

*Michael Grätzel on Light and Energy,*  
**Molecular Photovoltaics Mimic Photosynthesis.**

Perhaps the greatest challenge for our global society is to find ways to replace the slowly, but inevitably vanishing fossil fuel supply with renewable resources and at the same time avoid negative effects from current energy system on climate, environment and health. The quality of human life depends to a large degree on the availability of clean energy sources. Worldwide power consumption is expected to double in the next four decades due to the increase in world population and the rising demand of energy in the developing countries. This implies enhanced depletion of fossil fuel reserves, leading to further aggravation of environmental pollution. As a consequence of dwindling resources, a huge power supply gap of 14 terawatts is expected by 2050. This equals today's entire consumption, and thus threatens to create a planetary emergency of gigantic dimensions. Solar energy is expected to play a crucial role as a future energy source. The sun provides about 120,000 terawatts to the earth's surface which amounts to six thousand times the present rate of the world's energy consumption. However, capturing solar energy and converting it to electricity or chemical fuels, such as hydrogen, at low cost and using abundantly available raw materials remains a huge challenge.

Chemistry and materials science are expected to make pivotal contributions to the identification of environmentally friendly solutions to this energy problem. Learning from the ways green plants capture solar light and convert it to chemical energy, we have developed a photovoltaic cell based on films of nanometer-sized semiconductor oxide particles. The most advanced embodiment of the new solar cell employs the sensitization of mesoscopic titanium dioxide film by a molecular dye or semiconductor quantum dot [1-3]. The overall efficiency for solar energy conversion to electricity has already reached more than 12 percent, rendering the new photovoltaic cells competitive with thin film silicon devices. For the first time, dye sensitized solar cells accomplish the separation of light harvesting and charge carrier transport, opening up vast options for the choice of the molecular absorber material. The sensitizer or semiconductor quantum dot is placed at the interface between an electron and hole-conducting material. Upon photo-excitation the sensitizer injects an electron in the conduction band of the oxide and is regenerated by the injection of a positive charge in the electrolyte or hole-conductor. Impressive stability both under long-term light soaking and high temperature stress has been reached, fostering first industrial applications [4]. This field is currently receiving enormous attention, with a great increase in the number of publications over the last decade.

The advantage of dye sensitized solar cells (DSSCs) is that they can be produced at low cost, i.e. potentially less than 0.5 US\$/peak Watt according to industrial projections.

The DSSC does not require the expensive and energy-intensive high vacuum and materials purification steps that are currently employed in the fabrication of all other thin film solar cells. The low cost and ease of production of the new cell should benefit large-scale applications. Mass production of flexible light-weight modules by a role-to-role method and their commercial sales have started recently.

The materials used to make DSSCs are abundantly available so that the technology can be scaled up to the terawatt scale without running into feedstock supply problems. This new solar cell will promote the acceptance of renewable energy technologies, not least by setting new standards of convenience and economy.

#### **Literature:**

1. Grätzel, M., and O'Regan, B. "A Low-Cost, High-Efficiency Solar Cell Based on Dye-sensitized Colloidal TiO<sub>2</sub> Films" *Nature*, 353, 737-740, 1991.
2. Grätzel, M. et al., "Solid-state Dye-sensitized Mesoporous TiO<sub>2</sub> Solar Cells with High Photon-to-electron Conversion Efficiencies." *Nature*, 395, 583-585, 1998.
3. Grätzel, M., "Photoelectrochemical Cells." *Nature* 414, 338-344, 2001.
4. Grätzel, M., "Recent Advances in Mesoscopic Solar Cells." *Acc. Chem. Res.* 42, 1781-1798, 2009.

In 2008, the photovoltaic industry produced about 8 gigawatt peak of electric power, and the projection is that the capacity will reach about 300 gigawatt peak in 2030. The term "peak" indicates that this power would be generated in full sunshine. However, taking into account the seasonal and diurnal cycles, the average power is about 3-10 times lower. The goal is to cut down on fossil consumption and use renewable sources to cover energy demands. As mentioned above, the sun, in particular, supplies 120,000 terawatts to the earth, compared to the 14 terawatts of power the earth requires to cover all its present energy needs. The photovoltaic market has been growing, but still depends strongly on subsidies. There is thus plenty of room for new cells and new concepts. In the end, radical breakthroughs are needed to bring the costs down below the 0.05 US\$/KWh level, in order to become competitive with conventional energy suppliers. Moreover, we need to use readily available materials. A brief presentation of this discovery follows.

As Professor Stauffacher pointed out, the solar cell we have invented is the only photovoltaic device that uses dye molecules to absorb light and generate positive and negative charges, resulting in the conversion of solar to electric power. In this fashion, it mimics the primary process of natural photosynthesis, which has been operating in green plants and organisms for 3.5 billion years and hence is a well established

principle. In the green leaf, chlorophyll molecules absorb sunlight and generate electric charges, which, however, are not collected as electric current. Instead, they are converted by redox reactions at the membrane level to generate oxygen from water and reduce carbon dioxide to carbohydrates.

Using this principle of natural photosynthesis, our voltaic cell is the first to achieve the separation of the two functions of light absorption and charge carrier transport. In a conventional photovoltaic cell, these tasks are actually assumed by the same material. Thus, in silicon solar cells, the semiconductor – a sandwich of positively (p) and negatively (n) doped silicon – absorbs sunlight, resulting in the generation of electric charges. These need to be separated from each other first by the local electric field present at the p-n junction, which is followed by transport to the charge collectors. Thus, the silicon has to absorb light, separate the positive from the negative charges and conduct the charges to the two electric current collectors. Things get quite complicated, and ultra-pure materials are required to accomplish the photo-electric conversion at high efficiency. Solar grade silicon requires 99.9999 percent purity, which makes it expensive and energy-intensive to produce. The approach we have been taking is radical, but it is not entirely new, because the light energy conversion in photosynthesis uses a very similar principle.

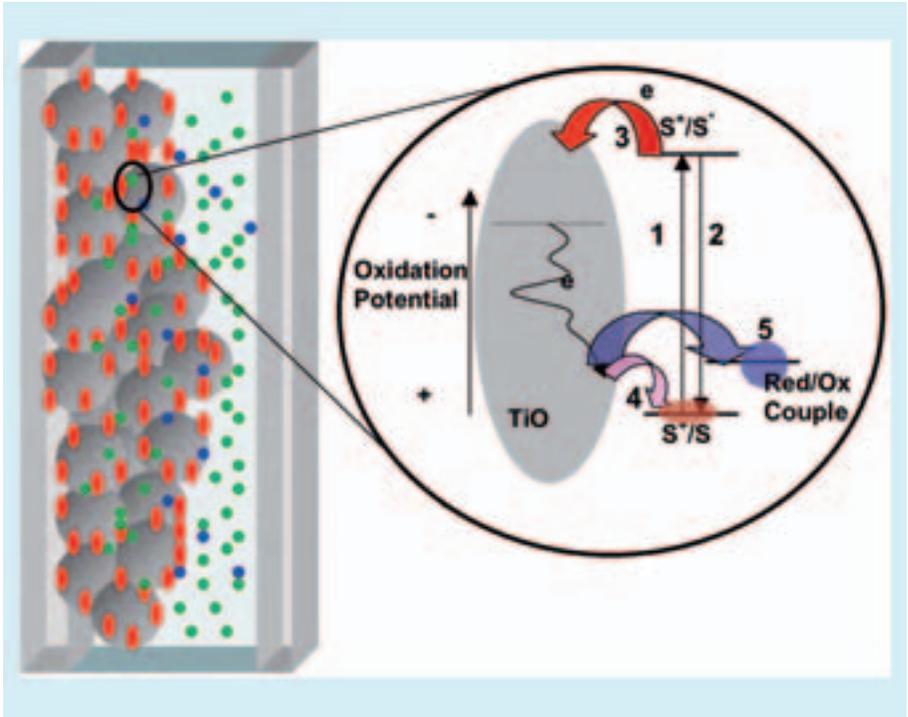


Figure 1

Figure 1 gives a fair summary of the whole invention. It shows a solar cell that appears as a coloured glass, where the photo-sensitized pigment is sandwiched between the front glass panel serving as the front electric contact and the back panel serving as the counter-electrode of the cell. The ease of fabrication of these cells is illustrated by the fact that the photoactive pigment layer can be applied to the front panel by screen printing, thus offering a large variety of options for different colours and patterning of these films. The cells can be made in ambient laboratory conditions without having to follow any expensive procedures like high vacuum deposition methods. Here we have printed the logo of the Ecole Polytechnique de Lausanne using a sensitizer with a beautiful red colour. That the patterned film really acts as an efficient photovoltaic converter, can be shown by the fact that the electricity produced by the solar cell spins a fan even under ambient light conditions. Note also that the coloured glass panel is transparent. In fact, our cell is the only one that can be made truly transparent, thus rendering it attractive for applications such as energy producing windows or glass facades in buildings. It also absorbs light from all angles, just as the green leaf renders its operation particularly efficient in diffuse light, i.e. cloudy skies or indoor conditions. A conventional photovoltaic cell captures light from one side only. Thus, the device shown in the picture captures ambient diffuse light and turns it into electric power. I could have shown the same experiment in this very room here, producing electricity from the light that is emitted by the fluorescent tubes. One company that has seen an immediate application for this effect is Logitech, which would like to power the keyboard of computers using our cells. They selected our cells because they are the most efficient in converting ambient light to electricity.

Ruth Dreifuss, the former Conseillère Fédérale, who is present today in the audience, personally witnessed this experiment some 15 years ago. At that time, she was the President of Switzerland and visited the Ecole Polytechnique Fédérale de Lausanne. She was accompanied by Queen Beatrix from the Netherlands with her husband Prince Bernhard, who were on a state visit to Switzerland. We built a solar cell glass panel that turned a small model of a windmill under illumination. Both the Queen and the Prince were enchanted by this demonstration, which received widespread press coverage in the Netherlands. This visit had a strong impact, and in fact, the Netherlands became the first country where our principle was adopted. First, our Dutch colleagues checked it out of course – they are very careful people – and they afterwards built a very strong research community that helped us to develop this technology.

Figure 2 is a schematic representation of the solar cell we presented in the seminal paper “A Low-Cost, High-Efficiency Solar Cell Based on Dye-sensitized Colloidal  $\text{TiO}_2$  Films”, published in *Nature*, vol. 353, in 1991. The paper has been cited over



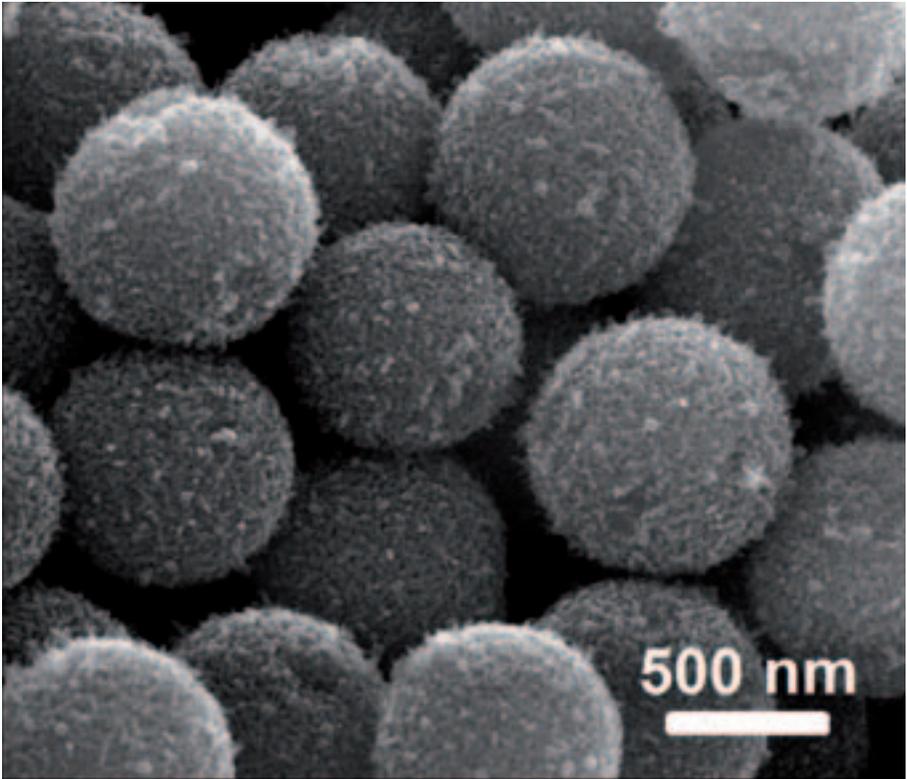
**Figure 2:** Schematic presentation of the operation of a mesoscopic dye sensitized solar cell. Light is captured by the sensitizer (S) that is attached to a nanometer-sized  $\text{TiO}_2$  particle producing the excited state  $S^*$  (1). This enables the sensitizer to inject an electron into the conduction band of the  $\text{TiO}_2$  (3). The interfacial electron transfer competes with deactivation of  $S^*$  (2). The oxidized sensitizer is regenerated by the electron donation from the reduced form of the redox couple present in the electrolyte. The conduction band electrons move through the  $\text{TiO}_2$  particle network to be collected as electric current. Competing with this process is their recapture by the oxidized form of the sensitizer (4) or redox couple (5).

5,000 times, so has since then become a classic. It shows the principle of operation of the dye-sensitized solar cell. The electron transporting material is constituted by a network of very small titanium dioxide ( $\text{TiO}_2$ ) particles, whose size is in the 20-30 nanometer range. These  $\text{TiO}_2$  particles are represented as grey balls in the diagram. The medium transporting the positive charges (holes) is either an electrolyte or a solid

p-type semiconductor, which is infiltrated in the porous network. Electric charges are generated from light by dye molecules that are anchored as a monomolecular layer at the surface of the nanocrystalline  $\text{TiO}_2$  film. These dye molecules are presented as red dots in the diagram. Following excitation by sunlight, the dye molecules inject electrons in the  $\text{TiO}_2$  particles and holes in the electrolyte or solid p-type conductor. In order to reach high conversion efficiencies with the solar cell, it is very important to collect these photo-generated charge carriers as electric current before they recombine. In order to achieve this goal, the charge carrier collection has to be significantly faster than their recombination. Contrary to conventional photovoltaic devices where electrons and holes are generated – and recombine – in the same semiconductor solid, in our cell, their recombination has to take place across the interface that separates the electron transporting material from the hole-transporting material. This offers the opportunity to retard the charge carrier recombination by judicious engineering of this interface. For present state-of-the-art solar cells, the transport of charge carriers is at least 100 times faster than their recombination. Hence, over 99 percent of the charges produced by the sensitizer under illumination can be collected as electric current, which explains why the solar cell operates very efficiently despite a highly disordered structure.

As research advances in this field, new nanostructures emerge, showing great potential to move the conversion efficiencies to higher levels. For example, Figure 3 shows an electron microscopy picture of beads consisting of agglomerated nanometer-sized  $\text{TiO}_2$  particles that have been sintered together to produce round balls of 500-800 nm size.

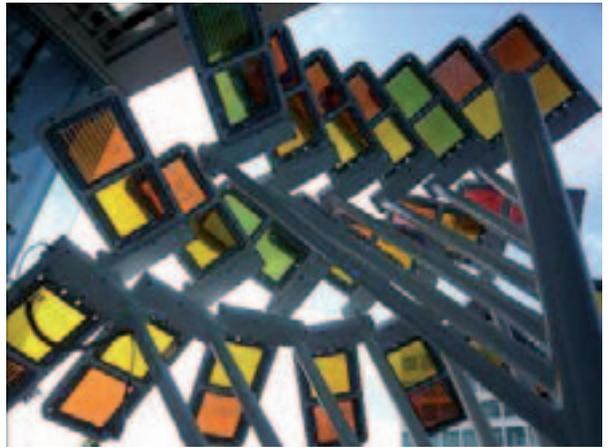
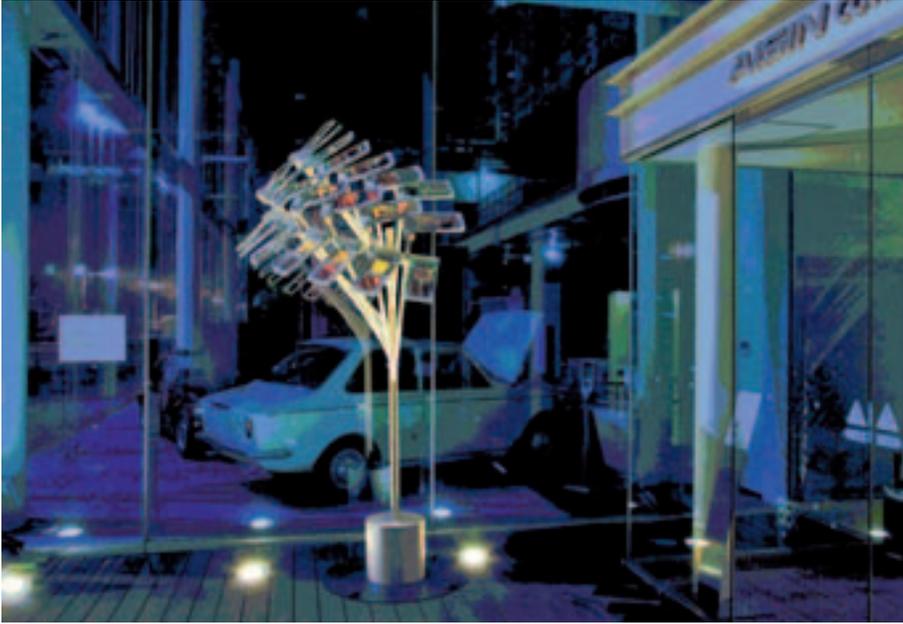
The mesopores in the interior of these beads generate a large internal  $\text{TiO}_2$  surface area, which is covered by dye molecules for efficient solar light collection. Amazingly, when visible light strikes these beads, it can be quantitatively converted to electric current, their light harvesting capacity being increased markedly over a simple nanocrystalline film by multiple scattering of photons increasing the optical path length. Thus, these new mesoscopic structures enhance photon capture by exerting a dual function to scatter light and photo-generate charge carriers. We can use different dyes in order to realize solar cells in a variety of colours, i.e. yellow, red, blue, green and black. The discovery of a new green dye has been remarkable, as dye sensitized solar cells based on this molecule achieve over eleven percent conversion efficiency. The chemical structure of this new green dye resembles that of chlorophyll, i.e. it is a macrocyclic compound composed of 4 pyrrol rings coordinating a zinc ion. The Japanese company Aisin Seiki in cooperation with Toyota has made artificial green leaves using a green dye which provides electric power under illumination.



**Figure 3:**  $TO_2$ , new porous structures.

There is a great enchantment with dye sensitized solar cells in Asian countries. I have just returned from an international photovoltaic congress in Korea, where seven sessions were held on our cells. Many interesting lectures on dye sensitized solar cells were presented there, illustrating the excellent level of research of the numerous groups working in this field. I shall now illustrate our invention with a few applications. Figure 4 shows multicoloured streetlamps in Japan, where transparent dye sensitized cells are used to charge a battery during the day, and then at night, the stored electric energy is used to power a light emitting diode (LED).

The beautiful lamps and electric power producing windows developed by Sony have a similar function, except that they capture ambient light and convert it to electricity,



**Figure 4:** *Streetlamps in Japan.*

which is again stored in a battery and used to power the LED. So we do not need any electric power supplies to run these lamps. Their appearance is extraordinary, as Sony designers have printed the dye-sensitized pigments in the form of beautiful motifs on the glass screen of the lamp. These cells look more like artwork than photovoltaic devices. I think that in the future, we shall not only increasingly mount conventional photovoltaic panels on the roof, but that we shall also see them penetrate our living space more and more. One particularly attractive application of dye translucent dye-sensitized solar cells – pursued by the Australian company Dyesol – is the electric power producing glass facade.

Dye sensitized solar cell modules are undergoing stability tests in outdoor conditions, for instance, on a building of 3G Solar Ltd in Jerusalem. The photocurrent flowing out of the modules in bright sunshine is 3 amperes, and the voltage is over 20 V. This is a very significant electric power output for each module. When we started our work we first measured microamperes of photocurrent with small laboratory cells. Hence the scale up of the devices has been over 1 million times.

The company G24 Innovations started the mass production of flexible solar cells in Cardiff, Wales, in October 2009. The cells are fabricated by continuous roll-to-roll production, and hence are low cost. They are used on bags or rucksacks to power electronic equipment – such as portable telephones – by ambient light.

For the future it is very important to motivate the younger generation to work in the renewable energy sector. Thus, in Japan a group of young people raised about 6,000,000 yen to build a race car powered by dye sensitized solar cells. It participated successfully in a race in Japan last year. I think that we shall witness a shift to electric or hybrid cars in the near future, and they could be powered at least for city traffic by solar energy.

Last but not least, I would like to again express my profound gratitude to the Balzan Foundation for selecting me as one of the laureates for this prestigious Prize. I am deeply indebted to my co-workers who have contributed in a decisive fashion to the success of our research. I would also like to acknowledge our sponsors. In particular, I must mention the Swiss National Science Foundation, which has generously supported our curiosity-driven, fundamental research over many years.