion at 510 °C, and 83% at 850 °C.

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Next one is called the sulphur iodine thermochemical water splitting. So, thermochemical water splitting is the conversion of water into hydrogen and oxygen by a series of thermally driven chemical reactions how it is taking place.

Say suppose we are having sulphuric acid H_2SO_4 , right. So, it is breaking into the half oxygen plus sulphur dioxide plus water more than 800 degree centigrade when we are heating that particular materials. Then these two again reacting each other and they are forming the H_2SO_4 , it is a reverse reaction basically. So, you can see that iodine plus sulphur dioxide plus $2H_2O$. So, basically it is coming from here to here. And then we are adding the iodine over there, so that it can produce the H_2SO_4 plus $2HI$, it is less than 120 degree centigrade, then $2HI$ it is again coming into the iodine and the hydrogen that is more than 300 degree centigrade. So, ultimately, we are getting this hydrogen gas from here. And also, H_2O we can split into the H_2 plus half O_2 .

With a suitable catalyst the high temperature decomposition of sulphuric acid achieves 10 percent conversion at 510 degree centigrade and 83 percent conversion at 850 degree centigrade.

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Process:

- The sulfuric acid can be decomposed at about $850\text{ }^{\circ}\text{C}$ releasing the oxygen and recycling the sulfur-dioxide.
- The hydrogen iodide can be decomposed at about $400\text{ }^{\circ}\text{C}$, releasing the hydrogen and recycling the iodine.
- The net reaction is the decomposition of water into hydrogen and oxygen.
- The whole process takes in only water and high temperature heat and releases hydrogen.
- All reagents are recycled; there are literally no effluents.

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So, process; so, as I told already, so the sulphuric acid can be decomposed at about 50 degree centigrade releasing the oxygen and recycling the sulphur dioxide. So, this is the number 1, equations if I take this is as a number 1.

Then, the hydrogen iodide can be decomposed at about 400 degree centigrade releasing the hydrogen and recycling the iodine. So, basically in this particular case whatever the H_2O and H_2 is generating, they are reacting over here and then that is coming in this particular picture and we are adding the iodine and the reaction is taking place less than 120 degree centigrade, again it is forming the H_2SO_4 and the hydrogen iodide. Then in this particular case actually what we are doing? We are adding the water.

The net reaction is the decomposition of water into hydrogen and oxygen. The whole process takes is only water and high temperature heat and release the hydrogen. In this particular case, it is generating the heat high heat temperature and the reaction is taking place more than 300 degree centigrade and ultimately it is generating the hydrogen gas which is coming over here as a product. So, all reagents are recycled, they are literally no effluents. So, from these particular case effluents means, we are not getting any kind of by products or maybe any kind of toxic gases which can be harmful to the environment itself.

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Gas separation needs in S-I cycles:

<p>O₂ & steam removal from H₂SO₄ decomposition reactants</p> <p>Benefits:</p> <ul style="list-style-type: none">✓ Increase H₂SO₄ conversion efficiency.✓ Concentrate SO₂ for the 2nd reaction.✓ Reduce reactor size for the 2nd reaction.	<p>H₂SO₄ /steam separation in a membrane process</p> <p>Benefits:</p> <ul style="list-style-type: none">✓ Less energy consumption than distillation.✓ Concentrate H₂SO₄ for the 1st reaction.✓ Reduce the reactor size for the 1st reaction.
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H₂ separation and purification process

Benefits:

- ✓ Increase HI conversion efficiency.
- ✓ Concentrate I₂ for the 2nd reaction.
- ✓ Reduce reactor size for the 2nd reaction.
- ✓ Purify H₂ for down stream applications.

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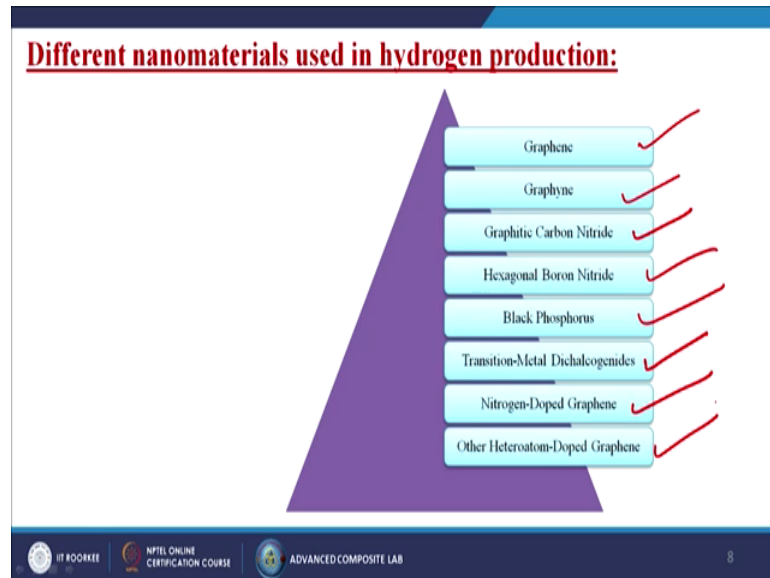
Now, gas separations needs in S-I cycles. So, oxygen and steam removal from H₂SO₄ decomposition reactance what are the benefits? Increase H₂SO₄ conversion efficiency, concentrate sulphur dioxide for the second reaction, reduce reactor size for the second reaction itself. If I talk about the sulphuric acid steam separations in a membrane process, in this particular case the benefits is less energy consumption than distillation, concentration sulphuric acid for the first reactions reduce the reactor size for the first reaction itself not into the second.

And if I talk about the hydrogen separations and the purification process, what are the benefits? Increase HI conversion efficiency, concentrate iodine for the second reactions, reduce reactor size for the second reactions, purify hydrogen for downstream applications. So, from this particular slides, we can understand that when we are using the oxygen or maybe the steam or maybe rather sulfuric acid or maybe the steam or maybe the hydrogen separation membrane. So, every time we have to use the pure materials over there and we can increase or decrease the size of the reactor depending upon that how much quantity of the hydrogen I required at the later stage. So, by this way we can optimize the whole reaction process.

Now, let us discuss about what type of materials are very very useful or maybe rather I can say that scientist does working on now to generate that hydrogen gas. So, basically, we can heard about so many times that about the graphene because it is a fantastic

material, it is not about for the hydrogen. Basically, nowadays the graphene is widely used for any applications, either it may be biomechanical, biomedical anywhere, energy storage device, energy generation device or maybe for some mechanical properties or may be polymer matrix composites, metal matrix composites people are using graphene worldwide.

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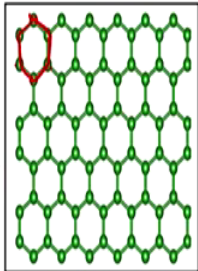


Another material that is called the graphyne, then graphitic carbon nitride, in short basically we are calling it as a GCN, then h-BN that is hexagonal boron nitride, then people are using the black phosphorus over there. Of course, they are converting the black phosphorus from the red phosphorus itself. Then this is also another wonderful material that is called the TMD, that is transition metal dichalcogenides. Then we are having some doped graphene like nickel doped or maybe the nitrogen doped graphene and some other heteroatom doped graphene also now people are using. So, now, I am going to discuss one by one into the subsequent slide.

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1. Graphene:

- Since its discovery in 2004 by Geim and Novoselov using their famous scotch tape method, graphene has become a leading research interest in various fields such as electronics, biomedical engineering, and electro catalysis.
- Graphene is a one-atom-thick 2D carbon crystal in which sp^2 -bonded carbon atoms are packed in a hexagonal lattice resembling a honeycomb (Figure).
- It is considered as the fundamental building block for other dimensional carbon materials, including 0D fullerenes, 1D CNTs, and 3D bulk graphite or other carbon architectures.
- The cause of such interest in graphene is due to its many unique properties, such as high theoretical surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), high modulus of elasticity (1.0 TPa); and good thermal ($5000 \text{ W m}^{-1} \text{ K}^{-1}$), and electrical conductivities (106 S cm^{-1}).



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Now, 1st we are going to discuss about the graphene. So, graphene its discovery in 2004 by Geim and Novoselov using their famous scotch tape method. So, simple they are having that graphite. What is graphene? Graphene is nothing, but a single layer of the graphite itself. So, they are having the tape. First, they have stick that material graphite on to that and then after that they are pulling so many time, so that the layer by layer separation will be taking place by which they have prepared the graphene material.

So, graphene has become a leading research interested in various fields such as electronics, biomedical, engineering and electrocatalysis as I told already. And here also whatever the materials we are going to discuss that basically are acting as a catalytic material or maybe the catalyst. So, that our hydrogen generation can be enhanced. So, graphene is a one atom thick 2D carbon crystal as I told already in which sp^2 bonded carbon atoms are packed in a hexagonal lattice resembling a honeycomb structure. This is the hexagonal structure of that graphene. So, it is having total 6 carbon atom together.

It is considered as the fundamental building block for other dimensional carbon materials including 0D fullerenes, 1D carbon nanotubes, 3D bulk graphite or other carbon architectures, it depends. So, either it can be 1D, it can be 0D, it can be 3D depending upon that which xyz which direction are into the nano meter range. So, when we are talking about that 0D, that means, all the sides are into the nano meter range. If we talk about the 1D, so one is into the macroscale, either it may be the micro level and wrist y

and z or may be x and y or may be the x or z are into the nanoscale. So, like this way we are classifying the whole materials in to the 0D, 1D, 2D, 3D directions.

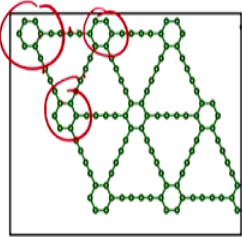
The cause of such interest in graphene is due to its many unique properties such as high theoretical surface area like 2630, 2630 metre square per gram, high modulus of elasticity that is almost 1.0 tera pascal and good thermal that is 500 watt per metre per kelvin and electrical conductivity is almost 106 siemens part centimetre. So, basically this is the wonderful properties of the graphene that is why people are widely using for every applications.

Now, let us discuss on to the second material that is called the graphyne.

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2. Graphyne:

- Graphyne is another allotrope of carbon that is a one-atom-thick planar sheet of sp and sp^2 -bonded carbon atoms arranged in a crystal lattice.
- Comprised of benzene rings (sp^2 -like carbon atoms) and acetylenic (sp -like carbon atoms) linkers, graphynes were named after their relationship to graphite and acetylenic components.
- They are differentiated as graphyne, graphdiyne (Figure), graphtriyne, etc. based on the number of acetylenic groups between two adjacent benzene rings.
- The synthesis of 2D graphdiyne is mainly based on bottom-up methods such as chemical vapor deposition (CVD) and gas/liquid or liquid/liquid processes using hexa-ethynyl-benzene as a precursor monomer.



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So, graphyne is another allotrope of carbon that is a one atom thick planar sheet of sp and sp^2 bonded carbon atoms arranged in a crystal lattice. So, one is the sp^2 , 6 atoms over there and then they are attaching with the sp bonding over there. So, that is why it is called the sp^2 , sp bonded carbon atoms.

Comprised of benzene rings. So, this is the benzene rings sp^2 like carbon atoms whatever I have already told and acetylenic sp like carbon atoms linkers, graphynes were named after their relationship to graphite and the acetylenic compounds. They are differentiated as graphyne or maybe the graphdiyne in figure, graphtriyne etcetera based on the number of acetylenic groups between two adjacent benzene rings. So, in between

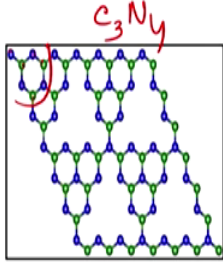
tube and adjacent benzene rings that how many are attached, whether it is single, double or maybe the triple one.

The synthesis of 2D graph dyeing is mainly based on bottom of methods such as CVD chemical vapour depositions and gas liquid or maybe the liquid liquid processes using hexa-ethynyl-benzene as a precursor monomer.

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3. **Graphitic Carbon Nitride: (GCN)**

- Carbon nitride is one of the first artificial polymers reported in the scientific literature.
- Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is a 2D crystal with a Vander Waals layered structure, and is considered to be the most stable allotrope of all the various carbon nitride materials.
- Analogous to graphene, the crystal structure of $g\text{-C}_3\text{N}_4$ can be described as a hexagonal carbon framework with N-substituted carbon through the sp^2 hybridization of carbon and nitrogen atoms.
- Two structural isomers of $g\text{-C}_3\text{N}_4$ exist and are synthesized using different precursors and condensation methods.



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In the 3rd one, we are going to discuss about the graphitic carbon nitride in short basically we are calling it as a GCN. So, carbon nitride is one of the first artificial polymers reported in the scientific literature. Graphitic carbon nitrides as I told already basically we are writing is like a $g\text{-C}_3\text{N}_4$ is a 2D crystal with a Vander Waals layered structure and is considered to be the most stable allotrope of all various carbon nitride materials.

Analogous to graphene the crystal structure of $g\text{-C}_3\text{N}_4$ can be described as a hexagonal carbon frame work with a N-substitute carbon through the sp^2 hybridization of carbon and the nitrogen atoms. So, now, we can see in every alternative there is one nitrogen atoms are present.

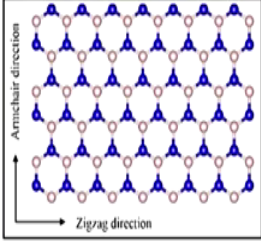
So, if we talk about this one. So, suppose if I cut this particular site, so what will happen? Here I am having 3 carbon over there right, so that is why it is V 3 and nitrogen 1, 2, 3, and 4, so N 4. So, that is why it is coming the C_3N_4 structure over there. Two

structural isomers of $g C_3 N_4$ exist and are synthesized during different precursors and condensation methods.

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4. Hexagonal Boron Nitride:

- Hexagonal boron nitride (h-BN) is another analogue of graphite and is also known as “white graphene”.
- Bulk h-BN has a layered structure with lattice constants of 2.50 Å and interlayer distances of 3.33 Å (Figure).
- Differing from graphene, h-BN is an insulator with a thickness dependent band gap.
- In electronic and optical devices, h-BN nanosheets have been used as dielectric substrates for graphene and MoS_2 -based heterostructures.
- However, pristine h-BN displays barely no performance for electro catalysis, limited by its poor conductivity and poor catalytic activity.



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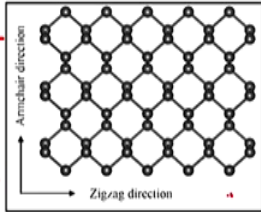
Next 4th one is called the hexagonal boron nitride. So, basically, we are calling it as a h-BN is another analogue of graphite and is also known as white graphene. Bulk H bn has a layered structure with lattice constant of 2.50 angstrom and interlayer distance of 3.33 angstrom. Differing from graphene h-BN is an insulator with the thickness dependent band gap. So, now, in electronic and optical devices h-BN nano sheets have been used as dielectric substrates for graphene and molybdenum sulfide based heterostructure because it is having a wide bandgap.

However, pristine h-BN displays barely no performance for electro catalysis, limited by its poor conductivity and poor catalytic activity. So, that is why people are trying to modify the h-BN by some doping or maybe the coating or maybe some kind of incorporations of the impurity inside it. So, that it can acts as a good conducting material.

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5. Black Phosphorus:

- Black phosphorus (BP) has a 100 year long history as its bulk form was first synthesized in 1914.
- BP is a layered semiconductor with an orthorhombic crystal structure; one phosphorus atom is covalently bonded with another three to form a puckered honeycomb structure in a single layer (Figure).
- The three bonds take up all three valence electrons of phosphorus, resulting in a band gap of ~ 2 eV which can be tuned by controlling its thickness.
- However, only a few works have been reported about its applications in electro catalysis, which may be due to its low stability under electrocatalytic conditions and poor electrical conductivity.



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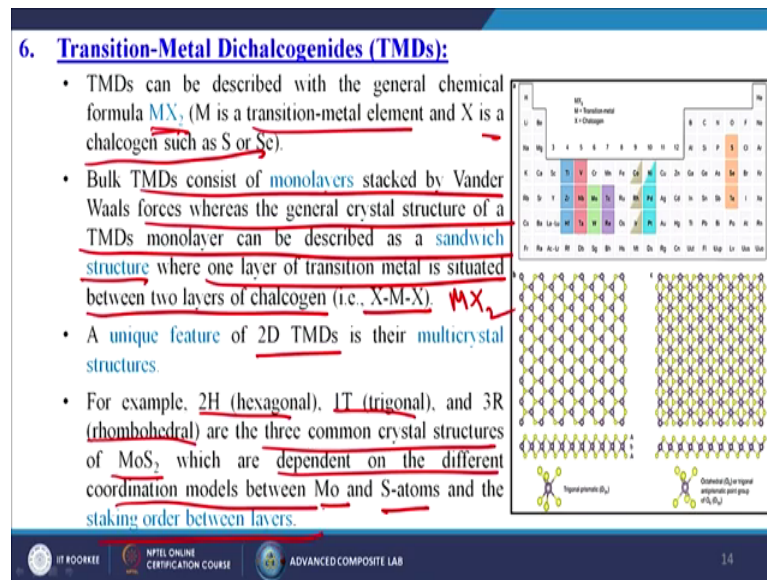
Next 5th one is call the black phosphorus. So, basically the black phosphorus in short we are calling it as a BP has a 100 year long history as its bulk from was first synthesized in the year of 1914. BP is layered semiconductor with an orthorhombic crystal structure, one phosphorus atom is covalently bonded with another three to form a puckered honeycomb structure in a single layer. So, basically this is the structure of that black phosphorus.

The three bonds take up all 3 valence electrons of phosphorus, resulting in a band gap of 2 electron volt which can be tuned by controlling its thickness. However, only a few works have been reported about its applications in electro catalysis which may be due to its low stability under electro catalytic conditions and poor electrical conductivity. So, that is also the another drawback for the black phosphorus.

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6. Transition-Metal Dichalcogenides (TMDs):

- TMDs can be described with the general chemical formula MX_2 (M is a transition-metal element and X is a chalcogen such as S or Se).
- Bulk TMDs consist of monolayers stacked by Vander Waals forces whereas the general crystal structure of a TMDs monolayer can be described as a sandwich structure where one layer of transition metal is situated between two layers of chalcogen (i.e., X-M-X).
- A unique feature of 2D TMDs is their multicrystal structures.
- For example, 2H (hexagonal), 1T (trigonal), and 3R (rhombohedral) are the three common crystal structures of MoS_2 which are dependent on the different coordination models between Mo and S-atoms and the stacking order between layers.



Then the 6th one is called that TMDs or may be that transition metal dichalcogenides. TMDs can be described with a metal chemical formula MX_2 basically. So, WS_2 , WSe_2 , MOS_2 , $MOSe_2$. So, these all are the examples of the TMDs or may be the transition metal dichalcogenides. M is the transition metal element and X is a chalcogen such as sulphur or maybe the seldodium.

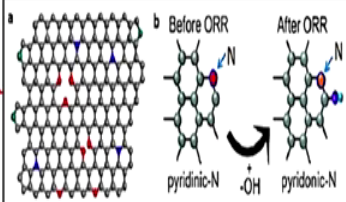
Bulk TMDs consists of monolayers stacked by Vander Waals force whereas the general crystal structure of a TMDs monolayer can be described as a sandwich structure where one layer of transition metal is situated between two layer of chalcogen, so X-M-X. So, that is why it is basically the MX_2 . A unique feature of 2D TMDs is there multi crystal structure. For example, 2H hexagonal, 1T trigonal and 3R that is rhombohedral are the 3 common crystal structures of MoS_2 which are dependent on the different coordination model between the molybdenum and sulphur atoms and the stacking order between the layers. So, basically that depends upon how you are arranging your materials over there.

So, basically this is the chalcogen one, sulfur, selenium and the tellurium and this is the transition metals over there.

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7. Nitrogen-Doped Graphene:

- N-graphene is the most studied graphene-based electrocatalyst due to its simple synthesis process and relatively good electrocatalytic performance.
- Nitrogen is of similar atomic size to carbon, but is more electronegative.
- Therefore, doping with nitrogen can change the electron configuration of graphene while minimizing the lattice mismatch after doping.
- Being the earliest studied and the most important metal-free electrocatalyst for the ORR, N-graphene has demonstrated some unique characteristics compared to metal-based electrocatalysts.
- N-graphene has tolerance to the fuel (e.g., methanol and CO) present in the anode chamber of fuel cells, which largely prevents the crossover effect.



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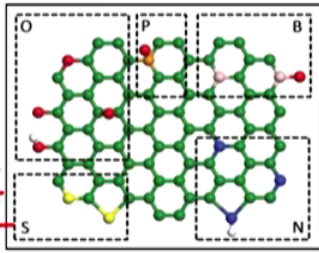
Next 7th one is called the nitrogen doped graphene. N-graphene is the most studied graphene based electro catalyst due to its simple synthesis process and relatively good electrocatalytic performance. Nitrogen is of similar atomic size to carbon, but its more electronegative. Therefore, doping with nitrogen can change the electron configuration of graphene while minimizing the lattice mismatch after doping. So, that is why the people are doing the nitrogen doping on to the graphene.

Being the earliest studied and the most important metal free electrocatalyst for the ORR, N-graphene has demonstrated some unique characteristics compared to metal based electrocatalysts. N-graphene has tolerance to the fuel like methanol and carbon monoxide present in the anode chamber of fuel cells which largely prevents the crossover effects, because while doing that this kind of gases at generating which can react with the electrode. But, in these particular case that N-graphene does not have any good reactions with the methanol or maybe the carbon monoxide that is why that n doped graphene can sustain for a longer time as a electrocatalyst material.

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8. Other Heteroatom-Doped Graphene:

- Besides nitrogen, other p-block elements (e.g., B, S, P) have been doped into the graphene matrix by physical or chemical approaches.
- Similar to nitrogen, the differing size and electro-negativity of these heteroatoms to carbon can also induce electron modulation which changes the electronic properties of pristine graphene.
- These kinds of electrocatalysts can usually be prepared by annealing GO with the appropriate heteroatom containing precursor at high temperatures (>900 °C).
- The doping level of these materials is normally lower than that of N-graphene.
- Doping graphene with heteroatoms of either higher or lower electronegativities than carbon ($\chi = 2.55$), such as N ($\chi = 3.04$), B ($\chi = 2.04$), and P ($\chi = 2.19$), can induce electrocatalytic ORR activity through intramolecular charge transfer in the graphene matrix.



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Then the last one is called the other heteroatom doped graphene. Besides nitrogen other p block elements like boron, Sulphur, phosphorus have been doped into the graphene matrix by physical or maybe the chemical approaches. Similar to nitrogen the differing size and electronegativity of these heteroatoms to carbon can also be induced electron modulation which changes the electronic properties of pristine graphene. These kinds of electrocatalysts can usually be prepared by annealing graphene oxides with the appropriate heteroatom containing precursor at high temperature that is more than 900 degree centigrade basically we are doing the doping.

The doping level of these materials is normally lower than that of N-graphene. Doping graphene with heteroatoms either higher or lower electronegativities than carbon that is χ equal to 2.55, such as N χ is equal to 3.04, boron 2.04 and phosphorus 2.19 can induce electrocatalytic ORR activity through intramolecular charge transfers in the graphene matrix. Actually, basically, the doping is taking place by two methods, one is called the interstitial doping, another one is called the substitutional doping. So, whatever the doping materials you are going to introduce that diameter is if it is equivalent with the carbon diameter then the substitution will be taking place, if it is larger then the interstitial will be taking place. So, in this manner it depends that which type of doping will be done on to these graphene material.

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Advantages:

- ✓ Water is an attractive feedstock since it can be recycled back into nature indefinitely.
- ✓ One side benefit of a nuclear reactor that produces both electricity and hydrogen is that it can shift production between the two.

Disadvantages:

- ✓ The efficiency and durability of reactant materials for thermochemical cycling need to be improved.
- ✓ Efficient and robust reactor designs compatible with high temperatures and heat cycling need to be developed.
- ✓ For solar thermochemical systems, the cost of the concentrating mirror systems needs to be reduced.

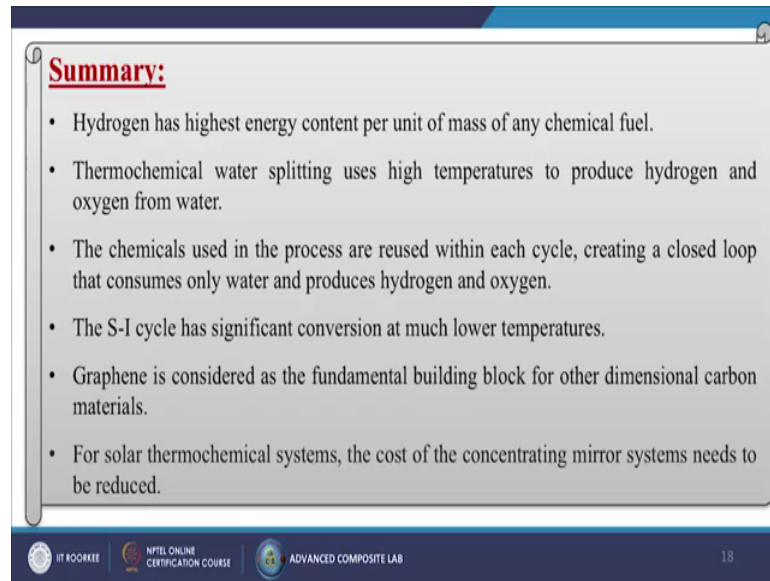
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Now, let us come to the advantages. Water is an attractive feedstock since it can be recycled back into nature in definitely. It is true. So, when we are making it into the hydrogen and oxygen and then later stage this again hydrogen oxygen comes together and there forming the water. One side benefit of a nuclear reactor that produces both electricity and hydrogen is that it can shift production between the two itself.

Now, of course, there are certain disadvantages. What? That efficiency and durability of reactant materials for thermochemical cycling needs to be improved because the efficiency is not up to that much level. Efficient and robust reactor designs compatible with high temperatures and heat cycling needs to be developed. Yes, because that reactor materials also should sustained at that particular higher temperature and the pressure. For solar thermochemical systems, the cost of the concentrating mirror systems needs to be reduced because they are very very costly materials.

Now, we have come to the last slide of this particular lecture. So, in summary we can say that hydrogen has a highest energy content per unit of mass of any chemical fuel that is why scientist, researchers are nowadays tending towards the hydrogen generation and the hydrogen storage. Thermochemical water splitting uses high temperatures to produce hydrogen and oxygen from the water. We have already seen through that we are breaking it into the oxygen molecules and the hydrogen molecules, so that we are getting plenty of oxygens and the plenty of hydrogens too.

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Summary:

- Hydrogen has highest energy content per unit of mass of any chemical fuel.
- Thermochemical water splitting uses high temperatures to produce hydrogen and oxygen from water.
- The chemicals used in the process are reused within each cycle, creating a closed loop that consumes only water and produces hydrogen and oxygen.
- The S-I cycle has significant conversion at much lower temperatures.
- Graphene is considered as the fundamental building block for other dimensional carbon materials.
- For solar thermochemical systems, the cost of the concentrating mirror systems needs to be reduced.

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The chemicals used in the process are reused within each cycle creating a closed loop that consumes only water and produce hydrogen and the oxygen because that is a very good environmental process for the society. The S-I cycle has significant conversion at much lower temperatures. Graphene is considered as the fundamental building blocks for other dimensional carbon materials. Though, we have discussed about so many materials as a catalyst, so that the hydrogen or maybe the oxygen production will be increased. For solar thermochemical systems the cost of the concentrating mirror systems need to be reduced, so that we can use that mirrors frequently to generate the hydrogen gas in the near future.

Thank you.