Solar Energy Conversion[*]

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Abstract. If solar energy is to become a practical alternative to fossil fuels, we must have efficient ways to convert photons into electricity, fuel, and heat. The need for better conversion technologies is a driving force behind many recent developments in biology, materials, and especially nanoscience.

The Sun provides Earth with a staggering amount of energy—enough to power the great oceanic and atmospheric currents, the cycle of evaporation and condensation that brings fresh water inland and drives river flow, and the typhoons, hurricanes, and tornadoes that so easily destroy the natural and built landscape. The San Francisco earthquake of 1906, with magnitude 7.8, released an estimated 10^{17} joules of energy, the amount the Sun delivers to Earth in one second. Earth's ultimate recoverable resource of oil, estimated at 3 trillion barrels, contains 1.7×10^{22} joules of energy, which the Sun supplies to Earth in 1.5 days. The amount of energy humans use annually, about 4.6×10^{20} joules, is delivered to Earth by the Sun in one hour. The enormous power that the Sun continuously delivers to Earth, 1.2×10^{5} terawatts, dwarfs every other energy source, renewable or nonrenewable. It dramatically exceeds the rate at which human civilization produces and uses energy, currently about 13 TW.

The impressive supply of solar energy is complemented by its versatility, as illustrated in Figure 1. Sunlight can be converted into electricity by exciting electrons in a solar cell. It can yield chemical fuel via natural photosynthesis in green plants or artificial photosynthesis in human-engineered systems. Concentrated or unconcentrated sunlight can produce heat for direct use or further conversion to electricity.[1]

Despite the abundance and versatility of solar energy, we use very little of it to directly power human activities. Solar electricity accounts for a minuscule 0.015% of

world electricity production, and solar heat for 0.3% of global heating of space and water. Biomass produced by natural photosynthesis is by far the largest use of solar energy; its combustion or gasification accounts for about 11% of human energy needs. However, more than two-thirds of that is gathered unsustainably—that is, with no replacement plan—and burned in small, inefficient stoves where combustion is incomplete and the resulting pollutants are uncontrolled.

Between 80% and 85% of our energy comes from fossil fuels, a product of ancient biomass stored beneath Earth's surface for up to 200 million years. Fossil-fuel resources are of finite extent and are distributed unevenly beneath Earth's surface. When fossil fuels are turned into useful energy though combustion, they produce greenhouse gases and other harmful environmental pollutants. In contrast, solar photons are effectively inexhaustible and unrestricted by geopolitical boundaries. Their direct use for energy production does not threaten health or climate. The solar resource's magnitude, wide availability, versatility, and benign effect on the environment and climate make it an appealing energy source.
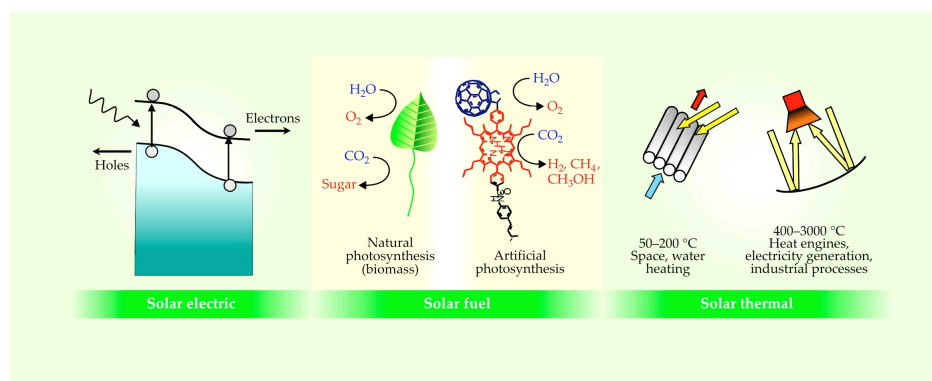

FIGURE 1. Solar photons convert naturally into three forms of energy—electricity, chemical fuel, and heat—that link seamlessly with existing energy chains. Despite the enormous energy flux supplied by the Sun, the three conversion routes supply only a tiny fraction of our current and future energy needs. Solar electricity, at between 5 and 10 times the cost of electricity from fossil fuels, supplies just 0.015% of the world's electricity demand. Solar fuel, in the form of biomass, accounts for approximately 11% of world fuel use, but the majority of that is harvested unsustainably. Solar heat provides 0.3% of the energy used for heating space and water. It is anticipated that by the year 2030 the world demand for electricity will double and the demands for fuel and heat will increase by 60%. The utilization gap between solar energy's potential and our use of it can be overcome by raising the efficiency of the conversion processes, which are all well below their theoretical limits.

RAISING EFFICIENCY

The enormous gap between the potential of solar energy and our use of it is due to cost and conversion capacity. Fossil fuels meet our energy demands much more cheaply than solar alternatives, in part because fossil-fuel deposits are concentrated sources of energy, whereas the Sun distributes photons fairly uniformly over Earth at a

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more modest energy density. The use of biomass as fuel is limited by the production capacity of the available land and water. The cost and capacity limitations on solar energy use are most effectively addressed by a single research objective: cost effectively raising conversion efficiency.

The best commercial solar cells based on single-crystal silicon are about 18% efficient. Laboratory solar cells based on cheaper dye sensitization of oxide semiconductors are typically less than 10% efficient, and those based on even cheaper organic materials are 2–5% efficient. Green plants convert sunlight into biomass with a typical yearly averaged efficiency of less than 0.3%. The cheapest solar electricity comes not from photovoltaics but from conventional induction generators powered by steam engines driven by solar heat, with efficiencies of 20% on average and 30% for the best systems. Those efficiencies are far below their theoretical limits. Increasing efficiency reduces cost and increases capacity, which raises solar energy to a new level of competitiveness.

TABLE 1. Photovoltaic conversion efficiencies. *As verified by the National Renewable Energy Laboratory. Organic cell efficiencies of up to 5% have been reported in the literature.

	Laboratory best*	Thermodynamic limit
Single junction		31%
Silicon (crystalline)	25%	
Silicon (nanocrystalline)	10%	
Gallium arsenide	25%	
Dye sensitized	10%	
Organic	3%	
Multijunction	32%	66%
Concentrated sunlight (single junction)	28%	41%
Carrier multiplication		42%

Dramatic cost-effective increases in the efficiency of solar energy conversion are enabled by our growing ability to understand and control the fundamental nanoscale phenomena that govern the conversion of photons into other forms of energy. Such phenomena have, until recently, been beyond the reach of our best structural and spectroscopic probes. The rise of nanoscience is yielding new fabrication techniques based on self-assembly, incisive new probes of structure and dynamics at ever-smaller length and time scales, and the new theoretical capability to simulate assemblies of thousands of atoms. Those advances promise the capability to understand and control the underlying structures and dynamics of photon conversion processes.

ELECTRICITY

Solar cells capture photons by exciting electrons across the bandgap of a semiconductor, which creates electron–hole pairs that are then charge separated, typically by p–n junctions introduced by doping. The space charge at the p–n junction interface drives electrons in one direction and holes in the other, which creates at the

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external electrodes a potential difference equal to the bandgap, as sketched in the left panel of Figure 1. The concept and configuration are similar to those of a semiconductor diode, except that electrons and holes are introduced into the junction by photon excitation and are removed at the electrodes.

With their 1961 analysis of thermodynamic efficiency, William Shockley and Hans Queisser established a milestone reference point for the performance of solar cells.[2] The analysis is based on four assumptions: a single p–n junction, one electron–hole pair excited per incoming photon, thermal relaxation of the electron–hole pair energy in excess of the bandgap, and illumination with unconcentrated sunlight. Achieving the efficiency limit of 31% that they established for those conditions remains a research goal. The best single–crystal Si cells have achieved 25% efficiency in the laboratory and about 18% in commercial practice. Cheaper solar cells can be made from other materials,[3] but they operate at significantly lower efficiency, as shown in the table above. Thin-film cells offer advantages beyond cost, including pliability and potential integration with preexisting buildings and infrastructure. A new approach, (Figure 2) used flexible, processable material, consisting of crystalline Si wires embedded in a plastic (polydimethylsiloxane) The wires allow effective capture and conversion of sunlight from inexpensive silicon, while the embedded structure offers the processability of organic materials such as photographic film. Achieving high efficiency from inexpensive materials with so-called third-generation cells, indicated in Figure 3, is the grand research challenge for making solar electricity dramatically more affordable.

The Shockley–Queisser limit can be exceeded by violating one or more of its premises. Concentrating sunlight allows for a greater contribution from multi-photon processes; that contribution increases the theoretical efficiency limit to 41% for a single-junction cell with thermal relaxation. A cell with a single p–n junction captures only a fraction of the solar spectrum: photons with energies less than the bandgap are not captured, and photons with energies greater than the bandgap have their excess energy lost to thermal relaxation. Stacked cells with different bandgaps capture a greater fraction of the solar spectrum; the efficiency limit is 43% for two junctions illuminated with unconcentrated sunlight, 49% for three junctions, and 66% for infinitely many junctions.

The most dramatic and surprising potential increase in efficiency comes from carrier multiplication,[4] a quantum-dot phenomenon that results in multiple electron hole pairs for a single incident photon. Carrier multiplication was discussed by Arthur Nozik in 2002 and observed by Richard Schaller and Victor Klimov two years later. Nanocrystals of lead selenide, lead sulfide, or cadmium selenide generate as many as seven electrons per incoming photon, which suggests that efficient solar cells might be made with such nanocrystals. In bulk-semiconductor solar cells, when an incident photon excites a single electron–hole pair, the electron–hole pair energy in excess of the bandgap is likely to be lost to thermal relaxation, whereas in some nanocrystals most of the excess energy can appear as additional electron–hole pairs. If the nanocrystals can be incorporated into a solar cell, the extra pairs could be tapped off as enhanced photocurrent, which would increase the efficiency of the cell.
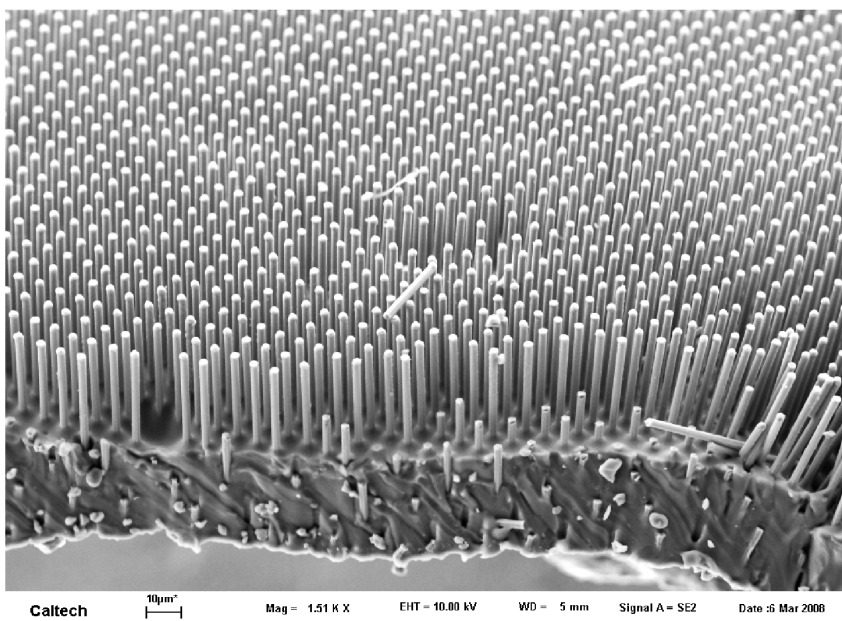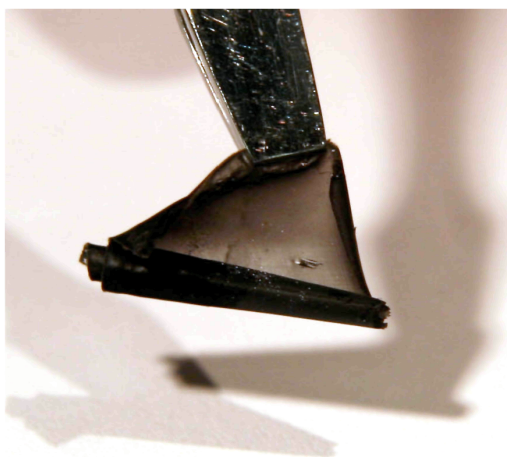
FIGURE 2. Photograph (upper) and scanning electron microscope (lower) of a flexible, processable material consisting of crystalline Si wires embedded in a plastic (polydimethylsiloxane). The wires allow effective capture and conversion of sunlight from inexpensive silicon, while the embedded structure offers the processability of organic materials such as photographic film. [J. Spurgeon, K. Plass, and N. Lewis, Division of Chemistry and Chemical Engineering, Caltech]
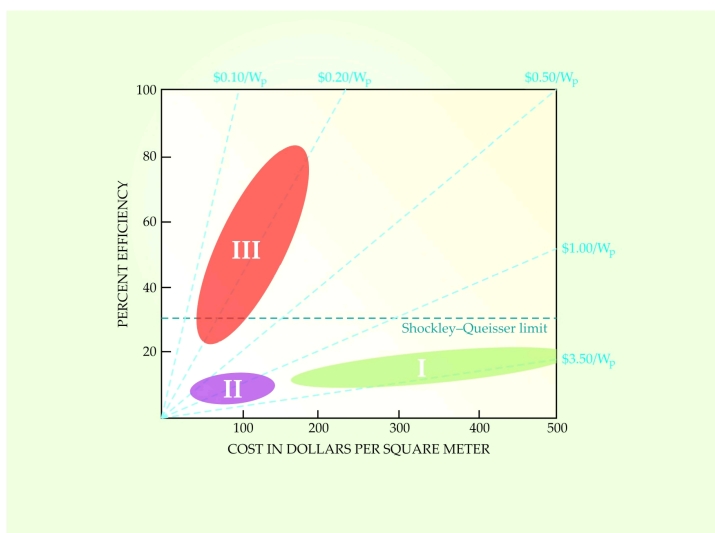
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FIGURE 3. The three generations of solar cells. First-generation cells are based on expensive silicon wafers and make up 85% of the current commercial market. Second-generation cells are based on thin films of materials such as amorphous silicon, nanocrystalline silicon, cadmium telluride, or copper indium selenide. The materials are less expensive, but research is needed to raise the cells' efficiency to the levels shown if the cost of delivered power is to be reduced. Third-generation cells are the research goal: a dramatic increase in efficiency that maintains the cost advantage of second-generation materials. Their design may make use of carrier multiplication, hot electron extraction, multiple junctions, sunlight concentration, or new materials. The horizontal axis represents the cost of the solar module only; it must be approximately doubled to include the costs of packaging and mounting. Dotted lines indicate the cost per watt of peak power (W_p). (Adapted from ref. 2, Green.)

Hot-electron extraction provides another way to increase the efficiency of nanocrystal-based solar cells: tapping off energetic electrons and holes before they have time to thermally relax.[5] Hot electrons boost efficiency by increasing the operating voltage above the bandgap, whereas carrier multiplication increases the operating current. Femtosecond laser and x-ray techniques can provide the necessary understanding of the ultrafast decay processes in bulk semiconductors and their modification in nanoscale geometries that will enable the use of hot-electron phenomena in next-generation solar cells.

Although designs have been proposed for quantum-dot solar cells that benefit from hot electrons or carrier multiplication, significant obstacles impede their implementation. We cannot attach wires to nanocrystals the way we do to bulk semiconductors; collecting the electrons from billions of tiny dots and putting them all into one current lead is a problem in nanoscale engineering that no one has solved yet. A second challenge is separating the electrons from the holes, the job normally done

by the space charge at the p–n junction in bulk solar cells. Those obstacles must be overcome before practical quantum-dot cells can be constructed.[5]

Dye-sensitized solar cells, introduced by Michael Grätzel and coworkers in 1991, create a new paradigm for photon capture and charge transport in solar conversion.[6] Expensive Si, which does both of those jobs in conventional cells, is replaced by a hybrid of chemical dye and the inexpensive wide-bandgap semiconductor titanium dioxide. The dye, analogous to the light-harvesting chlorophyll in green plants, captures a photon, which elevates one of its electrons to an excited state. The electron is then quickly transferred to the conduction band of a neighboring TiO_2 nanoparticle, and it drifts through an array of similar nanoparticles to the external electrode. The hole left in the dye molecule recombines with an electron carried to it through an electrolyte from the counter electrode by an anion such as I^-. In addition to using cheaper materials, the scheme separates the absorption spectrum of the cell from the bandgap of the semiconductor, so the cell sensitivity is more easily tuned to match the solar spectrum. The cell efficiency depends on several kinds of nanoscale charge dynamics, such as the way the electrons move across the dye–TiO_2 and dye–anion interfaces, and the way charges move through the dye, the TiO_2 nanoparticle array, and the electrolyte. The development of new dyes and shuttle ions and the characterization and control of the dynamics through time-resolved spectroscopy are vibrant and promising research areas. An equally important research challenge is the nanoscale fabrication of dye-sensitized cells to minimize the transport distances in the dye and semiconductor and maximize the electron-transfer rate at the interfaces.

FUEL

Over the past 3 billion years, Nature has devised a remarkably diverse set of pathways for converting solar photons into chemical fuel. An estimated 100TW of solar energy go into photosynthesis, the production of sugars and starches from water and carbon dioxide via endothermic reactions facilitated by catalysts. Although plants have covered Earth in green in their quest to capture solar photons, their overall conversion efficiency is too low to readily satisfy the human demand for energy. The early stages of photosynthesis are efficient: Two molecules of water are split to provide four protons and electrons for subsequent reactions, and an oxygen molecule is released into the atmosphere. The inefficiency lies in the later stages, in which carbon dioxide is reduced to form the carbohydrates that plants use to grow roots, leaves, and stalks. The research challenge is to make the overall conversion process between 10 and 100 times more efficient by improving or replacing the inefficient stages of photosynthesis. There are three routes to improving the efficiency of photosynthesis-based solar fuel production: breeding or genetically engineering plants to grow faster and produce more biomass, connecting natural photosynthetic pathways in novel configurations to avoid the inefficient steps, and using artificial bio–inspired nanoscale assemblies to produce fuel from water and CO_2. The first route is the occupation of a thriving industry that has produced remarkable increases in plant yields, and we will not discuss it further. The second and third routes, which involve more direct manipulation of photosynthetic pathways, are still in their early stages of research.

Nature provides many examples of metabolic systems that convert sunlight and chemicals into high-energy fuels. Green plants use an elaborate complex of chlorophyll molecules coupled to a reaction center to split water into protons, electrons, and oxygen. Bacteria use the hydrogenase enzyme to create hydrogen molecules from protons and electrons. More than 60 species of methane-producing archaea, remnants from early Earth when the atmosphere was reducing instead of oxidizing, use H_2 to reduce CO_2 to CH_4. Anaerobic organisms such as yeasts and bacteria use enzymes to ferment sugars into alcohols.

In nature, the metabolic pathways are connected in complicated networks that have evolved for organisms' survival and reproduction, not for fuel production. The efficient steps that are relevant for fuel production might conceivably be isolated and connected directly to one another to produce fuels such as H_2, CH_4, or alcohols. Hybridizing nature in that way takes advantage of the elaborate molecular processes that biology has evolved and that are still beyond human reach, while eliminating the inefficient steps not needed for fuel production. For example, the protons and electrons produced in the early stages of photosynthesis could link to hydrogenase to produce H_2, and a further connection to methanogenic archaea could produce CH_4. The challenges are creating a functional interface between existing metabolic modules, achieving a competitive efficiency for the modified network, and inducing the organism hosting the hybrid system to reproduce. The ambitious vision of hybrids that produce energy efficiently sets a basic research agenda to simultaneously advance the frontiers of biology, materials science, and energy conversion.

Artificial photosynthesis takes the ultimate step of using inanimate components to convert sunlight into chemical fuel.[7,8] Although the components do not come from nature, the energy conversion routes are bio-inspired. Remarkable progress has been made in the field.[8] Light harvesting and charge separation are accomplished by synthetic antennas linked to a porphyrin-based charge donor and a fullerene acceptor, as shown in Figure 4. The assembly is embedded in an artificial membrane, in the presence of quinones that act as proton shuttles, to produce a light-triggered proton gradient across the membrane. The proton gradient can do useful work, such as powering the molecular synthesis of adenosine triphosphate by mechanical rotation of natural ATP synthase inserted into the membrane. Under the right conditions, the required elements self-assemble to produce a membrane-based chemical factory that transforms light into the chemical fuel ATP, molecule by molecule at ambient temperature, in the spirit of natural photosynthesis.

Such remarkable achievements illustrate the promise of producing fuel directly from sunlight without the use of biological components. Many fundamental challenges must be overcome, however. The output of the above energy conversion chain is ATP, not a fuel that links naturally to human–engineered energy chains. The last step relies on the natural catalyst ATP synthase, a highly evolved protein whose function we cannot yet duplicate artificially. Laboratory approximations of biological catalysts have catalytic activities that are often orders of magnitude lower than those of their biological counterparts, which indicates the importance of subtle features that we are not yet able to resolve or to reproduce.
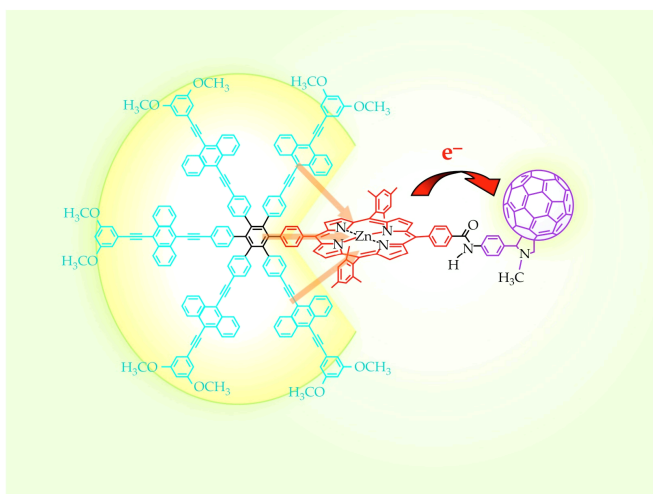
FIGURE 4. An artificial antenna–reaction-center complex that mimics the early stages of photosynthesis. The central hexaphenylbenzene core provides structure and rigidity for the surrounding wheel of five bis(phenylethynyl)anthracene antennas that gather light at 430–475 nanometers. The energy is transferred to a porphyrin complex in 1–10 picoseconds (orange arrows), where it excites an electron that is transferred to the fullerene acceptor in 80 ps; the resulting charge-separated state has a lifetime of 15 nanoseconds. Complexes such as the one shown provide the first steps in artificial photosynthesis. They have the potential to drive further chemical reactions, such as the oxidation of water to produce H_2 or the reduction of CO_2 to CH_4, alcohol, or other fuel. (Adapted from ref. 16.)

Solar fuels can be created in an alternate, fully nonbiological way based on semiconductor solar cells rather than on photosynthesis. In photoelectrochemical conversion, the charge-separated electrons and holes are used locally to split water or reduce CO_2 at the interface with an electrolytic solution, rather than being sent through an external circuit to do electrical work.[9] Hydrogen was produced at the electrode–water interface with greater than 10% efficiency by Adam Heller in 1984 and by Oscar Khaselev and John Turner in 1998, but the fundamental phenomena involved remain mysterious, and the present devices are not practical. A promising way to improve them is by tailoring the nanoscale architecture of the electrode–electrolyte interface to promote the reaction of interest. A better understanding of how individual electrons negotiate the electrode–electrolyte interface is needed before H_2 can be produced with greater efficiency or more complex reactions can be designed for reducing CO_2 to useful fuels.

HEAT

The first step in traditional energy conversion is the combustion of fuel, usually fossil fuel, to produce heat. Heat produced by combustion may be used for heating space and water, cooking, or industrial processes, or it may be further converted into motion or electricity. The premise of solar thermal conversion is that heat from the

Sun replaces heat from combustion; fossil–fuel use and its threat to the environment and climate are thus reduced. Unconcentrated sunlight can bring the temperature of a fluid to about 200 °C, enough to heat space and water in residential and commercial applications. Many regions use solar water heating, though in only a few countries, such as Cyprus and Israel, does it meet a significant fraction of the demand. Concentration of sunlight in parabolic troughs produces temperatures of 400 °C, and parabolic dishes can produce temperatures of 650°C and higher.[10,11] Power towers, in which a farm of mirrors on the ground reflects to a common receiver at the top of a tower, can yield temperatures of 1500 °C or more.[10,12] The high temperatures of solar power towers are attractive for thermo–chemical water splitting and solar–driven reforming of fossil fuels to produce H_2.[11]

The temperatures produced by concentrated sunlight are high enough to power heat engines, whose Carnot efficiencies depend only on the ratio of the inlet and outlet temperatures. Steam engines driven by solar heat and connected to conventional generators currently supply the cheapest solar electricity. Nine solar thermal electricity plants that use tracking parabolic-trough concentrators were installed in California's Mojave Desert between 1984 and 1991. Those plants still operate, supplying 354 MW of peak power to the grid. Their average annual efficiency is approximately 20%, and the most recently installed can achieve 30%.

Although those efficiencies are the highest for any widely implemented form of solar conversion, they are modest compared to the nearly 60% efficiency of the best gas-fired electricity generators. Achieving greater efficiency for solar conversion requires large-scale plants with operating temperatures of 1500°C or more, as might be produced by power towers. Another alternative, still in the exploration stage, is a hybrid of two conversion schemes: A concentrated solar beam is split into its visible portion for efficient photovoltaic conversion and its high-energy portion for conversion to heat that is converted to electricity through a heat engine.[10]

Thermoelectric materials, which require no moving parts to convert thermal gradients directly into electricity, are an attractive possibility for reliable and inexpensive electricity production.[13] Charge carriers in a thermal gradient diffuse from hot to cold, driven by the temperature difference but creating an electric current by virtue of the charge on each carrier. The strength of the effect is measured by the thermopower, the ratio of the voltage produced to the applied temperature difference. Although the thermoelectric effect has been known for nearly 200 years, materials that can potentially convert heat to electricity efficiently enough for widespread use have emerged only since the 1990s.[13] Efficient conversion depends on minimizing the thermal conductivity of a material, so as not to short–circuit the thermal gradient, while maximizing the material's electrical conductivity and thermopower. Achieving such a combination of opposites requires the separate tuning of several material properties: the bandgap, the electronic density of states, and the electron and phonon lifetimes. The most promising materials are nanostructured composites. Quantum-dot or nanowire substructures introduce spikes in the density of states to tune the thermopower (which depends on the derivative of the density of states), and interfaces between the composite materials block thermal transport but allow electrical transport, as discussed by Lyndon Hicks and Mildred Dresselhaus in 1993.[14] Proof of concept for interface control of thermal and electrical conductivity was achieved by 2001 with

thin-film superlattices of Bi_2Te_3/Sb_2Te_3 and PbTe/PbSe, which performed twice as well as bulk-alloy thermoelectrics of the same materials. The next challenges are to achieve the same performance in nanostructured bulk materials that can handle large amounts of power and to use nanodot or nanowire inclusions to control the thermopower. Figure 5 shows encouraging progress: structurally distinct nanodots in a bulk matrix of the thermoelectric material $Ag_{0.86}Pb_{18}SbTe_{20}$. Controlling the size, density, and distribution of such nanodot inclusions during bulk synthesis could significantly enhance thermoelectric performance.[15]
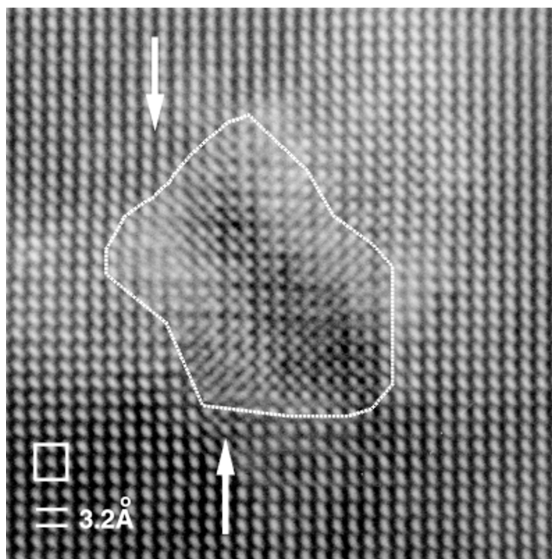

FIGURE 5. A nanodot inclusion in the bulk thermoelectric material $Ag_{0.86}Pb_{18}SbTe_{20}$, imaged with high-resolution transmission electron microscopy. Despite a lattice mismatch of 2–5%, the nanodot (indicated by the dotted line) is almost perfectly coherently embedded in the matrix. The arrows show two dislocations near the interface, and the white box indicates the unit cell. The nanodot is rich in silver and antimony relative to the matrix. (Adapted from ref. 15.)

STORAGE AND DISTRIBUTION

Solar energy presents a scientific challenge beyond the efficient conversion of solar photons to electricity, fuel, and heat. Once conversion on a large scale is achieved, we must find ways to store the large quantities of electricity and heat that we will produce. Access to solar energy is interrupted by natural cycles of day–night, cloudy–sunny, and winter–summer variation that are often out of phase with energy demand. Solar fuel production automatically stores energy in chemical bonds. Electricity and heat, however, are much more difficult to store. Cost effectively storing even a fraction of our peak demand for electricity or heat for 24 hours is a task well beyond present technology.

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Storage is such an imposing technical challenge that innovative schemes have been proposed to minimize its need. Baseload solar electricity might be generated on constellations of satellites in geosynchronous orbit and beamed to Earth via microwaves focused onto ground-based receiving antennas. A global superconducting grid might direct electricity generated in sunny locations to cloudy or dark locations where demand exceeds supply. But those schemes, too, are far from being implemented. Without cost-effective storage and distribution, solar electricity can only be a peak–shaving technology for producing power in bright daylight, acting as a fill for some other energy source that can provide reliable power to users on demand.

OUTLOOK

The Sun has the enormous untapped potential to supply our growing energy needs. The barrier to greater use of the solar resource is its high cost relative to the cost of fossil fuels, although the disparity will decrease with the rising prices of fossil fuels and the rising costs of mitigating their impact on the environment and climate. The cost of solar energy is directly related to the low conversion efficiency, the modest energy density of solar radiation, and the costly materials currently required. The development of materials and methods to improve solar energy conversion is primarily a scientific challenge: Breakthroughs in fundamental understanding ought to enable marked progress. There is plenty of room for improvement, since photovoltaic conversion efficiencies for inexpensive organic and dye-sensitized solar cells are currently about 10% or less, the conversion efficiency of photosynthesis is less than 1%, and the best solar thermal efficiency is 30%. The theoretical limits suggest that we can do much better. Solar conversion is a young science. Its major growth began in the 1970s, spurred by the oil crisis that highlighted the pervasive importance of energy to our personal, social, economic, and political lives. In contrast, fossil-fuel science has developed over more than 250 years, stimulated by the Industrial Revolution and the promise of abundant fossil fuels. The science of thermodynamics, for example, is intimately intertwined with the development of the steam engine. The Carnot cycle, the mechanical equivalent of heat, and entropy all played starring roles in the development of thermodynamics and the technology of heat engines. Solar–energy science faces an equally rich future, with nanoscience enabling the discovery of the guiding principles of photonic energy conversion and their use in the development of cost–competitive new technologies.

This article is based on the conclusions contained in the report[1] of the US Department of Energy Basic Energy Sciences Workshop on Solar Energy Utilization, April 18–21, 2005. We served as chair (Lewis) and co-chair (Crabtree) of the workshop and were principal editors of the report. We acknowledge the US Department of Energy for support of both the workshop and preparation of the manuscript.

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