Project Title: **Nanowires and Hydrogen Storage**

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Abstract:

The present report will focus on the nanowire technology and how it is being used for the hydrogen storage. The report starts with the introduction to the nanowires and just a brief discussion of the techniques involved in their synthesis like the top-down or the bottom-up approach. This is followed by the hydrogen storage and the various processes involved in the release of hydrogen from various materials like the process of photolysis, biophotolysis and thermo-chemical water splitting. These processes are then made use of in the various materials for adsorption/desorption of hydrogen like in carbon nanostructures especially the nanowires. Not only the carbon nanowires but other materials like AlN, ZnO and Mg can also be used for the synthesis of nanowires and they can be used for the storage of hydrogen.

ZnO, Mg, AlN and inorganic nanowires are studied for hydrogen storage. The porous Li-Mg-N-H NWs along with the Single Wall Nanotube (SWNT) are also considered as an option for the hydrogen storage. The process and the difficulties involved in it have been briefly mentioned.

Finally the disadvantages or the risks involved in working with the nanostructures have been outlined. The final part of the report gives a clue about the other possible options for the hydrogen storage like PIMs, MOFs and Clathrates.

Nanowires:

The size of the nanomaterials is in the range of 10^{-9}m and due to this small size the properties of these nanomaterials are very different than their macro counterparts. The quantum mechanical effects come into picture at this scale. If we have a nanomaterial with extremely small thickness or diameter with unconstrained length then we approach a 1-D structure which is known as nanowires.

These wires can be metallic made of metals like Ni, Au, semiconducting due to semiconductors like Si, InP or insulating due to insulators like SiO_2, TiO_2.

Applications: [1]

The nanowires are still under study and they have not yet been out for the industrial usage. Although they have been tested for various uses like improving the friction characteristics and replacing the carbon nanotubes but still a wide range of research is required to make them useful in practical life.

The nanowires are increasingly being studied to make FETs where they are used in the form of a T junction to make source, drain and substrate with just two nanowires. They can be used for the making of the non-volatile storage devices by the use of bistable nanoscale switches.

Another use of the nanowires is in the making of the resistances, FETs and diodes. The nature of the device depends upon the properties of the two nanowires placed orthogonal to each other and the layer between them. By programming these junctions, any of these devices can be obtained. They can be used for building single electron devices, scanning electron microscope tips etc.

Challenges Faced in Building Nanowire Devices [2]:

The major concern in the production of the nanowire devices is the contamination. Thus various traditional materials like the SiO_2 have been replaced by the new materials like HfO_2 and other high-k dielectric materials for the making of gate in the case of transistors. Also Ti and Ni have replaced Co for making the contacts. These are so called low-k dielectrics.

Also the use of Au can lead to contamination and thus cleaning solutions have to be used to remove it. In order to overcome this problem, Cu is now used to replace Au for particle-assisted nanowire growth.

After the nanowires have been built, the problem of addressing the problems associated with the devices comes into picture. The nanowires can be used to design the transistors. They can be used to design the FETs. But in order to design the FETs there are some issues that need to be addressed. These involve the series/contact resistance, gate length control etc.

There are also other challenges like the lack of knowledge about the risks associated with the nanotechnogy. The research on how this technology can affect humans and environment is going on and only after that we can think of using the nanostructures in our day to day life without any hesitation.

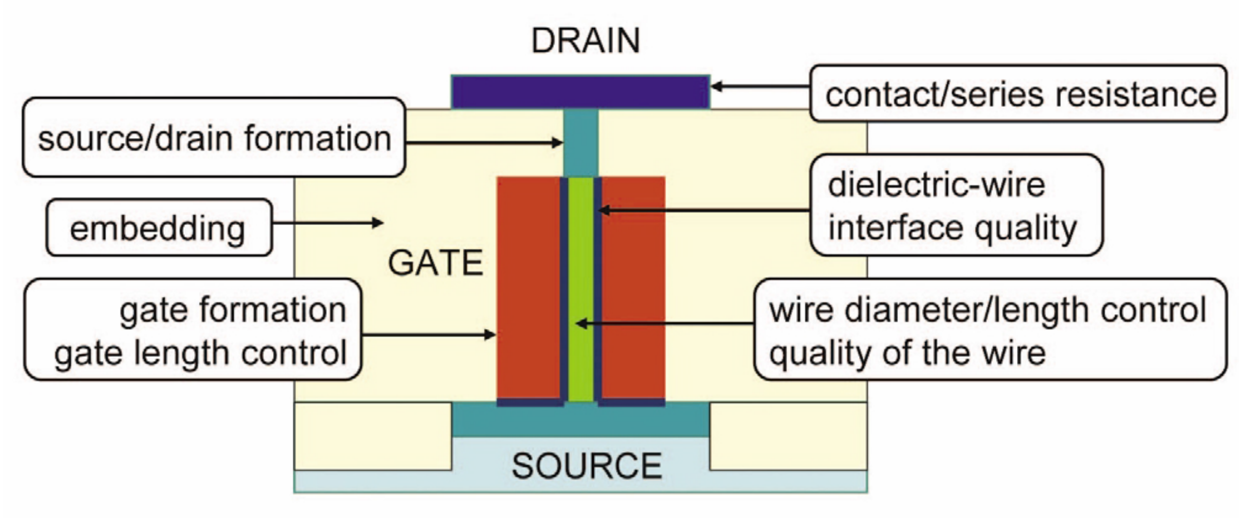

Fig 1 [2] : Figure Showing the Critical Areas of a Vertical Nanowire Transistor

Structure of Nanowires: [1]

The nanowires are not found in nature so they must be synthesized. They can be prepared from a variety of materials like the semiconductors like Ge, GaAs or oxides and alloys. NWs can be synthesized by the bottom-up or top-down approach. The top-down approach reduces a large piece of material into small pieces by the processes like lithography or electrophoresis. While in the case of the bottom-up approach, the constituent adatoms are combined. This is the preferred technique used now a days.

The manufacturing involves the laboratory techniques like vapor deposition, suspension and electrochemical deposition.

The nanowires have the diameter in the range of the few nanometers but their length can be several hundred micrometers. They can be aligned in any direction and can be placed on any surface and thus can be made into any orientation.

The nanowires can show crystalline as well as non-crystalline structure because they have periodic structure in only one direction (only in the axial direction) and can have any shape in the other direction.

Properties of Nanowires:

1. **Conductivity:** The conductivity of the nanowires is less and the reason can be the scattering from the wire boundaries when the man free path is less than the wire diameter.
2. **Edge effects:** As the nanowires shrink in size, the number of atoms on the surface of the nanowire can increase in number than the atoms in the bulk of the nanowire and this can lead to the defects and poor conductance.
3. The energy of the electrons going through the nanowire can assume only a discrete value, which is a multiple of Landauer constant, $G=2q^2/h$.

4. The conductivity is described as the sum of the transport by separate channels and hence thinner the wire, less are the number of the channels available and hence lesser is the conductivity.

Practical Methods for Nanowire Synthesis:

1. The top-down approach involves the lithographic techniques like e-beam lithography, ion-beam lithography. While on the other hand, the bottom-up approach involves the techniques like electro-deposition, assemble from units etc. Other techniques involve plasma arcing, laser ablation etc.
2. Visible light cannot be used in the making of nanoscale structures because the wavelength of visible light is 40nm which is higher than the size of the structures to be made. So the alternatives like x-ray beams or e-beams are used.
3. Chemical Vapor Deposition is one of the most important technique to synthesize the nanowires. This method is used when the nanosites have been already created and then the material coated on the surface is removed with the help of a chemical or electron beam.

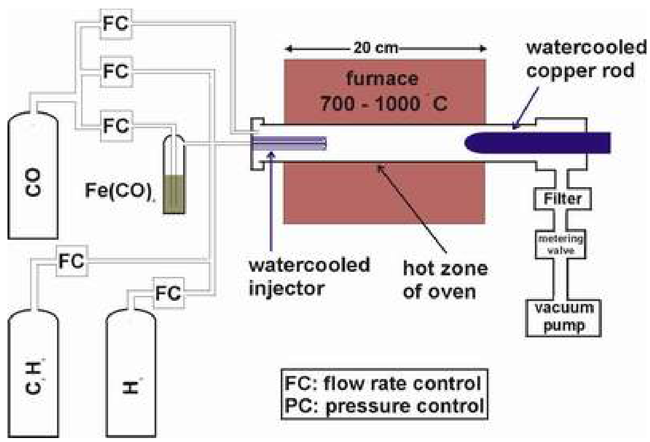

Fig 2 [3]: CVD Technique for Nanowire Synthesis

4. Apart from these methods there are certain other methods also like Vapor-liquid-solid method etc. but these methods are just been explained here to give an overview so all the methods are not listed.

Hydrogen storage [4] :

Hydrogen is stored in many ways so that it can be used for various purposes like as an energy source, as fuel for transportation like in ships and rockets. The methods used for the hydrogen storage involve the use of high pressures, cryogenics and chemical compounds that release H_2 upon heating.

Liquid hydrogen is used in the space shuttles but there is a problem of storage because it boils at around -252.882^{o}C and also this increases the insulation cost for the tanks.

The physical storage of hydrogen is mainly done by the following ways:

1. **Cryo-compressed Hydrogen:**
   This method uses cold hydrogen to achieve a high energy density. This method can increase the driving range of the vehicles. Companies like Toyota and BMW have already started to work on this technology.
2. **Glass Capillary Arrays:**
   A team of Russian, Israeli and German scientists have devised a new technique in which the glass capillary tubes can be used for infusion, storage and controlled release of hydrogen in mobile applications.
3. **Carbon Nanostructures:**
   Carbon nanostructures are also being considered as one of the options to store hydrogen. The hydrogen stored in them amounts to approx. 3.0 – 7.0 wt% at 77K which does not meet the standards set by the US Department of Energy. This is one of the reason why this option needs to be further explored in order to make it viable for future.

There are methods which are used to produce hydrogen now a days, these involve photolysis, biophotolysis, thermo-chemical water splitting etc. These processes involve the use of some chemicals or chemical reactions in order to produce hydrogen.

1. **Photolysis:**
   It is a process in which a particular compound can be broken down to produce a particular product in the presence of light. The light used need not be only visible light but can be of any type say UV or other depending upon the strength of the bonds that need to be broken in the target. Example of this is the breaking of water molecule in the presence of light to produce hydrogen.

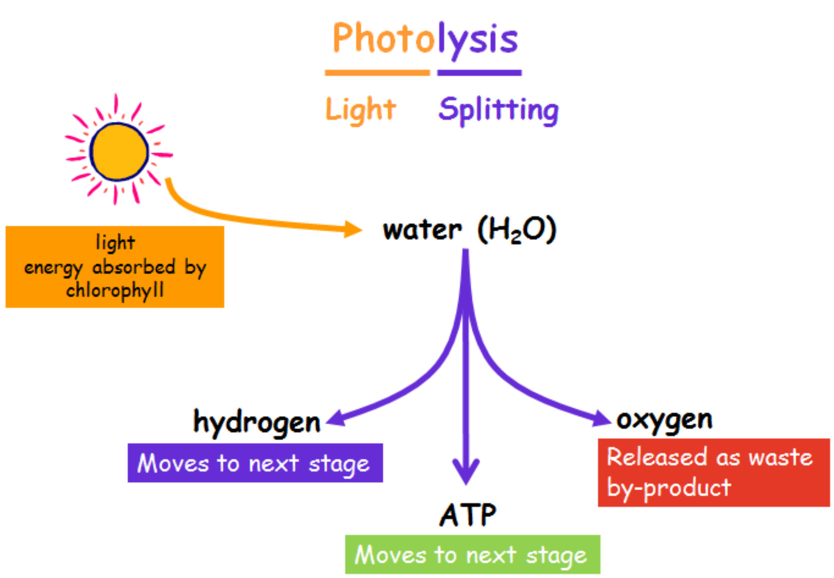

Fig 3 [5]: Principle of Photolysis

2. **Biophotolysis:**
This process involves the use of light for the production of hydrogen. In other words, it is a type of photolysis reaction for breaking a biochemical compound. Like for example the action of light on algae. This process still needs some research so that it may be used for practical purposes. The general reactions involved in this process may be written as: **[6]**

Water + Algae +TPN + Light → TPNH + Oxygen
TPN + Oxalacetate + Lyophilized R.Capsulata → TPN + Malate
Malate + Fresh R.Capsulata + Light → Hydrogen + Oxalacetate

After removing all the micro-organisms and the electron carriers, the overall equation can be simplified to:

Water + Light → Hydrogen + Oxygen

3. **Thermo-chemical Water Splitting: [7]**
The thermo-chemical water splitting cycles have now been known for about 35 years but they still need to be made cost-efficient. It is the splitting of water which mainly uses heat (thermo) to split water into its constituents i.e. hydrogen and oxygen. One of the example is iodine/sulphur cycle but this cycle also involves reactions other than the production of hydrogen. There is a need to capture these hydrogen reactions and to avoid the associated corrosion problems.

($830^{O}C$): $H_2SO_4 \rightarrow SO_2 + H_2O + 1/2O_2$
($120^{O}C$): $I_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$ (Bunsen Reaction)
($450^{O}C$): $2HI \rightarrow I_2 + H_2$
SUM: $H_2O \rightarrow H_2 + 1/2O_2$

Thus in this process, hydrogen is released at the end of the reaction in the third step and this is the step which needs to be controlled for the cost-efficient production. The overall reaction looks like as if water is being used for obtaining hydrogen so this process is also called water splitting otherwise it is just another form for the representation of the chemical reaction process.

The overall reaction can be drawn as:

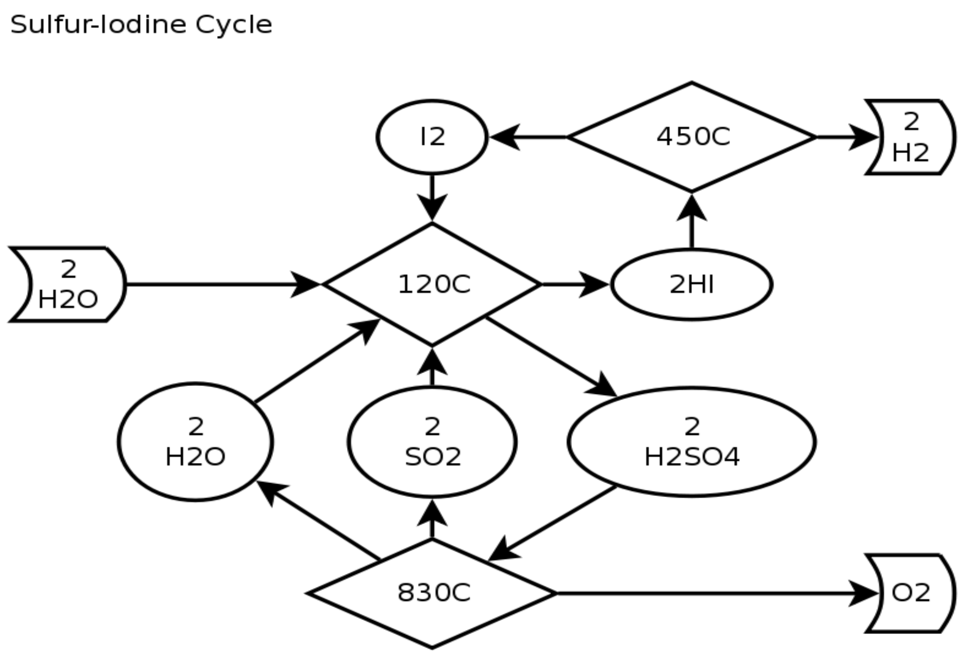

Fig 4 [7]: Iodine/Sulphur Thermo-chemical Process for the Production of Hydrogen

Nanowire Approaches for Hydrogen Storage:

The carbon nanostructures in the form of the nanotubes which may be single wall or multi wall can be used for hydrogen storage. They are cut and hydride is introduced in them and then they can be used for hydrogen storage. This process and the drawbacks associated with them will be discussed later in this report. Now we discuss various other techniques developed by the use of nanowires for hydrogen storage one by one:

1. Use of ZnO Nanowires: [8]

a. Overview:
The ability of ZnO to include other metals in place of Zn and increase or decrease its band gap is being exploited to be used for hydrogen storage and in optical studies. Addition of Mg can widen the band gap while the addition of Cd can reduce the band gap. Thus the ZnO nanowires are doped with Mg to form $Zn_{1-x}Mg_xO$ (x =0, 0.05, 0.1 and 0.2) by using techniques like molecular beam epitaxy, pulsed laser deposition etc.

b. Synthesis of Mg doped ZnO nanowires:
The synthesis involves a horizontal tube furnace (30cm in length and 4cm in diameter), a quartz tube (50cm length and 3cm diameter) with two gas inlets and gas flow control system. The temperature inside the tube is held constant within 10^0C and the air inside the tube is removed by the use of argon. Then oxygen is inserted with the flow of 100 SCCM at 900^0C and also 2g of Zn in an alumina boat is inserted in tube. After 8-10 min white cotton like product is obtained.

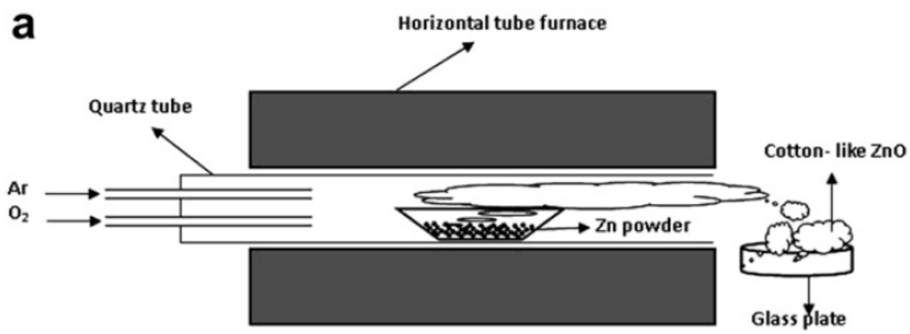

Fig 5 [8]: Synthesis of ZnO Nanowires

The doping with Mg is carried out by solid state reaction at vacuum pressure using powdered Mg (99.99%). The powder is then mixed with agate mortar for 30min and pressed to form pellets which are then wrapped in tantalum foil and sealed in silica at 10^{-5} torr. This setup is then heated for 12 hours at approx.600^0C and then cooled at room temperature at a rate of 10^0C/min.

c. Hydrogen Uptake of Undoped and Doped ZnO Nanowires:

The hydrogen absorption by the ZnO nanowires is shown in the graph below which shows that the higher hydrogen content in the doped nanowires than the undoped ones. The reason behind such a behavior is still under study but the reasons which are thought to be responsible for such a behavior involve physisorption of hydrogen molecule and chemisorption which includes the breaking of hydrogen molecule on the surface and moving to the interstitial sites.

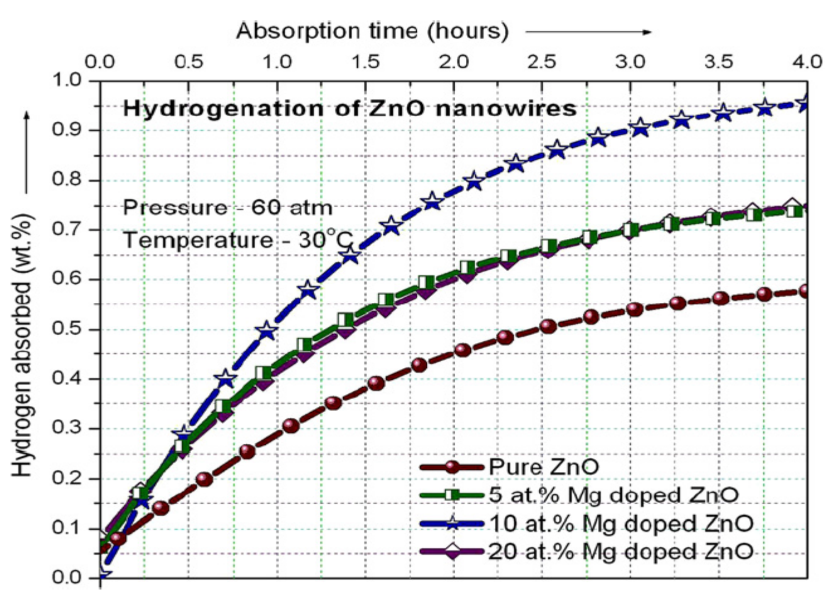

Fig 6 [8]: Hydrogen Storage Trend in Doped and Undoped ZnO Nanowire

d. Findings:

It is found that at room temperature (28^0C) and at a pressure of about 60 atm, about 1 wt% hydrogen can be stored in Mg doped ZnO nanowire. Approximately 75% of the stored hydrogen can be released upon heating at 40^0C under 1 atm. Also it has been found that the hydrogen is found in the lattice in the form of H^- ions located near the Zn^{2+} ions and oxygen vacancies, in the form of H^+ ions near the O^{2-} ions and the neutral ions at the neutral locations. However, in order to get the exact picture of the happenings, further research needs to be done in this field.

2. Hydrogen Storage in Mg Nanowires: [9]

a. Overview:

Physisorption needs cryogenic temperatures for hydrogen storage and release and this can create a problem while chemisorption is a fast process and needs to be controlled but is a feasible process and can be used in the laboratories to generate and store hydrogen in the nanowires. It has been found that chemisorption can lead to the hydrogen storage capacity of 7.7 wt% for a single wall carbon nanotube. In this part we will study how the size of the Mg particles can affect the absorption/desorption of hydrogen based on the Density Functional Theory (DFT).

Magnesium is considered as one of the favorable materials for hydrogen storage due to high gravimetric density of 7.6 wt%, low cost and good reversibility. The desorption kinetics is slow and hence leads to high desorption temperature of 573K at 1bar H_2. Thus this requires some alloying or doping. It has been found that the nanowires having diameter in the range of 30-170nm have lower desorption energy which can still be lowered by decreasing the diameter further. A reduction in the size of the MgH_2 nanowires can lead to unstable structures and thermodynamics. The following figure shows the different Mg nanowires:

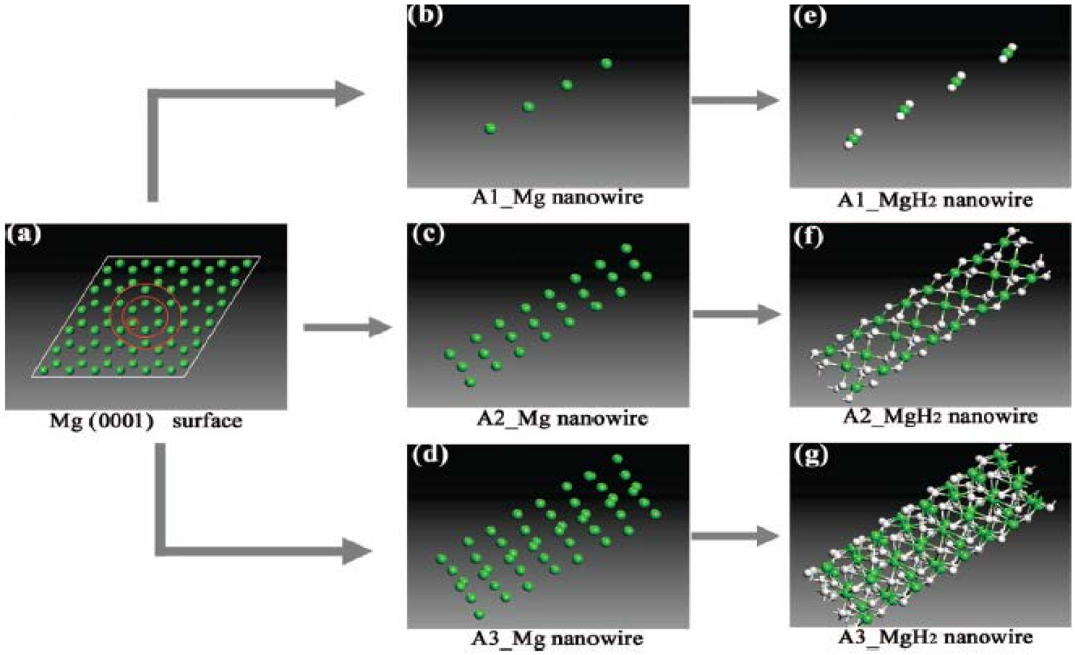

Fig 7 [9]: Mg surface (hexagonal close packed structure) and Different Mg Nanowires of Infinite Length: diameter increasing in the order A1, A2, A3

b. Density Functional Theory (DFT): [10]

This theory is used to study the electronic structure of many-body systems i.e. the molecules with atoms from different elements. Under this theory, the properties of these systems can be studied in terms of the functionals i.e. the functions of other functions. And these functions in this case is the spatially dependent electron density. Hence the name density functional theory.

c. Hydrogen Position:

The hydrogen atoms can be present either on the surface or inside the nanowire. The surface can have hydrogen on the top, bridge or 3-fold site while if we talk about the inner structure of the nanowire, hydrogen can be present at the tetrahedral site where it is 4-fold coordinated or at the octahedral site where it is 6-fold coordinated. The desorption reaction involved in this process is:

$$Mg_nH_{2m} = Mg_n + mH_2$$

Where n is the number of the Mg atoms in the supercell and m is half the number of the hydrogen atoms.

d. Findings:

It has been found that the hydrogen atoms prefer the bridge sites on the surface which are most energetically favorable. The calculations for the enthalpy using the above equation indicated that the decrease in the diameter leads to the enthalpy becoming more and more negative and hence unfavorable condition. The diameter range of 30-50nm is found to be most appropriate.

The only disadvantage involved in this process is that the nanowires collapse after few cycles of hydriding/dehydriding. If the diameter is increased beyond this limit, the thermodynamics of MgH_2 nanowire will approach that of bulk MgH_2 and that of Mg will approach bulk Mg. The hydrogenation process in A3 type of nanowire is shown below:

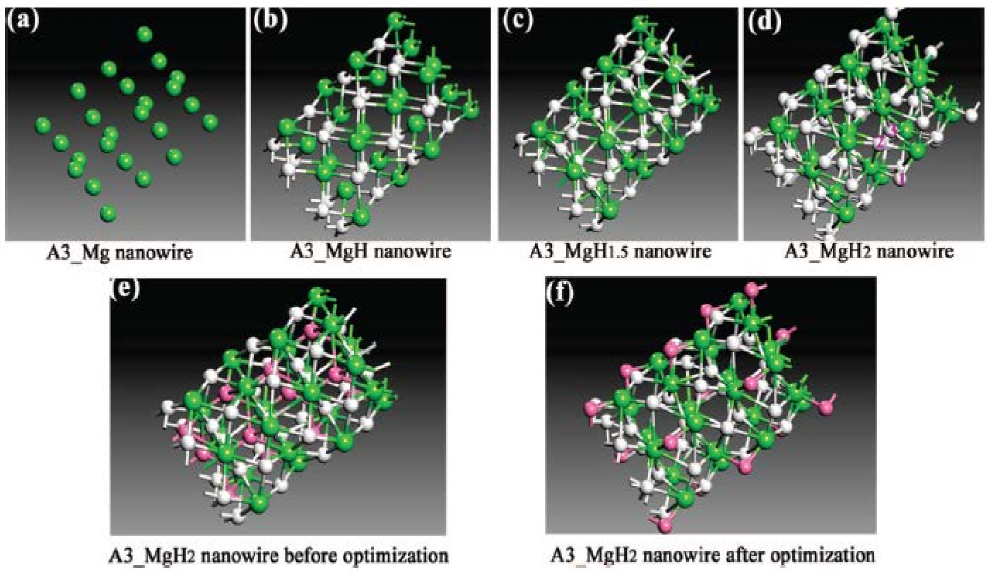

Fig 8 [9]: Hydrogenation in A3Mg and $A3MgH_2$ Nanowire. Optimization here refers to the movement of hydrogen atoms to energetically favorable positions

The A2 and A3 forms have been found to hold more hydrogen than A1 form because they are thermodynamically more stable. The hydrogen storage in A2 and A3 is 8.8 and 8.3 wt% as compared to only 7.6 wt% in the original structure of MgH_2.

3. Storage of Hydrogen in Inorganic Nanowires/Nanotubes: [11]

a. Overview:

There is a great demand for the cleaner and renewable sources of energy due to the increasing levels of CO_2 in the earth's atmosphere. And here the nanowires come into picture. They can be used for hydrogen absorption as well as desorption. Hydrogen is considered as one of the best alternatives for the present choice of fossil fuels because it is cleaner, non-toxic, light weight, highly volatile and also the oxidation product produced is water vapor which is again a clean product. Thus apart from the carbon SWNT, inorganic materials like the oxides, nitrides and carbides are also used to construct the nanostructures like nanowires. As already discussed in the above methods that the synthesis is possible by chemical methods like vapor-liquid-solid, hydrothermal synthesis etc. or by the physical methods like nanolithographic techniques.

b. Traditional Hydrogen Storage in PEC Cells:

The photo-electrochemical (PEC) cells are prepared using Si which is a low band-gap material with a band-gap of 1.12eV. Si is used to make the nanowire- based PEC cell using p-type nanowires by using vapor-liquid-solid method. Hydrogen is produced by the PEC electrolysis of water by the process known as photolysis which we have already discussed before. This hydrogen can then be used for various purposes like in the fuel cell stack. The wt% of hydrogen that can be produced could not be clearly established. The nanowires are utilized in making the PEC cells electrodes like for example Hematite which have proper band gap and is electrochemically stable. Nanowires overcome the problem of slow water oxidation at the interface leading to charge recombination in Hematite.

c. Using Nanowires for Cell Electrodes:

The anode and cathode used in the cell can both be semiconductors but they have to meet certain requirements like the energy of the valence band should be greater than the water oxidation potential of 1.23eV and the energy of the conduction band should be less than the water reduction potential of 0eV. Also the movement of the electrons i.e. the charge from the surface to the electrolyte should be faster than the decomposition reaction. Thus, considering all these factors, nanowires are seen as the best possible materials for the electrodes as explained in the above paragraph.

The nanowires have higher surface to volume ratio and hence provide larger area for the reaction to take place and hence generate larger current. Also due to the small dimensions of the nanowires, the distance through which the minority carriers have to diffuse is small and hence the reaction is almost free of recombination losses which was a major problem in the case of Hematite. The process involves the oxidation of water and the movement of the electrons to the opposite electrode for reduction. The long height of the nanowires helps in higher amount of light absorption and smaller diameter decreases the diffusion length. The charge can be transferred to the back-contact without the loss due to the random pathways i.e. there is proper charge confinement.

4. AlN Nanowire as Hydrogen Storage Material: [12]

a. Overview:

The materials used for the storage of hydrogen demand that they should be lighter than Al so that the gravimetric density of hydrogen stored in them is atleast 6 wt% and they should have the binding energies in between physisorption and chemisorption energies so that hydrogen can be adsorbed/desorbed in the temperature range of -20 to 50^0C at a pressure of maximum 100atm. In order to accomplish this, it was thought that the transition metal atoms present on the nanowires can bind hydrogen in quasi-molecular form and thus the H-H bond gets stretched and hence gets weaker and can be easily broken at room temperatures. However, these metal atoms can form clusters and hence undermine the hydrogen storage capacity.

b. Study Undertaken:

In order to avoid the cluster of these metal atoms, various light metal atoms are studied and it has been found that Al ions have strong affinity for hydrogen atoms and this decreases the interaction energy. The main concern is now to find the materials which can accommodate the aluminium ions in them without the issue of the clustering of metal atoms. The AlN (wurtzite structure) nanostructure has the unsaturated sites which results due to the movement from the four-fold geometry in bulk to two or three fold geometry in these nanostructures. These sites adsorb hydrogen atoms.

c. AlN Nanowire:

AlN nanowire is prepared by using a 5x5x2 AlN bulk supercell. The process involves the removal of all the Al and n atoms form the inner and the outer part and vacuum is used in the empty space in between to form the nanowires. The wire extends infinitely in the 0001 direction with three AlN pairs in the cross section. The nanowire with and without the hydrogen atoms attached is shown below. The desorption can be done in the general way of achieving a particular temperature at a particular pressure. The wt% of hydrogen is approx. 4.7 wt% in AlN nanowires.

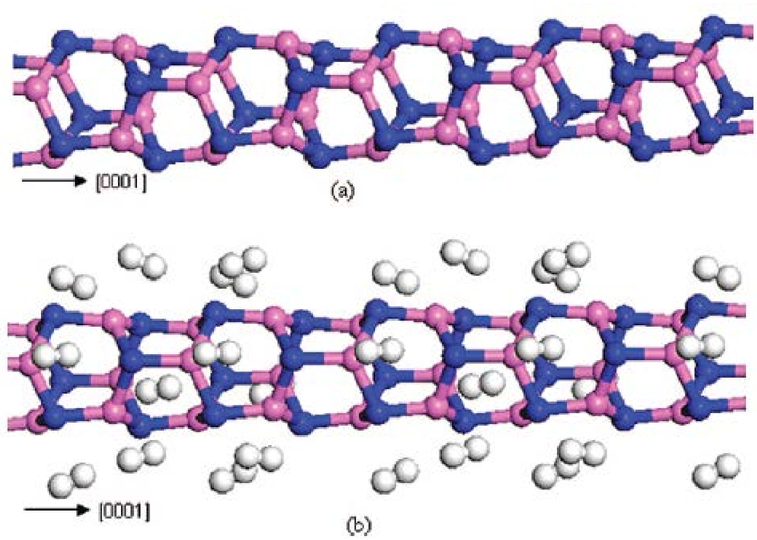

Fig 9 [12]: The AlN Nanowires (a) without and (b) with hydrogen atoms attached. Magenta Spheres are Al Atoms, Blue Spheres are N Atoms While the White Spheres are the Hydrogen Atoms.

5. Porous $Li_2Mg(NH)_2$ @C Nanowires for Hydrogen Storage: [16]

a. Overview:

There has been a constant search on how to obtain a solid-state hydrogen storage materials to use them as energy sources. After a long term research, it is found that the Li-N-H systems can reversibly store 11.5 wt% of hydrogen. One of the other form of this type of the system, $Mg(NH_2)_2$-2LiH composite is considered as one of the best options since it can store 5.6 wt% of hydrogen at a temperature of 90^0C under 1 bar of hydrogen pressure. This meets the requirements for the Proton Exchange Membrane (PEM) fuel cells. The overall reaction is:

$$Li_2Mg(NH_2) + 2H_2 \leftrightarrow Mg(NH_2)_2 + 2LiH$$

b. Process Involved:

There is often incomplete reaction of $Mg(NH_2)_2$ with LiH and hence it leads to the release of ammonia which is toxic. In order to prevent this there has to be a proper contact between the two and hence came the option for the nano-confinement of these complexes. The nanostructures used in his case are porous in nature which will preserve the shape and size of the materials used. This involves melt-infiltration and solution-infiltration but this process is slow so the technique of electro-spinning is used.

The Li-Mg-N-H composite is formed by electro-spinning using the precursors $Mg(NH_2)_2$ and LiN_3. The in-situ carbonization provides the carbon coating on the nanowires produced. The overall reactions involved in the process are:

$$3MgCl_2 + 2Li_3N \rightarrow Mg_3N_2 + 6LiCl$$
$$Mg_3N_2 + 4Li_3N + 12H_2 \rightarrow 3Mg(NH_2)_2 + 12LiH$$

The synthesis of the Li-Mg-N-H NWs is shown in the figure below:

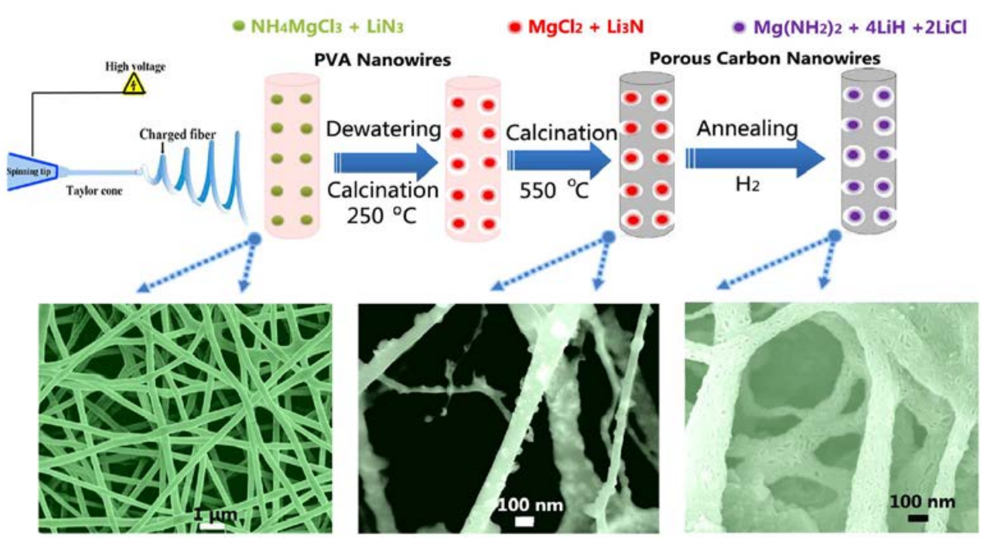

Fig 10 [16]: Diagram Showing the Fabrication of Li-Mg-N-H NWs

Electrospinning is the process of using electrical charge to draw fine fibres from a liquid especially at nano or micro scale. Calcination is the process of heating a material in the presence of air to remove the volatile part or for thermal decomposition.

c. **Findings:**
The desorption temperature of these nanowires has been found to be 78^0C as the onset and 113^0C as the peak. Also it is found that the release of toxic ammonia is somewhat reduced which helps in reversibility. The hydrogenation is fast with a capacity of 5.5 wt% at a temperature of 135^0C. The complete cycle of adsorption and desorption can be completed in an estimated time of 60 minutes with a release of about 5.2 wt% at the temperature of 105^0C. The only problem associated with this method is the degradation of hydrogen capacity due to the release of ammonia but this is a minor problem since the hydrogen content still remains at about 96% even after 20 cycles.

Nanotube Hydrogen Storage: [13]

Now a days, the SWNT are being used for the hydrogen storage. The nanotubes are gradually replacing the nanowires in the practical applications but the nanowires are still an important option for hydrogen storage. They cannot be used directly because in order to assess the amount of hydrogen stored in SWNT they have to be sonicated in dilute nitric acid solution with a high-energy probe. This process cuts the SWNT into shorter segments and introduces $TiAl_{0.1}V_{0.04}$ alloy, which is a metal hydride, which can be helpful in estimating the amount of stored hydrogen. The SWNTs which do not contain metal impurities are then used and this particular metal hydride is then added step by step to determine the wt% of hydrogen.

Reports on Hydrogen Storage:
All the reports on hydrogen storage so far have been divided into the following 3 categories by the researchers:

1. Un-physical reports with H/C ratios exceeding 2 (approx. 14 wt% H)
2. Reports matching the expectations with high surface area carbons (approx. 0 wt% H)
3. Reports which show the hydrogen percentage from 1-14 wt%

Carbon Nanostructures for Hydrogen Storage:

The storage of hydrogen by the use of the carbon nanotubes or graphite nanofibres (to almost 30-40 wt %) has been reported to be as an impossible task. Later on it was found that the molecular hydrogen phsisorption is possible but is only useful at the cryogenic temperature i.e. a temperature of below 123K and also there is a requirement of large surface area carbons. The atomic hydrogen can be obtained only at high temperatures of 400^0C. The physisorption limit is about 6 wt% while that of chemisorption is about 8 wt%. Chemisorption involves covalent bonding.

Efforts have been made to make it possible to adsorb hydrogen at room temperature but it is still not practically feasible. There is a strong need to study the surface and bulk properties of the materials so that effective adsorption of H_2 can be done but the involved properties are still under study. The study involves a huge cost and is often questioned because the % of hydrogen that can be stored in the carbon based materials like the nanowires etc. is very small so not many scientists agree to the research in this field.

Some of the common carbon structures that can be used for hydrogen storage are shown in the following figure:

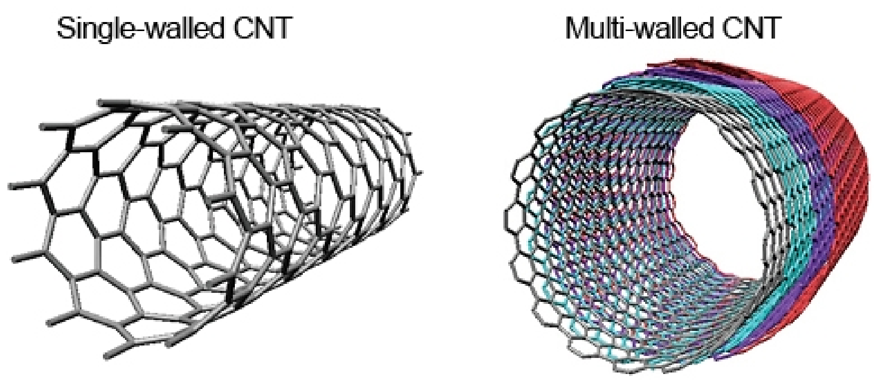

Fig 11: (a) Single-Wall Nanotube (SWNT) (b) Multi-wall Nanotube (MWNT)

Present Day Approach:

We saw the hydrogen storage for the different nanowires and the procedure used in them. The type of the tubes or wires i.e. the wires with different chirality or diameter can lead to different hydrogen storage capacities. The variation in the percentage of stored hydrogen can also be a result of the lack of control of the sonication step in different nanotubes or it can be the lack of technology to achieve the required conditions of temperature and pressure in the case of the nanowires.

The hydrogen storage in nanowires is higher in terms of wt% than the conventional method of storing it on the activated carbons. The following table provides a list of the materials used in hydrogen storage along with the density of hydrogen stored at the indicated temperature and pressure values.

Material	Density wt%	Temp (K)	Pressure (MPa)	Reference	Year
GNFs (herring bone)	67.55	RT	11.35	Chambers	1998
GNFs (platelet)	53.68	RT	11.35	Chambers	1998
Li-MWNTs	20	~473-673	0.1	Chen	1999
K-MWNTs	14	< 313	0.1	Chen	1999
GNFs (tubular)	11.26	RT	11.35	Chambers	1998
CNFs	~10	RT	10.1	Fan	1999
Li/K-GNTs (SWNT)	~10	RT	8-12	Gupta	2000
GNFs	~10	RT	8-12	Gupta	2000
SWNT (lo purity)	5-10	273	0.04	Dillon	1997
SWNT (hi purity)	8.25	80	7.18	Ye	1999
CN nanobells	8	573	0.1	Bai	2001
Nano graphite	7.4	RT	1	Orimo	2000
SWNT (hi purity + Ti alloy)	6-7	~300-700	0.07	Dillon	2000
GNFs	6.5	RT	~12	Browning	2000
CNFs	~5	RT	10.1	Cheng	2000
MWNTs	~5	RT	~10	Zhu	2000
SWNT (hi purity + Ti alloy)	3.5-4.5	~300-600	0.07	Dillon	1999
SWNT (50% purity)	4.2	RT	10.1	Liu	1999
Li-MWNTs	~2.5	~473-673	0.1	Yang	2000
SWNT (50% purity)	~2	RT	echem	Nutzenadel	1999
K-MWNTs	~1.8	< 313	0.1	Yang	2000
(9,9) array	1.8	77	10	Wang	1999
MWNTs	< 1	RT	echem	Beguin	2000
CNF	0.1-0.7	RT	0.1-10.5	Poirier	2001
(9,9) array	0.5	RT	10	Wang	1999
SWNTs	~0.1	300-520	0.1	Hirscher	2000
Various	< 0.1	RT	3.5	Tibbets	2001
SWNT (+ Ti alloy)	0	RT	0.08	Hirscher	2001

Fig 12 [13]: Hydrogen Storage in Various Materials (GNF: Graphite Nanofibres)

It has been found that in the case of nanotubes:

1. The amount of hydrogen stable at room temperature on SWNT basis is in between 5 to 10 wt%.
2. Initial heating in vacuum can be helpful in removing the pre-adsorbed species.
3. Oxidation of SWNTs in H_2O can improve the storage capacity by a factor of three.
4. Infrared absorption spectroscopy measurement of the original and the hydrogen containing samples showed that no new C-H bonds are formed in this process.
5. Hydrogen adsorption capacities can be different for the different SWNT materials i.e. the repeatability is poor.

Variation in Hydrogen Storage Capacity of Various SWNTs:

It was found that the different SWNT samples that are tabulated in the table above can have different storage capacities. On possible reason for such a variation can be the ultrasonic process which is used to cut them to introduce the metal hydride. Thus the manner in which the alloy particle is incorporated in the sample is of importance. The $TiAl_{0.1}V_{0.04}$ particles capable of making an intimate contact with the SWNTs may be seen as activators for the tubes for hydrogen storage.

It has been observed that the variation in cutting and alloy incorporation occur even when the external parameters like sonication time, sonication power and hydrodynamics are under control.

In order to overcome these problems, a new technique of dry-cutting is now being studied. Under this technique, it is found that the D/G ratio is an important factor for determining the degree of cutting in the nanowires. The D here refers to the D band which is the SWNT Raman mode at 1350 cm^{-1} while G refers to the G band which is the SWNT Raman mode at 1593 cm^{-1}. It has been found that the same increase in the magnitude of this ratio for all the samples under similar cutting technique leads to optimization of hydrogen storage capacities.

Risks and Hazards of Nanotechnology: [14]

We have seen that the nanowires can be used for hydrogen storage and this hydrogen can be used for the energy needs in future. But inspite of these advantages of the nanowires, there are certain disadvantages associated with this technology which are often ignored.

a. Since the nanotechnology deals with the particles at the nano-scale so the properties associated with materials can be quite different than the macro counterparts. These properties include the thermal conductivity, mobility etc.
b. The risks involved with the nanotechnology are still under study and not much is known about the effect of the nanostructures on the environment as well as the human health.
c. The risks involved using the nanostructures include toxicity, explosions, dust inhalation etc.

1. **Health Hazards:**
   In working with the nanostructures, the particles due to their high mobility, can enter the human body through skin, through air we breathe or through what we eat. This can lead to various diseases like lung cancer, inflammation of the airway, neurodegenerative diseases, lung cancer etc.

2. **Fire and Explosion Hazards:**
   Carbon-containing and metal dust can explode if they are allowed to form aerosol at a high concentration and if oxygen is present. Since the surface to volume ratio of the nanoparticles is very high so they are more prone to explosion than their macro counterparts. Thus, as the size is decreased, the particles become more prone to explosion.

3. **Environmental Hazards:**
   Very little is known about the impact of the nanostructures like nanowires etc. on the environment and only a few texts are available online which show the study undertaken in this direction. One of the major concern is that how these structures will affect the animals or the plants. They can enter the food chain through the microorganisms present in soil and plants which get affected by the waste discharged from the production facilities, wastewater treatment plants and others. Thus they can enter human body through fish or plants.

Risk Assessment and Safety Precautions:

The risk can be estimated by the general formula:
Risk = (toxicity) x (exposure)
It is important to evaluate the risk and then take the steps to avoid any damage. This includes four steps: identifying the hazard, assessing risk, preventing or controlling risk and evaluating the effectiveness of control measures. When working in an organization, there is generally a Material Safety Data Sheet (MSDS) which contains information regarding the behavior of the nanostructure under study and it can be used in case of emergency.

Exposure Control:

The exposure can be avoided by using liquid suspension instead of powdered material. Also the after effects can be avoided by using the High Efficiency Particulate Air (HEPA) Filter for 300nm nanostructures or Ultra Low Penetration Air (ULPA) Filter for 120nm structures. Mats can be used in the laboratories along with the hand protection like the latex gloves and eye protection.

Future Directions for Hydrogen Storage Material Design: [15]

1. We studied the storage of hydrogen in the nanowires so that the need for energy can be met. But now a days, the nanotubes are replacing the nanowires in this field too. For an instance, the SiC nanotubes are being used to store hydrogen which can give a storage capacity of about 7 wt% as compared to nanowires where it is only limited to about 6.5 wt% in most of the cases.
2. There is still need for great amount of research before we can fully rely on hydrogen as the medium of energy in our daily lives. We saw that there are two methods for hydrogen storage/desorption. These are physical and chemical methods. Both the methods have their own advantages and disadvantages. Like for example, most of the chemical methods work under favorable conditions but they are not reproducible.
3. Apart from nanowires and other nanostructures there are also some other materials which can be used for hydrogen storage like clathrates, zeolites and others. Clathrates are the materials which are made up of two or more entities. They have weak bond between them and one molecule encloses the other. Thus hydrogen can be stored in these materials and can be released later by varying the temperature or pressure.
4. It has been found by studies on various elements that the use of the lighter elements makes it possible to store more hydrogen in terms of the gravimetric density.
5. Other possible materials are the MOFs i.e. metal-organic framework which have good reversibility but the temperature required for the process falls in the range of 77K and hence somewhat not suitable for use in the practical applications.
6. Polymerization of monomers with rigid units or cross-linking of polymeric gels gives rise to the Polymers of Intrinsic Microporosity (PIM). The storage capacity is around 2.17 wt% at 77K and 10bar pressure but due to weak interaction with hydrogen, they cannot be used for practical purposes since their capacity to hold hydrogen at ambient temperature is quite low. They have large surface area due to their microporosity.

Thus, it is evident that there is still room for further studies and research in this field. There are many materials which can be options for better storage of hydrogen. Thus the future studies will mostly concentrate on overcoming the drawbacks involved in all the methods and discovering new materials for storage.

Conclusion:

We discussed the various materials in form of the nanowires which are possible for hydrogen storage. We started with the nanowires, what they are and how they are synthesized. Then we moved towards the hydrogen storage and it's desorption. We discussed why hydrogen storage is so important and what are the various methods that can be used to produce hydrogen?
Most of the report is based on the various types of the nanowires like the ZnO, Mg, AlN, inorganic, porous Li-Mg-N-H nanowires which are used today for the adsorption/desorption of hydrogen. Each part viewed the whole process involved.

At the end of the report, the disadvantages and problems associated with the working of the nanostructures are listed. It is listed that how they affect the environment as well as the human health and how they enter the food chain.

Finally the future works possible in this field have been listed. Few examples of the materials that can be used in future for hydrogen storage have been given. Apart from all of this, the search for novel materials that are able to store more than 10 wt% of hydrogen continues.

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