Chapter 12
Applications

12.1 Introduction

The ability of materials to dramatically change their properties at nanoscale has opened up the possibility of making new devices, instruments and consumer goods to function in a much better way than was possible earlier. We have seen in Chaps. 10 and 11 that nanomaterials have enabled us to design new products which were not possible using bulk materials. Rapid progress in the synthesis and understanding of nanomaterials in just a few years has led them to enter the world market in a big way. Figure 12.1 shows an overview of various fields in which nanomaterials have entered or are about to enter. In this chapter we shall briefly discuss some of these applications.

12.2 Energy

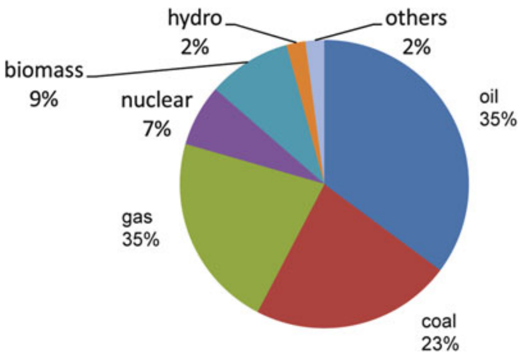
Nanotechnology is expected to play an important role in the field of 'energy' due to the availability of high efficiency and cost effectiveness of nanomaterials. We all know that natural energy resources like coal, oil and natural gas used in transportation, communication, agriculture, industry, houses and many other human activities are limited and depleting very fast. Future generations will have to look for alternative sustainable energy sources like nuclear, geothermal, wind, solar energy or hydrogen-based fuel cells to satisfy their requirements.

The world energy consumption is $\sim$13 TW per annum. The distribution of resources is roughly as follows: 4.66 TW from oil, 2.98 TW from coal, 2.89 TW from gas, 0.92 TW from nuclear, 1.24 TW from biomass, 0.28 from hydro and 0.28 TW from other renewable sources like solar, wind or geothermal. This can be seen in Fig. 12.2 as percentage distribution.

S.K. Kulkarni, *Nanotechnology: Principles and Practices*,
DOI 10.1007/978-3-319-09171-6_12

Fig. 12.1 Applications of nanotechnology

Fig. 12.2 Pie diagram showing the energy derived from different sources



There is a considerable amount of research going on to tap hydrogen fuel by splitting water (H_2O) using sunlight in the presence of nanomaterials (photocatalysts). Available hydrogen can indeed become a good source of fuel for automobiles and other transportation purposes. However storing hydrogen is not an easy job as it can readily catch fire. Material like carbon nanotubes, a special class of nanomaterials, is being investigated for its potential use as hydrogen storage material. Current cost of carbon nanotubes is very high, but scientists are trying to find inexpensive ways of making them on large quantities, which would help in future to use hydrogen fuel without risk. There are also attempts going on to increase the efficiency of solar cells for energy production using nanoparticles.

Numerous gadgets like laptops, cellular phones, cordless phones, portable radios, CD players, calculators etc. need rechargeable, light weight batteries or 'cells'. Presently, the batteries for such gadgets need to be either replaced with new ones or recharged quite frequently due to their low energy density or storage capacity. Attempts are being made to increase their energy density, for example by replacing the electrode materials. Some metal hydride nanoparticles like nickel hydrides or high surface area, ultra light weight materials like aerogels are found to be better options than the conventional materials in improved batteries.

Although there have been numerous efforts to tap various alternative energy sources than coal, oil and gas, main hurdle is the cost effectiveness. The solar energy, although spread over a large area of the earth's surface, is so much abundant on the earth that if one could harness it, the energy received on earth in one hour from the Sun is sufficient to satisfy the needs of entire human population on the earth for 1 year. About 120,000 TW of radiation from the Sun strikes the earth every year. However, so far all the attempts to tap the solar power (or other sources like wind, hydro etc.) have not turned out to be cost effective as compared to oil, gas or coal—the conventional energy sources (Box 12.1).

Box 12.1: History of Solar Cells

- **1839** – French scientist A.E. Becquerel understood the photovoltaic effect i.e. generation of voltage in a material due to incident photons.
- **1883** – Charls Fritts fabricated the first solar cell by using gold contacts with selenium. Efficiency of ~1 % was achieved.
- **1946** – Russel Ohl patented junction solar cell.
- **1954** – D.M. Chapin, C.S. Fuller and G.L. Pearson made diffused p-n junction solar cell in silicon.
- **1991** – Grätzel developed dye sensitized titania nanoparticles based solar cell with ~11 % efficiency. This marks the search for nanomaterials based solar cells other than silicon.

Globally the scientists and technologists are making efforts with domestic and international financial support to tap alternative sources of energy. In many nations there is a move against the establishment of new nuclear plants and even shut down the existing nuclear plants due to risk of fatal accidents. Nuclear waste, leakages and accidents can be dangerous for generations. Therefore in future we expect that the use of nuclear power plants will be on the decline.

Besides their depletion, the conventional energy sources also turn out to be problematic due to emission of carbon dioxide. Carbon dioxide once emitted does not dissociate easily and its equilibration by biomass and ocean takes place after several years. It is realized now that this has resulted into global warming, causing the melting of polar caps or huge glaciers at the north and the south poles of the earth. Glaciers while melting also release methane adding to the pollution. Already the pH of oceans is changing and at some places has resulted into de-colouration of the corals. Temperature rise by 4–5° would extinguish many species on the earth. This has already started disturbing the eco-balance and the whole world is quite concerned about it due to the obvious reasons. However, the modern life style also depends upon the increasing consumption of power. It is speculated that the 13 TW annual consumption of power by the earth population (earth population also is increasing) would increase the demand to 20 TW by the year 2050. From where is this energy going to come? One needs to find clean, safe sources of energy which are sustainable as well as cost effective.

Scientists are seriously considering solar energy as one of their best options (contribution to the energy generation by wind, geothermal, ocean tides etc. is not expected to be very high/cost effective). Solar energy spectrum extends from UV to infra red. One way to tap energy is to collect the thermal energy in concentrated manner to heat water, cooking purposes and so on. This is being done quite profitably in many places now. However, it is quite a marginal relief to the energy stress on the global scale. Another option is to use photovoltaic panels and store the energy in batteries and use it whenever required like usual switching of electricity. Advantage with photovoltaic panels is that they can work in remote places like in villages in isolation or in urban areas. The surplus energy can be transferred to the electric grid. Such installations have proved to be cost effective even with the crystalline silicon photovoltaic panels which are a bit expensive.

Currently, the photovoltaic (solar cells) are divided as first generation, second generation and the third generation. First generation solar cells are made using single crystalline silicon wafers and are nothing but p-n diodes. Although the efficiency of these cells in some configurations has reached as high as ~40 %, they are too expensive. The second generation of solar cells is based on the thin films of crystalline silicon, amorphous silicon, $CuInSe_2$ based cells and many other thin film solar cells. They are cost effective to some extent but not efficient. The third generation of solar cells is based on the nanocrystalline materials and technologists are hopeful that it would be efficient as well as cost effective.

Currently two types of solar cells viz. inorganic and organic are competing with each other in terms of research. Attempts are being made to improve the performance (efficiency increase) and reduce the cost of production/installation. Some hybrid designs are also being demonstrated.

Besides solar cells, efforts are made to improve the fuel cells. In the following sections we will discuss some of the photovoltaic solar cells, fuel cells and issues related to hydrogen generation and storage for energy supply.

12.2.1 Dye Sensitized Photovoltaic Solar Cell (Grätzel Cell)

The first solar cell based on nanomaterials is probably the dye-sensitized Grätzel cell, named after a scientist from Switzerland. Instead of using just one p-n junction like in the first or second generation solar cells it uses multiple junctions at each nanoparticle of TiO_2 and a dye molecule. Although the efficiency of such a cell is only ~11 % (claims upto ~15–16 % also are made), the cost effectiveness has been very attractive and hoped that even with lower efficiency the energy problems can be solved to some extent (Boxes 12.2 and 12.3). Besides, Grätzel cell has generated a new concept of utilizing efficient and cost effective nanoparticles for photovoltaics. Various hybrid solar cells using nanoparticles, CNTs, graphene, polymers and other materials are under intense research. It has been shown that there is no problem for the nanoparticle solar cells to reach the thermodynamic limit of ~90 % efficiency.

Box 12.2: Solar Spectrum

Energy received by the earth is in the form of an electromagnetic radiation (Fig. 12.3), in the range of ~250 to ~2,300 nm. Energy radiation from the sun results due to nuclear fusion as hydrogen gets converted into helium. In this process $\sim 6 \times 10^{11}$ kg hydrogen gets converted per second ($E = mc^2$, Einstein equation) to helium with $\sim 4 \times 10^3$ kg mass difference. This amounts to $\sim 4 \times 10^{20}$ J. Assuming that the mass of the Sun is 2×10^{30} kg, estimated life of Sun is more than 10 billion years. Thus practically solar energy is inexhaustible.

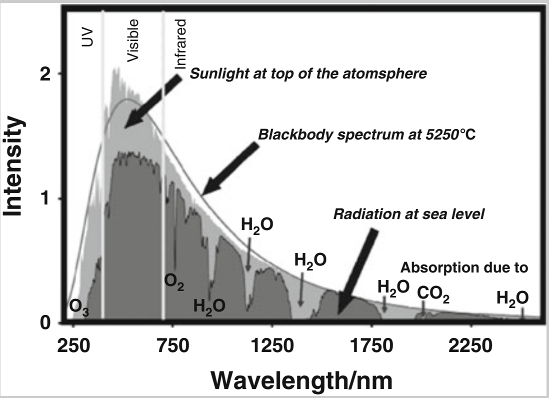


Fig. 12.3 The solar spectrum

(continued)

Box 12.2 (continued)

Solar energy spectrum, although continuous, is absorbed/scattered in certain regions of wavelengths due to some molecules like water, ozone or dust particles before reaching the surface of the earth. Therefore it is necessary to consider the solar intensity in free space, where there is no air. Usually intensity is measured (see Fig. 12.4) at different 'air mass' and referred to as AM0, AM1 or AM2. The angle between Sun and the Zenith is used to determine the atmospheric length the rays have to travel relative to the minimum path length. Minimum path length is when Sun is overhead at a point on the earth (at the sea level).

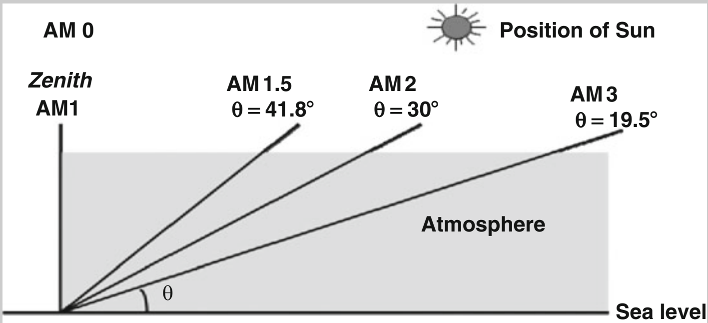


Fig. 12.4 Path of solar rays through atmosphere

Box 12.3: Solar Cells

Solar cells can obtain the energy from the sunlight to produce electricity. It is a sustainable, clean form of energy without consumption of any fuel. Large area solar cell panels can be constructed in order to produce large power or with smaller modules power can be locally delivered. Usually solar cell based panels or devices can last for 30–40 years without much maintenance.

Working principle of a solar cell can be understood as follows. Solar cell in its simplest form is a p-n diode (see Fig. 12.5) in a single material. The diode is formed by diffusing n-type dopant from one side of a p-type semiconductor or diffusing p-type dopant in n-type semiconductor. Electrons from n-side diffuse to p-type and combine with the holes and the built up charges on both

(continued)

Box 12.3 (continued)
the sides of the junction sets up an electric field by which a depletion region is formed which is devoid of any charges.

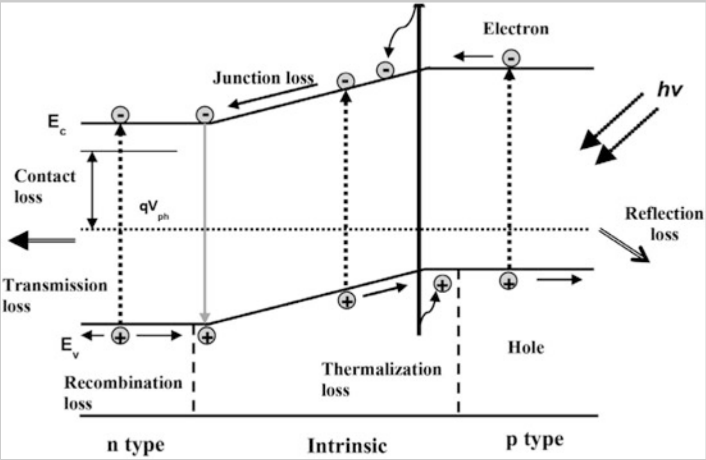


Fig. 12.5 Principle of a conventional photovoltaic solar cell

When a photon of energy larger than the energy gap is incident on the cell, electrons are excited to the conduction band and various processes as depicted in Fig. 12.5 take place. It can be seen that there are different sources of losses of photons and charges. There are many approaches adopted to minimize these losses using various materials and architectures.

Efficiency of a solar cell is defined as

$$\eta = \frac{I_{sc} V_{oc} FF}{P_s} \times 100 \tag{12.1}$$

where

$$FF = \frac{I_{mp} V_{mp}}{I_{sc} V_{oc}}. \tag{12.2}$$

The various values of current and voltages given in the equations are as shown in Fig. 12.6.

(continued)

Box 12.3 (continued)

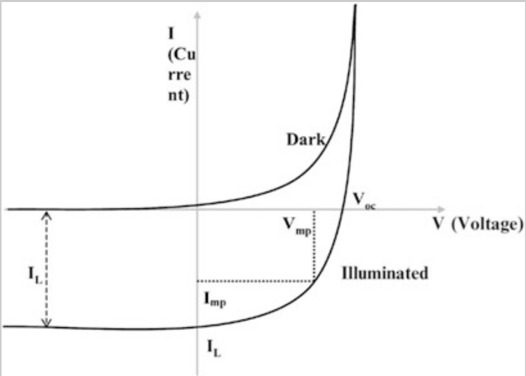


Fig. 12.6 I-V characteristic of a typical solar cell. I_{SC} is the short circuit current i.e. when $V = 0$, V_{OC} is the open circuit voltage i.e. when $I = 0$ and $P = I \times V$ i.e. the power output of the solar cell

For more details about the solar cell efficiency determination and terminologies the interested readers may refer to the literature or recommended books at the end of the chapter.

As illustrated in Fig. 12.7, TiO_2 particles are deposited on a glass substrate with a conducting coating like FTO (fluorinated tin oxide). The resistivity of a typical FTO coating, few nm thick is few ohm.cm. Usually ruthenium complexes are used to sensitize the titania particles. An iodine layer acts as an electrolyte. Another glass substrate coated with platinum serves as the second electrode. The two electrodes are connected to each other externally through a load to obtain the current.

The TiO_2 nanoparticles in a dye sensitized solar cell are randomly deposited. This is one of the obstacles for the generated charge carriers to reach the appropriate electrodes, reducing the efficiency of the cell. Attempts are therefore made to obtain organized nanoparticles and increase the efficiency. Nanotubes and some other porous media are being considered for this purpose.

Further, the solar cells using quantum dots of CdS, CdSe, PbS, and PbSe are being investigated with varied success. The reason for using these nanomaterials is that they can absorb the visible and/or IR part of the solar spectrum and can replace the liquid dye used in the dye sensitized solar cells. This kind of solar cell is often known as ‘Quantum Dot Solar Cell’ and is depicted in Fig. 12.8.

Lot needs to be done in order to obtain yet high efficiency quantum dot solar cells. Considering multiple junctions in a solar cell, interfaces need to be improved so that no charges are lost during the transport across the cell. Good n-type, p-type semiconductors compatible with the energy level diagram of quantum dots is a must. Addition of an anti-reflection coating is a challenge. Multiexciton generation in quantum dots could be very useful. Attempts are also made to use plasmonic structures (nanoparticles, rods or other shapes) in order to profitably use their strong visible light absorption capabilities.

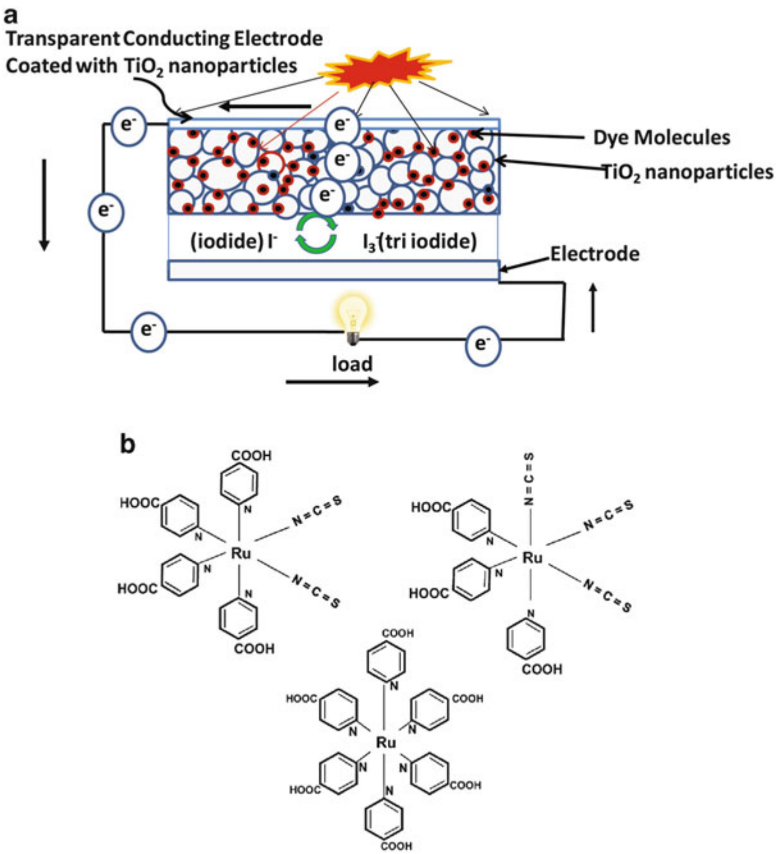


Fig. 12.7 (**a**) Schematic of a dye sensitized solar cell; and (**b**) Some dye molecules used in a dye sensitized solar cell

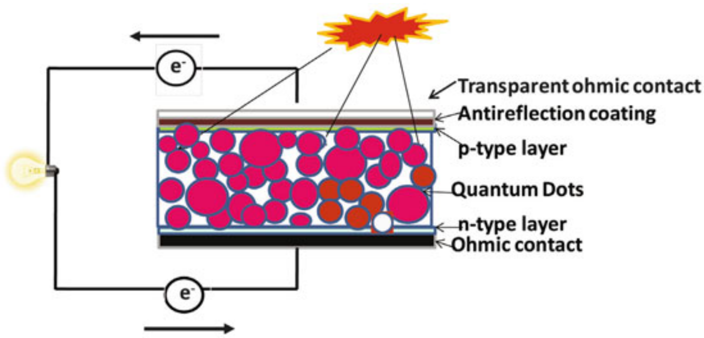


Fig. 12.8 A quantum dot solar cell

12.2.2 *Organic (Polymer/Small Organic Molecules) Photovoltaic Cells*

Although lots of efforts are being made to improve the efficiency and reduce the cost of the dye sensitized and quantum dot solar cells parallel efforts are going on to fabricate low cost organic solar cells using either small organic molecules or polymers. The most important advantage of use of organic/polymer is their low cost and the possibility of easy processing. Organic molecules can be processed by solution spinning, dipping or drop casting. They are easily deposited on flexible substrates like plastics.

There is the possibility of roll-to-roll process by which, just like newspaper printing (using inks), organic molecules can be printed. This should help in large scale production. Figure 12.9 shows some of the commonly used organic molecules in the organic solar cells. However, only few commonly used molecules or molecular units of polymers are shown here. The scientists are trying to use a large variety of low band gap semiconducting molecules. Often multilayer structures are also designed with different polymers. Inorganic nanoparticles (plasmonic materials like Au and Ag) also are used to increase the functionality like photon absorption efficiency of the organic cells.

The organic cells can be divided into three types: (1) A semiconducting polymer simply sandwiched between two electrodes as in Fig. 12.10a. (2) Two polymers, one electron donor and other electron acceptor are sandwiched between two conducting electrodes (Fig. 12.10b). (3) A bulk heterojunction (BHJ) in which a polymer capable of donating electrons is thoroughly mixed with (usually) an electron acceptor (fullerene based) polymer or molecules. This is illustrated schematically in Fig. 12.10c.

It is important that the excitons be efficiently generated in the semiconductor polymer and electron-hole (e–h) be separated. In a single layer polymer solar cell this is rather difficult. Once generated by absorption of photons, excitons just drift (excitons are charge neutral) and should not recombine. However, if there is an interface of acceptor and donor semiconductor polymer at the interface, they can be separated. Therefore, two polymer layer solar cell as in Fig. 12.10b is better than a single layer polymer solar cell (Fig. 12.10a). In order to absorb sufficient light the polymer thickness needs to be typically $\sim$100 nm which is much larger than the typical exciton diffusion length. Thus photogenerated e-h pairs recombine before reaching the interfaces and result into an inefficient solar cell. A better solution is then to blend the donor and acceptor polymers forming a large number of interfaces where the excitons may get formed and electron-hole get separated. The BHJs, therefore, have been widely investigated (Fig. 12.10c) with the hope of getting reliable, reproducible, inexpensive and efficient, flexible solar cells for the future.

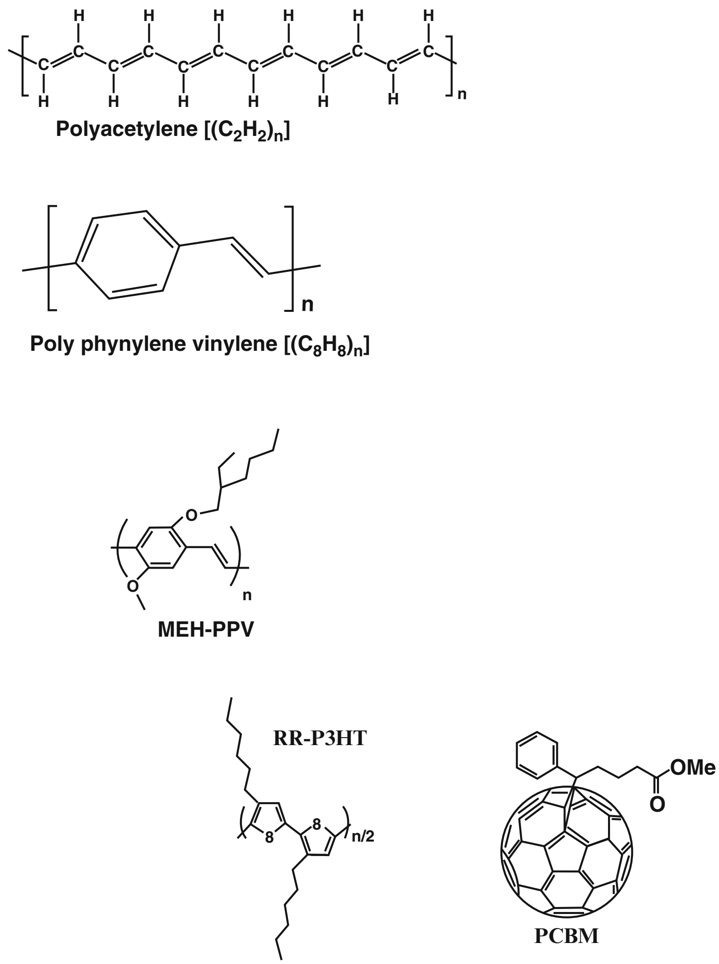


Fig. 12.9 Variety of organic molecules/polymers used in the organic solar cells

12.2.3 *Fuel Cell*

A fuel cell like photovoltaic cell is a strong candidate to provide electricity. It is an alternative source of energy. The first fuel cell was fabricated by Sir William Grove in 1839 but the name ‘fuel cell’ was coined in 1889 by Ludwig Mond and Charles Lanser. Grove used four cells in which he used hydrogen and oxygen gases to produce electricity which in turn was used to split water. The commercial application, however, came in 1960 when NASA started the use of fuel cells in the spacecrafts. Indeed in Gemini and Appollo spacecrafts the fuel cells were used

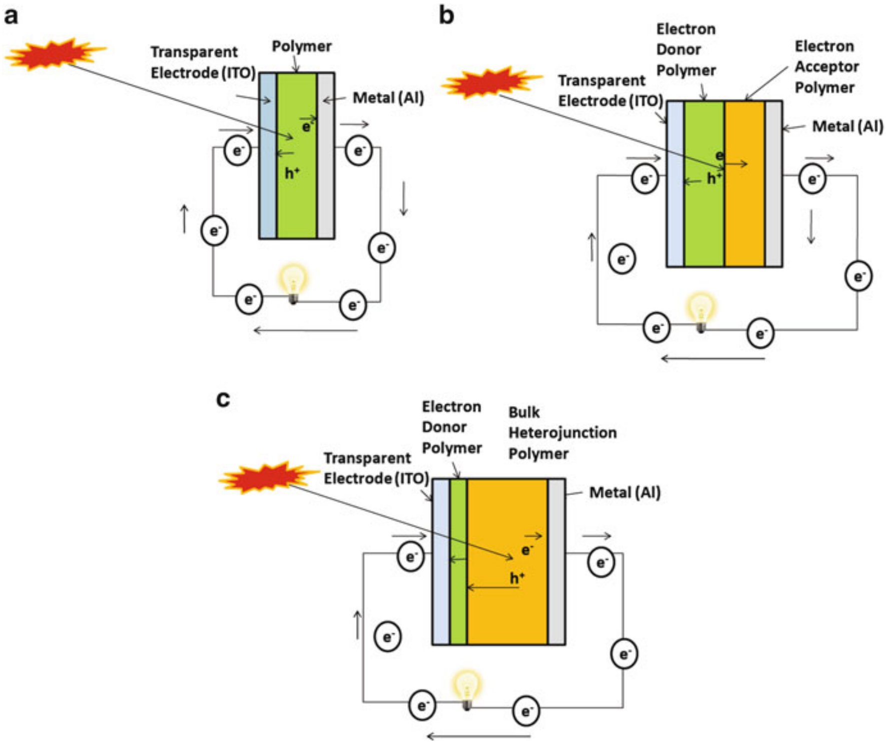


Fig. 12.10 (**a**) A single layer organic solar cell, (**b**) A bilayer organic solar cell and (**c**) A bulk heterojunction organic solar cell

to produce electricity (and water as the byproduct). Since then different fuel cells are being produced and some are in various installations in commercial buildings, hospitals, restaurants, airports and many other public places. They are also used for onboard applications in public transport or personal cars in few countries. The main advantage of the fuel cells is that most of them when used with hydrogen as the fuel provide electricity and heat with water as the byproduct. There is no emission of green house gases, and environment is not polluted. It also does not have moving parts so there is no acoustic pollution. Many automobile companies are trying to use fuel cells in their cars. The main hurdle being the use of hydrogen gas, its supply (stations) and associated risk of carrying high pressure gas onboard. Besides, the cost of fuel (H_2) and expensive electrode materials needs to be reduced. Here nanomaterials would become important. The expensive platinum electrodes can be replaced with porous, non-corrosive alternative electrodes and efforts are being made towards it. Some nanomaterials also are being considered as catalysts for the water splitting as a source of generating hydrogen. The photocatalysis using nanoparticles forms an important branch in nanoscience. Let us discuss now what are fuel cells, their types and how they function.

Currently there are six types of fuel cells in practice, viz.

1. Proton Exchange Membrane Fuel Cell (PEMFC)
2. Alkaline Fuel Cell (AFC)
3. Direct Methanol Fuel Cell (DMFC)
4. Phosphoric Acid Fuel Cell (PAFC)
5. Molten Carbonate Fuel Cell
6. Solid Oxide Fuel Cell (Box 12.4)

As mentioned above they are conceptually similar but vary in their use of electrolytes and sometimes fuel. This may lead to differences in their operating temperatures and also in efficiency. Without going into design and too many materials aspects (which would finally determine the efficiency as well as cost of the cell), a basic outline of these cells will be given.

Box 12.4: Nanotechnology and Fuel Cells

Use of nanomaterials in fuel cells is a hot research topic. Although conceptually simple, cost of fuel cells as well as hydrogen storage/transport and supply are daunting problems. Efforts are, therefore, being made to replace some of the expensive components in the fuel cells like platinum electrodes (catalyst used to dissociate or oxidize hydrogen and reduce oxygen) as well as to improve the electrolytes or polymer membranes using nanomaterials. Nanomaterials due to their size reduction can act as better catalyst sites as well as decrease the cost of the electrodes due to the small amounts needed. Attempts to use platinum nanoparticles and nanowires show some success in this direction. There are also attempts to replace even the costly platinum itself using nickel particles, carbon nanotubes and graphene in the form of composites. These can even be doped with suitable atoms to alter their electronic structure to make them effective catalysts. It is interesting that suitably developed nanocatalyst materials can work equally well for H_2 or methanol as a fuel, giving more flexible fuel option in the same cell. Moreover, attempts are made to use 'self cleaning' electrodes so that H_2 can be replaced with low grade and cheaper hydrocarbon gases as a source of fuel. The problem faced while using inexpensive hydrocarbon gases to replace H_2 is that after dissociation they deposit carbon on the electrodes making them inefficient in short time. With the use of 'self cleaning' nanoparticles the contaminated electrodes can be cleaned at operating temperature of the cells. This would lower down the cost of the cells. There are experimental demonstrations of such ideas at laboratory scale now. Graphene coated indium-tin oxide (ITO) nanoparticles are shown to split hydrogen and oxygen equally well. In the quest for reducing the cost of the fuel cells successful demonstrations are given by developing ultra thin (<100 nm) polymer electrolyte membranes.

(continued)

Box 12.4 (continued)
The electrolytes (Nafion) are also blended with sulphonic acid functionalized single wall carbon nanotubes. This improves the transport of protons from the anode to the cathode in the fuel cell.

Thus there are several attempts to reduce the cost of fuel cells as well as make them efficient using a variety of nanomaterials.

Similar to a battery, a fuel cell also transforms chemical energy into electricity. However unlike in a battery, a fuel cell needs a continuous supply of fuel flow viz. hydrogen gas. As illustrated in Fig. 12.11, a fuel cell consists of a solid polymer (usually Nafion) electrolyte sandwiched between two electrodes (usually platinum). Hydrogen gas is flowed in the anode region which catalytically splits in proton and an electron. The proton is conducted through the electrolyte and goes towards the cathode where it combines with the oxygen to form water molecule. The electron flowing in the external circuit assists to complete the reaction.

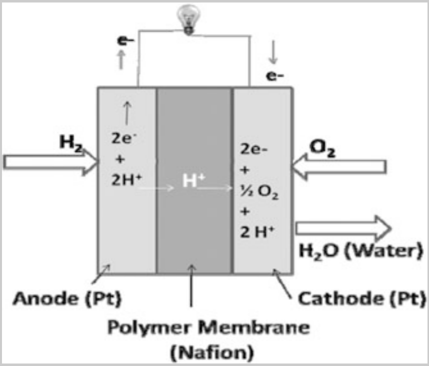


Fig. 12.11 A fuel cell concept

12.2.3.1 Proton Exchange Membrane Fuel Cell (PEMFC)

This cell works on hydrogen gas and oxygen as depicted in Fig. 12.11. It uses (usually) platinum electrodes and solid Nafion Membrane as the electrolyte. The reaction at the anode can be written as

$$H_2 \rightarrow 2H^+ + 2e^- \tag{12.3}$$

and the reaction at the cathode as

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{12.4}$$

Total reaction is

$$2H_2 + O_2 \rightarrow 2H_2O \tag{12.5}$$

This results into an external voltage equal to 1.23 V. The operating temperature of the cell is 350–400 K. The efficiency of the cell is 35–60 %.

12.2.3.2 Alkaline Fuel Cell (AFC)

The alkaline cell is similar to the PEMFC cell described above except the electrolyte. In this cell liquid KOH is used as the electrolyte for the conduction of protons from anode to the cathode. The fuel is same as in PEMFC. Its operation temperature is ~360–420 K and efficiency is ~35–55 %.

12.2.3.3 Direct Methanol Fuel Cell (DMFC)

As we will see below, often the fuel hydrogen gas is produced from methanol gas. Avoiding this step of hydrogen production and then using it for a fuel cell, in this cell methanol is directly used as the fuel. The reaction at the anode can be written as

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{12.6}$$

And that at the cathode as

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{12.7}$$

The electrolyte and electrodes are as in PEMFC cell. This cell produces 1.18 V output. Emission of CO_2 is undesired.

12.2.3.4 Phosphoric Acid Fuel Cell (PAFC)

In this cell the phosphoric acid HPO_3 is used as the electrolyte. It is corrosive in nature and can cause related problems. Other things remain the same as in PEMFC. The cell produces 1.23 V. The operating temperature of the cell is ~475–500 K and the efficiency is 35–45 %.

12.2.3.5 Molten Carbonate Fuel Cell

The electrolyte used in this cell is lithium and potassium carbonate. Cheaper nickel can be used as a catalyst. The fuel can be H_2, CO, CH_4 or hydrocarbon gas. The reactions at the anode and cathode can be

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \quad (12.8)$$

$$\frac{1}{2}O_2 + CO2 + 2e^- \rightarrow CO_3^{2-} \quad (12.9)$$

The operating temperature of the cell is rather high ~950 K. Efficiency of the cell is ~45–55 % or even better. The drawback is the emission of CO_2.

12.2.3.6 Solid Oxide Fuel Cell

This cell utilizes various solid oxides like zirconia (ZrO_2) or yttria (Y_2O_3) or yttria stabilized zirconia (YSZ) as the electrolyte and is a low cost, high efficiency cell. The operating temperature of the cell is ~1,300 K and efficiency is 50–60 %. The electrode reactions are as in PEMF. The cost can be reduced here by replacing the platinum electrodes with other electrodes.

In fact most of the research efforts to improve the efficiency of the fuel cells are directed towards the replacement of the electrode materials with efficient, high temperature stable, non-corrosive materials.

12.2.4 Hydrogen Generation and Storage

Hydrogen is one of the most abundant elements in our solar system. However it is not the most abundant element on the earth although it is a part of living beings, water, hydrocarbon gases, oil, polymers and many organic molecules. Hydrogen as a fuel does not emit harmful gases and is environmental friendly. Hydrogen gas chemical energy is basically converted into heat, water and electricity. In order to use hydrogen as a fuel it needs to be separated mostly as a gas and then stored either as pressurized gas in strong metallic cylinders, metal hydrides or some new storage systems like carbon nanotubes. It can then be transported and used as per demand. Here we discuss various sources of hydrogen production. It should be remembered that these reactions are accelerated in the presence of suitable catalysts and nanoparticles provide a good platform for this due to their large surface to volume ratio.

12.2.4.1 Partial Oxidation

In this case a hydrocarbon gas like methane is oxidized as follows

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad (12.10)$$

or

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \quad (12.11)$$

12.2.4.2 Methane Steam Reforming

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (12.12)$$

Above reaction needs heat to be supplied for it to take place (endothermic reaction).

Additional H_2 is produced from CO as

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (12.13)$$

Here nickel nanoparticles are used as catalyst.

12.2.4.3 Electrolysis of Water

The reaction of producing H_2 from water is simple

$$2H_2O \rightarrow O_2 + 2H_2 \quad (12.14)$$

However availability of electricity can be a hurdle.

12.2.4.4 Photo Electrochemical Cell (PEC)

Water splitting using photons (or solar energy) according to (12.14) is a possible way of getting hydrogen. Use of solar energy to produce H_2 and its use in fuel cells is the best way of getting energy particularly for transportation purposes. The major requirement is that the anode material should have a suitable band gap (semiconductor) to absorb visible radiation, should be robust, reusable, have a long life and should have large catalytic activity. Spherical nanoparticles, nanowires, nanotubes, nanoflakes and some other morphologies are being investigated as they can offer large surface area and catalytically favourable sites. In order to increase the efficiency of hydrogen production the catalytic anodes are modified by using TiO_2 nanoparticles doped with carbon as an anode and platinum as cathode for oxygen generation. Doping of TiO_2 is essential to utilize visible and the IR part of the solar spectrum, as the bulk band gap of TiO_2 itself is 3.2 eV and can increase in nanomaterials. Doping modifies the electronic structure and greatly accelerates the reactions. However, efficiency can be improved by using TiO_2 nanotube array which provides a diffusion pathway without considerable scattering. When UV light was used on such an anode array the photoconversion efficiency as high as ~16 % was obtained. TiO_2 itself needs to be coated on some transparent electrode through which the solar radiation can be incident on the PEC.

The transparent thin films (<100 nm) of Indium Tin Oxide (ITO), F doped ITO and F doped SnO_2 are the usual substrate materials for the anode nanomaterials deposition. The interface of transparent electrodes and catalytic materials can be a source of reducing the efficiency and need attention. Similar to TiO_2, ZnO nanostructures are suitable candidates for cathodes in PEC for hydrogen production. Aligned ZnO nanorods or other suitable ZnO nanostructures (also doped with Al, Ni or other transition metal ions) have been widely studied and used to improve the light absorption capability of their electrodes. Another suitable nanoparticle or nanorod material as potential anode candidate is α-Fe_2O_3. Nanorods of α-Fe_2O_3 doped with W or Cr ions serve as good anode materials. It is found that WO_3 itself in the form of nanowires, nanorods or nanoflakes is a potential candidate for anode in a PEC for hydrogen production. $WO_3/BiVO_4$ composite nanoparticles also show a great promise in hydrogen production due to their catalytic activity towards hydrogen. However, more research is necessary to fully exploit the nanostructures in the hydrogen generation and the field is far from maturity.

12.2.4.5 Biological Methods

Human waste, garbage and plant scraps are the biological sources of H_2. Fermentation or photosynthesis by bacteria and algae can produce hydrogen. Some organisms in water also can split water into H_2 by photosynthesis. However, tapping such resources is still under research. Nanomaterials also should be used to assist the degradation of bio-waste.

12.2.5 Hydrogen Storage (and Release)

The world wide pollution problem is caused mostly due to the emission of gases like CO_2, CO, NO_x etc. which are not easily absorbed by sea or environment easily. Use of hydrogen has been considered as a good option particularly for the on-board application in the vehicles as H_2 fuelled vehicles emit water molecules as their byproduct in a fuel cell. However storage of H_2 is challenging as it occupies much larger volume compared to gasoline for the same amount of energy release. Storing hydrogen as a pressurized gas and carrying it on-board is not a suitable option for the vehicles. There are also problems with gas pumping stations availability at suitable locations. Therefore the scientists are since long looking for the suitable options for hydrogen storage. Some of the materials considered so far can be metal hydrides, complex hydrides, nanotubes, nanofibres, nanoparticles, polymer nanocomposites, aerogels doped with TiO_2, Al_2O_3, MgO or Fe_3O_4 and Metal Organic Framework (MOF).

Ideally the hydrogen storage material should be light weight, inexpensive, available, and simple to use in the desired storage tank; hydrogen releasing temperature should be low, should get released fast and should have long life to undergo number of adsorption-release cycles. The storing material should have at least 6 wt% H storage capability and operating temperature should be less than 400 K. In this respect the research on materials shows that many nanoparticles as well as porous materials are suitable. MgH_2 nanoparticles with Al, Ni nanoparticles, $LiBH_4$, $LiBH_4 + ½ ZnCl_2$ doped with 3–10 nm Ni nanoparticles, alloys of Mg-Ni-Al, Ca-B-Ti alloys in the form of nanoparticles are investigated as H_2 storage materials. Various Alanates, particularly $NaAlH_4$ and Na_3AlH_6, in the nanoform are also under investigations for their suitability as hydrogen storage materials. Carbon in various forms like carbon nanotubes, fullerenes or graphene along with other materials like $NaAlH_4$, MgH_2 or MgH_2 + CNT + transition metal nanoparticles (<10 nm) hold a great promise as hydrogen storage materials. Fullerene C_{60} molecule alone is able to store 60 H atoms on its surface and some inside. It shows ~7.7 wt% hydrogen storage capacity but the hydrogen release temperature is larger than about 500 °C. However, scientists are hopeful to produce some nanocomposites in future for the suitable hydrogen storage for the on-board application with the capability of recycling or refueling the fuel cells.

12.2.6 Hybrid Energy Cells

We have seen in Sect. 12.2 that there are various types of photovoltaic (solar) cells using inorganic or organic materials. There are trials to improve the efficiency not just by using the nanomaterials of different shapes and sizes but even using organic-inorganic semiconductor layers or blending the materials with plasmonic and oxide materials/layers to improve the solar radiation absorption. Thus various functionalities of the nanomaterials are put together to achieve high efficiency and low cost solar cells to produce electricity.

However as seen from the previous section, the electricity can be obtained even from a battery or a fuel cell using chemical energy and the scientists as well as technologists are trying hard to tap from all the possible sources as reliability on the fossil fuel has not reduced. This is not only polluting our planet but making it difficult to satisfy the energy needs of the human population. In the present scenario, therefore, it is necessary that we tap all the possible resources. The energy demands have given rise to an idea that one should make some hybrid cells which make use of the mechanical, acoustic, thermal, chemical or solar energy to get electricity as per the availability of these resources. For each purpose separate cell is fabricated but can be used in isolation or simultaneously. Such cells need not be large but they are able to run cell phones, light emitting diodes, laptops etc. and they can take care of large load off of energy requirement. This is a new path in energy research using particularly nanodevices.

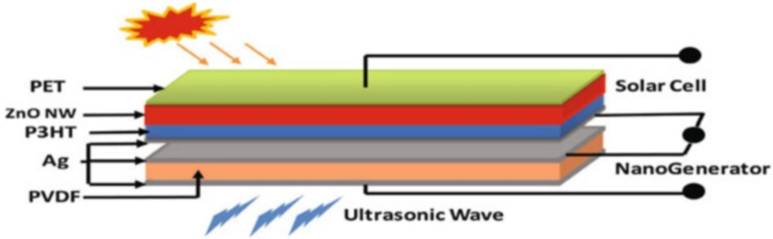


Fig. 12.12 A hybrid cell combining solar, mechanical and thermal energies

This has given rise to make 'nanogenerators'. Figure 12.12 illustrates schematically a hybrid cell which integrates thermal, mechanical and solar energies. The cell is flexible due to use of polyester (PET) substrate and flexible material layers.

In this cell, a polyvinylidene fluoride (PVDF) polymer film ~100 μm has been sandwiched between two thin silver layers acting as the electrodes. This forms a pyroelectric/piezoelectric nanogenerator. The solar cell is composed of ZnO nanowires grown on the PET substrate and the poly (3-hexylthiophene) or P3HT. The PET and Ag act as electrodes for the solar cell here. The silver layers for NG and Sc are separated by a small gap. The PVDF layer showed the generation of pyroelectric current and voltage (~ −24 nA and −2.5 V respectively at ~314 K and 31 nA and 3.2 V at 295 K). The same NG could use mechanical energy to generate piezoelectric current and voltage under compression. The ZnO and P3HT diode could produce with AM 1.5 with 100 mW/cm^2 light intensity 0.4 V and 31 μA current. By connecting NG and SC in parallel it was possible to show that there was always an output enough to drive an LED. Interestingly some scientists have made a hybrid cell on a few micrometre diameter sized single polymethymetacrylate (PMMA) fibre using ZnO nanowires and graphene nanogenerator, supercapacitor and solar cell. It is expected that such a concept of hybrid cell which is still in its initial stage would be used in future.

12.3 Automobiles

A car is made up of large number of parts and materials. Its body and various structural parts are made up of steel, some alloys, rubbers, plastics etc. Body structure should be strong, non-deformable or rigid, of desirable shape and size. It is known that nanotube composites have mechanical strength better than steel. Attempts are made to make composites that can replace steel. Currently the synthesis of nanotubes is not economically viable but attempts are being made so that they can be used on large scale. Cars are spray painted with fine particles. Nanoparticle paints provide smooth, non-scratchable thin attractive coating. Some research is going on to explore the possibility of applying a small voltage to change the colour of the car as desired.

It is possible to use special window glass materials. One can use 'self cleaning' glass so that it is not necessary to wash the windows with water. Self cleaning glass can be made by dissolving small amount of titania (TiO_2) nanoparticles in it while manufacture by melting together its other ingredients like silica (SiO_2), CaO, Ba_2O_3 etc. Titania is able to dissociate organic dust in presence of UV light available in the sunlight. Once dissociated it may fall down or simply evaporate. Even drops of waters on glass give hazy look. But TiO_2-containing glass can spread water evenly giving clear sight.

Besides main engine there are large number of small motors in a car. For example wipers, window glass movements, removing CD's from player all need motors. Their operations need one kind of motor or the other. Very powerful electric motors are made using what is known as shape memory alloys using nanoparticles of materials like Ni–Ti. They perform better and are less power hungry than other motors. Such motors are finding their way in automobiles.

Tyres of cars consume considerable amount of rubber which not only increase in price but also add to its weight. Increase in weight is related to reduction of speed and increase in fuel consumption. By using nanoparticle clay—better, light weight, less rubber consuming thinner tyres are possible. Newer cars are expected to employ such tyres. Emission of particles and poisonous gases like CO and NO from car exhausts is one of the biggest concerns in cities. Increasing number of vehicles means increased air pollution affecting a large portion of world population. Use of efficient nanomaterial catalysts is one solution to convert harmful emission into less harmful gases. Large surface area of nanoparticles is useful to produce better catalysts.

Another solution to overcome the pollution problem is to use hydrogen as a fuel. There are numerous advantages of using hydrogen as a fuel. First of all hydrogen as a part of water molecule is abundant on earth as compared to depleting oil used as petrol or diesel after refining. Dissociation of water into H_2 and O_2 is not a difficult process. Therefore abundant H_2 fuel can be made available. When H_2 fuel is burned it can only produce harmless water vapour. However main problem of using hydrogen fuel is its storage. Hydrogen gas is normally stored in a metal cylinder under high pressure. Carrying metal cylinders under high pressure not only can add to the weight of the vehicle but is also dangerous. Hydrogen in contact with air can catch fire. A solution to this problem has been suggested that it be saved in some other forms like metal hydride. Another solution is to store it in 'nanocylinders' of carbon nanotubes. In Sect. 12.2 we have already discussed fuel cells and hydrogen storage issues. Currently many improvements in techniques are necessary to make CNT synthesis economically viable.

Thus nanotechnology may turn out to be one of the indispensable technologies for automobile industries. What is being discussed for cars may equally be applicable to other automobiles.

12.4 Sports and Toys

Nanotechnology has already been introduced into sports equipment and toys. Tennis balls using nanoclay are able to fill pores in a better way and trap the air pressure inside. This increases the life of balls. Some of the international organisations have accepted such balls for their tournaments.

Good quality tennis racquets are made of carbon. Light weight and toughness or strength is necessary for such racquets. It is possible that carbon nanotube composites would serve as a high strength, light weight material for racquets.

In other games too, balls and other equipments using nanomaterials can be employed.

Toy industry also has been well geared to embrace nanotechnology. Eye movements of dolls, robot movements etc. are enjoyed by children but appear quite brisk. Nanotechnology-based motors are being used by toy industry now making the body part movements very smooth, swift and natural looking.

12.5 Textiles

Textile industry is also quite excited about nanomaterials. There are some clothes produced which would give pleasant look of synthetic fibre but comfort of cotton. Special threads and dyes used in textile industry are products of nanotechnology. The clothes made using nanotechnology would not require ironing or frequent cleaning. In fact some companies are using silver nanoparticles in washing machines which make clothes germ-free. Use of silver in either washing or directly in textile assures germ-free environment necessary for bandages, surgical purposes and child care items. The use of highly fluorescent colours from nano semiconductors is one possibility but even just by changing the distance between the particles or changing the size of the nanoparticles woven in the fibre one can change the colour of the clothes. This is because the optical properties of nanoparticles at wavelengths smaller than the wavelength of the incident light depend on their sizes. There are also proofs of the concept that using polymer threads one can weave or integrate solar cells in the clothes so that enough power is generated for charging cell phones or playing MP3 or some such devices. One can also weave in polymer transistors and other passive devices to fabricate a wearable computer. The masks or even fashionable clothes can be made which would either capture pollution or release insecticides when needed to kill e.g. mosquitoes. Thus there is plenty of room to design novelty of wearable textile. The ‘self cleaning’ carpets or tapestry washing away coffee or tea stains are already marketed. Thus the field of textile research is coming out with novel concepts and useful nano research.

12.6 Cosmetics

Nanoparticles are also important in cosmetics. Besides gold, silver, copper, platinum, and metal oxide nanoparticles like zinc oxide, alumina, silica and titanium oxide, liposomes, solid lipid nanoparticles and nanoemulsions are found to be used in the formulations of various cosmetics like face creams, lipsticks, body sprays, hair care products, sunscreens and so on. Due to their small size nanoparticles-based creams are preferred as they can be used in small amount and do not leave any gaps between them. This gives a smooth appearance. The small particles in some of the creams scatter light in such a way that appearance of the wrinkles is diminished. Some of the nanoparticles can also penetrate deep inside the skin and help repair the skin damages like wrinkles. Usually white sunscreens were used but TiO_2 and ZnO based sunscreens are transparent, much thinner than white screens yet serve in a better way by blocking the UV radiation and protecting the face. Silver nanoparticles in some of the creams are able to kill the bacteria and are able to maintain protection. Nano-based dyes and colours are quite harmless to skin and can be used in hair creams or gels. Nano-based cosmetics are becoming quite popular; however some research on the effect of nano-cosmetics on human bodies shows that some nanoparticles can harm human bodies.

12.7 Medical Field

A great revolution is taking place in biotechnology and medical field due to nanotechnology. The small size of nanoparticles, huge variety of nanomaterials from noble to highly reactive makes it possible to use them for the diagnostic purposes in the laboratory as well as treatments as nanoparticles can be injected, inhaled or digested for different treatments. It is also possible, as we have seen earlier, that they can be designed in different shapes like spheres, wires, rods, tubes or core-shell so that some functional molecules can be attached inside or outside as desired so that drug delivery or molecular recognition can be achieved. Traditional medicines have used gold and silver formulations. Nanoparticles can be good heat or light absorbers or magnetically active and used appropriately. The nanotechnology finds application in medical imaging, drug delivery, cancer and tumour detection and destruction in the early stages, surgery, wound healing, cardiology, Alzheimer and Parkinson treatment, diabetes treatment, dentistry, vision and hearing prosthesis, in body implants and so on. In this section we try to understand how nanotechnology is helping achieving imaging, drug delivery, cancer therapy, tissue welding and bones and muscles treatment areas.

12.7.1 Imaging

Conventionally X-rays and computed tomography (CT) are used for imaging. Iodine and gadolinium (Gd) or radioisotopes are often used as contrasting agents. Iodine compounds are injected in the body intravenously which in small quantities can get cleared out of the body quickly. The large quantity has the toxic effects and the patients have side effects. Gd delivered using dendrimers (branched polymeric supermolecules of specific size and shape having highly functional surface) are able to load very small quantities. Gold with large number of electrons is preferred in imaging. In order to make it economically viable, gold is used as a thin coating on silica, alumina or carbon nanostructures making it non-toxic, biocompatible, low cost material. For the Magnetic Resonance Imaging (MRI) silica core-shell particles with conducting metal coatings are developed.

Semiconductor nanoparticles or quantum dots (discussed in details in Chap. 8) are highly fluorescent materials and can be used for biological labelling. When surfaces of such particles are functionalized using some specific antibodies or molecules they can be targeted towards specific receptors in biological cells. This kind of targeting has conventionally also been done using some organic dyes. But they get easily photobleached and also require depending on the dye, particular excitation wavelength for emission to occur. Therefore the analysis is sequential and time consuming. However fluorescent semiconductor nanoparticles have a wide excitation spectrum and can be excited with any wavelength in the UV or blue range. The emission wavelengths depend upon the particle size and can be tuned in controlled way. Semiconductor nanoparticles are resistant to photobleach and preferred. Figure 12.13 shows the fluorescence obtained from CdSe nanoparticles of varying size. They have been simultaneously excited using a hand-held UV lamp. This type of excitation is not possible for simple dyes.

It is also possible to make 'microbeads' or 'core-shell' particles for biological labelling. Often CdSe or CdTe nanoparticles with high fluorescence ability are coated with thin layer of ZnS shell. The overall size of such a core-shell particle may be $<$10–15 nm. The shell may be water soluble, hence useful for biological application, whereas the core can be synthesized by a non-aqueous process and may not be biocompatible but highly fluorescent. Fluorescent nanoparticles can be trapped inside the silica or some polymer beads, encoded with appropriate molecules on the surfaces and used to target the specific recognition sites. By taking appropriate amounts of differently fluorescing nanoparticles an exhaustive colour library can be generated. Such microbeads are also useful as barcodes.

There are also imaging applications using silver and gold nanoparticles which have excellent photothermal and optical properties. By targeting the Ag or Au nanoparticles to the cell nucleus the molecular signals within the plasmonic field could be detected. This in turn enables to distinguish cancerous and healthy cell. The effect of drugs on the cancerous cell till its death also can be monitored. Such a technique known as 'targeted plasmonically enhanced single cell imaging spectroscopy (T-PESCIS)' has been reported.

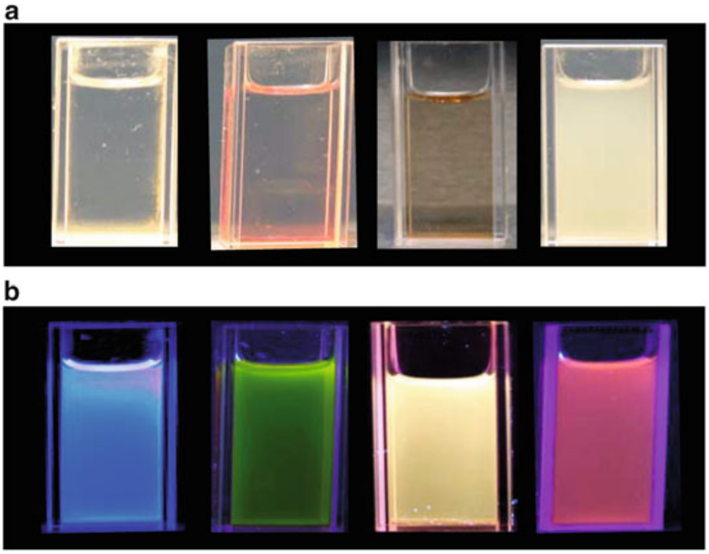


Fig. 12.13 In (**a**) the solution containing CdSe particles is under normal day light. In (**b**) the fluorescence produced by CdSe nanoparticles as the size of particles reduces (*red* to *blue*) can be seen. These are same solutions as in (**a**) but are illuminated with a hand-held UV lamp

Briefly, nano semiconductor as well as metal (plasmonic) particles are useful in imaging. However, it should be remembered that choosing the nanoparticles of appropriate size can be very challenging. Large nanoparticles can get accumulated in some body parts and lead to dysfunction of the organ. Very small size particles may simply not get detected or not stay in the body for long enough time to get detected. Semiconductor nanoparticles also show blinking. Thus there are still many challenges ahead.

12.7.2 Drug Delivery

In most of the conventional drug delivery procedures the drug circulates in the body. As a result, only small part of the loaded drug reaches the part which needs the treatment. Therefore the new approach is to do the 'targeted drug delivery' i.e. to use some molecular recognition systems or some coatings so that the drug is released only to the desired section of the body. Targeted drug delivery is quite important as it would avoid killing of healthy cells unlike in chemotherapy. There is considerable nanotechnology-based research going on to help diabetic, HIV etc. patients.

Use of appropriate nanoparticles like micelles, liposomes, nanospheres, core-shell particles, albumin-based nanoparticles or dendritic polymers enables to achieve these goals in the modern nanomedicine techniques. They are coated with small molecules, proteins or peptides. Often the nanoparticles themselves may be effective as they may store drug inside them and release when they get to the targeted site. Initial tests of various drug delivery systems, cancer or tumour therapies or detection have been successful using nanotechnology. Nanoparticles being very small are easy to inject and target towards specific portion in a body. Particle surface can be modified using some functional molecules which can then go to specific receptor site. Some of the important examples of drug delivery system are in cancer therapy, insulin delivery and treating Alzheimer as well as Parkinson disease.

The scientists have developed novel nanocarrier systems to deliver cancer treatment drug to cancerous cells without affecting the healthy cells. This avoids excessive drug circulating in the body causing toxic effects. Some of the drugs are also not easily soluble in many solvents. In such cases nanocarriers turn out to be effective means of drug delivery.

Diabetes mellitus or simply diabetes is a disease which increases the level of blood sugar in the body. There are Type I and Type II (and some more, less frequent) diabetes. The main cause of diabetes is that the insulin producing β-cells in pancreas either stop producing insulin or an insulin resistance (Type II) is developed which can be controlled by regular medication. In Type I insulin needs to be regularly injected in the patient's body. Insulin is a peptide which is broken down by enzymes and helps to lower the glucose level in the body. However, controlled dose of insulin is important otherwise it leads to hypoglycemia. Regular injections are also troublesome to the patients. Insulin pumps (external wearable or implanted inside the body) regularly supply insulin to the body. Yet, attempts are made to deliver controlled insulin in nanocapsules made of polymers, polyanhydride or polyster by injecting it in soft tissues. Unfortunately their oral formulation is not yet developed as polymeric forms are not very stable in the gastrointestinal track. Chitosans are also found to be useful in insulin encapsulation. Chitin is a natural polymer which gives strength and protection to the cells in animals. It is basically a polysaccharide $(C_8H_{13}O_5N)_n$. However, it is not very successful as its initial burst is difficult to control.

In order to protect the delicate network of central nervous system of our body, there is so-called blood-brain barrier which does not allow large molecules to enter our brain. This is done by epithelial cell lining of blood vessels in the brain. The epithelial cells are lyophilic through which small molecules can pass due to their transporter proteins. Some large molecules can be transported across the barrier to brain through such transporters if they are able to bind with them. Yet, many large molecules which can be potential drugs to cure Alzeimer and brain cancer are not able to pass the blood-brain barrier. The suitably modified polymeric nanoparticles in the form of liposomes loaded with drugs are able to pass the barrier and make drug delivery. Radiolabelled Fe^{3+} and Cu^{2+} metal chelator clioquinol has been transported across the blood-brain barrier through lyophilic nano drug carriers.

At present the drug delivery using nanostructured materials is an active research area.

12.7.3 Cancer Therapy

Genes control the growth and division of cells. If genes are damaged the cell growth is uncontrolled and obstructs the normal body functions leading often to death. There are various types of cancers but the main cause for cancer is the cell growth. If not treated in early stages, it is fatal. The early detection of cancer has been claimed to be possible due to nanotechnology based diagnosis. This would enable to treat the patients before it is too late. As discussed earlier the drugs can be encapsulated in nanocapsules and targeted towards desired parts of a body. Drug can then be delivered at desired rate, by opening the capsule using some external stimulus like magnetic field or infrared light or under some physiological conditions. Targeted drug delivery is quite important as it would avoid killing of healthy cells unlike in chemotherapy. In fact targeted chemotherapeutic drug delivery has been successful. In this the cancer cell target is exploded and destroyed when encountered.

Fluorescent, nanoporous, water soluble and biocompatible silica nanoparticles loaded with camptothecian, taxol and other hydrophobic, toxic drugs (such as β-lapochene) are successfully delivered in animal models to cancer cells and destroyed. As the cancer recognizing ligands are attached to the silica nanoparticles healthy cells are spared which can eliminate the side effects due to the treatment on patients. By this nanotherapy it would be possible to cure breast, stomach, bladder, neck and colon (greater part of large intestine) cancer. To successfully treat cancer β-lapochene is delivered to cancer cells in polymer implants which gets slowly released destroying cancer.

Phototherapy (see Fig. 12.14) is another method which is becoming popular. One can use gold coated silica nanoparticles and target them to the cancer cells. The scattered light from such particles enables the location where the particles are attached. In fact this enables imaging combined with treatment. The silica-gold core-shell particles sizes can be tuned in such a way that there is maximum absorption of the laser power. This is possible (see Chap. 11, Sect. 11.7) due to Surface Plasmon Resonance of gold nanolayer. The IR laser beams are available. The advantage of using IR is that it penetrates inside the body without affecting the body. Moreover, the laser power required to destroy the cancerous cells is half than that needed to destroy the healthy cells, so the laser is operated at low power anyway. The heat generated by the core-shell particles raises the local temperature which is sufficient to kill the cancer cell.

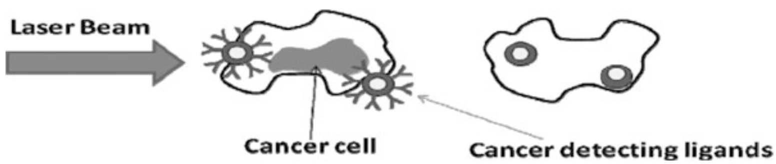


Fig. 12.14 Use of core-shell silica-gold nanoparticles to destroy cancer cells. Note that ligand are attached to the core-shell particles which identify the cancer cells and then with laser beam they can be destroyed

Instead of making gold core-shell particles, scientists have also coated gold nanoparticles with peptide lipid which encapsulated ‘silencing ribonucleic acid (siRNA)’ as the drug which were then directed towards cancer cells and then exposed to the laser beam. This also was an effective way of destroying cancer.

Another type of material useful in cancer therapy is magnetic nanoparticles. Magnetic particles with extremely small size can become superparamagnetic as discussed in Chap. 8. Every magnetic nanoparticle has a characteristic small size in nanometer range below which it becomes superparamagnetic. Such superparamagnetic particles (usually Fe_2O_3) when subjected to an AC magnetic field increase the local temperature around them by $\sim 4°–5°$ than the normal body temperature. This can destroy the cancer cells. This type of treatment is known as ‘hyperthermia’ and has a great application in the real world.

However, the above mentioned treatments are yet not available in the hospitals as they await the government approval.

Ideally a nanocarrier needs to be developed which will detect cancer in the early stage, destroy and even report that the cell death has occurred. Research in this direction has long way to go.

12.7.4 Tissue Repair

Tissues comprise of similar type of cells working in co-operative manner to give some functionality to body. There are four types of tissues viz. connective tissues, nervous tissues, muscle tissues and epithelial tissues. Connective tissues are responsible for body structure and support. They include fat and bones. Nervous tissues control the body processes. Muscle tissues enable movements of body parts. However, in body all actions are not voluntary but some muscles are continuously working on their own, involuntarily for body function like breathing. Epithelial tissues give inside and outside cover throughout the body.

Joining of tissues is important to repair the cuts, cartilage in joints, blood vessels, skin, cornea etc. For very long time this was done using chromophores or dyes as absorbers of laser power. With a small incision in the body an optical fibre can be inserted in the body for surgery using a laser. Specific lasers are required for specific dyes. Conventionally in the indocyanine green (ICG) dye an organic molecule is used in conjunction with infrared laser. However absorption is limited compared to now available gold nanoparticles (absorption is about 4–5 orders of magnitude more than dye molecules). Dyes also bleach fast or disintegrate. Gold nanoparticles on the other hand are quite stable. They can be tuned to desired/available laser wavelength in IR region, particularly if one uses different shapes like nanorod to tune the wavelength of absorption. Here the phenomenon of surface plasmon resonance (SPR) discussed in Chap. 7 is responsible for the strong absorption of light. The absorbed heat by the gold particles is used to heat the tissues which get sutured. This is joining of the tissues without stitches which reduces surgery related pain and infections. Although laser welding of tissues using gold nanoparticles has been successfully demonstrated in quite a few laboratories in the world, it also has not come in practice for human beings.

The scientists are developing better body implants than available so far. The body implants should be strong and biocompatible. Body cells should be able to grow on them and hold in place. Growth of artificial muscles also is being one of the aims of nanotechnology. Much work is going on in understanding how the nature does it all and mimic it.

12.8 Agriculture and Food

May be it is urban or rural population in developed, developing or undeveloped country, food is the basic requirement. Importance of agriculture, therefore, needs no explanation. The agricultural raw products after cultivation and production need processing and proper packaging before they reach the consumers. Nanotechnology in more than a decade now is emerging not only for higher yield but also to lower the various inputs like pesticides, herbicides or reduce the requirement of water. Pesticide DDT was very popular in the twentieth century but due to its toxicity is banned now. Traditional method of increasing the yield of the crop has been to grow different crops alternately.

Most of the nanotechnology research in agriculture is related to sensing the soil condition, growth of plant parts and provide adequate amount of fertilizers, pesticides or herbicides as per the requirement. This can help proper and economical growth of the crop. Efficient and smart sensors are obviously the requirement (a smart sensor would sense the presence of a disease and release the pesticide/herbicide in adequate quantity). This is through what is termed as '*precision farming*' in which use of computers, global position sensing (GPS) and remote sensing can be made. For this variety of sensors will have to be spread in the fields. Some of these ideas are in their infancy but scientists dream of bringing them into reality.

Some groups are trying to investigate plants of tomato, soybean, rice, wheat, corn and so on which are consumed on a large scale. The nanoparticles of Au, Ag, Cu, CuO, SiO_2, Fe_2O_3 and ZnO, fullerenes, and carbon nanotubes are under investigation to use them catalyze fertilizers or pesticides more effectively or use as sensors. Interaction of synthetically made nanoparticles and naturally present nanoparticles in soil, however, is not known yet. Thus a major thrust in agriculture research using nanomaterials is expected to find out ways and means to produce healthy and large quantity of agriculture products.

Healthy raw crop is the first important step that needs to be achieved. However, lot of agriculture products if not processed and delivered properly, can result into waste of energy, man-power and money. Lot of major food product producing companies have turned their attention to use nanotechnology in packaging, increasing the shelf life of products, maintaining odour and taste of products, increasing food nutrition value etc.

The food companies are using some innovative ideas of nanotechnology. It is known that omega-3 fatty acid reduces blood clotting, decreases platelet aggregation, improves insulin response in diabetic patients, reduce obesity and help prevent cancer growth. Fish (tuna and others), soyabean, tofu etc. are rich in omega-3. Tuna fish oil odour smells bitter and unpleasant making it difficult to take it in food. The scientists have encapsulated tuna fish oil in a biocompatible capsule which bursts only after reaching stomach.

Ice-creams with 1 % fat as compared to usual ice-creams with 16 % fat are produced by reducing the size of particles which give ice-creams a texture.

Bioavailability for nutrition can be increased using nano self-assemblies of micelles. The nutrients enter blood stream from stomach and are made available. The technology is used to reduce cholesterol and this would be useful also to deliver vitamins. A company has produced the nano product which not only reduces the energy needed for cooking but extends oil life used in deep frying.

Packaging is very important in preserving food for long time as well as transporting it to long distances. A company has used SiO_2 nanoparticles in making air-tight wrappers which preserve food for longer time. Nanoplastic wrappers are produced using zinc oxide nanoparticles as catalysts which are antibacterial, UV and temperature resistant and fire-proof in nature. Nylon-based nanocomposites are used to bottle the beer to make a barrier for CO_2 and O_2 to keep the clarity, flavour and increase the shelf life. Emphasis of food preserving and packaging industry is to use nanocapsules inside so that flavour, odour are triggered only when used. Colours and nutrients also get added only when product is either opened or is being consumed. Capsules are dormant until then. It is also possible to attach colour strips to qualify if the food is good to eat or already started becoming stale. This would be convenient for food packages in big malls. Briefly, lot of revolution using nanotechnology is underway in agriculture and food supply.

12.9 Domestic Appliances

Use of silver nanoparticles is made in refrigerators, air purifiers or air conditioners and water purifiers. It is well known for long time that silver has antibacterial property. That is why it has been used as utensils material since long. But recent research has shown that silver nanoparticles are much more effective and only small quantity of them is required. Therefore some manufacturers have special nanoparticles lining in refrigerators, air conditioners or even in washing machines.

Food in refrigerators can remain fresh and prevent fungal growth for longer time than ordinary refrigerators. The clothes washed in silver nanoparticles lined washing machines are claimed to stay sterile for about a month. This should be quite useful in hospitals. Air conditioners or water filters with silver nanoparticles also are claimed to have advantages and are being marketed with very little additional price.

Some of the building blocks like window materials can be based on nanomaterials. One can maintain the inside temperature of the houses reducing heating/cooling effects due to outside weather using appropriate window materials like aerogels which are highly insulating but can be made transparent for window purpose. Self cleaning glasses also are useful for windows. One can also use some window coatings to adjust the interior lighting of the houses. Dye sensitized solar cells can be an integrated part of modern architecture increasing the aesthetic appearance as well as satisfying local power requirement of the house or a building. Thus nanomaterials are quite useful.

12.10 Space, Defense and Engineering

Space and defense scientists also are trying to adopt nanomaterials as alternative materials and replace the conventional materials. Very low density materials known as aerogels (Chap. 11) are nano porous materials (i.e. materials having small nanosized pores in them). Aerogels can be of various materials. Their density is typically 0.01–0.8 g/cm^3. One can compare this density with that of iron which is $\sim$7.8 g/cm^3. So one can get an idea of how light aerogels are. Naturally it is very good to use for various applications in spacecrafts and defense to reduce the weight. Even some special light weight suits, jackets etc. can be made using aerogels as they can be made such that they are poor conductors of heat. Even some special high temperature materials which are otherwise difficult to make can be made at lower temperatures using nanomaterials.

In space, mainly solar energy is used to power the satellites or space crafts. Some of the solar cells currently in use have reached an efficiency of $\sim$30 % at air mass zero (AM0). Some solar cells are approaching an efficiency of $\sim$40 %. However there is still a concern in reducing the weight of materials used in solar cells. It is speculated that future spacecrafts would be powered with luminescent dye sensitized nanoparticle based or nanoparticle-based solar cell arrays.

Space vehicles also need high performance, multifunctional materials which can withstand harsh and extreme environments during launching and in space. Materials should also sustain high or low temperature and high or low pressure. For some parts light weight polymers are quite attractive. Low processing temperature, possibility of having them as fibres, coatings or thin films makes polymers attractive as internal insulation in solid rocket motors. Polymer composites using silica fibres and nanoparticles have larger Young's modulus, low temperature coefficient of expansion and high impact strength.

It can be seen from Fig. 12.15 that nanoparticles in polymer composites are better radiation protectors as compared to microparticles-based composites.

In satellites better ignitors of nanocrystalline materials are being considered. Alumina particles are used in solid propellants. Nanoparticles of alumina are at least six times better than the conventional particles. A nanocomposite of Fe_2O_3 and aluminium burns much faster and is more sensitive than conventional thermites.

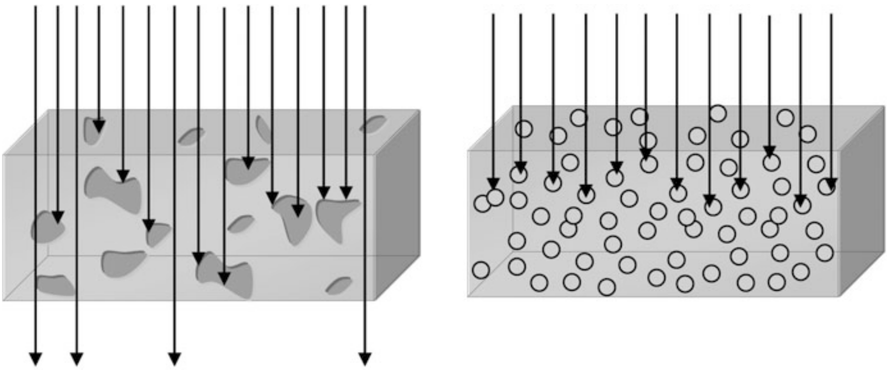


Fig. 12.15 Nanoparticle-Polymer composites

In aircrafts, superior property, specially fatigue resistant materials are required. Fatigue strength usually decreases with time. Some nanomaterials have better fatigue strength and life is increased by ~200–300 %.

There is always a fear that terrorist or enemies may use dangerous microbes or viruses as weapons. Quick detection of biological weapons is the urgent need of defense departments and other public offices to 'on the spot check' the dangerous traffic of harmful biological weapons or epidemic. For example it becomes necessary to detect anthrax or SARS patients immediately. Nanotechnology is expected to play an important role in these areas.

Some of the chemicals used in warfare are VX, HD, GD and GB. Some nanoparticle oxides like CaO, Al_2O_3 and MgO interact with such chemicals much faster than microparticles and are ideally suited for fast decomposition of warfare chemicals.

As was discussed in Chap. 11, the new kinds of structures based on metamaterials will be useful in cloaking or making the objects invisible. This will have considerable defense applications.

Further Reading

M.A. Green, *Third Generation Photovoltaics, Advanced Solar Energy Conversion* (Springer, Berlin/New York, 2003)

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A.W. Miziolek, S.P. Karna, J.M. Mauro, R.A. Vaia, *Defense Applications of Nanomaterials*. ACS Symposium Series 891 (2005)