

Beyond the Shockley-Queisser Limit

PV Efficiency Improvements via Downconversion and Upconversion

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Spring 2024

Executive Summary

This paper explores novel photonic techniques of downconversion (DC) and upconversion (UC) to enhance the efficiency of solar cells beyond the traditional bounds. While multijunction cells have been the mainstay in surpassing the Shockley-Queisser limit, this research investigates the potential of modifying the solar spectrum to match the absorption characteristics of a single-junction crystalline silicon solar cell, thus addressing the incongruence between the solar spectrum and the cell's absorption capacity. Theoretical foundations suggest that through DC and UC, where the former refers to the splitting of high-energy photons to multiple lower energy photons and the latter to the combining of low-energy photons to exceed the bandgap, solar cells could theoretically achieve significant efficiency gains. Lanthanide-doped materials emerge as a primary candidate for these processes, offering many energy levels for potential transitions. Despite theoretical advantages, practical application of DC and UC layers has led to a modest efficiency improvement, raising questions about their commercial viability. Challenges such as the nonlinearity of UC processes, the need for spectrum and emission tuning to align with the solar cell's functional range, and long-term stability under ambient conditions are addressed. Ultimately, this paper concludes that while DC and UC hold promise theoretically, multijunction cells remain the more proven path to high-efficiency solar cells in the immediate future. Advances in material science and photonic engineering, however, could eventually realize the integration of DC and UC layers, potentially revolutionizing the solar energy landscape.

Problem Statement/Objective

Over the last 50 years, photovoltaic (PV) cell conversion efficiencies have steadily climbed higher. While progress has been seen across cell technologies, creating multijunction cells that better align with the solar spectrum has been the most fruitful approach. The highest recorded efficiency to date is from a four-junction cell based on Group III-V cell technology, which achieved an efficiency of 47.6% [1]. (Note that this is a concentrator cell that uses optical devices to focus sunlight.) The multijunction approach relies on adapting the PV cell to fit the solar spectrum, but what if we could approach this the other way around—modifying the solar spectrum to the PV cell? For this report, I wanted to investigate the novel techniques of downconversion (DC) and upconversion (UC) for further improving solar cell efficiency. These are methods that could compensate for the incongruence between the solar spectrum and relatively narrow absorption characteristics of solar cell materials.

Before we get to the theoretical limit for the efficiency of a $p-n$ junction solar cell established by Shockley and Queisser, there is a simpler theoretical limit to these cells' efficiencies that we can obtain by looking at the solar spectrum and doing some simple math. For simplicity and ease of comparison to historical calculations, we'll consider a single junction crystalline silicon solar cell with a bandgap of 1.1eV. In order for solar energy to be absorbed by this cell, the photons must have at least 1.1eV of energy. We can easily solve for the cutoff wavelength above which no energy can be absorbed, as shown in Equation 1.

$$1.1 \text{ eV} = \frac{hc}{\lambda} \rightarrow \lambda = 1128 \text{ nm}$$

Equation 1. h is Planck's constant in electron volts (4.14×10^{-15} eV) and c is the speed of light (3×10^8 m/s).

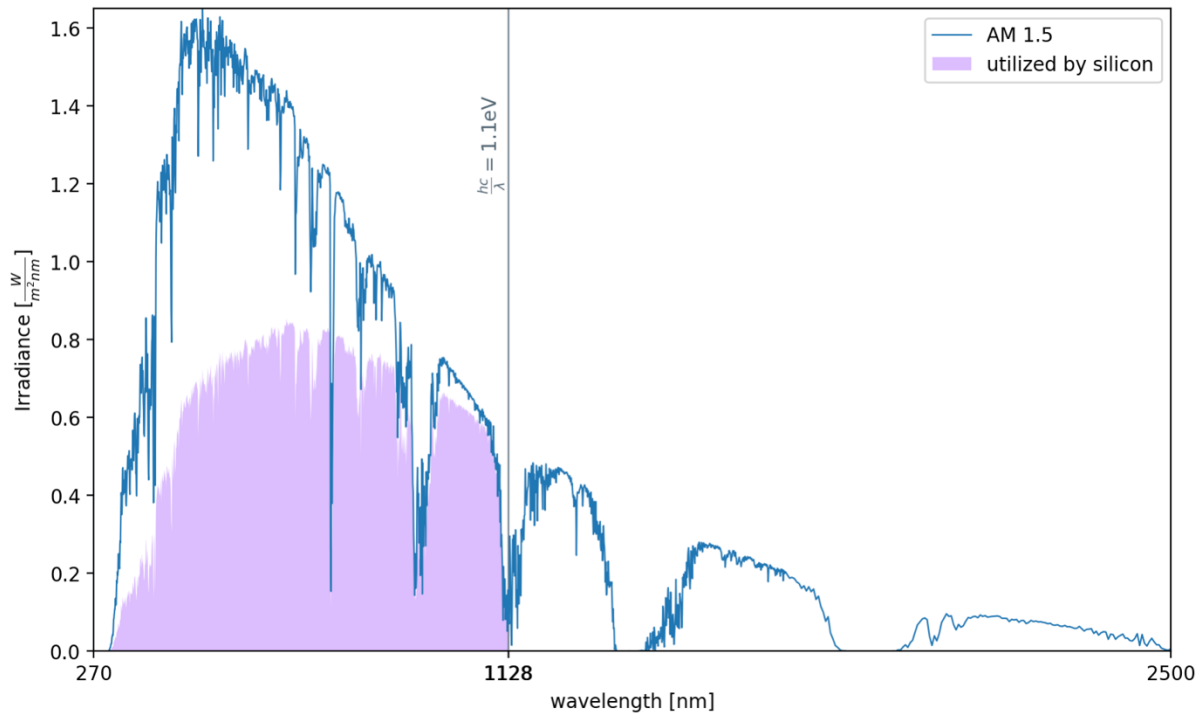


Figure 1. Single junction silicon solar cells have a fundamental limit on how much of the solar spectrum they can absorb. Original work.

Further, for shorter wavelengths, all the energy beyond 1.1 eV is wasted. We can illustrate this on a plot, showing the AM 1.5 spectrum irradiance vs. wavelength and the portion that a silicon solar cell is able to capture. (The AM 1.5 data was retrieved [2]). The irradiance capture by the silicon cell is calculated as in Equation 2.

$$I_{Si}(\lambda) = I_{AM\ 1.5}(\lambda) \times \frac{1.1\ \text{eV}}{\frac{hc}{\lambda}}$$

Equation 2. Portion of the spectrum absorbed by a silicon solar cell.

Integrating the area under the silicon curve compared to the area under the AM 1.5 curve, we see that the silicon solar cell can absorb almost 50% of the 1000 W/m² available.

*Don't look at this 50% number and think that I think a Silicon solar cell has a theoretical maximum efficiency of 50%; I know the real number is around 31% due to thermalization, recombination, etc. I am just illustrating how much of the solar spectrum is not even available to the Silicon cell. Shockley and Queisser referred to this figure as **ultimate efficiency** [3].*

How can we tap into the remaining 50% of the solar spectrum? One valid and commercially practiced method is multijunction cells. Another is concentration of sunlight. We covered these in class, so I wanted to investigate other methods, hence the topic of this paper: downconversion and upconversion. DC is also sometimes referred to as “quantum cutting”. DC occurs when a photon with energy at least twice the bandgap is downconverted into 2 photons

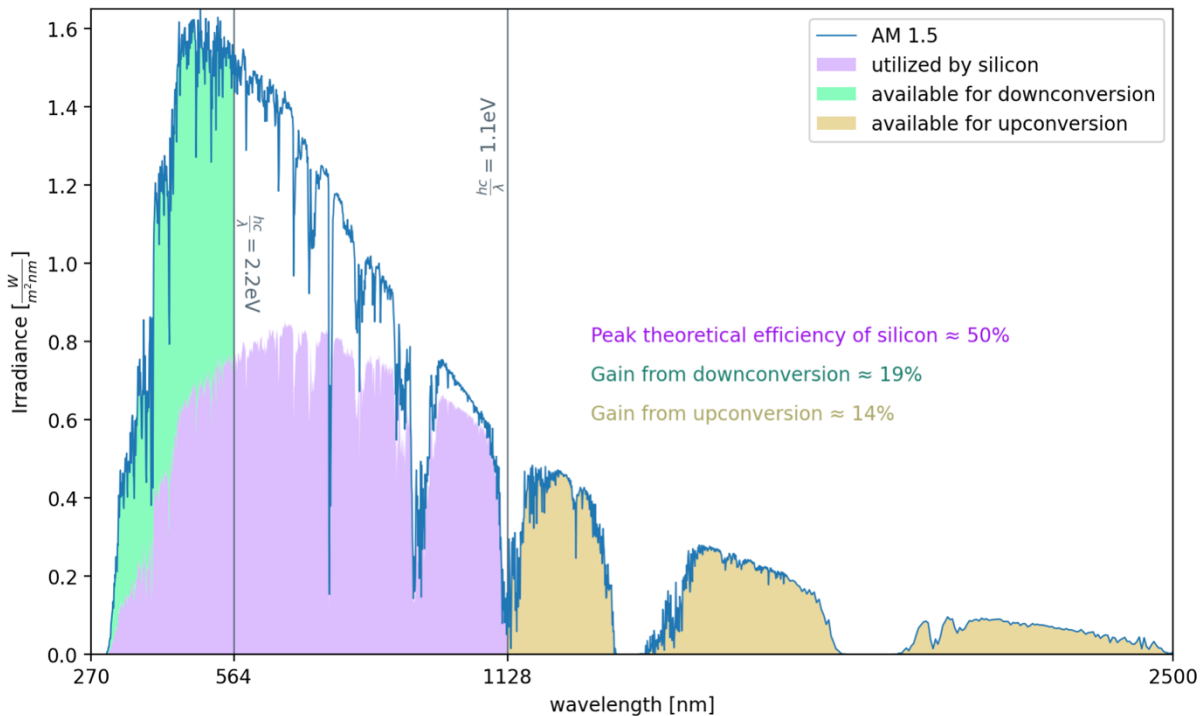


Figure 2. The AM 1.5 spectrum showing potential for upconversion and downconversion to improve efficiency. Original work.

with **lower** frequency (hence **down**) but still enough energy to excite an electron across the bandgap. UC is when photons with less energy than the bandgap can accumulate their energy and produce a higher frequency photon that then has enough energy to excite an electron across the bandgap. Figure 2 shows the potential gains in efficiency with DC and UC. There is more potential for efficiency gains with DC, about 19%, compared to 14% theoretical improvement with UC.

Theoretical Framework

UC and DC are not merely figments of science fiction. Both conversions have been demonstrated experimentally and theories have been developed to explain how they work [4]. In fact, the concept of DC was first explored in 1957 by D.L. Dexter [5].

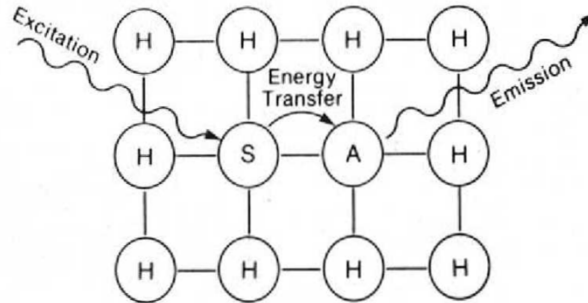


Figure 3. Luminescence. H = host, S = Sensitizer, A = Activator. Reproduced from [6].

DC and UC are examples of luminescence, so in order to understand their underlying mechanisms, first we'll cover the basics of luminescence. Luminescence can be defined as the absorption of photons by a substance which is then followed by a photon emission that is not a result of high temperatures [6]. Photon emission as a result of high temperature, rather, would be incandescence. We call substances that exhibit luminescence phosphors. Phosphors are created by doping a host material with a small amount of foreign ions. We call the foreign ion that can be excited to luminescence an **activator**. We call a foreign ion that can transfer its energy to a neighboring activator a **sensitizer**, or sometimes a **donor** [6]. Figure 3 shows the relationship of sensitizers, activators and the host lattice.

Now let's define an important term, external quantum efficiency (EQE). EQE refers to the number of electrons generated per incident photon at a given wavelength. This includes absorbed, transmitted, and reflected photons. When Shockley and Queisser established their theoretical limit in 1960, they assumed an EQE of 1 (unity) [3]. DC is all about achieving an EQE greater than unity. In UC, EQE is by definition less than 0.5.

DC can occur via a few different mechanisms. In the simplest scenario, as shown in figure 3, a single high energy photon is absorbed by the DC material, causing an electron to jump up two energy levels. The electron then relaxes in two sequential stages with each relaxation emitting a lower frequency/energy photon. If the energy of the two photons is at least as much as the bandgap of the solar cell, then two electrons will be excited in the solar cell [4].

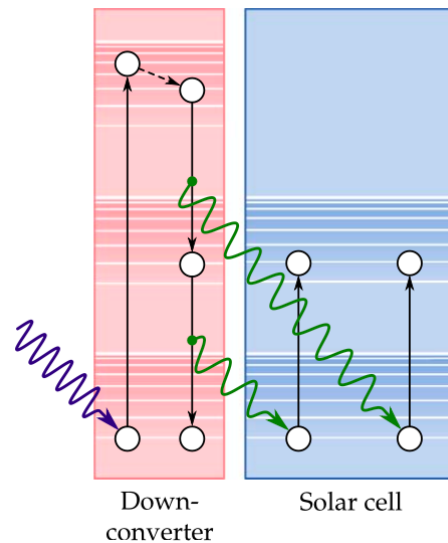


Figure 4. The simplest DC scenario, reproduced from [4].

In another mechanism called cooperative energy transfer (CET), a high energy photon excites a single donor (shown in figure 4). The donor then transfers its energy to nearby acceptors. If the acceptors then emit efficiently, the result is two emitted photons for a single absorbed photon [7]. This version of DC is typically modeled using Monte Carlo simulations [4].

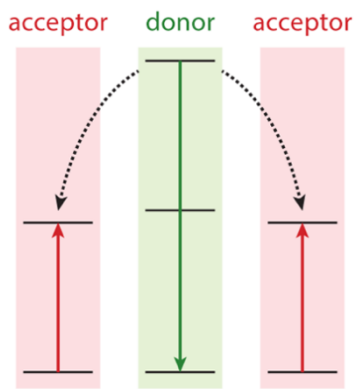


Figure 5. DC via cooperative energy transfer where a single excited donor transfers energy to two neighboring acceptors, reproduced from [7].

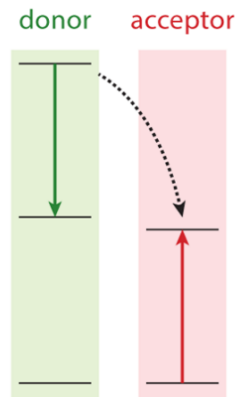
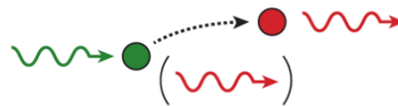


Figure 6. DC via cross relaxation where a donor transfers some but not all of its energy to an acceptor, reproduced from [7].

A third, similar mechanism, called cross-relaxation is shown in figure 5. In this case, the donor that was excited by a high energy photon transfers part of its energy to a single acceptor. Now both the donor and acceptor are in an intermediate state, and both have the potential to emit a lower energy photon.

With this in mind, we can explore the various mechanisms of UC, three of which are shown in figure 7. The simplest form is shown in figure 7a. Excited state absorption (ESA) occurs when two photons are sequentially absorbed by an electron, and then a single photon is emitted. The energy levels of the activator must be such that it can facilitate the absorption of a second photon [8].

Next in figure 7b, we have energy transfer upconversion (ETU). Here both a sensitizer and an activator absorb a low energy photon. Then the sensitizer undergoes nonradiative

relaxation, transferring its energy to the activator. Finally, the activator emits a high energy photon [8].

Third, in figure 7c, I show the UC flavor of CET. Notice the similarity between this and DC CET—it’s basically the reverse. Two sensitizers absorb low energy photons and then cooperatively, simultaneously transfer their energy to the neighboring activator. The activator then emits the high energy photon [8]. There is a fourth mechanism called the photon avalanche effect that involves ESA and cross relaxation, but the workings are a bit beyond my ability to comprehend.

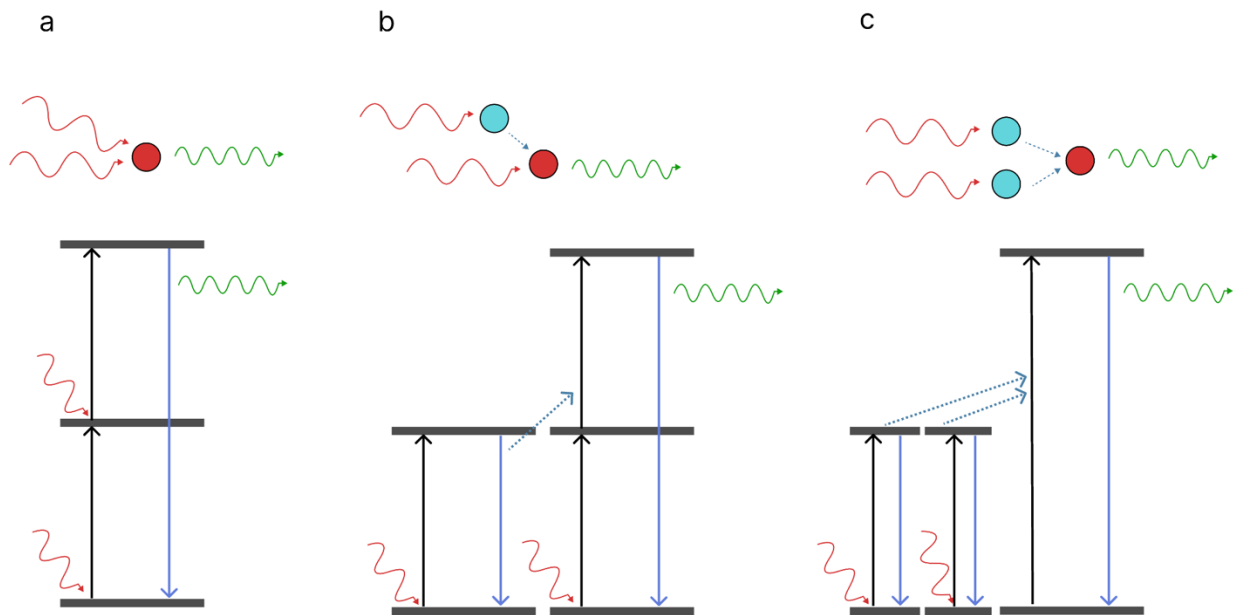


Figure 7. UC schemes adapted from [8]. In my diagrams, the red circles are activators and the blue circles are sensitizers. Dashed lines indicate nonradiative energy transfer. ESA is shown in a, ETU in b, and CET in c.

Materials

For both DC and UC, the general approach to achieving these processes is by adding a thin layer with the converting material on top (on bottom for UC) of a solar cell. The standard approach to a DC material is doping an oxide or fluoride with lanthanide ions. Lanthanides are

rare earth metals with atomic numbers from 58 to 71—elements such as Terbium (Tb) and Ytterbium (Yb). Lanthanides have the useful property of having many energy levels in the 4f orbital, which allows multiple intraband transitions [4]. This makes them very suitable for wavelength conversion. A downside to using lanthanides is that the DC layer often ends up highly reflective, lowering efficiency, but there is potential to use an antireflection layer between air and the converter. There also might need to be second antireflection layer between the converter and the silicon layer to avoid reflection of the downconverted photons [9]. One of the first demonstrations of DC with a lanthanide doped yttrium fluoride material yielded 140% quantum yield. Since then, yields close to 200% have been achieved [9].

Counterintuitive as it may seem, lanthanide ion doped materials are also a common approach to UC. On the surface, it seems like DC and UC are polar opposite processes, but they are actually just both wavelength conversions. Due to the abundance of energy levels in lanthanides, different wavelength conversions can be achieved with slightly different material compositions. Erbium (Er) has been a popular choice as the dopant for UC, as it absorbs light in the range of 1460-1580 nm [9]. As mentioned, the UC layer has been experimentally shown to work best when layered below the silicon layer, as shown in figure 8. Adding the UC layer as a thin film has been accomplished with chemical and physical vapor deposition [8].

Another approach to creating DC materials is to use nanomaterials, as materials with nanoscale dimensions can have significantly different chemical and optical properties compared to the same material as bulk [4]. There are two flavors of nanomaterials that can be used: nanophosphors and quantum dots.

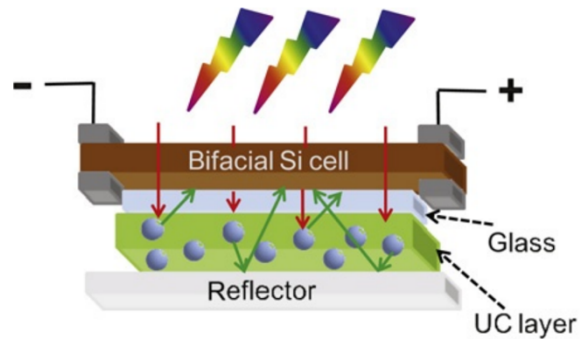


Figure 8. UC material layered below a bifacial solar cell. Reproduced from [9].

Nanophosphors consist of a crystalline host material with a nanometric size, to which a dopant is added at a low concentration. In order to take advantage of quantum confinement effects, the particle size must be between 3 and 5 nm [10]. Nanophosphor synthesis methods can be physical like sputtering or chemical like precipitation in the presence of capping agents [10]. A group was able to achieve 3% efficiency gains with a solar cell layered with this material, but this was with when illuminated with a concentrated 400nm laser beam [11].

Nanocrystal quantum dots are promising because they have a narrow emission band and their optical absorption and emission ranges can be tuned by varying the size of the dot. Examples of semiconductor materials used in the quantum dots are CdS, CdTe, PbS, and InP, to name a few [12]. There has also been research in creating a quantum dot based on perovskites, as they have exhibited low-threshold and ultrastable stimulated emission under atmospheric conditions.

Practical Applications and Challenges

Despite great theoretical improvements, the greatest efficiency gain in practice for a DC layered silicon cell has been just over 2% [4]. This was a screen-printed monocrystalline silicon cell with a layer of Europium (Eu) doped yttrium hydroxide nanotubes [13]. Most experimental work on DC materials appears to be under narrow band illumination.

Experiments with UC in silicon solar cells under AM 1.5 irradiance are also few and far between. Experiments have mostly been proof-of-concepts using a narrow band of intense long wavelength light tuned specifically to the UC material. The best results in the few real-world-conditions experiments have been an efficiency increase of only 2%, much less than the theoretical prediction of 10% [8]. A couple reasons for this poor efficiency improvement are the nonlinearity of the UC process low absorption coefficients. Research has suggested this could be improved by adding a light-concentrating material [9].

One challenge with creating a UC layer is that not only does its absorption band need to be tuned, but it also needs to emit light of the right wavelength that can most efficiently be absorbed by the solar cell. Some promising UC materials like Yttrium oxide have to be ruled out because their emissions are outside the functional range of the solar cell [8].

In order for DC and UC layers to become common in commercial PV, efficiency gains must account for increased fabrication costs. Further, this extra layer on the PV must be able to withstand ambient weather conditions over a long term. This kind of degradation study has not yet been performed [4].

Conclusion

I think it's safe to say we are decades away from DC and UC layers becoming commonplace, if it ever happens at all. Conversion technologies are still largely in the research and development phase. They are not technologically mature enough to be considered for commercial use at scale. Further, their cost-effectiveness is still very uncertain and would depend on improvements across the board in material costs efficiency gains. At this point in time, multijunction cells are a much more proven way to surpass the Shockley-Queisser limit. In 1980, Alexis De Vos figured out that a theoretical infinitely junctioned cell could achieve 68% efficiency under 1 sun irradiance [14].

In light of these considerations, the integration of DC and UC technologies into widespread solar applications remains a challenge for the foreseeable future. While the theoretical prospects are encouraging, practical deployment hinges on scientific breakthroughs that bridge the gap between current limitations and the ambitious targets set by researchers like De Vos. Nonetheless, continued research into multijunction cells and other innovative approaches to exceed the Shockley-Queisser limit is crucial. Such endeavors are key to advancing solar technology and unlocking the full potential of renewable energy sources, which could have significant implications for the global energy landscape.

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