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Advanced Materials for innovative solar cell technologies

Part I: Fundamentals, historical development and market potentials

Summary

To achieve the 2050 climate targets set out in the Paris Agreement, novel "emerging photovoltaics" (EPVs) that enable flexible, ultra-thin and, above all, lightweight photovoltaic (PV) modules will be used alongside classic siliconbased technologies. Innovative materials, socalled "advanced materials", open up new application areas and possibilities. Such novel PV systems are based on, for example, perovskite semiconductors, quantum dots, organic polymers or dyes, all of which can be produced easily and cost-effectively. Besides traditional power generation in the form of groundmounted and roofmounted systems, they open up new fields of application such as e.g. portable small devices, building-integrated power generation on facades or window surfaces, or in the transport industry. However, before widespread commercial use is possible, some research and development work is still necessary, especially where increased efficiency and service life are concerned. Since the PV market is currently almost exclusively supplied by silicon-based technologies, and because EPVs do not hold a significant market share, it is not possible to derive future market trends from previous or current ones. Instead, they must be estimated on the basis of existing market segments into which the technology can potentially penetrate. It is necessary to differentiate between application areas where power generation is the main focus and those where local energy supply by PV is the goal, but where the solar cells must fulfil additional functions. As a result, the benefit of EPVs does not lie exclusively in electricity generation per se, but in the possibilities opened up by a targeted local power supply, not taking into account electricity grids.

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Introduction

Renewable energy sources, including photovoltaics (PV), are expected to replace fossil fuels in the future. To achieve the 2050 climate targets set out in the Paris Agreement, which also provide for climate-neutral electricity generation, renewable energy technologies, including the PV markets, must grow very quickly. For Austria, potentials of approx. 26.7 gigawatts (1.6 GW are currently installed) have been identified, 1 of which at least approx. 11 GW should be achieved by 2030.2 To achieve this goal, novel "emerging photovoltaics" (EPVs) can and should be used alongside classic, silicon-based and relatively heavy solar panels, enabling the use of flexible, ultra-thin and, above all, lightweight PV modules. Innovative materials ("advanced materials" or AdMs) are used and open up new fields of application because of their new and improved properties. At the same time, their use can contribute to making applications and manufacturing processes more environmentally friendly. EPVs are based, for example, on perovskite semiconductors, quantum dots, organic polymers or dyes. In addition to traditional power generation in the form of groundmounted and roofmounted systems, EPVs have great market potential as they open up new fields of application such as e.g. the energy supply of portable small devices such as the "Internet of Things"3, buildingintegrated power generation on facades or window surfaces, or power generation in the agricultural sector through integration into glass or plastic greenhouses. This dossier (part I) provides an overview of the technical background and historical development of such innovative solar cell technologies as well as their future market potentials. In part II of the dossier, the AdMs used will be analysed in terms of their environmental friendliness and sustainability, whilst also presenting their significance in a circular economy.

Fundamentals and historical development

Solar cells convert light into electrical energy. In so doing, light particles (photons) are absorbed by a semiconductor structure and converted into electrical charge pairs. Solar cells with a single light-absorbing layer can achieve efficiencies of up to 30% under laboratory conditions. Socalled stacked solar cells (also called tandem or multi-junction solar cells) with several absorber layers of different materials can even convert almost 50% of the incident sunlight into electrical energy (Figure 1, violet area). After the absorption of light by the absorber layer, the photon energy is briefly stored in the form of a chemical potential. Ultimately, electrical energy is released via an external consumer, e.g. the public electricity grid.

After the discovery of the photovoltaic effect by Alexander Becquerel in 1839 and the production of the first photovoltaic element based on the semiconductor material selenium by William G. Adams and R.E. Day in 1877, it took almost 80 years until the first efficient solar cell could be produced. In 1953, the first crystalline silicon solar cells with an efficiency of about 4% were produced at Bell Laboratories in New Jersey by Daryl Chapin, Calvin Fuller, and Gerald Pearson. A few years later, efficiencies above 10% could be achieved. The first PV modules were used in space travel. Since the mid-1980s, efficiencies of approx. 27% have been achieved (Figure 1, blue area). Because of the initially very high costs of crystalline silicon technology, alternative semiconductor materials were sought before long. For this purpose, polycrystalline silicon was investigated on the one hand because it is easier and cheaper to produce; on the other hand, various thin-film solar cells were developed. These use very thin absorber layers and thus very small quantities of materials. Consequently, thin-film modules made of amorphous silicon4, cadmium telluride or so-called chalcopyrite have been developed and commercialised in recent decades. Chalcopyrite consists of e.g. copper, indium, gal-

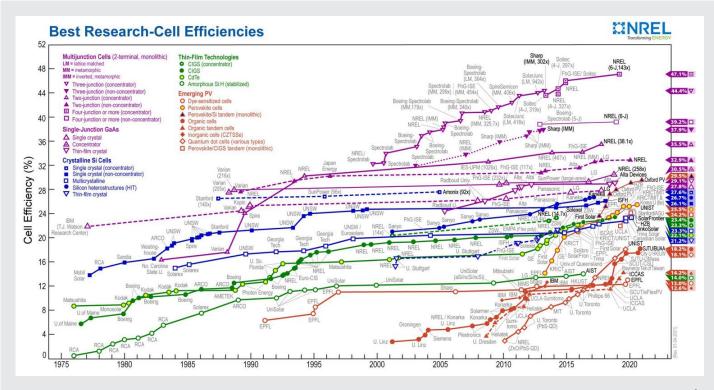


Figure 1: National Renewable Energy Laboratory (NREL) – Historical development of conversion efficiencies of the most powerful solar cells in research.⁶

lium, and selenium, and is also known as CIGS. Many of these technologies have been able to achieve efficiencies above 20% in recent years (Figure 1, green areas). Because of the enormous reduction in costs for crystalline and polycrystalline silicon technologies in recent years, thin-film technologies currently play a subordinate role on the world market despite all the progress made: currently, their share of the global market is less than 5%5, whereas in 2010 they still held a market share of over 15%.

Novel photovoltaic technologies

As well as these thin-film technologies, there are novel ("emerging") PV technologies (EPVs) which use newly developed semiconductor materials and where alternative component concepts are being realised. Perovskite solar cells, organic solar cells, quantum dot solar cells, and dye-sensitized cells have been particularly successful in recent years (Figure 1, red areas). These components have very similar architectures (Figure 2) and are being extensively researched at present.

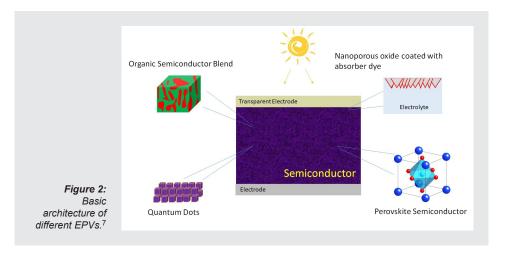
The various EPVs are characterised by the possibility of simple manufacturing processes and low costs. Printing and coating processes, very thin light-absorbing layers, and the use of inexpensive materials make the various technologies seem attractive. However, none of the "emerg-

ing" solar cells are technically fully mature. For widespread use, improvements in particular still need to be realised in terms of efficiency, their stability, and manufacturing processes.

Organic solar cells

The first organic solar cell was patented by Melvin Calvin and David Richard Kearns in 1959.⁸ In their experiments, they attempted to engineer a solar cell that resembled the reaction centre of photosynthesis. However, unlike the natural model of photosynthesis, this had a very low efficiency (< 1%), which led to the idea not being pursued for a long time. In 1986, Ching W. Tang

published an article on the development of an organic solar cell with an efficiency of 1%. ⁹ His patent on these organic solar cells from the KODAK laboratories, however, already dated back to 1977. ¹⁰ In 1992, Niyazi Serdar Sarıçiftçi discovered the light-induced charge transfer between an organic semiconductor and fullerene molecules. ¹¹ Thanks to the use of these materials, solar cells with an efficiency of approx. 2% could be produced. That same year, these so-called "bulk heterojunction solar cells" were patented by Sarıçiftçi and Heeger as an invention. ¹² This work resulted in intensive efforts to further improve the efficiency of organic solar cells. Following the synthesis of a variety of new organic





semiconductors, it is now possible to produce components with an efficiency of up to 18% (Figure 1, ● Organic (solar) cells). Organic solar cells are characterised by particularly simple manufacturing processes and low material consumption. Layers of a few 100 nanometres can be produced costeffectively using very simple processes (printing or deposition from the gas phase onto a surface). The typical structure of an organic solar cell is shown in Figure 3 a). In comparison, Figure 3 b) illustrates the structure of a quantum dot cell, and Figure 3 c) a perovskite solar cell.

Organic solar cells are typically built onto transparent plastic or glass substrates, which feature an electrode that is also transparent. This electrode uses conductive oxides such as indium tin oxide, doped tin or zinc oxide, but also conductive polymers such as doped poly(3,4-ethylenedioxythiophene). The transport layers 1 and 2 consist of different oxides or organic materials and establish the electrical connection to the light-absorbing semiconductor layer (coloured areas in Figure 3). For the semiconductor layer, different organic semiconductors are combined. Aluminium is vapourdeposited as the counter electrode. The components must be hermetically encapsulated to protect them from environmental influences such as ingress of oxygen or water or water vapour. For this purpose, the solar cells are embedded between two barrier layers consisting e.g. of silicon dioxide.

At present, organic solar cells do not yet play a major role on the global market, despite efforts to commercialise this technology for some time. Numerous research institutes and universities are working on optimising the technology, developing the first prototypes. Right now, primarily lightweight and flexible products are being developed; moreover, lots of research is being undertaken to make both electrodes transparent. The resulting semitransparent photovoltaic elements could be used in facades and windows amongst other things. In general, organic PV modules are, however, particularly suitable for portable applications.

For successful commercialisation of organic photovoltaics, a number of problems still need to be solved. On the one hand, significant differences still exist between the efficiencies of cells (approx. 18%) and small modules (approx. 12%) under laboratory conditions when compared with the first products on the market (5-7%). This shows that basic research and industrial development are still relatively strongly decoupled from each other. On the other hand, organic photovoltaic development is still hampered by the limited service life of the components. It is true that a product service life of several years is already possible today, which is quite sufficient for applications in electronic consumer products, However, to meet the demands placed on conventional PV modules (at least 20-25 years), the expected service life is still insufficient. Here, too, it is evident that basic research and industrial development must be much more closely interlinked to fully exploit the potential of organic photovoltaics.

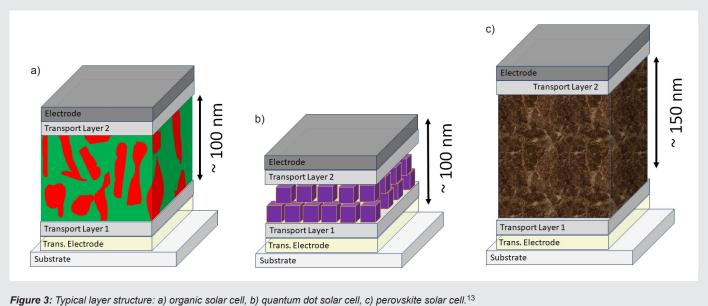
The dye-sensitized cell

The sensitisation of photochemically active materials with the help of integrated dyes has been known for a very long time; the process was first used in a photoelectrochemical cell by James Moser in 1887. In his doctoral thesis from 1968.

Helmut Tributsch presented the dye-sensitized electrode of titanium oxide (TiO_x) as a solar cell. ¹⁴ Despite some efforts, the first efficient solar cell was not produced until 1991 by Brian O'Regan and Michael Grätzel¹⁵, and has since then also become known as the "Grätzel cell". Individual dye molecules were deposited on a nanoporous titanium dioxide layer, with a liquid electrolyte connecting the two electrodes whilst being responsible for the charge transport (Figure 4). A typical Grätzel cell consists of a glass substrate, a fluorine-doped tin oxide layer, a partially porous titanium dioxide layer that is coated with dye molecules, an electrolyte, and an electrode. The manufacturing process is very simple and cost-effective.

The first Grätzel cell demonstrated an efficiency of approx. 7%, which could be increased to 13% over the years (Figure 1, O Dye-sensitized cell). This makes the dye-sensitized cell the PV technology with the lowest efficiency. For a long time, attempts were made to substitute the liquid electrolyte in the cell structure with a solid transport layer to improve both service life and efficiency. Only by using perovskite semiconductors, which replace the dye and the electrolyte, could efficiencies be increased significantly (see section on perovskite solar cells).

In recent years, some attempts have been made to use dye-sensitized cells in various applications, e.g. at the SwissTech Convention Center in Lausanne or at the Science Tower in Graz where parts of the facade were designed with semitransparent dye-sensitized cells (Figure 5). The use of different dyes and the modules' high transparency allow for an aesthetic design of large glass surfaces. The efficiency of these modules in relation to power generation is, however, limited to



rigure 3. Typical layer structure. a) organic solar cell, b) quantum dot solar cell, c) perovskite solar cell.

just a few percent. In total, only a small number of dye-based solar modules were built and installed. With the advent of perovskite solar cells, as described in more detail below, research activities regarding dye cell technology decreased.

Perovskite solar cells

Perovskites are minerals with a characteristic crystal structure ABX3, where A and B (Pb2+) are cations and X negatively charged halogen ions. They were named after the Russian politician and mineralogist Lev Alekseyevich von Perovski (1792-1856). In perovskite solar cells, semiconducting, lead-containing perovskite materials are used as light-absorbing layers, which also have this crystal structure. However, the first experiments with solar cells based on this technology were only carried out in 2009 by Tsutomu Miyasaka and his team at the University of Yokohama (Japan). The light-absorbing layer of this dyesensitized cell was replaced by a thin methylammonium lead iodide layer. The first experiments resulted in an efficiency of approx. 4%. In the last 10 years, efficiency could be increased to >25%. Changes in the layer structure and the development of improved perovskite absorbers led to this impressive development (Figure 1, OPerovskite cells).

Figure 3 c) shows the typical structure of a perovskite solar cell. The layer structure is similar to that of organic solar cells or dye-sensitized cells; by now, it is possible to produce mechanically flexible, very thin, and foil-like perovskite solar cells (Figure 6). The production of perovskite solar cells follows similar processes to those of organic solar cells. Their mechanical properties and low weight also resemble those of organic solar cells.

The commercialisation of perovskite solar cells is currently being pursued with great intensity. On the one hand, modules for portable and smart

Figure 4: Structure of a dye-sensitized/Grätzel Transparente Electrode solar cell.16 Light Dye O Glass Figure 5: Semitransparent "Grätzel facade" at the Counter Nanoporous Electrolyte SwissTech Convention Electrode TiO₂ Center in Lausanne. 17

products as well as components for highly efficient stack cells are being developed. For successful commercialisation, a number of problems

still need to be solved. For example, little is yet known about the actual service life of perovskite solar cells. There are initial indications that those

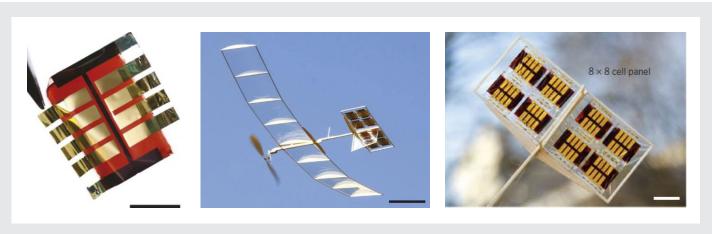


Figure 6: Flexible perovskite solar cell. 18 Size of scale bar: image on the left 1 cm, in the middle 10 cm, on the right 2 cm.



cells in the prototypes investigated so far are likely to have a long service life, but this still needs to be verified under real conditions. Furthermore, there is still very little information available on perovskite solar cells under real production conditions. One of the keys to the success of this technology will be whether the "record-breaking efficiencies" of cells produced in the laboratory can also be achieved in mass production. Many experts also consider the use of water-soluble lead salts (e.g. methylammonium lead iodide) as problematic because of the possible impact lead has on the environment and health (see part II of the dossier). Despite great efforts, it has not yet been possible to develop a lead-free perovskite absorber with similar properties or efficiencv. As a result, research is currently focussed on finding particularly good sealing methods for these solar cells to prevent the release of lead. Nevertheless, even then a residual risk remains, for instance in the event of a fire. Moreover, suitable concepts for waste management must be developed to prevent the release of lead-containing materials from these cells into the environment, and to improve recyclability.

Quantum dot solar cells

Quantum dot solar cells are based on the concept that the optical and electrical properties of semiconductor materials can be changed by reducing the size of the crystals into the nanometre range. As a result, semiconductors that are normally unsuitable for this application (e.g. lead sulphide or cadmium selenide) can also be used in photovoltaics. The first quantum dot solar cells

were certified in 2010 with an efficiency of approx. 2% (Figure 1, Quantum dot cells). In the following years, it was possible to increase efficiency to approx. 10% by using sulphide quantum dots. More recently, perovskite nanoparticles made from lead iodide have been used in quantum dot solar cells, achieving efficiencies of up to 18%.

Figure 3 b) shows the typical structure of a quantum dot solar cell. The layer structure is similar to that of organic solar cells. The manufacturing methods and corresponding benefits are also very similar. At present, the markets show no major tendencies to commercialise the quantum dot solar cell. Moreover, there are only few reliable data on the service life of the components that make up quantum dot solar cells. In addition, the use of quantum dots seems problematic for many reasons, particularly where material components containing lead or cadmium are concerned.

EPVs and their market potentials

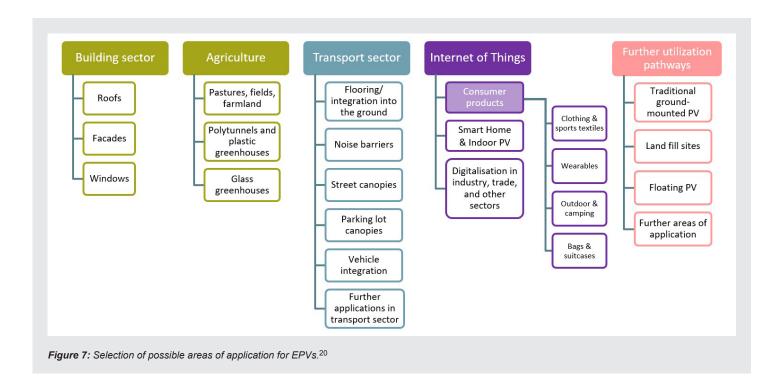
As already outlined in the introduction, the silicon solar cell has become the dominant cell in conventional PV panels globally over the past decades. Despite the many changes that have been made to this solar cell, there are some areas in which EPVs could be used to a greater extent in the future. Factors such as e.g. construction, weight, material flexibility or aesthetic design will, however, be decisive for their aplication. Low manufacturing costs can also play a

decisive role in the medium term. The use of low-cost conventional printing processes for mass production will also be crucial. EPVs are attracting widespead interest in research and industry, but so far only a few commercial products are available on the market. As the photovoltaic market is dominated by the classic silicon module, it is hardly possible to deduce how the market will develop in the future. Previous "market trends" in small niches have had no significance so far. Instead, trends must be estimated on the basis of existing market segments into which the technology can potentially penetrate.

Since efficiencies of cell technologies can differ drastically between the laboratory and industrial production conditions (see Figure 1), the market potential can primarily be deduced by areas that have potential for development. As part of the research project "SolarCircle" a rough estimate was given for the market potential in Austria.

Figure 7 shows a selection of possible EPV application areas listed by greatest anticipated potential. A distinction must be made between areas of application where power generation (as a substitute for other energy sources) is the main focus, and those areas where energy is needed locally but the amount required is limited, or where solar cells have to fulfil additional functions.

Where general power generation is concerned, classic large-scale ground-mounted or roof-mounted PV systems (nowadays also more of-ten on building facades) have become the norm.





In such settings, yielding the highest possible amount of energy is important. Large, efficient modules covering different surfaces can be used, with the classic silicon solar cell being suitable for such applications. However, there are special circumstances in the building sector where the use of such modules is not an option²³, e.g. where listed buildings are concerned (Gründerzeit (1840-1914) houses with a footprint of approx. 20 km2 in Austria)²¹, or because of structural requirements (exceeding e.g. the maximum load-bearing capacity; affects approx. 100 km² roof surface of existing commercial or industrial buildings in Austria)22. In such cases, it is possible to use either individually designed modules and integrate these into the roof area, or use lightweight PV films that can be rolled out. Such products, based on silicon and thin-film technologies, already exist, but EPVs could play a greater role in the future. EPVs could also be used in the design of facades and windows of modern buildings.24

In the agricultural sector, integrating EPVs e.g. into glass and plastic greenhouses is conceivable as there are around 6 km² of commercial glass and plastic greenhouses in Austria. ²⁵ Special solar greenhouses are already being tested. ²⁶ EPVs are particularly suitable for these applications because of the low weight and flexible design options. Moreover, semitransparent and perfectly colour-coordinated PV glasses might have a positive impact on the yield. Research on matching glasses to specfic needs of plants is already in progress. ²⁷

In the transport industry, the expected possible uses are particularly diverse: solar cells integrated into the ground are very costly and have rarely been used to date, yet it is not uncommon to see classic solar cells on noise barriers, traffic lights or parking machines. They are also used for canopies in parking areas which have great potential because of the available surface area. ²⁸ Moreover, integrating EPVs specifically into ve-

hicles could be a relevant field of application since colour design, weight, and the possibility of using printing processes play a major role in this area.²⁹ The cells can either be integrated directly into the surface of the vehicle or yield additional electricity when integrated into the interior of the vehicle in the form of tailor-made "indoor solar cells". Buses³⁰ and trains in particular have great market potential for EPVs because of their large external surfaces.

The "Internet of Things" (IoT) and digitalisation applications are considered another large area of interest for EPV use, with digitalisation applications increasingly finding their way into the private, commercial, and public sectors. EPVs (perhaps in combination with small storage units) can be used for safe and efficient power supply of networks, portable devices, and distributed sensors³¹ – not only outdoors, but also indoors. The latter feature in particular allows for quick and costeffective retrofitting of production facilities as well as existing buildings. Equipped with adapted, relevant sensor technology, this can be done without the need for rewiring power cables or regular battery changes. For 2023, a global indoor PV market with a volume of around 850 million USD has been forecast.32 In 2022, the IoT market is expected to have around 50 billion devices in circulation globally.33

Another potential market segment for EPVs is the outdoor and camping industry. Even in this industry, IoT devices are selling fast, e.g. smartwatches and wearables which already feature solar glasses. ³⁴ Energy self-sufficient camping equipment with integrated or optional PV modules could also be successfully launched on the market. In future, EPVs could play a greater role in this field, for example in the form of e-textiles ³⁵⁻³⁶ that are sewn into tents, clothing, backpacks, etc. However, durability and reliability of the EPVs will be key for successful application.

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Conclusion

The development of novel, flexible, and lightweight solar cells (EPVs) on the basis of "advanced materials" has made great progress in recent years. Although there are still some barriers for widespread commercialisation, these have the potential to open up niches in the traditional PV market in the future and thus contribute to renewable electricity generation. Because of their versatility, they are particularly suitable for use in the IoT and digitalisation sector. Today, they are already used in small portable electronic devices and in the building sector. In the future, they could become a building block for resilient energy and infrastructure systems. Technologically mature EPVs could therefore play a role in all areas of life in the future. The benefit of EPVs does not always lie in the electricity generation per se, but in the possibilities opened up by a targeted local power supply independent of grids.



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