Chemistry Innovations in Sustainable Development

Sustainability Education for High Schools: Year 10-12 Subject Supplements

Lesson 10: Green Chemistry

Dealing with Greenhouse Gases

Developed by:

The Natural Edge Project

Griffith University

Funded by:

Port of Brisbane
Here for the future

As part of the:

Sustainable Living Challenge

Acknowledgements

The development of the '*Sustainability Education for High Schools: Year 10-12 Subject Supplements'* has been supported by a grant from the Port of Brisbane Corporation as part of the Sustainable Living Challenge. The Port of Brisbane Corporation is a Government Owned Corporation responsible for the operation and management of Australia's third busiest container port. Its vision is: *'To be Australia's leading port - here for the future'*. Sustainability for the Port of Brisbane Corporation means making economic progress, protecting the environment and being socially responsible. In response to the recent drought, and the wider global debate on climate change, the Port is committed to working with the port community to showcase the Port of Brisbane as a sustainable business precinct. Initiatives aimed at reducing the Port of Brisbane's ecological footprint include energy efficiency, a green corporate fleet and constructing green buildings.

The development of this publication has been supported by the contribution of non-staff related on-costs and administrative support by the Centre for Environment and Systems Research (CESR) and the Urban Research Program (URP) at Griffith University; and the Fenner School of Environment and Society at the Australian National University. The material has been researched and developed by the team from The Natural Edge Project. Versions of the material have been peer reviewed by Cameron Mackenzie, Queensland Department of Education, and Ben Roche, National Manager, Sustainable Living Challenge, University of New South Wales.

Project Leader: Mr Karlson 'Charlie' Hargroves, TNEP Director

Principle Researcher: Ms Cheryl Desha, TNEP Education Director

TNEP Researchers: Mr Michael Smith, Mr Peter Stasinopoulos

Copy-Editor: Mrs Stacey Hargroves, TNEP Editor

The Natural Edge Project

The Natural Edge Project (TNEP) is an independent non-profit Sustainability Think-Tank based in Australia. TNEP operates as a partnership for education, research and policy development on innovation for sustainable development. TNEP's mission is to contribute to, and succinctly communicate, leading research, case studies, tools, policies and strategies for achieving sustainable development across government, business and civil society. Driven by a team of early career Australians, the Project receives mentoring and support from a range of experts and leading organisations in Australia and internationally, through a generational exchange model. TNEP's initiatives are not-for-profit. Our main activities involve research, creating training and education material and producing publications. These projects are supported by grants, sponsorship (both in-kind and financial) and donations. Other activities involve delivering short courses, workshops, and working with our consulting associates as we seek to test and improve the material and to supplement the funds required to run the project. All support and revenue raised is invested directly into existing project work and the development of future initiatives.

Enquires should be directed to: Mr Karlson 'Charlie' Hargroves, Co-Founder and Director, The Natural Edge Project charlie@naturaledgeproject.net www.naturaledgeproject.net

Lesson 10: Green Chemistry

Dealing with Greenhouse Gases

The increase in concentrations of greenhouse gases in the atmosphere over the last two centuries has generated the climate change that we have experienced to date and will experience over the next couple of decades and beyond ... It is neither desirable, nor remotely feasible, to seek to lower the climate change risk by substantially slowing the rise in living standards anywhere, least of all in developing countries ... There is a path to Australia being a low-emissions economy by the middle of the 21st century, consistently with continuing strong growth in material living standards.

Professor Ross Garnaut, *Garnaut Review* (2008)[1]

Educational Aim

This lesson aims to highlight the potential role of Green Chemistry in helping to mitigate climate change through innovations in: 1) reducing greenhouse gas emissions, and 2) removing (sequestering) greenhouse gases from the atmosphere. The lesson briefly discusses the types of greenhouse gas (GHG) emissions and some exciting chemistry innovations in sequestering GHGs and reducing GHG emissions.

Key Words for Searching Online

CO_2 and non-CO_2 Greenhouse Gases, Photosynthetic Centre, Solar Cells, Biomimicry, alternative synthetic pathways, biomass feedstock.

Key Learning Points

1. Chemists and chemical engineering have a significant role to play, in collaboration with other professionals, to address human induced climate change. Just as chemical engineering knowledge and innovations helped to catalyse the fossil-fuel based prosperity in the second half of the 20th Century, chemical engineers can now choose to work on innovations that can help catalyse sustainable development and 'sustainable prosperity' in the 21st Century.
2. In particular, as summarised by the Intergovernmental Panel on Climate Change (IPCC),[2] society faces a major challenge to stabilise and then reduce GHG *concentrations* in the atmosphere. A key part of this challenge is to significantly *reduce the GHG emissions* entering the atmosphere, as well as potentially *capturing GHGs* in the atmosphere. The 2008 Australian *Garnaut Review* report refers to this as 'substantial decarbonisation' of our way of life.[3]

---

[1] Garnaut, R. (2008) *The Garnaut Climate Change Review*, Cambridge University Press, Cambridge, see 'Synopsis of Key Points'. Available at http://www.garnautreview.org.au/index.htm. Accessed 4 December 2008.
[2] IPCC (2007) *IPCC Fourth Assessment Report: Climate Change 2007*, IPCC.
[3] Garnaut, R. (2008) *The Garnaut Climate Change Review*, Cambridge University Press, Cambridge.

3. It is important to understand the difference been the natural greenhouse effect and the enhanced greenhouse effect. The natural greenhouse effect is caused by greenhouse gases which occur naturally in the earth's atmosphere. The main natural greenhouse gases are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and water (H_2O). These gases absorb and re-radiate the sun's heat, helping to warm the planet and providing a temperature range that is suitable for life as we know it. Without these natural greenhouse gases, the temperature of the earth's atmosphere would be approximately 34 degrees Celcius lower than it is today.[4]

4. There are five classes of human-induced or 'anthropogenic' greenhouse gases, as well as CO_2, which are recognised by the IPCC which contribute to the 'enhanced' greenhouse gas effect and global warming:[5]

   1) Nitrous Oxide (N_2O)
   2) Hydrofluorocarbons (HFCs)
   3) Perfluorocarbons (PFCs)
   4) Methane (CH_4)
   5) Sulfur Hexafluoride (SF_6)

5. Chemists and Chemical Engineers can make a significant contribution to reduce these anthropogenic GHGs as well as CO2 in numerous ways, through ensuring good design of factories and processes. As the world engages in agreements to stabilise and then reduce GHG concentrations in the atmosphere, everyday products and services will increasingly be required to use materials and processes that emit less, and where possible even take GHGs out of the atmosphere.

6. As CO_2 is the main contributor to global warming of all the greenhouse gases - contributing 62 per cent[6] - one of the opportunities to make a difference in the 21st century for chemists and chemical engineers will be to find more effective ways to sequester and reduce CO_2 emissions. Students may have heard of research areas such as 'geo-sequestration' which is about capturing GHGs and storing them underground, and 'clean coal' which is about creating electricity from coal with fewer emissions.[7] Consider the following additional examples of ways chemists and chemical engineers are innovating to reduce CO_2 emissions:

   1) More than a decade ago in 1998, Toshiba announced that it had developed a new lithium silicate based material that can absorb up to 400 times its own volume in carbon dioxide (CO_2), effectively 'sequestering' this GHG from the atmosphere.[8] This rate of CO_2 absorption is faster than achieved previously, and can be carried out at room temperature. Then captured CO_2 can either be pumped underground and stored (geo-

[4] United Nations (2002) The Kyoto Protocol – A Protocol of the United Nations Framework Convention on Climate Change. Available at: http://unfccc.int/kyoto_protocol/items/3145.php. Accessed 14 December 2008.

[5] Intergovernmental Panel on Climate Change (IPCC) (2001) Climate Change 2001: The Scientific Basis, Cambridge University Press, Cambridge.

[6] See – Environmental Protection - NOAA's Greenhouse Gas Index Finds Increase In Carbon Dioxide, Nitrous Oxide. May 1, 2006 at http://www.eponline.com/articles/54025/ Accessed 11 December 2008

[7] Smith, M., Hargroves, K., Stasinopoulos, P., Stephens, R., Desha, C. and Hargroves, S. (2007) Energy Transformed: Sustainable Energy Solutions for Climate Change Mitigation, The Natural Edge Project (TNEP), Australia. Available at http://www.naturaledgeproject.net/Sustainable_Energy_Solutions_Portfolio.aspx Accessed 11 December 2008

[8] The A to Z of Materials (AZOM) (2003) 'Carbon Dioxide Absorbing Lithium Silicate Ceramics from Toshiba', *AZOM*. Available at http://www.azom.com/details.asp?ArticleID=2052. Accessed12 December 2007; and Toshiba Corporation (2003) 'Toshiba Group Announces Breakthrough in CO2 Absorbing Ceramics'. Japan Corporate News Network. Available at www.japancorp.net/Article.asp?Art_ID=5358. Accessed 11 December 2008.

sequestration) or be used to make polymers, which in turn can be used to make new kinds of plastic that are strong and durable.[9]

2) Over the last decade significant investment has been made into research and development to create electricity with lower GHG emissions, through solar cell technology that mimics the photosynthetic centre of plants.[10] In nature, plants capture CO_2 in the presence of sunlight to convert it to energy and sugar for cell growth. Leaves convert CO_2 and water into carbohydrates and oxygen through a process called ‘photosynthesis’. This ‘distributed’ form of energy conversion (via the thousands of leaves growing from the tree) means that small, low-temperature de-centralised forms of energy generation can be effectively used. Although the process is perhaps not very ‘efficient’, it is highly resilient – plants can function over a wide range of climatic and sunlight conditions.

3) The issue of finding alternative energy sources for transportation and electricity that emit fewer GHGs is a hot topic of research for chemists and chemical engineers, especially in the area of improving the battery storage of energy. If costs for such batteries can be significantly reduced intermittent sources of renewable energy, such as wind power, may cost effectively be used to provide a constant (or ‘base’) load of electricity that can compete with conventional fuels such as petrol for transportation, and coal and nuclear for electricity (see Lesson 12).

4) Leading chemical companies like Dupont and Dow have committed to sourcing more of their materials from renewable crops which themselves absorb significant amounts of CO_2 from the atmosphere. Kenaf for example, is an extremely fast growing plant that absorbs more CO_2 than almost any other crop. The plant can be made into paper, and can also be used to produce a superior plastic which is biodegradable and can be used in electronic products.[11]

7. As the other 5 ‘non-CO_2’ GHG groups are responsible for 38 per cent of anthropogenic global warming, finding methods to reduce these emissions is also a very important research area for chemists and chemical engineers. In particular, these emissions are often associated with very specific industrial applications and are produced in small quantities that are much stronger than CO_2. So, if they can be designed out of the industrial process, this can have a significant impact on addressing climate change. For example:

1) The magnesium industry is in the process of phasing out sulphur hexafluoride (SF_6) by 2010 through a voluntary partnership with the US EPA and the International Magnesium Association.[12] Nike has already phased out all SF_6 from its manufacturing facilities.[13]

2) Dupont has significantly reduced its GHG emissions by reducing and replacing the non-CO_2 GHGs (HFCs, PFCs, N_2O and CH_4), including reducing N_2O emissions from nylon production by 80 per cent.[14]

---

9 De La Pena, N. (2007) *Sifting the Garbage for a Green Polymer*. New York Times. Available at www.nytimes.com/2007/06/19/science/19poly.html?partner=rssnyt&emc=rss Accessed 11 December 2008

10 Collings, A.F. and Critchley, C. (eds) (2005) *Artificial Photosynthesis: From Basic Biology to Industrial Application,* Wiley Publications. Available at www.wiley.com/WileyCDA/WileyTitle/productCd-3527310908,descCd-tableOfContents.html. Accessed 12 December 2007.

11 See Metaefficient.com - *Kenaf* at www.metaefficient.com. Accessed 12 December 2007.

12 See US Climate Change Technology Research Program - *Research and Current Activities: Reducing Emissions of Other Greenhouse Gases* at www.climatetechnology.gov/library/2003/currentactivities/othergases.htm#sf6. Accessed 12 December 2007.

13 See Nike – 2001 Corporate Social Responsibility Report at http://www.nike.com/nikebiz/gc/r/pdf/environment.pdf Accessed 11 December 2008.

14 See Dupont Environmental Performance - *Greenhouse Gas Emissions* at http://www2.dupont.com/Sustainability/en_US/Performance_Reporting/data_summary.html#5. Accessed 3 February 2007.

3) ST Microelectronics (ST), a Swiss-based US$8.7 billion semiconductor company, has been able to set a goal of 'zero net GHG emissions' by 2010 while increasing its production 40-fold.[15]

8. Green chemists and green engineers can also help reduce GHG emissions by creating 'low carbon' manufactured materials. This could be achieved by reducing the amount of energy needed to make different products, and also by reducing 'inputs' (i.e. resources) and 'outputs' (i.e. waste). Traditionally, chemistry has focused on an 'A + B = C' approach. However, Nature uses slower and often more complex, but less energy-intensive and resource-intensive, methods. While plants have access only to air, a few trace minerals and water from the soil and energy from the sun, they carry out very complex chemical transformations. For example, using complex biomolecular reactions, plants can take a molecule 'A', add 'B' to get 'D', then take away 'E', add some 'F', bits of 'G', 'H' and 'I' to get 'K', then combine 'D', 'K' and a few dozen other complex molecular gymnastics to finally come up with the desired product 'C'!

9. Nature offers researchers the possibility of remaking and re-designing high energy chemical processes to achieve low energy alternatives, through the field of 'biomimicry' (i.e. innovation that is inspired by Nature).[16] For example, designing processes to make a strong silk fibre based on the spider's web using natural proteins and high-performance materials that produce no harmful waste products. This material can then be used in applications such as scratch-proof glasses, unbreakable windshields and nosecones for space shuttles (see Brief Background Information).

10. With these examples and opportunities in mind, it is clear that chemistry will play a major role in stabilising and then reducing the concentration of GHGs in the atmosphere over the coming decades. A key challenge for our generation is perhaps how to speed up the process of making such innovations 'normal' or 'mainstream' in society.

[15] ST Microelectronics (2003) *Sustainable Development Report,* ST Microelectronics. Available at http://www.st.com/stonline/company/environm/sustdev/sustdev03.pdf. Accessed 12 December 2007.
[16] Benyus, J.M. 2002, Biomimicry: Innovation Inspired by Nature, HarperCollins Publishers Inc., New York.

Brief Background Information

Overview of the range of GHG Emissions[17]

The four main natural greenhouse gases are carbon dioxide, methane, water and nitrous oxide which contribute to the natural greenhouse gas effect. There are five classes of human induced, or 'anthropogenic' greenhouse gases, as well as CO_2, recognised by the Kyoto Protocol[18] which contribute to the enhanced greenhouse gas effect which are causing global warming. The main six man made greenhouse gases identified by the Intergovernmental on Climate Change (IPCC) as causing climate change are Carbon Dioxide (CO_2), Methane (CH_4), Nitrous Oxide (N_2O), Hydrofluorocarbons (HFCs), Perfluorocarbons (PFCs), and Sulphur Hexafluoride (SF_6). Approximately 38 per cent of global warming is due to the emission of non-CO_2 greenhouse gases, which have significantly higher global warming potentials and atmospheric lifetimes than CO_2 , as shown in Table 10.1. The only exception is methane (CH_4), which has a global warming potential of 21 times CO_2 but an atmospheric lifetime of only 10 years compared to 50-200 years for CO_2. However, due to CO pollution from cars the average atmospheric lifetime of CH_4 has now risen to 12 years. N_2O is a greenhouse gas that has a global warming potential (GWP) of 310 times that of carbon dioxide (CO_2) and an atmospheric lifetime of 120 years.

Table 10.1. Six Kinds of Greenhouse Gases and Global Warming Comparisons

Symbol	Name	Common Sources	Atmospheric Lifetime (years)*	Global Warming Potential	Percentage of American Emissions (%)
CO_2	Carbon Dioxide	Fossil fuel combustion, forest clearing, cement production, etc.	50-200	1	79.9
CH_4	Methane	Landfills, production and distribution of natural gas and petroleum, fermentation from the digestive system of livestock, rice cultivation, fossil fuel combustion, etc.	12	21X	9.5
N_2O	Nitrous Oxide	Fossil fuel combustion, fertilizers, nylon production, manure, etc.	150	310X	5.8
HFC's	Hydrofluorocarbons	Refrigeration gases, aluminum smelting, semiconductor manufacturing, etc.	264	Up to 11,700X	1.8
PFC's	Perfluorocarbons	Aluminum production, semiconductor industry, etc.	10,000	Up to 9200X	
SF_6	Sulfur Hexafluoride	Electrical transmission and distribution systems, circuit breakers, magnesium production, etc.	3,200	Up to 23,900X	

*Standard Industry Classification

Source: Energy Information Administration (1998); IPCC (2001)[19]

[17] Energy Information Administration (1998) 'Form EIA-846: Manufacturing Energy Consumption Survey', and 'Form EIA-810, Monthly Refinery Report', Energy Information Administration; Intergovernmental Panel on Climate Change (IPCC) (2001) *Climate Change 2001: The Scientific Basis*, Cambridge University Press, Cambridge.

[18] United Nations (2002) The Kyoto Protocol – A Protocol of the United Nations Framework Convention on Climate Change. Available at: http://unfccc.int/kyoto_protocol/items/3145.php. Accessed 14 December 2008.

[19] Energy Information Administration (1998) 'Form EIA-846: Manufacturing Energy Consumption Survey', and 'Form EIA-810, Monthly Refinery Report', Energy Information Administration; Intergovernmental Panel on Climate Change (IPCC) (2001) *Climate Change 2001: The Scientific Basis*, Cambridge University Press, Cambridge.

Modelling by the Massachusetts Institute of Technology in America has confirmed this, showing that including strategies to reduce non-CO_2 emissions reduces the costs of climate change abatement by two-thirds. Companies like Dupont, IBM and STM Microelectronics are making significant reductions to GHGs by not ignoring non-CO_2 emissions. The benefits for companies addressing these non-CO_2 greenhouse gases is best shown by DuPont's experience:[20]

In the 1990s the company Dupont set itself the goals of reducing its GHGs by 65 per cent (which has now shown to be saving Dupont US$2 Billion).[21] Setting this target helped Dupont to look for new and creative ways to reduce GHGs. As Charles O. Holliday Jr. Chairman, CEO and Chief Safety, Health and Environment Officer, DuPont stated, *'As a company, Dupont believes that action is warranted, not further debate. We also believe that the best approach is for business to lead, not wait for public outcry or government mandates. From our experience of the past 10 years, we know that integrating environmental considerations into our business strategies enhances our ability to achieve sustainable growth'.*[22]

Dupont was able to significantly cut back on GHGs by reducing and replacing the non-CO_2 Greenhouse gas emissions of HFCs, PFCs, N_2O and CH_4, as shown in Figure 10.1. Dupont's biggest achievement was reducing N_2O emissions from nylon production by 80 per cent.

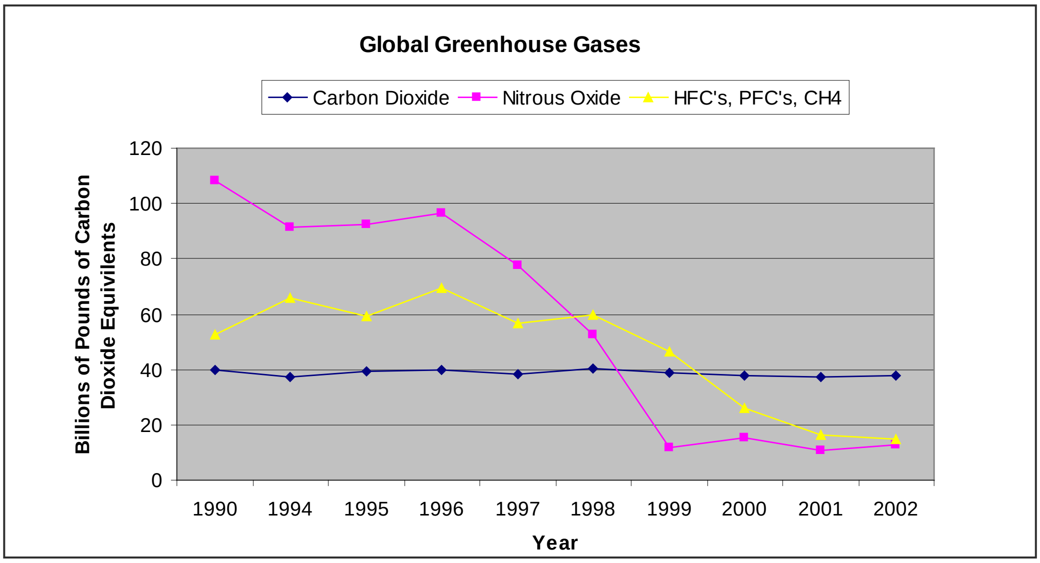

Figure 10.1: Trends of Global Greenhouse Gases Emissions for DuPont from 1990-2002

Source: DuPont [23]

Other companies are achieving significant greenhouse gas reductions by reducing onsite emissions of these gases. IBM[24] has achieved a 10 per cent reduction in onsite non-CO_2 PFC emissions between 2000 and 2005 while also saving US$791 million through a 65 per cent

[20] Dupont (2003) *Sustainable Growth 2003 Progress Report,* Dupont. Available at http://www2.dupont.com/Social_Commitment/en_BR/SHE/usa/us1.html. Accessed 12 December 2007.
[21] The Climate Group (2004) *Carbon Down, Profits Up*, The Climate Group. Available at www.theclimategroup.org/assets/Carbon_Down_Profit_Up.pdf. Accessed 12 December 2007.
[22] See The Climate Group - *DuPont: Corporate, Science and Technology* at http://www.theclimategroup.org/index.php?pid=421. Accessed 12 December 2007.
[23] See Dupont Environmental Performance - *Greenhouse Gas Emissions* at http://www2.dupont.com/Sustainability/en_US/Performance_Reporting/data_summary.html#5. Accessed 3 February 2007.
[24] IBM (2003) *Environment and Well-Being report,* IBM, p8. Available at http://www-8.ibm.com/ibm/au/environment/annual/2003.html. Accessed 12 December 2007.

reduction in CO_2 emissions (1990-2002).[25] The magnesium industry is in the process of phasing out SF6 by 2010 through a voluntary partnership with the US EPA and the International Magnesium Association.[26] Nike has already phased out all sulphur hexafluoride (SF6) from its manufacturing facilities. ST Microelectronics (ST), a Swiss-based US$8.7 billion semiconductor company, set a goal of zero net GHG emissions by 2010 while increasing production 40-fold.

> *The main sources of ST's GHG emissions are ~45 percent energy use, ~35 percent PFC and SF_6 emissions and ~15 percent transportation. Its strategy is to reduce on-site emissions by investing in co-generation (efficient combined heat and electricity production) and fuel cells (efficient electricity production). By 2010 cogeneration sources should supply 65 percent of ST's electricity with another 5 percent coming from fuel switching to renewable energy sources. The rest of the reductions ST is seeking are through improved energy efficiency (hence reducing the need for energy supply) and reforestation projects (to sequester carbon).*
>
> **ST Microelectronics, 2003**[27]

Thus, chemists and chemical engineers have a potentially pivotal role in helping the world reduce GHG emissions, because chemistry underpins all industries and society's way of living. The following examples and fields demonstrate the exciting areas where chemists and chemical engineers are working to make a difference in reducing GHG emissions.

Mimicking Photosynthesis in Plants[28]

The solar energy that hits the Earth's surface can meet current global anthropogenic (human) energy demands 10,000 times over. However, current human made solar cells are only about 15-30 per cent efficient at converting the sun's energy into electricity - in nature, plants convert the energy of sunlight much more efficiently than this. So to improve our solar energy conversion efficiency, we might ask the question: *How does nature collect and store solar energy?* Even after two or three centuries of investigation, the complete answer to this question is not entirely understood. Fortunately though, enough is understood to be practically useful. We know, for example, that solar energy is collected by the green leaves of plants, which contain the pigment *chlorophyll*. When chlorophyll absorbs sunlight energy, electrons in molecules are excited and transferred to other molecules in the leaf. This process is the first step of photosynthesis, which is the process plants use to convert sunlight, carbon dioxide and water into carbohydrates and oxygen.

For over 30 years many unsuccessful attempts have been made to create a solar cell based on the photosynthesis principle, such as covering titanium dioxide with a layer of chlorophyll - but this only has an efficiency of about 0.01 per cent. Since this initial research, a number of significant improvements have been made. One form of 'artificial photosynthesis' is based on the concept of a dye, similar in performance to chlorophyll, which can absorb light and generate electrons. These electrons enter the 'conduction band' of a high-surface-area semi-conductor

---

[25] Presentation by Ravi Kutchibhotla, Corporate Program Manager for Energy Management, IBM cited in The Climate Group (2004) *Carbon Down, Profits Up*, The Climate Group. Available at www.theclimategroup.org/assets/Carbon_Down_Profit_Up.pdf. Accessed 12 December 2007.

[26] See US Climate Change Technology Research Program - *Research and Current Activities: Reducing Emissions of Other Greenhouse Gases* at www.climatetechnology.gov/library/2003/currentactivities/othergases.htm#sf6. Accessed 12 December 2007.

[27] ST Microelectronics (2003) *Sustainable Development Report,* ST Microelectronics. Available at http://www.st.com/stonline/company/environm/sustdev/sustdev03.pdf. Accessed 12 December 2007.

[28] See Dyesol - *Dyesol* at www.dyesol.com. Accessed 13 November 2007.

film like titanium dioxide ('titania' - a fine white powder), and move through an external circuit, converting light into 'green' power.

A new solar energy technology called 'Dye Solar Cell' (DSC) that mimics the photosynthesis process using dye and nanotechnology is also of great interest to the Japanese and European Union Photovoltaics Industry. DSC was developed in 1998 by Michael Graetzel at EPFL, a research institute in Switzerland. Rather than using a single large (titania) semi-conductor, the technology uses a nano-porous titania 'sponge', where each particle is around 20 nanometers in diameter. This increases the effective surface area available for absorbing the light, and each particle is coated with a dye monolayer such as ruthenium dye. The dye behaves like chlorophyll in plant photosynthesis – when it absorbs light, an electron is excited and transferred to the titania. The titania, which is a semiconductor, then transfers the charge to an external circuit, generating an electric current. DSCs are more efficient in low or variable light conditions than existing silicon solar cells, which means that they could be cost effectively integrated into often-shaded buildings or small communication devices such as mobile phones.

Dyesol[29] is a solar cell technology that integrates several DSCs into a single module, and is now in its third generation of design. The modules can be used as is, or can be connected in series or parallel to form 12 Volt or 24 Volt solar panels. Dyesol's manufacturing processes are relatively simple, have a low capital outlay, and are fairly clean. The raw materials are cheap and relatively benign. The Dyesol technology is different from conventional photovoltaic technology because it contains the following characteristics:

- ***Photo-electrochemical cells:*** charge separation occurs on the interface between a semiconductor and an electrolyte (i.e. the dye).
- ***Nano-particulate cells:*** it is not a dense film such as silicon, but a 'light sponge' cell.
- ***Dye-sensitised cell:*** like the leaf-pigment *chlorophyll*, a dye monolayer chemically absorbed on the semiconductor is the primary absorber of sunlight. Free charge carriers are generated by electron injections from dye molecules excited by the absorption of sunlight.

Many other leading research groups around the world are also researching and investigating other materials and processes that mimic other key parts of the photosynthetic process.[30] For example, consider that photosynthesis can occur in the leaves of plants, in bacteria, and in algae. During the photosynthesis in green plants and algae, water is split into oxygen, protons and electrons:

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+$$

Both the protons and the electrons are used further in the photosynthesis. In natural photosynthesis a light-harvesting (LH) antenna system with a large optical cross-section (for example the LH2 complex as shown in Figure 10.2) absorbs a photon that is funnelled by energy transfer (ET) to the reaction centre. The study of *artificial photosynthesis* can roughly be separated into the study of *artificial antenna complexes* and the study of *artificial reaction centres*. In both cases, the artificial systems copy the functions of the natural systems. However, the molecules can be quite different chemically.

Figure 10.2 shows a diagrammatic representation of the photoactive part of the light harvesting antenna complex 'LH2', which is found in the purple bacterium *Rhodobacter sphaeraides*. This

[29] See Dyesol - *Dyesol* at www.dyesol.com. Accessed 13 November 2007.
[30] Jeffrey R. *et al* (2004) 'Molecular Electronics: From Basic Chemical Principles to Photosynthesis to Steady-State Through-Molecule Conductivity to Computer Architectures', *Australian Journal of Chemistry*, Vol. 57, pp1133-1138; Collings, A.F. and Critchley, C. (eds) (2005) *Artificial Photosynthesis: From Basic Biology to Industrial Application,* Wiley Publications. Available at www.wiley.com/WileyCDA/WileyTitle/productCd-3527310908,descCd-tableOfContents.html. Accessed 13 November 2007.

antenna complex (or 'chromophore') consists of two bacteriochlorophyll (BChl) ring systems, with 18 red and 9 green 'units' (or rings), respectively, and 9 carotenoid molecules (yellow strings). Each chromophore is confined to this geometry by the surrounding protein (not shown here).

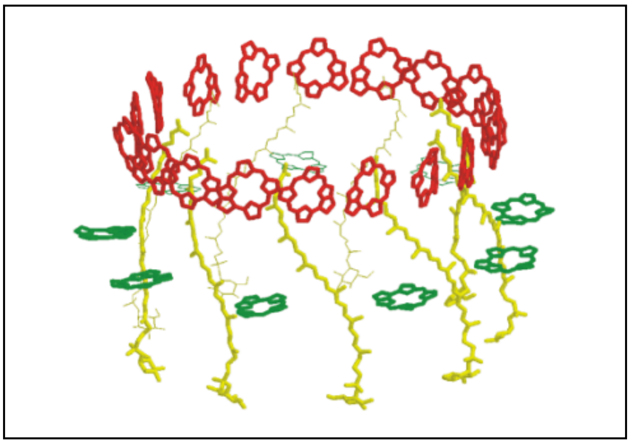

Figure 10.2: The photoactive part of the light harvesting antenna complex

Source: Arizona State University Photosynthesis Centre[31]

It is difficult to use BChls as chromophores in artificial antenna systems because they are not chemically stable. Better candidates to mimic the natural antenna system include chemically stable molecules that efficiently absorb light and, most importantly, are able to efficiently transfer the captured energy to other parts of the antenna. Many research groups are investigating *porphrin* array structures that can do this (see Figure 10.3).[32] For example, Artificial porphyrin systems designed to mimic light capture in nature are currently under investigation.

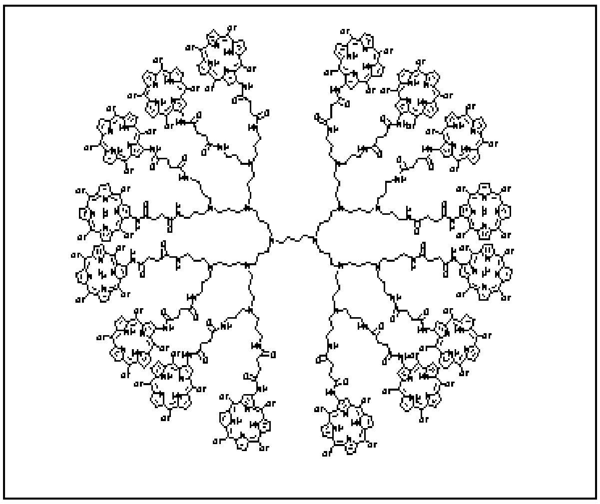

Figure 10.3: A diagram of the 'Porphyrin array'

Source: Crossley, M. *et al* (2005)[33]

Another potential future research innovation is described by Professor Chris Pickett, Associate Head of the Biological Chemistry Department, John Innes Centre, [34]

[31] For an overview of artificial photosynthesis see Arizona State University Photosynthesis Centre - *Artificial Photosynthesis and Bio-Inspired Catalysis* at http://photoscience.la.asu.edu/Photosyn/Director's%20Message.html. Accessed 13 November 2007.
[32] Kamat, P.V. *et al* (2004) 'Supramolecular Photovoltaic Cells Based on Composite Molecular Nanoclusters: Dendritic Porphyrin and C60, Porphyrin Dimer and C60, and Porphyrin-C60 Dyad', *Journal of Physical Chemestry B*, Vol. 108, pp12865-12872.
[33] Crossley, M., Sintic, P., Hutchison, J. and Ghiggino, K. (2005) 'Chemical Models for Aspects of the Photosynthetic Reaction Centre: Synthesis and Photophysical Properties of Tris- and Tetrakis-porphyrins that Resemble the Arrangement of the Chromophores in the Natural System', *Organic and Biomolecular Chemistry*, Vol. 3, pp852-865.

One notion that is currently holding the imagination of many research workers is to use the high-reduction potential electrons yielded by photochemistry… [to] *generate molecular hydrogen (H2). While hydrogen is not of much use to photosynthetic organisms, it is of great interest to humankind as an energy carrier and combustible fuel. If the electrons used in this process were to be extracted from water, as in photosynthesis, we could avail ourselves of an ideal method of energy generation: solar energy yielding hydrogen from water! This is an exciting early step in developing a sustainable system for producing electricity from hydrogen. In Nature iron–sulphur enzymes catalyse a range of important chemical reactions that industry can only do by using precious metal catalysts and/or high temperatures and pressures. Based on Nature's blueprint we are a step closer to building an iron-sulfur catalyst for reactions fundamental to a sustainable hydrogen economy.*

Creating Low Carbon Manufactured Materials

The overwhelming proportion of modern industry relies on 'heat, beat and treat'[35] methods to produce and manipulate materials, and to generate energy. The heat, beat and treat approach involves industrial processes running at very high temperatures. The process then uses high pressure extruders to force the fibres into alignment as they are drawn out. These processes are obviously extremely toxic and high in energy. Nature, on the other hand, manufactures an amazing array of products and yet it does it with low energy flows, at room temperature with no persistent toxics. Everything that is an output of a process is food for some other process - the loops are closed. Yet nature can create ceramics at room temperature that are tougher than the toughest ceramics industry can make. A spider produces a waterproof silk that is five times stronger than steel and five times tougher than Kevlar without needing high temperatures and sulphuric acid.

Drawing inspiration from the field of science called 'biomimicry' (i.e. design inspired by Nature) and realising the superior performance of the spider web, *Spinox,* a company based in the United Kingdom, is currently developing a biomimetic silk-producing device. The current version is hand-held, spinning a protein silk which is naturally golden in colour. At 15 microns, it is four times thicker than spider's silk.

Consider another example of the abalone shell. It manufactures an inner lining, stronger than our best ceramics, but it does it in seawater at ambient temperature immediately next to the creature's body. Research groups such as Sandia National Laboratories[36] are researching methods of mimicking the abalone to create high-performance materials for applications such as scratch-proof glasses, unbreakable windshields and nosecones for space shuttles.

Many engineers and designers will claim that they *must* use these traditional high energy methods of manufacture, but green chemists utilising insights from Nature are finding new ways to manufacture materials at low temperature. So, the question is: *how does Nature manufacture materials and generate energy?* The most significant difference between industrial manufacturing and natural manufacturing is the choice of materials. Nature mostly uses polymers, relying heavily on proteins for functionality, but also uses mineral compounds for special purposes.

[34] Mathias, R. (2005) 'Nature Points the Way to a Sustainable Hydrogen Economy', *Innovations Report: Forum for Science, Industry and Business*, 11 February, 2005. Available at www.innovations-report.com/html/reports/life_sciences/report-40161.html. Accessed12 November 2007. See also the Official John Innes Centre website at www.jic.ac.uk. Accessed 12 November 2007.

[35] For additional information see Biomimicry Guild/Rocky Mountain Institute - *Biomimicry Database* at http://database.biomimicry.org/start.php. Accessed 13 November 2007.

[36] Padilla, M. (2003) 'Sandia researchers create nanocrystals nature's way', *Sandia Lab News*, August 8, 2003, Sandia National Laboratories. Available at http://www.sandia.gov/LabNews/LN08-08-03/labnews08-08-03.pdf. Accessed 12 November 2007.

Consider the following four examples of Nature's 'tricks of the trade' for manufacturing materials which assist in reducing energy demands, from Janine Benyus's book, *Biomimicry: Innovation Inspired by Nature*: [37]

– ***Life-friendly Conditions:*** *'… nature's first trick of the trade is that nature manufactures its materials under life-friendly conditions – in water, at room temperature, near animals' bodies, without harsh chemicals or high pressures.'*

– ***Ordered Hierarchical Structure:*** this *'seems to be nature's second trick of the trade. From the atomic level all the way to the macroscopic, precision is built in, and strength and flexibility follow.'*

– ***Self Assembly:*** this *'is nature's third trick of the materials trade. Whereas we spend a lot of energy building things from the top down – taking bulk materials and carving them into shape – nature does the opposite. It grows its materials from the ground up, not by building but by self-assembling.'*

– ***Use of Templates*****:** *'nature's fourth trick of the trade – the ability to customise materials through the use of templates. Whereas we muddle by in our industrial chemistry with final products that are a mish-mash of polymer-chain sizes, with most too long or too short to be of ideal use, nature makes only what she wants where she wants and when she wants. No waste on the cutting room floor.'*

[37] Benyus, J. (2002) *Biomimicry: Innovation Inspired by Nature,* HarperCollins, New York, p97.

Key References (Alphabetical Order)

1. Anastas, P.T. and Warner, J.C. (2000) *Green Chemistry: Theory and Practice,* Oxford University Press, Oxford.
2. Anastas, P.T. and Williamson, T.C. (1998) *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes,* Oxford University Press, Oxford, UK.
3. BioMatNet: An EPOBIO project that makes available the results from European Commission suppored research in the area of renewable bioproducts. See http://www.biomatnet.org/home.html. Accessed 3 February 2007.
4. See US EPA –Innovation in Plastics *: Cargill Dow – Plastic from Corn* at http://www.epa.gov/osw/inforesources/news/2005news/01-corn.htm Accessed 13 December 2007.
5. Lancaster, M. (2002) *Green Chemistry: An Introductory Text,* The Royal Society of Chemistry, Cambridge, UK.
6. Pollard, G. (2005) *Catalysis in Renewable Feedstocks: A Technology Roadmap v1*, BHR Group. Available at http://www.bhrgroup.co.uk/extras/renewcatsumm.pdf Accessed 3 February 2007.
7. Smith, M., Hargroves, K., Stasinopoulos, P., Stephens, R., Desha, C. and Hargroves, S. (2007) Energy Transformed: Sustainable Energy Solutions for Climate Change Mitigation, The Natural Edge Project (TNEP), Australia. Available at http://www.naturaledgeproject.net/Sustainable_Energy_Solutions_Portfolio.aspx Accessed 11 December 2008
8. USA EPA website - *Greenhouse Gas Emissions: Non-CO_2 Greenhouse Gas Programs* athttp://www.epa.gov/climatechange/economics/mitigation.html . Accessed February 2007.
9. Various case studies are located at the US EPA website - *Presidential Green Chemistry Challenge* at http://www.epa.gov/greenchemistry/pubs/pgcc/presgcc.html. Accessed 12 December 2007.
10. Weaver, P*.,* Jansen, L., van Grootveld, G., van Spiegel, E. and Vergragt, P. (2000) *Sustainable Technology Development*, Greenleaf Publishing, Sheffield, UK.