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With Photovoltaics, Solar Energy Is Here to Stay

by Vaidyanathan (Ravi) Subramanian and Pawan Pathak

Until the turn of the 20th century, mankind was content with exploiting wood, coal, and petroleum for meeting all of its energy needs. Since the last century it began to dawn upon us that fossil fuels can be a finite resource. The last century has also seen notable advancements in technology leading to significant changes in our life style that has made us more energy dependent. Due to this ever increasing and aggressive dependence on fossil fuels, by several estimates we have reached a point where we cannot expect to continue using fossil fuels in the same manner to power our economy. For example, the availability of petroleum and its economical production will ultimately become a challenge, although we are not there yet. Coal can be regarded as a longer term fuel source compared to petroleum if we consider all grades and availability around the globe. However, in recent decades it has became abundantly clear that continued use of fossil based fuels can interfere with the environment leading to potentially irreversible climate change.

These changes can negatively alter our way of life. Therefore, there is an urgent need to examine alternative sources of energy, provided that their use is sustainable and contributes to maintaining our lifestyle without any drastic changes. Since the turn of the 20th century the notion that coal and petroleum will be *the* sources of energy to support our economies and be the driver that sustains our way of life and our environment, is slowly being replaced (Fig. 1).

From an energy standpoint, the challenges to the present and future generations are two-fold. The first is to identify energy sources that are sustainable and the second is to develop technologies that can harness these sources efficiently. Eco-friendly solutions to energy generation must become an integral part of the energy generation process in the future. This mindset will guide us to seek a lasting solution for meeting our energy needs and ensure that future generations do not wait until reaching a precipice that could force us to consider a lifestyle altering decision.

Solar Energy and Its Overarching Benefits

Solar energy has been available for billions of years, ever since the Sun came into existence. The moment the planetary system formed, the planets began to evolve by interacting with the energy from the Sun. Once the Earth was created and the conditions started to become conducive for sustaining life, evolution started to take root. The environment became conducive for the formation of the earliest and rudimentary microorganisms. In due course, these microorganisms, mostly simple and unicellular, began to thrive in all parts of nature. Later, complex cell structures began to evolve in the Earth's environment. At some point plants began to take shape. The plants and microorganisms began to thrive by interfacing directly with sunlight or using the nutrients available in the Earth's environment. These are the earliest and natural examples of the Sun's participation in Earthly evolution. Steadily the evolution of variants of these microorganism and more complex cellular structures (trees and animals) began to occur, much earlier than primitive man evolved. Other attempts, primarily manmade, to leverage the potential of the Sun to date is summarized in this retrospective of solar power as a one-stop-shop for all our energy needs.

Evolution of the Use of Solar Energy

The ancient Greeks are generally believed to be the first to realize the potential of the Sun's energy and to utilize it in an organized manner. They were able to design buildings in such a manner that light was allowed in to illuminate the living quarters. The Romans built upon this concept and were able to use glass as a medium to regulate the Sun's energy for domestic purposes. They were also able to leverage solar energy using the concept of green houses. Since then there have been several applications that have evolved around the use of solar energy as a primary power source.[1] Figure 2 provides a comprehensive list of efforts that are currently being pursued to harness energy from the Sun. This article focuses on the use of the Sun's energy for electricity generation. In the subsequent pages, we present some of the current state-of-the-art technologies in harnessing solar power as a sustainable and long term energy source using photovoltaics as a platform.

Solar to Electricity Conversion or Photovoltaics

The generation of electricity using solar energy was brought to the fore by French physicist, Edmund Becquerel, who developed the photovoltaic cell in 1839. The photoelectric effects, the phenomena in the cell, were explained by Nobel Prize winner Albert Einstein. When a photon of energy $E = h\nu$ (h = Planck's constant and ν = frequency of light) strikes a semiconductor surface, electron-hole pairs are generated in the material; the flow of these electrons constitutes an electric current. Since this discovery, research into photovoltaics has seen steady progress leading to the evolution of new materials, their assembly, and advancements in processing techniques, resulting in cells that produce power in a sustainable manner for a distributed supply.[2]

The technology of the photovoltaic (PV) solar cell is considered to have evolved across three generations.[3] The first generation represents the traditional solar cell and mainly focuses on silicon as the primary

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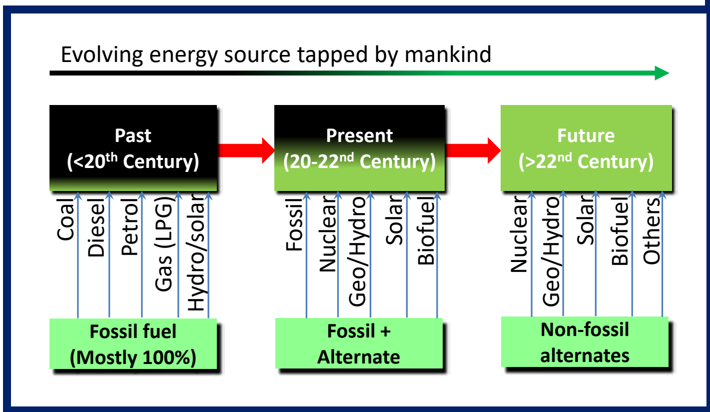

Fig. 1. *The major contributors towards the energy portfolio accessible to mankind in the past and present and the options available to us in the foreseeable future.*

material. Silicon is a unique element with four electrons in its outmost orbital and forms tetravalent bonds with other neighboring silicon atoms. The performance of a silicon-based device depends on the atomic arrangement of silicon.[4] The common arrangements are crystalline (ordered) or amorphous (disordered) as indicated in Fig. 3(i) and (ii) respectively.

Intrinsic or undoped Si is not as effective in demonstrating PV response and therefore an impurity is often added (or doped) in the Si to alter its electronic properties.[5] Pentavalent or trivalent atoms such as phosphorus or boron that give it a characteristic n-and p-type behavior respectively, are used for this purpose as shown in Fig. 3(i). The n- and p-type silicon can be integrated to form a single p/n junction solar cell with or without an intermediate intrinsic silicon layer as shown in Fig. 3(iii). Photoillumination of such a cell produces a DC current that can be used in the external circuit to power a device. The Shockley Queisser efficiency (SQE) analysis provides a theoretical limit of the performance of a single junction cell by correlating the spectral absorbance range and the possible bandgap energy required to the maximum efficiency of the cell. For a solid state single p/n junction crystalline silicon solar cell, this value is estimated to be ~33% under 1 sun (normal solar irradiance of ~100 mW/cm^2) as indicated in Fig. 3(iv).[6] Practically reported numbers are ~25% for a crystalline device.[7] This decrease is attributable to surface reflection and charge recombination/thermal losses.[8] The efficiency generally reduces as the crystallinity of the Si reduces. An increase in solar radiance typically achieved by solar concentration improves the single junction device performance across the spectral range of interaction. However, there are other approaches, where one can leverage structural design to achieve efficiencies beyond the SQE.[9] Further, one can assemble multiple absorber layers together that can interact with a broad spectral range to improve cell performance.

Silicon is the preferred material of choice because it offers advantages such as wide availability (produced from silica or sand). Broad ranging applications based on the extent of its crystalline characteristics are possible. Silicon solar cells are classified as monocrystalline, polycrystalline, amorphous, or hybrid. The techniques used for preparing the silicon depend on the crystallinity, dopant level, and type of substrate (hard surface or flexible ribbon-type) in the device. Based on the type of silicon and its physical features (hard or flexible) they can be used to produce power for various applications. Modular panels containing several of these silicon based cells can be assembled together in series/parallel configurations to generate a significant amount of electricity from the Sun. The technology for this class of material has matured over the last several decades. Today, silicon-based solar cells continue to be the dominant and most dependable of all solar cell technologies.[10] They produce energy for a broad range of applications from extraterrestrial (space) to residential and commercial complexes.

Second-generation devices are a class of cells that evolved to be recognized as very thin films comprising of a few to several layers of different materials that still lead to thicknesses that are in the order of several micrometers. Amorphous silicon-based cells are also included here since it is possible to produce them on a flexible substrate with the expenditure of relatively less energy than crystalline Si solar cells. Other representative examples include cadmium telluride (CdTe) cells or multi-component copper indium sulfide or copper indium gallium sulfide/selenide (CIGS) cells.[11] These cells are also single junction devices and are generally cheaper compared to first-generation crystalline solar cells due to lower processing cost. The raw materials for these cells could be an issue as noted recently or lead to environmental problems.[12] They are less efficient than some of the top performing single generation crystalline silicon cells but are catching up with efficiencies in the 20% range.[13]

The third-generation devices represent several organic, inorganic, and hybrid material classes that demonstrate unique optoelectronic properties. These cells are classified based on the type of light absorber materials as organic dyes, quantum dots, polymer, and the more recent organic perovskites cells. The key components of these cells are two conducting substrates that sandwich a semiconductor (optional in some cases), a light absorber, a redox medium and/or a hole transport medium in a configuration as shown in the exploded schematic of Fig. 4(i). Substrates are hard and inflexible such as indium or fluorine doped tin oxide glass or flexible and conducting polymer with at least the illumination side transparent. The substrate material is often a large bandgap oxide which shows good adhesion to the substrate, offers high surface area (usually due to a porous structure), and facilitates the transport of electrons once they are generated in the sensitizer. The photosensitive component absorbs light and injects electrons into the underlying semiconductor. Although each of the four sensitizer type is slightly different, the general cell operation involves the transport of the generated electrons through the external circuit constituting a photocurrent. A suitable redox medium that is matched to the sensitizer energetics serves as the medium for regeneration of the photosensitizer. Titanium dioxide is the most popular of the large bandgap semiconductor used as the substrate.

A characteristic aspect of the dye is it absorbs visible light and transition from a ground state, also called lowest unoccupied molecular orbital (LUMO), to an exited state, or the highest occupied molecular orbital (HOMO).[14] After attaining this excited state, the electron is injected into the semiconductor as indicated in Fig. 4(ii). It is reduced by the redox couple as it transitions to the ground state while the oxidized couple collects the electron from the cathode completing the circuit. Ruthenium-based dyes (e.g., N719), its variant, or N719 with additives are considered promising photo absorbers in the dye solar cell class.[15] These dye-based cells have been extensively developed and are at a point where they are considered competitive in the commercial domain.

Quantum dots are unique in that they display size dependent opto-electronic properties. The physics of quantum confinement principles state that when an object is confined and limited in its mobility to a small space, it demonstrates the property of an isolated atom, where the energy levels are discretized. Adhering to this principle are some semiconductor nanoparticles that absorb light to produce electron-hole pairs in discretized conduction and valence bands that are set based on the size of the nanoparticle. For example,

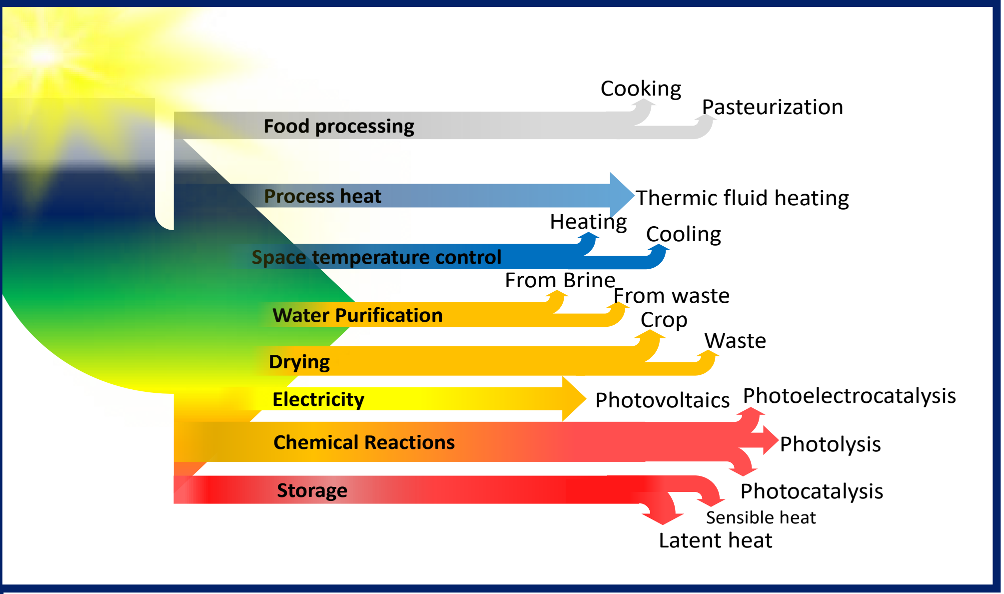

Fig. 2. *The omnipresent nature of solar energy has led to the development of broad overaching application.*

the chalcogenide CdS can be assembled as a heterostructure with TiO_2 to form a heterogeneous photoresponse electrode.[16,17] The choice of the semiconductor and its size is determined such that its conduction band is more negative to the conduction band edge of the substrate to allow photogenerated electrons to cascade to the oxide and exit at the substrate generating photocurrent as indicated in Fig. 4(iii). Chalcogenides are a class of semiconductors that demonstrate interesting size dependent optical/electronic responses and multiple exciton generation which can allow for theoretical cell efficiencies in ~40% range.[18] Nanoparticles of these material classes demonstrate widening bandedge positions as the physical size reduces allowing one to tune the bandgap to facilitate absorbance of light of various wavelengths spanning the visible and IR domain. An appropriate electrolyte redox couple is used to replenish the electron to the semiconductor. CdX (X = S, Se, or Te), PbX (X = S, Se, or Te) are materials that are photo responsive as well as demonstrate size quantization effects in the visible and IR domain.[19]

The polymer cells are very similar to the dye-sensitized solar cells (DSSCs). The electron donors are of various types ranging from photo responsive fullerene derivatives to conjugate polymers. Just as in the DSSCs these photoresponsive materials absorb light and produce electron-hole pairs. An oxide layer serves as the electron receptor. It may be optional if the photo responsive component and the hole transporter form an effective heterojunction and the in-built potential can drive the charges to separate. Examples of hole transport polymer are Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate (PEDOT:PSS).[20] The conducting hole transport may also be used with DSSCs to avoid using an expensive counter electrode such as platinum. The salient features of this class of cells include low processing temperatures, production on flexible substrates (roll-to-roll processing), light, and scalability.[21] Their efficiencies are however lower than the DSSCs.

Organic perovskites are a recently identified new class of inorganic-organic hybrid compounds comprised of an alkyl-halogen complex with a metal center and halogen moiety. Their role is very similar to organic dye. The small band gap, high charge carrier mobility, apparent tolerance of defects, and high exciton coefficient of perovskites materials have made them ideal for photovoltaic devices. Once the excitons are generated, the electron transport occurs by a pathway similar to the DSSC. However, the specific hole transporting agent is juxtaposed next to the perovskite and intimately mixed to enhance the efficiency of exciton separation, as indicted in Fig. 4(iv). Alkyl NH_4.MX (where M = Pb, X = Br, Cl, I) or halide perovskite cells have been extensively tested for their photo responsiveness.[22] They are coupled with with Spiro-MeOTAD (abbreviated name) as the hole transporting agent. However, stability is one of the major issues of perovskite solar cells and research groups around the world are intensively working to address this issue.[23] The contents of the cell require full encapsulation because moisture can significantly impede cell performance. Research in this type of solar cell has been dramatic with overall cell efficiencies close to ~22%. Other cells that are included in this third generation category are the tandem and multifunction cells. These devices consist of several absorber materials that principally broaden the spectral range to improve device efficiencies.

Conclusions and Future Outlook

Harnessing the power of the Sun using photovoltaics is a very real and practical option for sustainable energy generation. The development of photovoltaic technology has opened several avenues across three generations of photovoltaic technologies that can be considered as successful pathways for electricity generation. The

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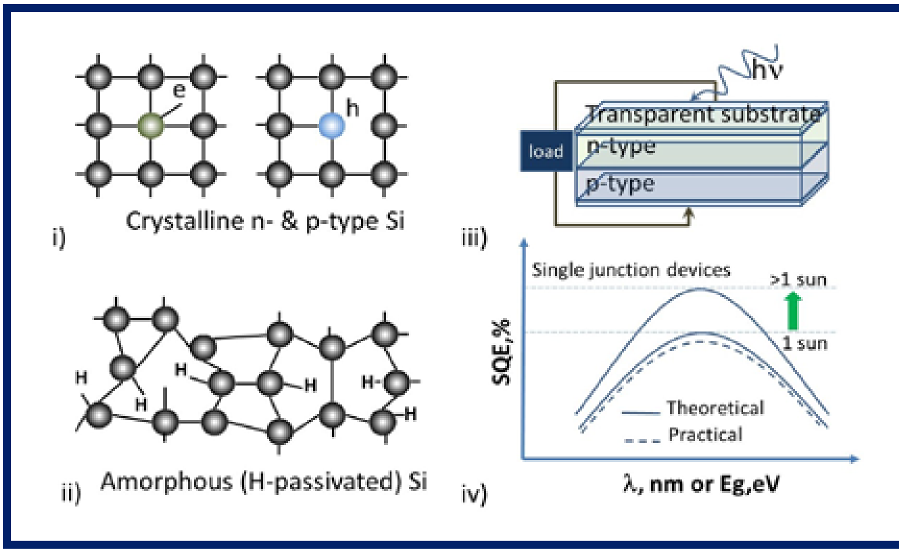

FIG. 3. *Lattice structure of (i) crystalline and (ii) amorphous silicon, (iii) structure of a pn junction silicon solar cell, and (iv) sketch of the Shockley Queisser efficiency plot with reference to wavelength or bandgap of photoresponse material forming single junction devices.*

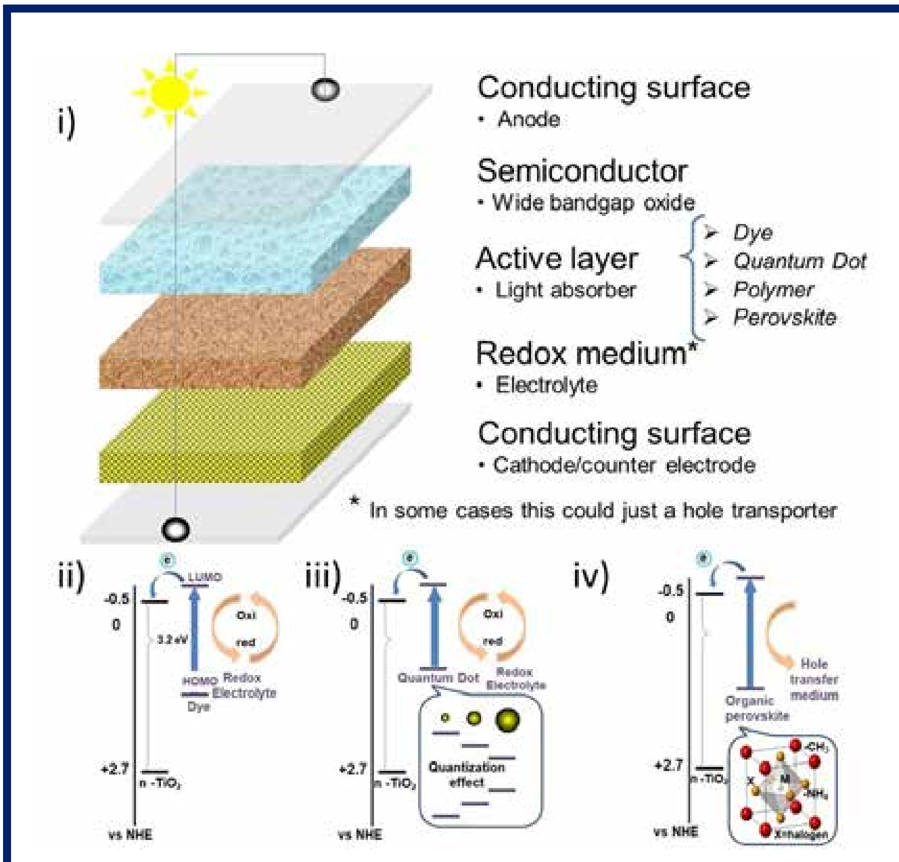

FIG. 4. *(i) The exploded view of the different layers in a typical third generation solar cell. The energetics of the (ii) dye sensitized,(iii) quantum dot (inset) size quantitation effect, and (iv) organic perovskite solar cells (insert) structure of an organic sensitizer.*

success of single crystalline solar cells for space applications set the standard for photovoltaics and continues to be implemented as evident from the recent Mars missions. However the traditional dominance of silicon is now being challenged by second- and third-generation cells. CdTe, CIGS, quantum dot, and perovskite solar cells provide unique properties that can be leveraged for niche applications and are expected to make inroads into applications ranging from off-grid power, portable devices, smart textiles, and building integrated photovoltaics. From a price standpoint as well the solar cell producing power well below a dollar per kW has made photovoltaics increasingly attractive and less dependent on government subsidies for market penetration. Some of the key future challenges include lowering of manufacturing cost, improving cell performance efficiency, and addressing material stability. Together these technologies will ensure that photovoltaic technology continues to be a relevant pathway for sustainable energy generation.

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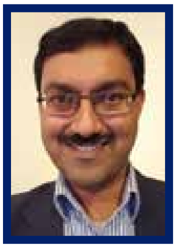
About the Authors



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Pawan Pathak has recently graduated with a PhD in chemical engineering from the University of Nevada, Reno. Prior to this he earned a MS in physics from the same university. He is an expert in wet chemical processing of oxides, chalcogenides, and heterostructures of oxide-chalcogenide nanocomposites. He has been recognized as an outstanding graduate student on multiple occasions at the university. He has several publications and a patent. He is currently a postdoctoral research scientist at the University of Central Florida, Orlando, in the Department of Mechanical and Aerospace Engineering. He may be reached at ppathak3210@gmail.com.

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