



NANOYOU Teachers Training Kit in Nanotechnologies

Chapter 3 – Energy

MODULE 2- Applications of Nanotechnologies

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Contents

<i>Solar Energy</i>	6
<i>Photovoltaics</i>	7
<i>Nanocrystals</i>	8
<i>Biomimetic approaches using nanotechnologies</i>	8
<i>Artificial photosynthesis</i>	9
<i>Quantum dot sensitised solar cells</i>	10
<i>Lotus-mimicking PV coatings</i>	11
<i>Solar energy storage</i>	12
<i>Solar heating</i>	12
<i>Hydrogen Society</i>	12
<i>Hydrogen production</i>	13
<i>Nanotechnologies for improving photoinduced water splitting</i>	14
<i>Hydrogen storage</i>	15
<i>Solid metallic nanostructured supports</i>	16
<i>The hydrogen fuel cell</i>	17
<i>Proton exchange membrane fuel cell</i>	18
<i>Thermoelectricity</i>	19
<i>Rechargeable Batteries</i>	21
<i>Nanotechnologies to impact energy capacity, battery power, charge rate and lifetime</i>	21



NANOYOU Teachers Training Kit – Module 2- Chapter 3

<i>Nanomaterials as alternatives to conventional electrodes</i>	22
<i>“Paper battery”</i>	23
<i>Battery operation range, lifetime and safety</i>	23
<i>Supercapacitors</i>	24
<i>Energy Saving</i>	25
<i>Catalysis</i>	25
<i>Advanced materials</i>	26
<i>Insulators and “smart” coatings</i>	26
<i>Energy-harvesting materials</i>	27
<i>Efficient lighting</i>	28
<i>Efficient energy transport</i>	29

Chapter 3: Applications of Nanotechnologies – Energy

Today's world energy demands are satisfied mainly via the combustion of fossil fuels. Of the 210 million barrels of oil equivalent per day used worldwide, about 85 million barrels come from oil; the rest comes from coal (23%), gas (17%), biomass (17%), some fission (5%), a small amount from hydroelectric power (6%) and almost none from renewable resources (**Figure 1**).

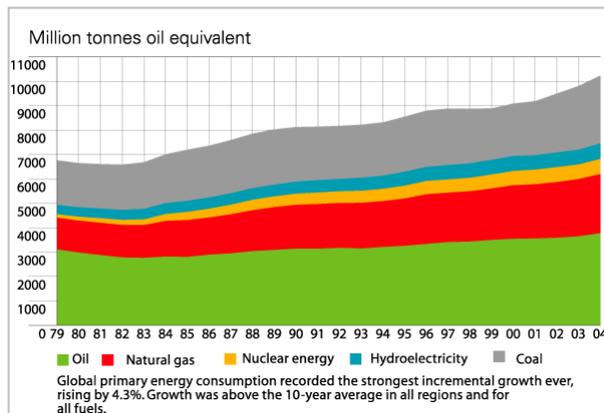


Figure 1 Global primary energy consumption.

It is estimated that by 2050 we will need twice the amount of energy that we are burning or consuming today (about 14 Terawatts, TW) and that most energy will have to come from solar, wind and geothermal (50%) energy. By then it is expected that the world's population will rise from today's 6.3 billion to 9 billion people. Relying on fossil fuels (oil, coal and natural gas) to "feed" the world's future energy needs is not a responsible

environmental option, since there is some evidence that the combustion of fossil fuels is the

main cause of the high levels of greenhouse gases such as carbon dioxide (CO₂) that are accumulating in the atmosphere, with consequent dramatic worldwide climatic changes.

Ranking	Problem
1	Energy
2	Clean Water
3	Food
4	Environment
5	Population
6	Disease
7	War/Terrorism
8	Poverty
9	Education
10	Land

Table 1: List of the most important problems facing humanity in the next 50 years (adapted from R. E. Smalley, Future Global Energy Prosperity: The Terawatt Challenge, Materials Matters Bulletin, Vol. 30, June 2005, 412-417).

But the problem is not limited to the environmental impact of using fossil fuels. The availability of fossil fuels is limited and the supply presently decreasing; consequently, as the demand for energy increases, so does the cost of fossil fuels. Affordable energy is instrumental for basically every aspect of our present societies,

including preserving global peace. In fact, in the list of the most important problems facing humanity in the next 50 years, energy is on the top (**Table 1**). The reason is that affordable energy is fundamental for dealing with the other problems listed there: the availability of clean water, food, down to poverty and education.

So we are presently facing an “*energy challenge*” and there is an urgent need for energy resources alternative to fossil fuels. Of these, renewable energy sources that are CO₂-neutral¹ (solar, wind, geothermal, hydro, etc.) are an option. However, a tremendous technology breakthrough will need to occur in the next years to make the conversion of these energy resources an efficient and economically viable option. Solar energy is an excellent example. Every day the Earth is hit by 165,000 TW of solar power; in the words of Nobel Prizewinner Richard E. Smalley, every day “we are bathed in energy”.² The problem is that renewable energy sources like solar energy are not constant in time and evenly distributed geographically (**Figure 2**). Therefore, solar energy collection, conversion, storage and distribution are major challenges: the entire process needs to be efficient and cost effective. Current

¹ CO₂-neutral here designates an energy carrier that does not directly produce CO₂ upon conversion (like solar energy or hydrogen).

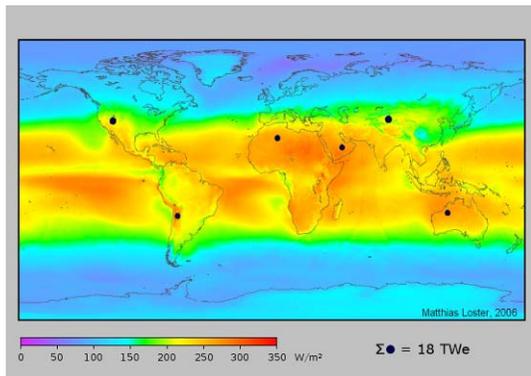
² ‘Energy challenge’ discussed by Professor R. E. Smalley see <http://smalley.rice.edu>

solar panels have about 15-20% energy conversion efficiency and they are very expensive. Since solar light is only available during part of the day, suitable storage solutions also need to be found.

Another alternative energy carrier is hydrogen, but hydrogen fuel cell technology will have to face a number of issues (e.g. hydrogen extraction, hydrogen storage, fuel cell lifetime and cost, just to mention a few) before a hydrogen economy can become a reality. Solving the future energy challenges requires not only advances in the field of energy conversion and storage, but also energy saving, considering how much energy is wasted today using conventional incandescent lights. As discussed in this paper, nanotechnologies not only have the potential to solve many of the issues that the energy sector is facing, but their application to this sector has already resulted in advanced research projects and some commercial realities.

Solar Energy

Among the renewable sources of energy, solar energy holds a great potential. Solar light, however, is not constant, it is only available during part of the day, and it is geographically uneven: some countries receive a much higher illumination than others. **Figure 2** gives an idea of the area that should be covered worldwide in order to produce a little more than the world's current total primary energy demand (assuming a conversion efficiency of 8%). The main problem associated with this form of energy is not



its supply, but the development of devices that will allow its efficient and cost-effective conversion into electric current.

Figure 2. Solar power systems installed in the areas defined by the dark disks could provide a little more than the world's current total primary energy demand (assuming a conversion efficiency of 8%). Colours in the map show the local solar irradiance averaged over three years (Image credit: http://www.ez2c.de/ml/solar_land_area/)

The second biggest problem is its storage and efficient transport. The areas that are most irradiated are desert, therefore in most cases remote from the main urban centres, so transporting this energy where it is most needed becomes a challenge. Making solar energy a viable alternative to fossil fuels therefore

requires a series of advances that will most likely be possible through fundamental research into solar energy conversion, storage and transport. Many of these advances are likely to be enabled by nanotechnologies.

Photovoltaics

A photovoltaic (PV) device is a device which converts solar energy into electricity. In a **conventional photovoltaic cell** there are two separate material layers, one with a reservoir of electrons that functions as the negative pole of the cell, and the other having vacancies of electrons, the electron holes, that functions as the positive pole. When sunlight or other light sources are absorbed by the cell, enough energy is provided to the cell to drive the electrons from the negative to the positive pole, creating a voltage difference between them. In this way, the cell can serve as a source of electrical energy. The efficiency of a PV depends on the type of semiconductor it is made of, and on its absorbing capacity. All semiconductors absorb only a precise “energy window” (the “band gap”) which is **just a fraction of the entire solar energy available**. Presently, maximum energy conversion efficiency (around 15-20%) in a PV cell is obtained when it is made of crystalline silicon (Si). This is an excellent conduction material, abundant and widely used in electronics, but has the main drawback of being very expensive to produce, which is reflected in the high cost of current PVs. This has limited their use. Alternative, cheaper materials, such as TiO_2 , can be used in PV technology. TiO_2 is a well known non-toxic semiconducting material, but has the characteristic of absorbing only the UV region of the solar spectrum, which represents only about 5% of the total solar energy available. This material therefore leads to cheaper PVs but with lower energy conversion efficiency.

As will be discussed here, nanotechnologies offer the possibility of introducing alternative materials and fabrication methods to produce cells with tailored absorption characteristics in order to absorb a larger portion of the solar energy spectrum. In order to meet the “energy challenge” through solar energy, conversion efficiencies in the order of 45% are needed so research in this area is very intense and numerous different types of nanomaterials are being investigated. In order to reach this ambitious goal, devices must be made of materials that absorb the visible part of the solar spectrum, which represents about 46% of it.

There are basically two approaches being investigated:

1. Development of silicon nanocrystals engineered to absorb more solar energy;
2. Biomimetic approaches, where the photovoltaic device is engineered to mimic the best known solar-conversion process ever made, the natural photosynthesis molecular machine.

Nanocrystals

The limitation of silicon is not only related to its processing cost. Due to its indirect band gap, silicon is weak in absorbing light – only a fraction of the solar spectrum is absorbed. This is where nanoscience can help: in sufficiently small nanocrystals the band gap becomes quasi-direct, which gives rise to strong light absorption. Thus the optical properties of silicon can be improved by adding nanocrystals. One such example is silicon-based tandem solar cells, where the top cell is based on nanocrystals, while the bottom cell is a standard silicon cell. Inside the solar cells the nanocrystals are used to increase the generation of current.

Biomimetic approaches using nanotechnologies

Nature has developed a “splendid molecular machine”³ that enables the conversion of solar energy into chemical energy through a process called photosynthesis. In this process solar energy is converted into stored chemical energy (in the form of carbohydrates). The process is an amazing example of a natural nanotechnology which serves as an inspiration for creating biomimetic devices capable of converting solar energy into other forms of energy. In photovoltaics the aim is conversion of solar energy into electricity, to be used for powering electrical appliances. In photosynthesis, light is “captured” by light-harvesting antennae (e.g. chlorophyll) in which photons are absorbed, exciting electrons to higher energy states. **The pigment in the “antenna” absorbs strongly in most of the visible region of the solar spectrum.** The energised electrons are transferred to a series of reaction centres which are called Photosystem I and Photosystem II. In these reaction centres a series of photochemical electron transfer reactions occur involving quinines. Eventually the energy is transferred through proton bonds to another reaction centre where the energy is stored in the bonds of the ATP molecule, which reacts further to form NADP⁺. In the final step of the process, hydrogen is taken from water (forming NADPH), releasing

³ P.D. Boyer, ‘The ATP synthase – a splendid molecular machine’. *Annual Review of Biochemistry*. 66 (July 1997), 717-49.

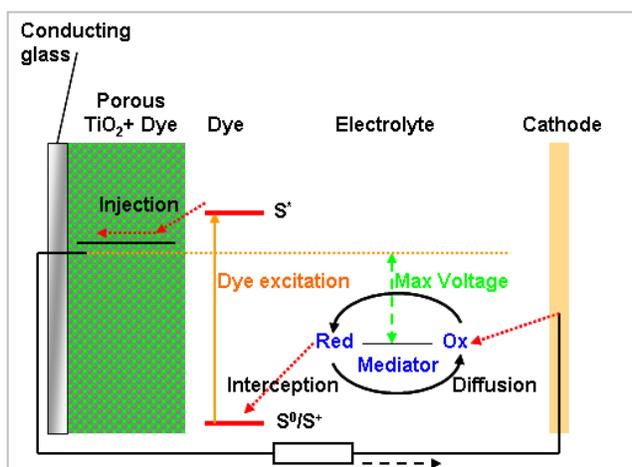
oxygen as a by-product. The NADPH stores energy until it is used in the next step of the reaction to provide energy for the formation of C-C bonds, consuming carbon dioxide in the process. The end product is carbohydrates. Therefore the overall process consumes water and carbon oxide, and produces carbohydrates, which are the fixed form of carbon that is the food base for all animal life.

Artificial photosynthesis

Some researchers have been able to extract the complex Photosynthesis I from spinach and use it to power solid-state electronic devices. This represents an example of a biomimetic solid-state photosynthetic solar cell. Creating the interface is not trivial because in the plant the complex requires salts and water to function, which obviously cannot be used in electronic devices, so surfactants are used instead. The device is made of alternating layers of conducting material (gold), biological material, semiconducting layer, and a conducting layer on top. The conversion efficiency of the device is 12%.

Dye-sensitised solar cell

The second approach is a hybrid between conventional photovoltaics, which uses semiconducting materials, and artificial photosynthesis. To date this seems the most promising approach to improve PV efficiency. In this approach, to the surface of the semiconductor (e.g. TiO_2) are attached some other strongly absorbing species (“dye”) which mimic the function of the chlorophyll. These type of cells are called dye-sensitised cells, or “Grätzel cells” from the name of their inventor, or **photoelectrochemical cells** (PEC). The complex dye molecules (called sensitisers) are attached to the surface of a mesoporous titanium oxide. The difference from a classical thin-film PV is that there light is absorbed in a semiconductor layer, whereas in **the Grätzel cell absorption occurs in the dye molecules**.



The *dye molecules* act somewhat like an antenna (mimicking chlorophyll), meaning that more of the light of a particular colour can be captured but also that a wider range of colours of light can be absorbed compared to pure TiO_2 , in this way increasing the efficiency of the device (**Figure 3**).

Figure 3. Schematic representation of the operation of the dye-sensitised electrochemical photovoltaic cell (Grätzel cell). (Image credit: L Filippini, iNANO, Aarhus University, own work).

In the Grätzel cell the anode is made of **mesoporous dye-sensitised TiO₂** and receives electrons from the photo-excited dye which is thereby oxidised. The oxidised dye in turn oxidises the mediator, a redox specie that is dissolved in the electrolyte. The mediator is regenerated by reduction at the cathode by the electrons circulated through the external circuit. The mesoporous nature of the titanium oxide provides an enormous internal surface area, thereby reducing the amount of material needed in the cell. The titanium oxide films are produced from a nanoparticle suspension (which is synthesised to form a stable porous material). Specific synthetic dyes are under development to increase light absorption. These cells are extremely promising because they are made of low-cost materials and do not need elaborate apparatus to manufacture. Current scale-up of production utilising polymer materials and roll-to-roll continuous production has the potential to produce the large areas of solar cell required to capture significant amounts of solar energy. Some companies, such as DyeSol, are already producing and selling these types of solar cells, with conversion efficiencies of about 12% (**Figure 4**).



Figure 4. A dye solar cell (DSC) commercialised by DyeSol (source: www.dyesol.com)

Quantum dot sensitised solar cells

Another possibility is to use semiconductor nanocrystals (known as quantum dots, QDs) instead of the photosensitive dyes used in the Grätzel cell. For example, CdS, CdSe, InP and InAs quantum dots have been combined with mesoscopic networks of TiO₂ nanoparticles to obtain **quantum-dot-sensitised solar cells (QDSSCs)**. In general, QDs offer several advantages compared to organic dyes such as those employed in a Grätzel cell: **they provide the ability to match the solar spectrum better because their absorption spectrum can be tuned with particle size**. An important nanotechnology discovery that has a great potential to increase the efficiency of these types of solar cells was reported in May 2006 by a team at the Los Alamos National Laboratory. Researchers from this group found that when nanoparticles of less than 10 nm in diameter made of lead and selenium (PbSe nanoparticles) are illuminated with light they absorb one photon of light but produce up to three electrons. When today's photovoltaic solar cells absorb one photon of sunlight, the energy gets converted to one electron, and

the rest of the photon's energy is lost in heat. Therefore PbSe nanoparticles produce at least twice the electrons compared to conventional semiconductors, a process known as “carrier multiplication”. This nanotechnology discovery could boost the efficiency of today's solar cells from 20-30% to 65%.

***NANOYOU DILEMMA-** The use of nanomaterials in photovoltaic promises to greatly improve the efficiency of these devices. When nanomaterials are encapsulated or contained within a photovoltaic cell, the risk of them coming into contact with the user is very low. The problem may occur when the device comes to the end of its lifetime. There may be problems with disposal of the device, especially if the regulation and control of these devices lags behind their development. In the **NANOYOU Role Play Card Game- Nano-based solar cell** (see www.nanoyou.eu/en/decide) we ask students: “Should solar cells incorporating nanoparticles be commercially manufactured before any associated risks are fully established?”*

Lotus-mimicking PV coatings

The lotus leaf is characterised by being extremely water-repellent, so much that water simply rolls off its surface dragging dirt during the droplets' motion. The consequence is the extreme cleanness of the leaf, which in fact is a symbol of purity in some Indian cultures. The super-hydrophobic properties of the lotus leaf are a consequence of its micro- and nano-topography, as well as its surface chemistry (see **Chapter 2**). Superhydrophobic surfaces are useful to **improve the performance of solar cells**. One of the problems with this technology is that they are kept outdoors and therefore prone to become very dirty. This layer of dirt “masks” the catalytic areas of the solar cells and so reduces their efficiency and lifetime. Coating the solar panel with a superhydrophobic coating keeps the panel considerably cleaner. Because of the nano-surface roughness, the coating is transparent to UV light, a necessity for these types of devices. The superhydrophobic coating is also durable, which further improves the solar panel lifetime.

In one research project, PV cells have been coated with a nanostructured coating which increases the absorption of light. The coating mimics the lotus leaf so it is super hydrophobic, with the effect of also conferring self-cleaning properties on the PV surface.

Solar energy storage

Storage of electrical power is critical for making solar energy a primary power source. The best place to provide this storage is locally, near the point of use. Ideally every house, every business, every building should have its own local electrical energy storage device, an uninterruptible power supply capable of handling the entire needs of the owner for 24 hours. If this were done using today's lead-acid storage batteries, such a unit for a typical house capable of storing 100 kilowatt hours of electrical energy would take up a small room and cost over \$10,000. Through advances in nanotechnology, it may be possible to shrink an equivalent unit to the size of a washing machine, and drop the cost to less than \$1,000.

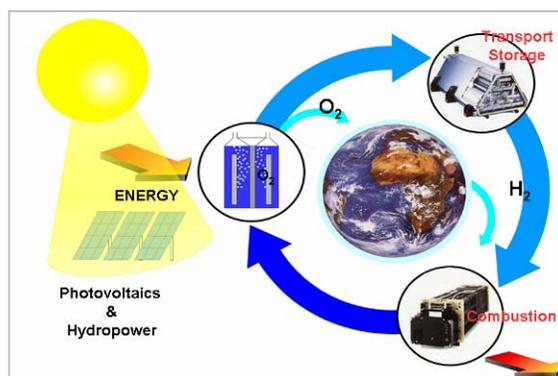
Solar heating

Solar energy can also be used as a heating source to produce hot water, and heat homes and offices. Current systems are able to convert 25-40% of solar radiation into heat. The principle of solar heating is straightforward: a material absorbs sunlight energy and releases it in the form of heat directly to a water source or a heat exchange element (heat pump). Any material that can enhance surface area or have improved absorption properties would improve this technique. Numerous nanomaterials do so. Since the sun is a variable source that produces a diffuse energy, controlling the incident solar radiation is difficult because of its changing position. Nanotechnologies can be used to fabricate complex nano-structured mirrors and lenses to optimise solar thermal collection. Also aerogels with nanopores are used as transparent and thermally isolating material for the cover material of solar collectors.

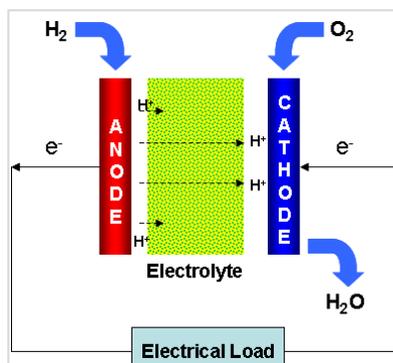
Hydrogen Society

Hydrogen (H_2) can, in principle, be a future environmentally friendly energy carrier when it is produced from renewable energy. The ideal scheme would be to produce hydrogen by splitting water molecules using solar light (as shown in **Figure 5**). H_2 could then be used as an energy carrier to provide electricity in our homes, fuel our cars, etc.

Figure 5. The ideal combination of photovoltaic and hydropower.



The idea of a fuel cell was first conceived in 1839 by Sir William Grove who thought that **electricity could be produced by reversing the process of electrolysis**, in which hydrogen and oxygen are produced by the electrolysis of water.



Hydrogen fuel cells use hydrogen and oxygen as fuel to generate electricity. The fuel molecules in the cell must be ionised to react. The ionisation must be catalysed by the electrodes, and an electrolyte must conduct the formed ionic species so that they can react (**Figure 6**). The sub-product of this reaction is only water – no

Figure 6. Schematic representation of a hydrogen fuel cell. (Image source: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution Share Alike 3.0).

CO₂ is produced during the conversion of H₂ to electricity. The result of the electrochemical process is a maximum of 1.2 V and 1 W cm⁻² of power.

The three fundamental elements of a hydrogen fuel cell are therefore: the fuel (H₂ and O₂), the catalyst and the electrolyte. At present, there are problems associated with each of these elements, making the fabrication and operation of H₂ fuel cells technically challenging and very expensive. However, the technology is developed enough and the worldwide research so intense that consumer goods powered by fuel cells are likely on a large scale.

Hydrogen production

The first problem is associated with the nature of the fuel, hydrogen. Although hydrogen is abundant in nature it is not freely available, it needs to be extracted from a source, such as hydrocarbons (e.g. methane), which produce CO₂ upon extraction, or water. Extraction of hydrogen from water is better. Ideally H₂ should be extracted using a renewable energy source (solar, wind, geothermal, etc.). One of the most promising methods of hydrogen generation is its photochemical extraction from water using sunlight. The idea is to use sunlight to split water into hydrogen and oxygen. This is accomplished routinely and has been for over 3.5 billion years by photosynthetic organisms, but to make it happen artificially is a real challenge!

Nanotechnologies for improving photoinduced water splitting

In principle, visible light at wavelengths shorter than 500nm has enough energy to split water into hydrogen and oxygen. However, water is transparent to this visible range and does not absorb this energy. Therefore, the combination of a light-harvesting system with a water-splitting system is necessary to implement the use of sunlight to split water.

Simple as the concept might sound, several technical challenges must be overcome before this technology can become commercially viable. **Table 2** compares the cost of producing hydrogen from a series of sources, and shows how to date only extraction from fossil fuels is economically viable. Therefore fundamental research is necessary to overcome the limitations of photochemical water decomposition to produce H₂.

Source	US\$/GJ
H ₂ from coal/oil/natural gas	1-5
H ₂ from natural gas minus CO ₂	8-10
H ₂ from coal minus CO ₂	10-13
H ₂ from biomass	12-18
H ₂ from nuclear energy	15-20
H ₂ from wind energy (via land)	15-25
H ₂ from wind energy (via sea)	20-30
H ₂ from solar cells	25-50

Table 2. Comparison of the cost of different types of H₂ sources. For a sustainable economy to exist, the price must be lower than 5 US\$/GJ (Adapted from T.R. Jensen, Hydrogen Fuel Cells, *Aktuel Naturvidenskab* 2004, www.ird.dk with permission from author).

In 1972 A. Fujishima and K. Honda demonstrated the photoelectrolysis of water with a TiO₂ photoanode using platinum as a counter-electrode. Although the reaction is possible, before it can become viable (i.e. both economic and efficient) as a source of hydrogen, two main problems need to be solved.

The first is the limited light absorption of wide-band gap semiconductors (such as TiO₂), in the visible range of the solar spectrum

This problem has already been mentioned in the PV section as it applies to both technologies. Basically photovoltaics and photoinduced water splitting implement the same concept of using sunlight to excite electrons but they differ in how the excited electron (e-h pairs) are used: to drive a current (in PVs) or to drive a chemical redox reaction (in photoinduced water splitting).

As discussed in the previous section, nanotechnology is leading the way in solving some of the problems associated with solar energy conversion with the introduction of nanostructured materials that have

high solar energy absorption rates. Along this approach, the group under the direction of Dr. Misra at the University of Nevada has developed **titanium dioxide (TiO₂) nanotube arrays** having a modified band gap for generating hydrogen by splitting water using sunlight.

The second problem in photoinduced water splitting is the fast electron-hole recombination, which lowers the efficiency of the process. In simple terms, photocatalysis involves harvesting solar photons in a semiconductor (the TiO₂ surface) and subsequent conversion of these photons to electronic excitations, which then induce the desired water-splitting reaction. The excited electron hole pair, though, has a high tendency to recombine. Nanostructures offer the opportunity to minimise the distances (and thus the times) over which charges have to survive and be transported after excitation. Deposition of small noble metal islands (<5nm) or metal nanoparticles enhances the photocatalytic activity of systems that use TiO₂ as the photocatalytic surface. This effect is due to the charge separation across the metal-semiconductor interface. More recent nanotechnology approaches include the use of carbon-doped titania nanotubes arrays, SWCNTs and nanostructured hematite films.

Hydrogen storage

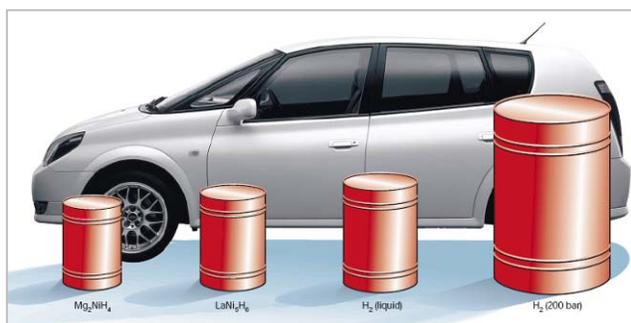


Figure 7. Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image credit: Reprinted by permission from Macmillan Publishers Ltd: Nature (L. Schlapbach, A. Züttel, 'Hydrogen-storage materials for mobile applications', Nature (2001) 414: 353-358), Copyright © 2001.

The combustion of hydrogen is straightforward with no detrimental by-products: $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$. However, a problem exists that relates to its **storage** and **transport** which need to be both efficient and safe. The problem is easily seen by comparing the energy-to-volume ratio for gaseous hydrogen (3.0MJ/L) to that of conventional gasoline (32.0MJ/L). This means that, given the same volume, the energy produced by hydrogen is about ten times lower than that from conventional gasoline. This obviously represents a problem for storing hydrogen in a vehicle; for example: a big, heavy tank would be required to store and transport the required amount of hydrogen (**Figure 7**). Some possible solutions are to use liquid hydrogen (8.5MJ/L), to use compressed hydrogen or to store hydrogen in a solid metallic support such as metal complexes (hydrides).

The use of compressed hydrogen implies using liquid tanks that need to be made of a very strong yet lightweight material. This material should also have outstanding insulating and pressurisation properties, in order to avoid hydrogen leakage. This problem can potentially be solved using nanotechnology to develop new materials with exceptional properties in terms of strength and density.

Solid metallic nanostructured supports

	H ₂ -inhold		Pressure/ Temperature
	Mass- energy density (weight %)	Volume- energy density (g/L)	$p(\text{H}_2)$ in bar (¹)
Pressure tank	4.6	25	300
	ca. 6	58	700
Metal hydride			Temperature in °C (²)
MgH ₂	7.6	110	350
LaNi ₅ H ₆	1.4	121	ca. 50
TiFeH ₂	1.9	107	ca.50
Complex metal hydrides			
LiBH ₄	18.5	121	380
NaBH ₄	10.7	114	400
LiAlH ₄	10.6	87	>125
NaAlH ₄	7.5	94	210
Mg ₂ FeH ₆	5.5	150	320

Table 3. Comparison between various hydrogen storing systems. Notes to table: (1) Hydrogen pressure in a gas tank (700 bar is the target); (2) Temperature for H₂ release at $p(\text{H}_2)=1$ bar, without catalyser. (Adapted from T.R. Jensen, Hydrogen Fuel Cells, Aktuel Naturvidenskab 2004, www.ird.dk)

Solid metallic supports are probably the most viable option for hydrogen storage⁸. In this approach hydrogen is “loaded” to a solid support and extracted from it when needed. The main challenges here are the material loading capacity and the regeneration kinetics to re-extract the hydrogen from the support. The best material would achieve an optimum compromise between having hydrogen too weakly bonded to the storage material, which means a low storage capacity, and a too strongly bonded to the storage material, which would require high temperatures to release hydrogen. Nanotechnology can contribute in this field by developing new molecules that allow high hydrogen loading

capacity and acceptable regeneration kinetics. Researchers aim at developing nanomaterials that are light in weight, low in volume, have high loading capacities, good regeneration kinetics and are low in cost.



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Two candidate materials are complex metal hydrides, which have an intermediate bonding of hydrogen, and nanostructured carbon-based materials, such as carbon nanotubes. The properties of some complex metal hydrides as H_2 storage materials, such as $LiBH_4$, $NaBH_4$ and $NaAlH_4$, are summarised in **Table 3**. In Figure 4 the schematic representation of sodiumaluminiumhydride ($NaAlH_4$) is shown. The structure can be imagined as a salt made of sodium ions (Na^+ , yellow) and a complex ion of aluminium (Al, orange) and hydrogen (blue), AlH_4^- (other examples of complex ions are the ion sulphate SO_4^{2-} and the ion phosphate PO_4^{3-}).

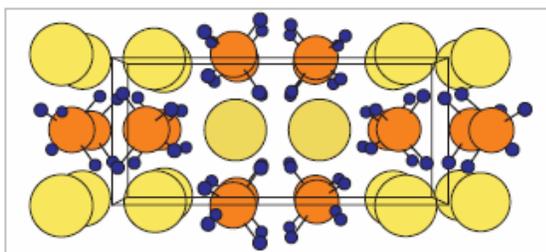


Figure 9. A schematic representation of sodiumaluminiumhydride ($NaAlH_4$), a promising complex hydride for hydrogen storage. Image from: T.R. Jensen, Hydrogen Fuel Cells, *Aktuel Naturvidenskab* 2004, www.ird.dk, *Naturvidenskab* 2004, www.ird.dk

The hydrogen fuel cell

In order for hydrogen fuel cells to become an economically viable alternative to combustion chambers, two other main problems need to be addressed: the **nature of the catalyst** and that of the **electrolyte** in the cell.

Currently, the electrodes in a fuel cell are made of a metal such as platinum (Pt), which is a rare, expensive metal, also sensitive to the CO and sulphur species that are dispersed in the atmosphere. These de-activate the Pt surface (a phenomenon called “poisoning of the catalyst”). Fuel cells operate at high temperatures ($>70\text{ }^\circ\text{C}$) since the poisoning agents at these temperatures tend to de-adsorb. Nanotechnology is already actively involved in addressing some of the issues concerning fuel cell catalysts. Improvements in this area through nanotechnology concern (1) increasing the material catalytic activity; and (2) reducing of rare metal usage. Since the current generated at an electrode is proportional to the active surface of the catalyst, fuel cells that have higher power density can be formed from nanomaterials, which have a higher surface area to volume ratio. Electrocatalytic material properties are also proportional to particle size, so nanoparticles and nanomaterials have increased catalytic activity compared to bulk materials. This characteristic can lead to a reduction of rare metal usage, for example by using carbon nanomaterials as a support for the dispersions of nano-sized Pt, thereby reducing the weight of Pt needed to produce the same surface area of active Pt catalyst. Carbon

nanomaterials are particularly suitable since they act both as a support for the Pt nanomaterial and as a conductor. Suitable carbon nanomaterials are carbon foams containing nanopores, different types of nanotubes and single walled nanohorns.

Proton exchange membrane fuel cell

The electrolyte conventionally used in fuel cells is aqueous KOH operating at about 70 °C (liquid alkaline cell). It leads to corrosion of the electrodes, reducing the cell lifetime, and operates at high temperatures, decreasing the thermodynamic efficiency of the cell. A solid electrolyte is preferred, therefore **modern hydrogen fuel cells use a proton-permeable membrane made of a polymer** (e.g. Nafion®), which has a high proton conductivity due to the presence of water molecules in its structure. In a Proton Exchange Membrane Fuel Cell (PEMFC) the proton ions generated at the platinum anode pass through the proton conducting membrane to the platinum cathode, where they combine with oxygen and form water (Figure 10 illustrates the operational principle of a PEMFC).

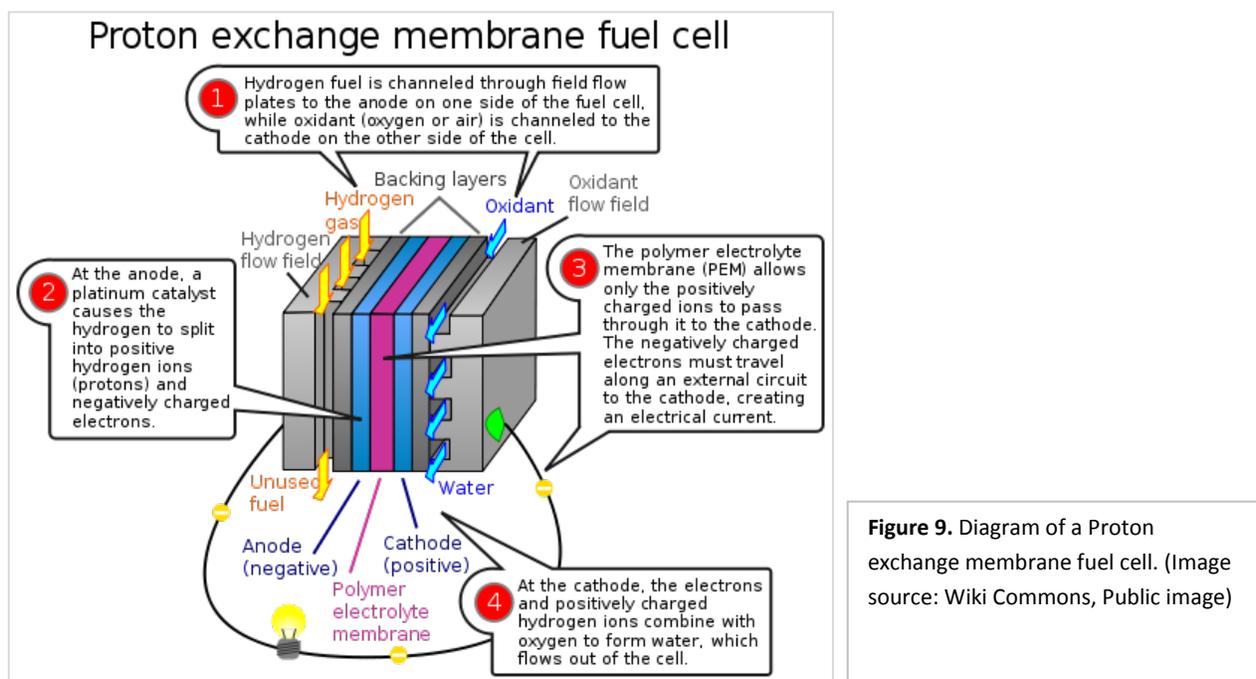


Figure 9. Diagram of a Proton exchange membrane fuel cell. (Image source: Wiki Commons, Public image)

Proton Exchange Membrane Fuel cells (PEMFC) are the most likely fuel cells to achieve commercialisation for automotive purposes thanks to their low operating temperatures and their

inherent properties of being lightweight, producing high current densities and containing no corrosive materials.

An area where improvement is urgently needed, however, is the nature of the solid membrane. Nafion[®], for instance, is expensive, subject to degradation through dehydration at operating temperatures above 100°C, and is not fabricated with nanoscale control; therefore it has pores that are not uniform in size and distribution, so that the active sites on the membrane surface (directly involved in proton binding) are randomly exposed. Other 3-D solid electrolytes have been investigated, but they have the problem of either having very low conductivity (reducing the efficiency of the cell) or requiring high temperatures to operate.

In this context, nanotechnologies can aid in the development of nano-structured solid membranes to increase proton conductivity, cell efficiency and durability. These include ceramic electrolyte membranes (e.g. metal-oxane membranes) and nano-structured solid electrolytes or fillers fabricated with nanoscale control. In addition, fuel cell assembly, durability and cost could in principle be improved by employing nanotechnology to fabricate sturdier cells able to withstand the large changes in temperature required in some applications, such as automotive operation.

Thermoelectricity

Thermoelectric materials (TE) are functional materials that have the double property of being able to convert heat to electricity, and vice versa. Thermoelectricity can be generated in all conductive materials. When a temperature gradient is applied across a wire, electrons diffuse from the hot to the cold part due to the larger thermal speed of the electrons in the hot region. Consequently, a charge difference builds up between the hot and cold region, creating a voltage and producing an electric current. Alternatively, a current can be applied to the wire to carry heat away from a hot section to cooler areas.

Thermoelectric materials can therefore be used for either cooling or power generation. Although current devices have a low conversion efficiency of around 10 per cent, they are strongly advantageous as compared to conventional energy technologies, since the converters have no moving parts and are therefore both reliable and durable. Also, they are scalable and hence ideal for miniature power generation, and no pollutants are released into the environment. If significantly improved thermoelectric materials can be developed, thermoelectric devices may replace the traditional cooling

system in refrigerators. They could also make power generators in cars obsolete by utilising heat from the exhaust gases, or they could possibly be used to convert huge amounts of industrial waste heat into electricity.

Despite their enormous potential, thermoelectric materials have not yet fulfilled their huge promise, and are currently employed only in niche applications, most notably by NASA to generate electricity for spacecraft that are too far from the sun for solar cells to operate. The problem is that for the process to be efficient, the thermoelectric materials need to be a good electrical conductor but a poor thermal conductor, so that the temperature difference inside the material remains. More specifically, thermoelectric materials are ranked by their figure of merit, ZT , which is defined as $ZT = S^2 \sigma T / k$, where S is the thermopower (or Seebeck coefficient), σ is the electrical conductivity, k is the thermal conductivity and T is the absolute temperature. To be competitive with conventional refrigerators and generators, thermoelectric materials with $ZT > 3$ must be developed. Yet in five decades of research, the room-temperature ZT of bulk semiconductors has increased only marginally, from 0.6 to about 1.0. The challenge lies in the fact that S , σ and k are interdependent: changing one alters the others, making optimisation extremely difficult.

However, in the last years, there have been reports of dramatic increases in the properties of TE materials. In all these cases, the material has been found to be nanostructured. Researchers are studying these nanomaterials in detail to understand whether this is a result of quantum confinement or photon dynamics and transport. What is clear is that to have optimum properties, the material needs to have high symmetry at the nanoscale level, and needs to incorporate heavy elements because of their low thermal conductivity.

Some examples of nanostructured TE materials are half-Heusler alloys (ZrNiSn), Zn_4Sb_3 , skutterudines, and novel PbTe-materials (e.g. LAST-18, SALT-20 and LASTT).

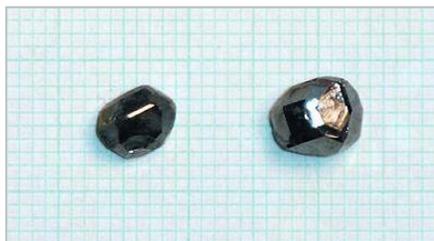


Figure 11. Clathrate crystals produced at iNANO are among the target materials for NASA's high-temperature thermoelectric converters for future Mars missions. Heat for the converters will be provided by radioactive sources. (Image courtesy of iNANO, Aarhus University.)

Rechargeable Batteries

Rechargeable batteries are energy storage devices used to power small electronic equipment such as mobile phones and personal computers, where high power and light weight are important. These same attributes are required for electric vehicles, hybrid electric vehicles, power tool and backup power subsystems. In simple terms, a battery is an electrochemical device that generates DC through a coupled set of reduction-oxidation (“redox”) reactions. The positive electrode is reduced (“captures electrons”) and the negative electrode is oxidised (“releases electrons”). The battery consists of a positive electrode

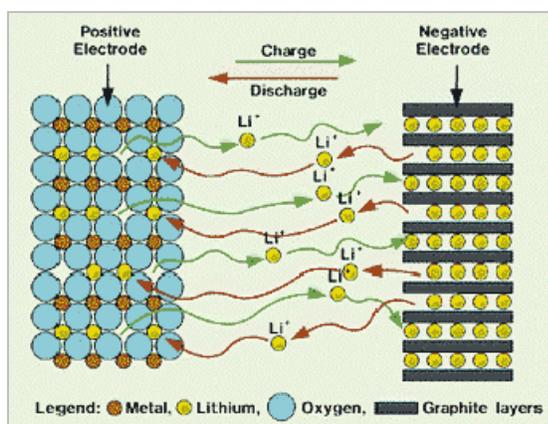


Figure 12. Schematic representation of a lithium-ion battery.

facing a negative electrode divided by a porous separator that prevents the electrodes from touching, and an ionic electrolyte, which is a conduction medium that ensures movement of the ions from one electrode to the other. Intercalation-based batteries using the small lithium (Li⁺) ion are the most used. These batteries have at least one redox-active electrode with an open crystal structure with “holes” capable of intercalating Li⁺. For example, oxidation of Co in LiCoO₂ expels Li⁺ which is taken up in a graphite electrode. When the battery is charged, the Li⁺ moves from the positive electrode to the negative one via the electrolyte. On discharge, the opposite occurs, releasing energy in the process. Ideally, the structure of the redox-active crystal should be capable of reversibly intercalating the small Li⁺ ion.

Nanotechnologies to impact energy capacity, battery power, charge rate and lifetime

Current problems with lithium rechargeable batteries involve a number of issues, the first being the battery energy capacity: in order to allow ions and electrons to move quickly into and out of the active material (allowing fast charging and discharging) the material must be deposited as a thin film. This limits the amount of active material that can be incorporated into the battery (energy capacity). For high-capacity batteries, thickness is increased in order to have more energy storage with the drawback of slower charging.

The second issue concerns the battery power: an important attribute of large format batteries is their capability of delivering power quickly. Power is restricted by the ion removal capability in lithium-

batteries which depends on the electrochemical properties of the battery. There is then the problem of charge rate: batteries need to be recharged, and recharging times are now in the order of hours. The time of charge is restricted by the incorporation rate capabilities of Li^+ inside the graphite electrode.

Lithium-battery lifetime also needs to be improved: in current batteries, every time Li^+ enters/exits the graphite electrode, the pores of the electrode need to expand or shrink. This repeated expansion and shrinkage fatigues the graphite particles, which as a result break apart, reducing battery performance.

Nanomaterials as alternatives to conventional electrodes

Nanocrystalline composite materials and nanotubes can be used to replace the conventional graphite or Li-graphite electrode. These can be fabricated to have voids having the same size as the lithium ions they have to accommodate. This allows packing much more active material into an electrode, increasing energy capacity. A nanostructured electrode with voids having the same size as the lithium ions increases the battery life and also ensures high charge rates. In the future, nanotechnology will also allow a move away from flat layers of electrode materials to positive and negative electrodes that interpenetrate. This 3D nano-architecture could improve the mobility of ions and electrons, thereby increasing battery power.

In this context it is interesting to note the work reported in December 2007 by Yi Cui and colleagues at Stanford University on the use of silicon nanowires as anode material. Bulk silicon has been investigated in the past as an alternative material to graphite since it has a low discharge potential and the highest theoretical charge capacity (more than 10 times that of existing graphite anodes). However, silicon bulk anodes (containing silicon films or large silicon particles) have shown short battery lifetime and capacity fading due to pulverisation and loss of electrical contact between the active material and the current collector. These problems arise from the fact that the volume of silicon anodes changes by about 400% during battery cycling as a result of the anode swelling (battery charging) and shrinking (battery discharging) as lithium ions enter and exit the anode.

The group at Stanford University replaced a conventional bulk silicon anode with one formed of silicon nanowires (SiNW), grown directly on the metallic current collector. In this way they were able to achieve the theoretical charge capacity of silicon anodes (ten times that of current ion-lithium batteries) and to maintain a discharge capacity close to 75% of this maximum. The work has been patented and the discovery has great potential for commercial high-performance lithium batteries.

“Paper battery”

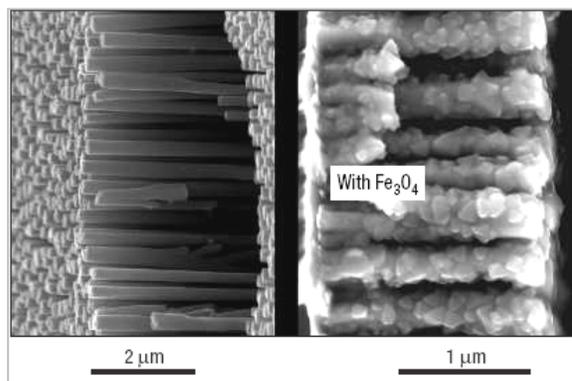
Some exciting work recently reported by scientists at Rensselaer Polytechnic Institute uses a composite material that combines high energy capacity with flexibility. The researchers found that they could combine nanotubes (which are highly conductive) with a layer of cellulose, the material used to make paper. In this way they were able to obtain “paper batteries” which can be rolled or folded just like paper without any loss of efficiency. This opens the opportunity to have batteries moulded to assume a particular form. Like all batteries, the paper version comprises electrodes, electrolyte, and a separator. The first electrode is formed by vertically aligned multiwalled carbon nanotubes, deposited on Si substrates. Plant cellulose is cast on top of the layer, solidified, and dried to form the porous separator. The middle paper layer is then impregnated with an ionic liquid which acts as the electrolyte; this can be an organic salt that is liquid at room temperature. The ionic liquid contains no water, so there is nothing in the batteries to freeze or evaporate. This expands the working temperature range of the battery, which can withstand extreme temperatures from 195 K to 450 K. To make a battery, the second electrode is formed by coating the paper side with lithium oxide. Interestingly, the same material can be used to make a supercapacitor simply by folding the paper in half, so that there is a carbon electrode at both top and bottom. The team were also able to fabricate dual-storage devices containing three electrodes that act as both supercapacitors and batteries.

Battery operation range, lifetime and safety

Li-batteries are at present limited in their operating temperature range. Below 0°C and above 50°C the batteries cannot be recharged, and above 130°C they become unsafe due to thermal runaway. Thermal runaway, which is due to reaction of the graphite with the electrolyte, can also occur due to battery impurities. Finally, Li-batteries are made of toxic metals and are therefore harmful for the environment.

Battery safety can be increased if the graphite electrode in a lithium-battery is replaced with a nanostructured material that is inert towards the electrolyte. Nanotechnology can also be employed to use alternative active materials which are less expensive and non-toxic to the environment. For example, the non-toxic magnetite (Fe_3O_4) has been employed as the active material in a high-capacity Cu nano-architected electrode (**Figure 13**). Nanostructured lithium batteries are becoming a commercial reality, such as the Altairano NanoSafe™ and 123 Systems Batteries.

Figure 13. Cross-sectional views of Cu-nanostructured current collector before (left) and after (right) Fe₃O₄ deposits. (Image credit: Reprinted by permission from Macmillan Publishers Ltd: P. L. Taberna et al., 'High rate capabilities Fe₃O₄-based Cu nano-architected electrodes for lithium-ion battery applications' Nature Materials (2006) 5:567-573, copyright 2006.)



Supercapacitors

Supercapacitors are another way of storing electricity that can benefit from nanotechnology. They are needed in devices that require rapid storage and release of energy, for instance hybrid-electric and fuel-cell powered vehicles. They are constructed of two electrodes immersed in an electrolyte, with an ion permeable separator between them. Each electrode-electrolyte interface represents a capacitor, so the complete cell can be considered as two capacitors in series. The focus in the development of these devices has been on achieving high surface-area with low matrix resistivity. The most remarkable property of a supercapacitor is its high power density, about 10 times that of a secondary battery. The maximum power density of a supercapacitor is proportional to the reciprocal of its internal resistance. A number of sources contribute to the internal resistance and are collectively referred to as Equivalent Series Resistance (ESR). Contributors to the ESR include the electronic resistance of the electrode material and the interfacial resistance between the electrode and the current-collector. Carbon, in its various forms, is currently the most extensively used electrode material in supercapacitors. A typical commercial supercapacitor can produce a power density of about 4 kW/kg. Nanotubes can be used to increase the power density of supercapacitors, since the nanoscale tubular morphology of these materials offers a unique combination of low electrical resistivity and high porosity in a readily accessible structure. Single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) are under investigation. Research has shown that the use of thin film electrodes with multi-walled aligned nanotubes increases the specific power density (laboratory results of 30 kW/Kg have been reported), thanks to reduction of ESR.

Energy Saving

Energy saving can be achieved in numerous ways, such as improving insulation of residential homes and offices; more efficient lighting; and using lighter and stronger materials to build devices which would then require less energy to operate. Also, a large portion of energy is lost during its transport, so there is a need for a more efficient electric grid to transport energy. Nanotechnologies can potentially be applied to all of these energy-saving materials and technologies.

Catalysis

Catalysis is of vital importance in our society and constitutes a cornerstone of life from biological processes to large-scale production of bulk chemicals. The availability of plentiful and inexpensive chemicals relies on industrial catalytic processes and without them it would be impossible to maintain the current living standard of the present human population. Other technologies also depend on catalysis, including production of pharmaceuticals, means of environmental protection, and production and distribution of sustainable energy. As already discussed in some of the previous sections, many technological advances required to **make alternative energy carriers to fossil fuels – such as sunlight and hydrogen – an economically viable option rely on optimising a catalytic process.**

For instance, for water to be split into hydrogen and oxygen with sunlight to feed a fuel cell, researchers need to improve the activity of the catalyst, e.g. TiO_2 .

A typical heterogeneous catalyst consists of a few nanometre-wide catalytically active nanoparticles dispersed on a highly porous support material which can have surface areas up to 250 m^2 per gram. The manufacturing of structures on the nanometre scale has been a central issue in catalysis research and development for decades. This fact relates to the structure of a heterogeneous catalyst, which requires control of materials ranging from macroscopic dimensions down to the nanoscale. Heterogeneous catalysis therefore has in a sense always had a nanoscience component. Since catalytic action takes place at a surface, and catalytic materials are often very expensive (as they use rare materials such as Pt), the goal for chemists has always been to fabricate catalysts with as high a surface-to-volume ratio as possible, so as to maximise the surface exposed to the reaction and minimise the amount of catalyst required.

Advanced materials

Nanotechnology can offer some indirect energy saving solutions by developing materials with better properties. One example is materials with improved strength which make constructions leaner and thus lighter, with an indirect energy saving, for instance in the transport sector (both on the road and in the air). Since a large fraction of the fuel consumption in a car is weight-related, making cars with lighter materials would be a very efficient way of saving energy. Higher tensile strength can be exploited as well as higher possible loads, so that with the same amount of material, stronger components can be built. For instance wind turbines could be capable of sustaining higher wind speeds if they were made of high-strength nanomaterials. Better creep resistance is an advantage in virtually any system for thermal power generation due to the higher operating temperature which is allowed and the concurrent higher efficiency. Nano-coatings with improved corrosion properties have a longer service life in aggressive environments and thus have potential for energy saving throughout their entire lifecycle (e.g. extraction, production, operation, disposal and recycling).

Insulators and “smart” coatings

Insulation is a very effective way of minimising energy consumption, for instance in homes and offices. Nanotechnology offers the possibility of developing new materials with improved insulating properties. One example is nanoporous aerogels to improve thermal insulation. A commercial example is represented by Aspen Aerogels products. This company produces flexible aerogel nanoporous insulation blankets (e.g. Cryogel™) designed for cryogenic applications (for instance, for insulating pipes and tanker ships). These insulation blankets can be cut as normal textiles and installed faster than traditional materials, and their low thermal conductivity requires less material to be used. Additionally, Aspen’s products are resistant to compression and inherently hydrophobic so they can be exposed to water for long periods without damaging the products’ outstanding thermal properties. Nanotechnology applied to indirect energy saving can be found in the form of “smart” materials such as electrochromic and photochromic coatings used for darkening window. They reduce indoor heating in summer, so less air-conditioning is required to keep the atmosphere cool, with consequent energy saving. Another example of nanotechnology applied to smart coatings is the use of a family of wavelength-selective films that is used to manufacture “heat mirrors”.

One of these materials is indium-tin-oxide (ITO), an infrared absorber. A 0.3 nm ITO coating on glass provides more than 80% transmission for the wavelengths predominant in sunlight. The transmission properties of the window can be varied by changing the thickness and material composition of the

coating, so that a combination of materials could be used to produce smart windows that reflect solar energy in summer but transmit solar energy in winter.

Energy-harvesting materials

Numerous innovative electronic devices under development have nano-scale components (see **Chapter 4 – “Information and Communication Technologies”**). Nanodevices do not use much energy, and if the little they need could be scavenged from vibrations associated with footsteps, heartbeats, noises and airflow, a whole range of applications in personal electronics, sensing and defence technologies would open up. In order to be able to do so, an “energy-scavenger” having nano-scale dimensions needs to be included in the device. Also, energy gathering of this type requires a technology that works at low frequency range (below 10 Hz), ideally based on soft, flexible materials. A group working at Georgia Institute of Technology has now come up with a system that converts low-frequency vibration/friction energy into electricity using piezoelectric zinc oxide nanowires grown radially around textile fibres. A piezoelectric material that makes use of piezoelectricity was discovered in 1883 by Pierre Curie and his brother Jacques. They showed that electricity was produced when pressure was applied to selected

crystallographic orientations. Piezoelectricity is thus the induction of electrical polarisation in certain types of crystals due to mechanical stress. ZnO nanowires are such a type of piezoelectric nanomaterial. In the work mentioned above, researchers have grown ZnO nanowires radially around a fibre of Kevlar, which is a material known for its strength and stability. By entangling two fibres and moving them by sliding them back and forth, a relative “brushing motion” is created, which in turn produces an output current.

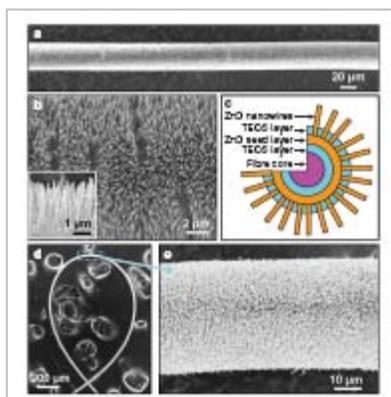


Figure 14. Kevlar fibres coated with ZnO nanowires. (a) An SEM image of a Kevlar fibre covered with ZnO nanowire arrays along the radial direction. (b) Higher magnification SEM image and a cross-section image (inset) of the fibre, showing the distribution of nanowires. (c) Diagram showing the cross-sectional structure of the TEOS-enhanced fibre, designed for improved mechanical performance. (d) SEM image of a looped fibre, showing the flexibility and strong binding of the nanowire layer. (e) Enlarged section of the looped fibre, showing the distribution of the ZnO nanowires at the bending area. Reprinted by permission from Macmillan Publishers Ltd.: Qjin et al. “Microfibre-nanowire hybrid structure for energy scavenging” (2008), 451, pp. 809-13, copyright 2008.

A mechanical energy (sliding motion) is converted into electricity via a coupled piezoelectric-semiconductor process. This work shows a potential method for creating fabrics which scavenge energy from light winds and body movement. In the future these type of nano-energy scavengers could be incorporated in textiles to power personal electronics.

Efficient lighting

Another important application of nanotechnology in the area of energy saving is the production of more efficient lighting devices. Conventional incandescent lights are not energy efficient, a large portion of their energy being dispersed in heat. Solid state light devices in the form of light emitting diodes (LEDs) are attracting serious attention now as low-energy alternatives to conventional lamps. The need is to engineer white-light LEDs as a more efficient replacement for conventional lighting sources. One proposed solution is to use a mixture of semiconductor nanocrystals as the intrinsic emitting layer for an LED device. Simply mixing several colours of nanocrystals together to achieve white light is a possibility, but this would result in an overall reduction of device efficiency through self-absorption between the various sizes of the nanocrystal. An important result that can potentially resolve this problem has come recently from the work of some researchers at Vanderbilt University. They found that crystals of cadmium and selenium of a certain size (called “magic sized” CdSe) emit white light when excited by a UV laser, a property that is the direct result of the extreme surface-to-volume ratio of the crystal. This material could therefore be ideal for solid state lighting applications.

Organic light emitting diodes (OLEDs) represent a promising solution for lighting applications as well as for low cost, full-colour flat panel displays. Quantum dots (QD) are another class of nanomaterials that are under investigation for making more efficient displays and light sources (QD-LEDs). Quantum dots are characterized by emitting saturated and monochromatic light; the colour emitted depends on the size of the QD and the light is emitted under certain conditions, e.g. when current passes to them via conductive polymer films. Recently even white-emitting quantum dots have also been fabricated. Therefore quantum-dot based LEDs are promising light sources and for use in flat-panel displays. The structure and properties of OLEDs and of QD-LEDs is described in detail in **Chapter 4 – “Information and Communication Technologies”**.

NANOYOU DILEMMA- *The use of quantum dots in polymer composites for new forms of light emitting devices (QD-LEDs) is extremely promising for the development of alternatives to conventional light bulbs. In the NANOYOU Role Play Card Game- Revolution for the light bulb (see www.nanoyou.eu/en/decide) we ask students to reflect on the safety aspects of these devices. Like other materials used in electronics (e.g., transistors), quantum dots are often made of toxic metals like cadmium, although in extremely small amounts. Therefore QD-LEDs would need to be properly managed once disposed of, as is the case for all electronics, but even in this case. However, it is not known yet what method should be used to dispose of them, what sub-products they would form, and if disposed improperly, if they could represent an environmental hazard. The dilemma is: “Do we implement the quantum dot technology within an energy efficient light source even though some health and environmental risks remain unanswered?”*

Efficient energy transport

One area where there is a large margin for improvement is in the transport of electric current. As the world’s power demand increases, the burden on the electricity infrastructure grows. This has been recently shown in some nation-wide blackouts like the one that occurred in the north-east of the USA in 2003, and in Italy in the same year. Therefore, a major challenge is to develop new transmission line materials that are lighter and have less energy loss than copper. Single carbon nanotubes (CNT) have the remarkable property of weighing one-sixth as much as copper but with similar or even better conductivity and negligible eddy current loss. This material thus has the potential to overcome some of the limitations of current transmission materials. Before this can become a reality, however, advances their production are needed. At present, scientists produce CNTs often less than 100 nm in length and with widely varying electrical conduction properties. The challenge for the future is therefore to produce nanotubes with controlled properties. Also, the manufacturing must be cost-effective and able to produce cables of fibres with desired electrical properties. At present, therefore, this application remains a vision.