Michael Graetzel’s Research Achievements

Graetzel pioneered fundamental studies of electron and energy transfer reactions in mesoscopic systems, a field where he has an outstanding track-record and to which he contributed major scientific breakthroughs. His groundbreaking investigations have opened up several new research fronts, providing the basis for a whole set of important discoveries with large impact both on the fundamental scientific and applied industrial level. Indeed, all of today studies on organic, quantum dot and perovskite solar cells can be traced to his seminal discovery of dye-sensitized solar cells, also known as “Graetzel” cells. He established the general validity of this revolutionary concept further by showing that reducing the feature size of any inorganic and organic light harvesting materials to the mesoscopic domain enables quantitative collection of photo-generated charge carriers even if their diffusion length is much inferior to the light absorption length. He also was the first to use mesoscopic systems to realize the efficient generation of fuels from sunlight mimicking the life sustaining process of natural photosynthesis and to enhance the power and storage capacity of lithium ion batteries. Below is a short summary of his research achievements.

Colloidal Semiconductor Nanocrystals
Graetzel was the first to prepare colloidal nanocrystals of II-VI chalcogenides and oxide semiconductors, such as CdS and TiO₂ and to study their optoelectronic properties. He conceived the idea of preparing monodisperse semiconducting particles of small enough dimensions to render scattering of light negligible. These have the advantage of yielding optically transparent solutions, allowing him to follow the dynamics of charge carrier reactions down to the femtosecond range by laser flash photolysis. Graetzel used a short laser pulse to generate electron-hole pairs in the colloidal nanoparticles and monitored the time course of their reactions using transient absorption spectroscopy. In this fashion he was able to obtain a wealth of information on the dynamics of interfacial charge transfer and electron-hole recombination in semiconductor nanocrystals [1, 2] which greatly assisted him in the subsequent realization of dye sensitized solar cells. The latter employ mesoporous films formed by arrays of TiO₂ nanocrystals as a key constituent. A crucial experiment in this respect involved the sensitization of the colloidal TiO₂ nanocrystals and mesoporous films by judiciously designed ruthenium complexes. The latter were endowed with carboxylated bipyridyl ligands to firmly anchor them to the oxide surface. Graetzel observed strikingly high external quantum efficiencies for photocurrent generation reaching an unprecedented level of 44% [3]. Subsequent femtosecond time resolution laser experiments showed the injection of the electron from the ruthenium complex into the conduction of the TiO₂ to occur within a picosecond [4] while the back-electron transfer to the oxidized sensitizer was orders of magnitude slower.

His findings laid the foundation to the development of semiconductor quantum dots showing size quantization effects in their optical properties. Studies on these colloidal quantum dots have been pursued over the last three decades on a world-wide scale and they have found first commercial applications as light emitters in television sets. Research on colloidal semiconductors continues in an unabated fashion and has produced extra-ordinary findings such as multi-exciton formation by a single photon and the slowing down of hot carrier cooling. Both effects are enhanced by quantum confinement effects and hence are much stronger in the nanocrystals than in bulk semiconductor materials.

Molecular Photovoltaics and Mesoscopic Solar Cells
Graetzel created the field of molecular photovoltaics, being the first to conceive and realize photosystems based on dyes as light harvesters that can rival and even exceed the
performance of state-of-the-art solar cells based on solid state p-n junctions. He is credited with moving the solar cell field beyond the principle of light absorption via diodes to the molecular level exploiting sensitization of wide band gap semiconductors oxides by dyes, for light energy harvesting. Key to his success was the introduction of a new paradigm in photovoltaics. Instead of using the conventional planar p-n junction cell architecture, he employed an array of colloidal semiconducting oxide nanoparticles to adsorb the sensitizer molecules. By introducing a mesoporous semiconducting oxide film as electron-selective contact to support the sensitizer he was able to increase the photocurrents in full sunlight several thousand times. Due to their huge internal surface area the nanoparticle array achieves very efficient light harvesting even at monolayer surface coverage by dyes, pigments or quantum dots while on a flat surface the sensitizer would produce a very week photo-response.

Graetzel's invention of mesoscopic solar cells presented a new paradigm in photovoltaic technology. The prototype of this new photovoltaic family is the dye-sensitized solar cell (DSC), also named "Graetzel cell", which employs dye molecules, pigments or semiconductor quantum dots to sensitize a mesoporous wide band gap semiconductor film. The landmark paper he published in Nature in year 1991 [5] had a huge impact being cited some 23’000 times until now (source: Web of Science June 2021). According to an analysis by Nature in year 2014 (volume 513) this publication ranks by citations amongst the top 100 papers of all time published across all domains of science. His revolutionary approach has allowed very high efficiencies to be reached in a photovoltaic conversion process that separated, for the first time, light harvesting and charge carrier transport mimicking successfully the primary process in natural photosynthesis. A further breakthrough [6] was realized with the molecular engineering of a new donor-acceptor porphyrin sensitizer achieving an efficiency record of 12.4 % in conjunction with cobalt complexes as redox mediators. Due to its beautiful green color and its high efficiency this sensitizer is presently employed commercially for electricity producing photovoltaic glass facades. Further computation-assisted molecular engineering of this type of donor-acceptor porphyrins allowed realizing panchromatic light harvesting across the while visible spectrum increasing the solar to electric power conversion efficiency (PCE) to 13% [7]. By using molecularly engineered donor acceptor chromophores and replacing the iodide/triiodide by Co(bipy)₃ complexes as redox couple the PCE of dye sensitized solar cells has meanwhile been raised further to 14.5 %. A recent breakthrough was achieved with DSCs using Cu(II/I)bipy₂ derivatives as redox mediators which realized efficiencies close to 35% for the conversion of ambient light into electricity. This has allowed dye sensitized solar cells into to take a leading position in the harvesting of ambient light for powering electronic devices opening up opportunities for widespread applications.

Graetzel initiated the use of ionic liquids as the redox electrolytes in the DSC, which initially contained volatile solvents. He and his team developed new hydrophobic ionic liquids displaying a low viscosity [8] which have found widespread applications and are now produced commercially. Further substantial advances in performance were achieved by introducing eutectic mixtures of imidazolium salts as redox active ionic liquids where the charge transport is accelerated by a Grotthuss-type exchange mechanisms [9]. The breakthroughs made by his team in this area have dramatically increased the stability of the dye sensitized solar cells under prolonged light soaking or heat stress, fostering their practical development for outside deployment. Several companies are now manufacturing ionic liquid based Cs on a commercial scale.

Graetzel pioneered also the use of solid state DSCs, replacing the liquid electrolyte by solid organic hole conductors. Specifically, his group introduced the triarylamine derivative spiro-
MeOTAD as a hole transporting material [10,11] which is now widely applied. Starting from low efficiencies below 1 % the PCE reached over 10 percent within a few years. The advantage of employing a solid hole conductor is that it is nonvolatile, shows faster charge carrier transport and is chemically less aggressive than a redox electrolyte. These advantages enabled the recent amazing rise of perovskite solar cells (PSCs) which currently reach a certified efficiency of 25.2 percent using the mesoscopic architecture of solid state C and hole conductors from the spiro-MeOTAD family.

**Perovskite Solar Cells**
Graetzel's work on dye sensitized solar cells and in particular his introduction of their solid state version employing spiro-MeOTAD as hole conductor [10] engendered the stunning development of perovskite solar cells (PSCs) which has become the most promising innovation in the recent history of photovoltaics. A vast number of scientists and engineers apply currently this embodiment in conjunction with metal halide perovskites pigments in particular methylammonium lead iodide (MAPbI₃) as light harvester. The development started with a paper by Miyasaka’s in 2009, who applied MAPbI₃ nanoparticles as sensitizers in liquid electrolytes based DSCs. However, the stability of the cells was poor due to rapid dissolution of the MAPbI₃ in the polar solvent and its power conversion efficiency (PCE) was low i.e. 3%. In year 2012 solid-state PSC versions using a solid state embodiment were announced by the groups of Kanatzidis, Miyasaka/Snaith and Graetzel/Park [12], which showed dramatically improved stability and a PCE of around 10%. This sparked a rapid progression of publications reaching currently a number of over 10'000. Introducing a sequential method for deposition of the perovskite films. Within a year's time Graetzel augmented the PCE from 10% to 15% [13], a stunning increase by common photovoltaic standards. His group also pioneered the use of multi A-cation perovskite formulations and discovered a way to stabilize the perovskite phase of FAPbI₃ (FA= formamidinium) by the addition of methylammonium or cesium ion [14,15]. Using these formulations his group reached as the first in the world a certified PCE of over 21 % showing the success of this approach. At present the certified PCE of such multiplication, solution-processed perovskite solar cells (PSCs) is 25.5 % exceeding the performance of the market leader polycrystalline silicon. Recent cost projections show that the levelized cost of electricity (LCOE) production by PSCs may be 2 -3- times cheaper than that of the PV market leader silicon. Together with the group of his colleague Lyndon Emsley, Graetzel introduced sophisticated solid-state NMR spectroscopy as a powerful tool to characterize these complex mixtures and study the interaction between its components. A serious caveat of PSCs has been their notorious instability to light thermal stress and moisture. Also, the currently employed spin coating procedure involving anti-solvents used to produce the high efficiency laboratory cells is difficult to upscale. These issues have put in question the outlook for practical applications of PSCs [14]. Graetzel has made outstanding contributions to realize stable and efficient PSCs that show promise for large-scale practical deployment (15-18)

**Mesoscopic Photosystems for the Generation of Fuels from Sunlight**
The Graetzel group leads research in the field of photosystems that accomplish the fuel generation by sunlight. His discoveries in the area of photoelectrochemical cells [19] have played a pivotal role for the development of technologies that can provide renewable and storable energy sources in the future. In this domain he also pioneered the use of mesoscopic light harvesting materials, in particular semiconducting oxides that show a strong absorption in the visible domain, such as Fe₂O₃ (hematite) and Cu₂O. The role of the mesoscopic morphology of these photosystems is different from that of the oxide nanoparticle arrays in DSCs. Their key advantage is that due their small feature size they can achieve near quantitative collection of the photo-generated charge carriers even for materials where the charge-carrier diffusion length is much shorter than the light absorption length [20]. This
allows to substantially enlarge the choice of absorber materials that carry out photoelectrochemical transformations very efficiently in sunlight. Thus, a compact Fe$_2$O$_3$ film contacted by water produces a very poor photo-response in sunlight due to the fact that most of the holes generated by sunlight recombine with electrons before they can reach the surface to react with water to produce oxygen. This is due to the fact that their diffusion length in the iron oxide is over 100 times shorter than the light absorption length. By contrast, a mesoscopic structure of Fe$_2$O$_3$ with a feature size of a few nanometer achieves quantum yields of over 60 % for oxygen generation from water. Using a tandem of two mesoscopic photosystems, including Mn-doped Fe$_2$O$_3$ nanorods and perovskite solar cells allowed to achieve the photoelectrochemical generation of hydrogen and oxygen from water splitting by visible light [21]. In year 2014 the Graetzel group introduced perovskite solar cells as light harvesters to split water into hydrogen and oxygen by sunlight, reaching a solar to hydrogen energy conversion efficiency (STH) of 12.3 % [22]. A similar efficiency of 13.4 % was obtained for the direct solar conversion of CO$_2$ to CO and O$_2$. [23]. Meanwhile the STH efficiency has been boosted further to reach a new record of 18.7 % with a perovskite/silicon tandem cell [24].

**Rechargeable lithium ion batteries.** Graetzel introduced the concept of using nanoparticle arrays as active materials in lithium ion batteries. This speeds up by 100 - 1000 times the rate of discharging and charging increasing the power output of the battery by the same factor. This concept was protected by a patent with Graetzel as coinventor filed in 1996, Together with 2 partners, Graetzel founded High Power Lithium (HPL) a company that commercialized the concept. The company was sold to Dow Chemical, which now offers nanostructured battery cathode materials developed by HPL such as lithium manganese phosphate on the market.

**References**


Atomic-level passivation mechanism of ammonium salts enabling highly efficient perovskite solar cells

Nature Communications 10, 3008 (2019)

A vacuum flash–assisted solution process for high-efficiency large-area perovskite solar cells


Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20 %.


Identifying champion nanostructures for solar water-splitting


Perovskite-Hematite Tandem Cells for Efficient Overall Solar Driven Water Splitting


Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth abundant catalysts


Solar conversion of CO2 to CO using Earth-abundant electrocatalysts prepared by atomic layer modification of CuO


TiC-Supported Pt Nanocluster Electro catalysts and Perovkite/Silicon Tandem Cells Enabling 18.7 % Solar Water Splitting

The discoveries of Michael Grätzel have launched new social-economic developments in the field of solar electricity and fuel generation as well as in lithium ion battery technology. These are summarized below. His ingenious concept of employing sensitized nanostructured junctions in photovoltaic cells has created a new paradigm in photovoltaics.

**Photovoltaics.** The revolutionary concept of employing sensitized nanostructured junctions in photovoltaic cells opened up technical breakthroughs in the PV field which are reflected by the evolution of the patent disclosure in this field over the last 2 decades. The first patent was granted in the USA in 1991, as shown in Figure 1 below and this was followed by a series of other patents. However, during the last 15 years the practical development of dye sensitized solar cells has taken off exponentially, the number of patents filed reaching over 3000 today. The patent history associate with this technology is shown in Figure 2. The unique selling propositions of today’s embodiments of dye sensitized solar cells are: i) the ease and low cost of their production. ii) the energy pay back times is 10 times shorter than for silicon. iii) the feed stocks required to make the cells are abundant iv) flexible, light weight versions of the cells can be fabricated by a roll to roll process. v) look-through glass panels of different color can be realize offering esthetically attractive solutions for building integrated PV producing electric power from sunlight. vi) the cells outperform silicon in diffuse daylight and indoor light. vii) the cells can capture light from all angles and their performance is much less sensitive to higher temperatures than that of Si cells. These features have opened up new markets for products based on dye-sensitized photovoltaics.
Professor Graetzel’s employer, the Ecole Polytechnique Fédérale de Lausanne, which owns Graetzel’s inventions has licensed his patents to a number of companies which are engaged in the commercial development of his cells. Roll-to-roll mass production of flexible light weight PV modules for ambient light harvesting has started in 2009 by the British company G24 Innovations Ltd. Since a number of companies such as the Swedish company Exeger (www.exeger.com) as well as the Japanese giants Ricoh (https://www.ricoh.com/release/2020/0204_1/) and Fujikura (https://dsc.fujikura.jp/en/?gclid=EAIaIQobChMIpP2oy9_78AIIVhOR3Ch1PXw6DEAAAYASAAEglFmPD_BwE) are selling products on the market. In March 2019 Exeger announced a strategic partnership with the Japanese Company Softbank to accelerate product development and world-wide deployment of its DSC-based, flexible Powerfoyle cells (https://www.exeger.com/product/applications/). This unique cell design generates electricity from ambient light with unprecedentedly high yield outperforming the best conventional photovoltaic cells by a large margin: https://www.forbes.com/sites/heatherfarmbrough/2021/02/15/look-no-leads-how-a-revolutionary-swedish-solar-technology-is-providing-endless-light/?sh=35cc68c3419d Two recent articles on dye-sensitized solar cells for efficient power generation under ambient lighting were published by the Graetzel group in Nature Communications 2021, 12 1777. and Nature Photonics, 2017, 11, 372-378. Figure 3 shows examples of commercially produced portable electronic devices powered by dye sensitized solar cells. In 2019. The report Sustainability in New and Emerging Technologies projects that IoT’s will reduce fuel consumption 3.5 trillion kWh annually and enable one gigaton benefit in
CO₂ emissions. Powering the IoT by DSCs from ambient light enables a further dramatic reduction in the electricity consumed by the IoT and in CO₂ emission which will entail large benefits to mankind.

Graetzel played a pivotal role in the recent development of perovskite solar cells (PSCs) that directly emerged from the DSC, triggering a second revolution in the history of photovoltaics. Their meteoric rise to reach a solar to electric power conversion efficiency of 25.5% has prompted large commercial investments. A plant with a capacity of 100 Megawatt is presently being built by Oxford PV in Germany. The ISE-Fraunhofer Institute projects the marked share of dye sensitized and perovskite photovoltaics to be 15 - 20 % by year 2030 corresponding to several hundred Gigawatt of renewable power.

In summary, Graetzel’s innovations in photovoltaics will provide clean and sustainable energy at low cost from the abundant solar source and in this fashion make a large contribution to the well-being of the human society.

**Figure 3.** Exeger products which use their Powerfoyle ([www.powerfoyle.com](http://www.powerfoyle.com)) photovoltaic cell design based on dye-sensitized photovoltaics to supply electric energy for their autonomous operation powered by ambient light. Recent examples include a bicycle helmet capturing sunlight for electric power production. [https://www.pocsports.com/collections/cycling-helmets/products/omne-eternal](https://www.pocsports.com/collections/cycling-helmets/products/omne-eternal)

Meanwhile several companies have started production and sales of electric power producing translucent glass panels based on Graetzel’s dye sensitized solar cell technology. A summary of the projected market evolution over the past few years is shown in Figure 4 and two examples for commercial installations of DSSC panels are shown in Figure 5.
### Table 7  Market share of PV panels by technology groups (2014-2030)

<table>
<thead>
<tr>
<th>Technology</th>
<th>2014</th>
<th>2020</th>
<th>2030</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon-based (c-Si)</td>
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<tr>
<td>Monocrystalline</td>
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<tr>
<td>Poly- or multicrystalline</td>
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<tr>
<td>Ribbon</td>
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<tr>
<td>a-Si (amorph/micromorph)</td>
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<td></td>
<td></td>
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<tr>
<td>Thin-film based</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Copper indium gallium (di)selenide (CIGS)</td>
<td>2%</td>
<td>5.2%</td>
<td>6.4%</td>
</tr>
<tr>
<td>Cadmium telluride (CdTe)</td>
<td>5%</td>
<td>5.2%</td>
<td>4.7%</td>
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<tr>
<td>Other</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Concentrating solar PV (CPV)</td>
<td></td>
<td>1.2%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Organic PV/dye-sensitised cells (OPV)</td>
<td></td>
<td>5.8%</td>
<td>8.7%</td>
</tr>
<tr>
<td>Crystalline silicon (advanced c-Si)</td>
<td>0.7%</td>
<td>25.6%</td>
<td></td>
</tr>
<tr>
<td>CIGS alternatives, heavy metals (e.g. perovskite), advanced III-V</td>
<td>0.6%</td>
<td>9.3%</td>
<td></td>
</tr>
</tbody>
</table>


**IRENA: End-of-Life Management of Solar Photovoltaic Panels, 2010**

**Figure 4.** Projected market share of PV panels by technology group (2014-2030)

**Figure 5.** First Applications of dye colored semi-transparent photovoltaic glass panels

Left: DSSC panels produced by the company Solaronix (www.solaronix.ch) mounted at the façade of the new Swiss High Tech Convention Center in Lausanne Switzerland. Right: The first energy noise barrier made with dye sensitized solar cell panels by HGlass S.A.
Rechargeable lithium ion batteries. Graetzel introduced the concept of using nanoparticles as active materials in lithium ion batteries. This speeds up by 100 - 1000 times the rate of discharging and charging increasing the power output of the battery by the same factor. This concept was protected by a patent with Graetzel as coinventor filed in 1996, see figure 6. Together with 2 partners, Graetzel founded High Power Lithium (HPL), a company that commercialized the concept. The company was sold to Dow Chemical, which now offers nanostructured battery cathode materials developed by HPL such as lithium manganese phosphate on the market.

Figure 6. United States Patent granted to Graetzel and two co-inventors in 1996. It protects the use of nanoparticulate materials as components for lithium ion batteries.