The solar age

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It is appropriate that the International Year of Light will see us capture more of our energy needs from light than ever before. The global photovoltaic (PV) power capacity is estimated to rise to over 230,000 MW in 2015, a stunning growth of over 600 % since 2010 (Figure 1) to reach 4.4 % of total global electricity capacity. This surge in PV installations has outstripped all expectations (and revised expectations) from the International Energy Agency and even Greenpeace. Early PV growth was fuelled by aggressive subsidy programmes, particularly in Germany, that aimed to make this renewable energy source competitive with energy from fossil fuels. However, it is less widely known that price parity has already arrived, with solar PV beating existing energy sources directly on price in some parts of the world. This article will briefly review the rise of solar PV and provide a glimpse of new materials being developed for the next PV revolution, including research activities in New Zealand.

The long-awaited arrival of solar PV

Enough solar energy falls on the surface of the earth in one hour to satisfy our current global energy needs for an entire year. Solar energy is the only renewable energy source that can even come close to meeting our energy needs. Scientists and engineers recognised this potential long before the invention of the photovoltaic cell; Thomas Edison reportedly enthused about the idea of replacing fossil fuels with solar energy in conversation with Henry Ford in 1931.

Life on earth began harvesting solar energy with the evolution of photosynthesis more than two billion years ago. It is reasonable to ask whether the easiest way to capture more solar energy might be to use what nature has already developed and grow biofuels. However, photosynthesis has a power conversion efficiency of only 0.3 %, which diminishes further when accounting for the energy required to recover the biofuel. Green plants did not evolve as power plants. They evolved to survive.

The present solar revolution is based on solar PV cells. Single junction PV cells can have power conversion efficiencies up to the thermodynamic limit of 33 %, and are commonly around half this in consumer PV panels. Unlike solar thermal, which generates low-grade heat energy, solar PV directly generates energy in the form that is most useful to us—electricity.

PV capacity has grown at a steady exponential rate since the technology become technically, if not economically, viable more than twenty years ago, as shown in Figure 1. Installed PV capacity has continually doubled approximately every two years throughout a time when the landscape was constantly changing;

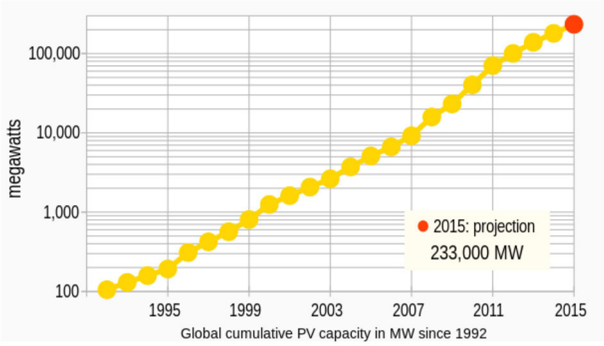

Figure 1. Cumulative global photovoltaic capacity since 1992 [1].

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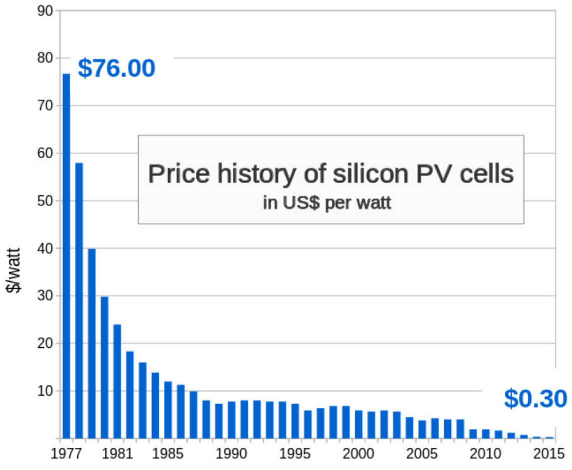
policies, subsidies, and manufacturers have frequently come and gone. Behind this enduring exponential growth is an important message: exponential behaviour is found in different aspects of almost all technologies. From his analysis of the history of technology [2], futurist Ray Kurzweil notes that, ‘we won’t experience 100 years of progress in the 21st century—it will be more like 20,000 years of progress (at today’s rate)’. Technology is always embedded in a complex network; not only does a given piece of technology improve, but the tools used to manufacture and improve it also improve, thus fueling exponential improvements. This exponential behaviour is manifest, for example, in the growth of computer processor speeds, and in the growing performance and falling price of flat-screen televisions. This idea is familiar to anyone who notices how quickly consumer electronics are outdated. For the exponential scaling to apply to energy is profoundly important. Whereas fossil fuels are priced according to the supply and demand for a finite resource, solar energy is virtually unlimited—the price reflects the cost of converting it to electricity. In other words, the price depends on a technology; solar PV obeys the exponential scaling laws of other technologies and can only get cheaper.

The global PV module price is shown in Figure 2, normalised in $US per peak watt (Wp). The present price of $0.30 /Wp means that a typical household system with a 10 kW capacity now costs only $3,000. Only ten years ago, the same system was closer to $40,000. This staggering price reduction is also predicted in the exponential view of technology. The production cost of a given piece of technology decays according to a power law with cumulative production. As the price drops, increased demand, in turn fuels accelerating production. Additional factors like the price of silicon and stimulation from subsidies have certainly also affected the historical price of silicon PV technologies, but the overall price reduction is not from any one thing. As Ken Zweibel of George Washington University remarked, ‘Instead of death by a thousand cuts, it’s more like life by a thousand cost cuts.’



Source: Bloomberg New Energy Finance & pv.energytrend.com

Figure 2. Price history of PV modules [3].

This virtuous cycle has driven the price so low that solar PV now competes directly with the grid in some parts of the world. Europe’s largest PV plant is currently nearing construction near Bordeaux in France. The 300 MW plant could power a city the size of Wellington under full sun, and it occupies only a few square kilometres of otherwise arid land. In the USA, the 100 MW Playa Solar 2 power plant in Nevada recently agreed to sell its power to utility company NV Energy at a rate of $US0.0387 /kW h [4]. This is nearly 70 % cheaper than the US National average electricity price, and well below the cost of electricity from coal, natural gas, or nuclear [5] when normalised by the cost over the entire lifespan. Warren Buffett, whose investment company owns NV Energy and other utilities, sees solar PV as being an increasingly important part of the global energy future on financial grounds. The dawning of the solar age begins with the tipping point of price parity rather than an environmental revolution.

Advanced materials and nanotechnology for the next PV revolution

The operating principles and basic design of a solar PV cell are very simple. PV cells comprise a semiconductor sandwiched between a pair of electrodes, as depicted in Figure 3. The origin of the PV effect in semiconductors relates to their electronic band structure. Electrons in the valence band require additional energy to cross the bandgap and occupy the conduction band. This additional energy can come from light absorption, provided that the photon energy exceeds the semiconductor bandgap. Thus, absorbed light can create an electric potential in the semiconductor, and when a current flows, electrical power extracted is simply the product of the photovoltage and the current.

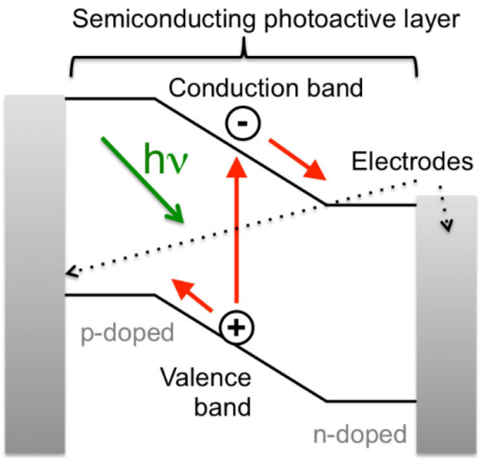


Figure 3. Basic operation of a PV cell.

Beyond these simple principles, the devil is in the details. Electrodes must be able to extract electrical charges before recombination takes hold, giving rise to a kinetic competition that is determined by both intrinsic factors and extrinsic factors that can be controlled by device engineering. Competing effects dictate the engineering of layer thicknesses; more light is absorbed in thicker semiconductor layers, but charge recombination losses will dominate if the layer is too thick. In order to let light access the active semiconductor, at least one of the electrodes must be optically transparent, making the choice of electrode material subject to severe physical constraints on the relationship between transparency and conductivity.

Today’s PV industry is built on silicon—the same semiconductor that dominates the electronics industry. The basic research into silicon PV cells was largely completed by the 1980s. The subsequent developments that have brought solar PV to global prominence today have been through manufacture engineering and the economics of scale. Nevertheless, there has been a resurgence of basic PV research aiming to develop the next generation of PV cells that can be printed from low-cost, non-toxic, and earth-abundant materials, often using nanotechnology. Some promising aspects of this research will be discussed below.

Printable semiconductors for PV cells

One of the disadvantages of silicon PV cells is that the semiconductor is processed in batches on glass substrates that can withstand the high temperatures required to reach sufficient material purity, control doping, and establish electrical contacts. Heavy and inflexible substrates contribute to the module, transport, and installation costs, as well as slowing the manufacturing process. An alternative is to print layers of semiconductor materials and electrodes onto lightweight and flexible substrates like plastics. Roll-to-roll processing under ambient conditions could simplify and accelerate manufacturing, but new semiconductor materials are required for this to be effective.

The prospect of low-cost, printable PV cells came a significant step closer with the discovery of optoelectronic devices based on organic polymer semiconducting materials [6]. Conjugated polymer light-emitting diodes were followed shortly afterwards by polymer-based PV cells whose active layers were deposited from viscous inks [7, 8]. The low efficiencies of these early devices reflected some fundamental differences between the physics of disordered organic semiconductors and their crystalline inorganic counterparts.

One of the most consequential differences between organic and inorganic semiconductors is their dielectric constant. A dielectric constant of ε >10 means that the Coulomb attraction between photogenerated charge pairs is readily screened in inorganic semiconductors like silicon, allowing facile charge separation and photocurrent generation. On the other hand, the substantially lower value of dielectric constants found in organic semiconductors (ε ~ 3 to 4) leads to the formation of charge pairs that are bound via strong Coulomb interactions. This effect, along with the intrinsic disorder found in conjugated polymer films, means that organic semiconductors retain a strong molecular character that contrasts with the electronic band structure of their inorganic counterparts.

Overcoming the strong barrier towards charge separation in organic PV cells requires a mixture of at least two different materials in the active layer, as shown in Figure 4. By matching materials with electronic energy levels that drive electrons into one phase and positively charged holes into the other, the Coulomb binding energy can be overcome to efficiently generate photocurrent. Understanding this key charge separation process has been a research priority in recent years in order to guide the design of better materials.

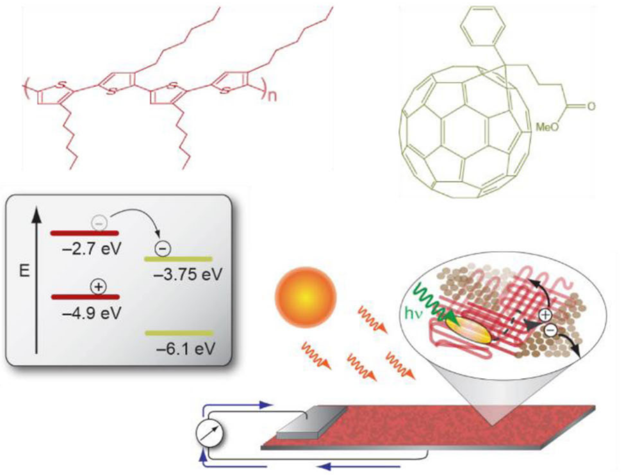


Figure 4. Typical organic polymer (left) and fullerene (right) components of an organic PV cell, whereby the energy level offset drives interfacial charge separation in a nanostructured blend of the two.

New Zealand researchers (including one of the present authors) are contributing to our understanding of charge separation in organic PV cells through the 'materials for energy capture and utilisation' research area of the MacDiarmid Institute. Together with Prof. Keith Gordon (University of Otago), we apply laser spectroscopy to probe the electronic structure and dynamics of the key excited states. For example, transient absorption spectroscopy, depicted in Figure 5a, uses short (~100 fs) laser pulses to generate excitations in a photovoltaic film and probe the subsequent optical absorption spectra. Figure 5b shows how the transient absorption spectrum of a typical organic photovoltaic blend evolves over time; spectral changes on the sub-picosecond timescale reflect bound excitons being converted to charge pairs, and the signal decay over hundreds of nanoseconds is due to charge recombination. This sets the timescale by which photogenerated charges must be extracted from an efficient device.

We recently discovered that the efficiency of a broad range of materials is universally defined by the yield of charge pairs that achieve a critical separation on a sub-nanosecond timescale [9]. This yield may be enhanced by the interplay of ordered and disordered polymer phases [10]. We also found that charge separation occurs via excited states that are substantially more

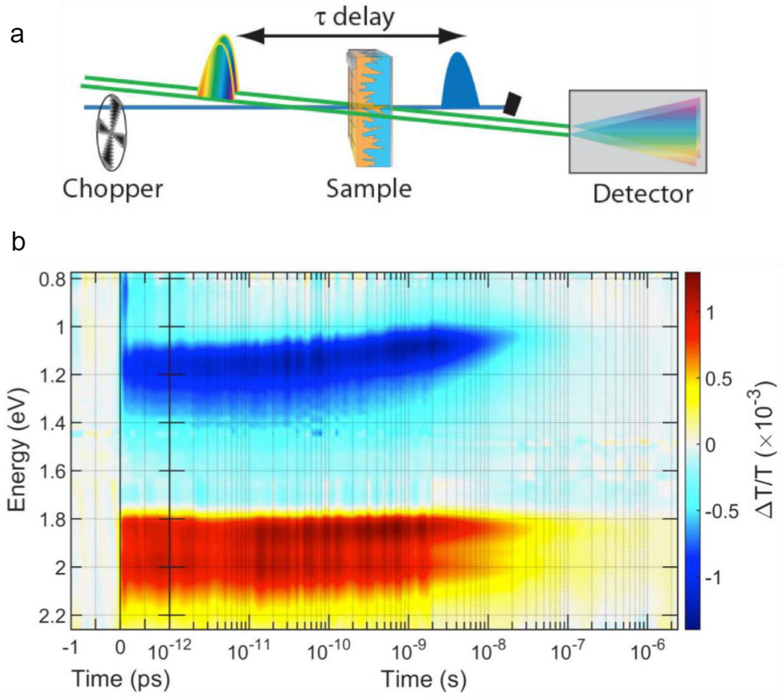


Figure 5. (a) Schematic of transient absorption spectroscopy using ultrafast laser pulses. (b) Transient absorption spectral map of an organic PV film.

delocalised than previously thought, which may be important to circumventing bound charge pair states [11]. The power conversion efficiency of organic photovoltaic cells has recently surged to over 11 % as a result of a global push to develop new active-layer materials [12]. Synthetic organic chemistry opens enormous possibilities of new materials whose chemical structures determine the optical absorption, electronic conductivity, solubility, degree of structural order, mixing behaviour, and stability – all critical parameters for organic PV cells. Understanding how to collectively optimise these parameters has challenged the research community to work across research disciplines. With a number of relatively efficient organic PV materials now available, new challenges include developing large-scale printing processes and prolonging device lifetimes.

The search for solution-processable semiconductors with high photovoltaic power conversion efficiencies was considerably boosted with the discovery of organometal halide perovskite (OMHP) PV cells in 2012 [13, 14]. The active-layer materials comprise metal halide (e.g. lead iodide) complexes and methylammonium cations that form a perovskite crystal structure (Figure 6) when deposited from solution, and they can now produce power conversion efficiencies of over 20 % [12].

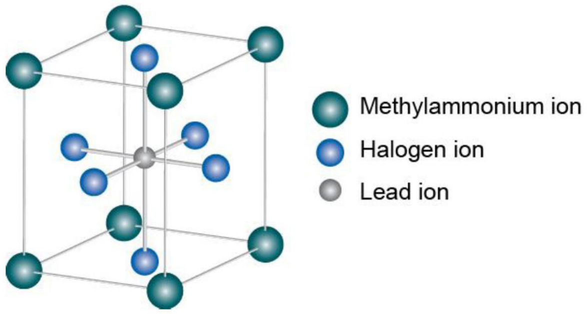


Figure 6. Structure of the OMHP $(CH_3NH_3)PbI_3$ used in efficient PV devices.

Many of the same tools used to study organic PV cells have been applied to OMHP PV cells in order to understand what makes them so efficient. They are a direct bandgap semiconductor, which means that only a thin layer is required to absorb all light. We have found that photoexcitation directly generates free charge carriers, thus circumventing the charge separation problem that dominates organic PV cells [15]. Both electron and hole charge carriers are long-lived and highly mobile, meaning that photocurrent is easily extracted before recombination occurs. When charge carriers are not extracted, they recombine radiatively (via photon emission), which has brought about other promising photonic applications, for example optical gain media for lasers [15, 16].

Aside from exploring the fascinating photophysical properties of OMHP materials, significant research effort is now directed at understanding their stability. OMHP PV cells suffer significantly poorer stability than organic PV devices, along with hysteresis effects. As well as chemical degradation in the presence of moisture and oxygen, OMHPs exhibit structural phase changes on account of the rotational freedom of methyl ammonium cations and migration of halide anions. If these problems can be resolved, the future of OMHP PV technologies looks very promising.

Transparent electrodes in PV cells – the nanotechnology approach

The sandwich structure of a solar cell requires several constituent parts that must all have the correct interaction with the incoming light. Besides the active layer where charge carriers are photogenerated, there are the electrode materials that act as the anode and the cathode of the PV cell. For most electronics applications you would choose a metallic electrode with a high conductivity {of the order of (10^3 to 10^5) S cm^{-1} where the Sieman (S) is the unit of conductivity and S = Ω^{-1}}. Most of us have an inherent feeling for what makes an efficient electrode and we also know that metals look shiny and bright rather than being optically transparent. In a PV cell it is essential for at least one of the electrodes to be transparent to light, to allow the interaction with the photoactive materials to take place. Most transparent materials, including glass and many plastics, are electrically insulating, with conductivities of the order of 10^{-13} S cm^{-1} for glass and 10^{-23} S cm^{-1} for polyethylene terephthalate, respectively. Nanomaterials play a crucial role in overcoming these incompatible material constraints for PV electrodes. This is a research focus of one of the present authors, working in the cleanroom fabrication facility in the School of Chemical and Physical Sciences at Victoria University of Wellington.

The industrial standard material for transparent electrodes is indium tin oxide (ITO) [17]. Films of ITO maintain the excellent transparency of indium oxide, with transmittance of almost 90 % at 550 nm, while tin doping increases the conductivity to 10^3 S cm^{-1}, corresponding to a sheet resistance R_{sh} (resistivity of sheet material divided by sheet thickness, a quantity having the dimensions of ohms but usually written as 'ohms per square', Ω sq^{-1}) of around 10 Ω sq^{-1} [18–20]. For comparison, the conductivity of silver, a very good electrical conductor, is only two orders of magnitude higher at 6.21×10^5 S cm^{-1} [21] whereas the glass and plastic insulators referred to above have conductivities 16 to 26 orders of magnitude lower! Expensive vacuum deposition techniques such as sputtering are used to produce these ITO films [17]. Aside from the operational expense, a high proportion of the raw materials are wasted, which is problematic owing to the scarcity and the costs of indium [22]. For the next generation of solar PV cells, and for applications in flexible and integrated electronics for which photoactive materials such as polymers and perovskites have shown promise, it is desirable to produce the electrodes using solution processing (e.g. printing) near room temperature. Nanomaterials offer researchers the chance to explore these options.

Recent work in the field of transparent nanomaterial electrodes has included the development of a range of flexible novel materials, flexibility being desirable because it is not possible to bend ITO layers and still maintain good conductivity, as the material is brittle and the conduction paths can be easily broken. These novel materials include silver nanowires [23, 24], carbon nanotubes [25–27], graphene [28] and composite materials, such as carbon nanotube/nanowire mesh structures [29] and doped inorganic and metal nanowire multi-stacked layers [19]. These nanomaterial based electrodes all share the following performance properties: low sheet resistances of 10–120 Ω sq^{-1}, transparency of the order of 90 % in the visible region, and the ability to be deposited onto plastic substrates (e.g. by spray coating) and maintain electronic performance even after significant bending.

Work carried out at Victoria University of Wellington by summer scholar Charlotte Duda shows the simplicity of the fabrication. Figure 7 shows an optical photograph of the experimental setup. Two large gold contact pads span the area of sides of a glass slide, and are then bonded to thin wires to allow for in-situ monitoring of the current across the film. The glass substrates are secured onto a hotplate using polyimide tape (yellow regions extending from the middle of the glass slides). A dilute solution of silver nanowires in methanol is then sprayed onto the substrate, which is held at a temperature of 60°C. The slight elevation of temperature ensures that the solvent is evaporated immediately and does not form part of the nanowire network. Due to the excellent transparency of the silver nanowire films, it is not possible to see the film.

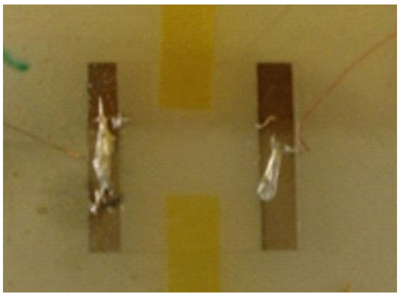


Figure 7. Photograph of a conducting silver nanowire network film deposited onto glass. The edge of the glass is coated with a traditional electrode material (here 35 nm of gold), which is optically opaque.

In order for nanowire films to have good electrical conductivity, the nanowires must form a percolating network, as depicted in Figure 8a, with low resistance between the nanowire-nanowire junctions. In order to measure the sheet resistances, similar films are prepared with electrodes fabricated in the van der Pauw, 4-point probe geometry to eliminate contact resistances from the measurements [21]. Sheet resistances of the order of 10–120 Ω sq^{-1} were achieved, demonstrating an excellent combination of the transparency and conductivity required for solar PV electrode applications.

Figure 8b shows a scanning electron microscope image of a silver nanowire network. The network is relatively dense with several layers of nanowires forming a mesh structure, but the transparency is still of the order of 85 % to 90 %. The conduction increases as more silver nanowires are deposited, although too many nanowires reduces the optical transparency of the films. Such effects are a bigger problem for the carbon nanotube (CNT) systems compared to the silver nanowires, owing to the need to have a larger volume of carbon nanotubes to achieve a reliable percolating network. To achieve similar sheet resistances in our tests, the CNT network was only 60 % to 70 % transparent over the same optical range.

In contrast to designing effective photoactive layers it is the lack of interaction with light that is important. These results, together with those discussed from the literature, show the promise of the nanowire electrode system for new transparent conductors. The nanowire network materials have been integrated with organometal halide perovskite [27] and solid-state dye-sensitized solar PV cells [24], showing the immense promise for the next generation of nanomaterial PV cells. Furthermore, these transparent electrodes are also suitable for flexible and stretchable electronics [23, 30] which have further applications such as flat screen display technology and integrated healthcare.

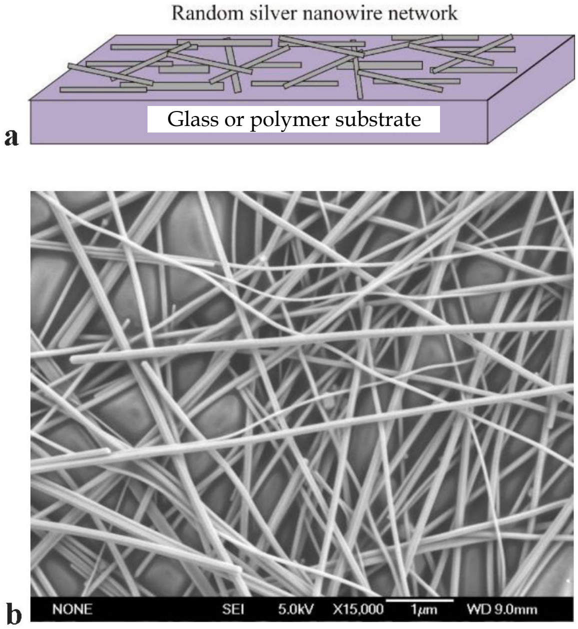


Figure 8. (a) A schematic image of a percolating random silver nanowire network for transparent electrode applications. (b) Scanning electron microscope image of a silver nanowire network deposited onto a polymer substrate. The nanowire matrix is several nanowires thick and appears dense at the microscale, but the samples maintain excellent optical transparency.

Outlook

In conclusion, the outlook for solar PV technology has never looked brighter. Exponential scaling laws of technology explain the exponential growth of solar PV capacity around the world and comcomittantly falling prices. With PV-generated electricity costs already competing with fossil fuels in some parts of the world, the financial case for solar PV technologies means that they will deliver an increasing amount of our energy in the future.

The surge in solar PV installation is based on silicon PV technology that was developed decades ago. The next generation of PV materials is currently being developed, with New Zealand nanotechnology researchers making significant contributions. Organic polymers and hybrid organometal halide perovskites are being developed as PV active layers that can be printed into flexible rolls. Facile processing also underpins the development of transparent electrodes, where nanomaterials offer a route to combining electrical conductivity with optical transparency, while maintaining mechanical flexibility. With these developments in the pipeline, PV technologies can only get more cost effective and more widely deployed.

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