Chapter 10 Optically Coupled Upconversion Solar Cells



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Abstract Conventional solar cells do not use photons with energy less than the band gap. Upconversion uses sensitizers to enable capture of the remaining light. Since upconversion is a nonlinear process, efficient device design requires detailed knowledge of the coupling of sunlight to the sensitizer. This chapter describes the properties of the principal components of an upconversion-augmented solar cell.

Keywords Upconversion · Fusion · Photovoltaics · Optics · Energy

10.1 The Solar Spectrum

Blackbody Radiation

Solar energy systems start with the capture and storage of sunlight. The sun emits light because it is hot. Owing to the equipartition theorem, hot objects which are coupled to the electromagnetic field emit electromagnetic radiation. A blackbody is an object which is maximally coupled to the electromagnetic field. The spectrum of blackbody spectral irradiance is the Planck law,

$$\frac{8\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1},\tag{10.1}$$

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where *h* is Planck's constant, *c* is the speed of light, k_B is the Boltzmann constant, λ is the wavelength, and *T* is the temperature of the sun, which is often modeled with 5800 K. For the sun, the spectrum of this radiation is slightly modulated by atomic and molecular spectral lines [1].

Definition 1 Irradiance : Power per area.

Definition 2 Spectral Irradiance: Power per area per wavelength. Spectral irradiance is used to describe the power of light incident on a solar energy device when the spectrum of the light is important.

! Warning

Field installations of solar cells are illuminated fairly uniformly. However, most laboratory light sources do not provide uniform irradiance. Since upconversion is a nonlinear phenomenon, small irregularities in irradiance may cause large experimental errors.

Optical Properties of the Atmosphere

The spectrum of sunlight at ground level varies in both predictable and surprising ways [2]. This presents a challenge for solar cell engineers. The performance of solar energy devices varies with the solar spectrum. It is necessary to have a standard spectral irradiance into order to define the performance of devices. The accepted standard is AM1.5G. It is illustrated in Fig. 10.1. The performance of a device under standard conditions does not predict the performance of the device in a particular field installation.

Definition 3 AM1.5G: The standard solar spectral irradiance. This standard is an appropriate reference for the development of devices. "AM" indicates "Air Mass." "1.5" indicates that the path length of atmosphere's absorption is 1.5 times the mass of the atmosphere above sea level. The air mass is greater than 1 because sunlight usually does not travel perpendicularly to Earth's surface. As an example "AM0" would indicate the spectral irradiance in space near Earth's orbit. "G" indicates global; the irradiance includes scattered light as well as light which has come directly from the sun. The standard irradiance is 1 kW m^{-2} .

The Earth's atmosphere contains molecules. The optically active vibrational modes of these molecules, such as the O–H stretching mode of water, absorb sunlight. The overtones of these modes also absorb light. As a result, there are a series of absorption lines in the near-infrared portion of the solar spectrum, as observed from Earth's surface. Sunlight is subject to Rayleigh (elastic) scattering. Rayleigh scattering is stronger at higher photon energies. As a result, blue and UV

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Solar Spectral Irradiance (W m⁻² nm⁻¹)

sunlight are attenuated. Some of the scattered light eventually reaches the ground, but it comes from a different direction than the direct sunlight. Ozone molecules in the atmosphere attenuate some ultraviolet light [3].

As discussed in Chap. 2, the efficiency of upconversion increases with irradiance. Presently, upconversion materials only capture a limited portion of the solar spectrum. If the goal is to achieve the highest upconversion quantum yield, then it is best to capture the green-blue region of the spectrum. This is not usually an option in applications.

For optically coupled upconversion solar cells, the energy efficiency of converting a particular wavelength of light into current by way of upconversion cannot be greater than the efficiency of direct conversion; adding the extra step always results in energy loss. Therefore, as discussed in Chap. 3 and Ref. [4], in practical devices, only the red and infrared regions of the spectral irradiance are used via upconversion. Therefore, the details of AM1.5G in the infrared region are important to efficient device design.

Reflective Concentration

AM1.5G provides 1 kW m^{-2} . To achieve efficient upconversion, greater irradiance can be helpful. Concentration is an increase in irradiance created by a reduction in the area which is illuminated. A large area of mirrors can be used to collect sunlight into a smaller area, resulting in increased illumination. This concept was known in ancient Greece, but claims of its practical application by Archimedes are not supported by evidence [5]. A lens can also be used [6]. Historically, a lens concentrator played an important role in combustion research [7]. Solar concentrators continue to be used as thermal energy sources in industry and cooking.

Definition 4 Concentration: The brightness of sunlight, expressed in units of AM1.5G, which is the same as 1 kW m^{-2} when integrated over the entire spectrum. These units are informally called "suns" or " \odot ".

! Warning

Illumination with 1 kW m^{-2} of monochromatic light is not equal to illumination with one sun of irradiance. For a given device, not all parts of the solar spectrum are used equally. A device designed to operate efficiently with a monochromatic light source may be inefficient in sunlight. When reporting illumination conditions, it is important to detail how an irradiance measurement was converted to suns.

Reflective solar concentrators are expensive. Lens-based concentrators are even more costly. The Earth rotates relative to the sun. As a result, the location of sunlight reflected off a ground-mounted mirror changes over time. Typically, the illuminated device is built to be the same size as the region of concentrated illumination. In order to utilize reflective concentration on a photovoltaic device, a mechanical tracking system is required to ensure the concentrated light reaches the device[8]. There are also fundamental efficiency limits [9, 10].

Luminescent Concentration

Luminescent concentration[11, 12] achieves an increase in irradiance by a different mechanism from reflective concentration. Where reflective concentration uses ray optics, luminescent concentration uses both ray optics and quantum mechanics.

The typical luminescent concentrator consists of a slab of material. Owing to the index of refraction *n* of the material, the slab is a waveguide. Light inside the concentrator reaches the surface at an angle θ away from perpendicular. If θ > arcsin (1/*n*), then all of the light is reflected. When this happens repeatedly at both the top and bottom of the slab, the light is guided to the edge of the slab. The aim of

a luminescent concentrator is to achieve an irradiance at the edge of the slab which is greater than the irradiance of the sun.

The material of the slab is designed to absorb as much of the solar spectrum as possible. Instead of converting the light to current, the slab material emits light at a different wavelength. Typically the emission is in a random direction.

Luminescent solar concentration runs into two difficulties. First, the random direction of emission often does not meet the requirement $\theta > \arcsin(1/n)$ for total reflection, defeating the waveguiding function. Second, it is challenging to create a material which absorbs sunlight but does not absorb its own emission. Even a low level of absorption can ruin a solar concentrator if the optical path that light takes from the center of a concentrator to the edge is meters long.

The concept of a luminescent solar concentrator is that it can cheaply collect light from a large area and deliver it to a small, expensive device. Thus far, cheap photovoltaics have outcompeted that design. For applications where upconversion is necessary, the usefulness of luminescent solar concentrators may be increased. Since the efficiency of upconversion is nonlinear, luminescent solar concentrators that produce a high irradiance but poor energy efficiency may, in the future, enable efficient upconversion. In addition, luminescent solar concentrators convert the broad spectrum of the sun into a relatively narrow emission spectrum. This greatly simplifies the design of the absorption spectrum of upconversion materials.

10.2 Attenuation of Sunlight by Solar Cells

There are two geometric strategies available for assembling optically coupled upconversion solar cells. The upconversion device can be on the sun side of the solar cell, or it can be on the shadow side of the solar cell. Generally, the shadow side is selected. In addition to absorbing the light that a solar cell cannot capture, upconversion materials are able to absorb some of the light that the solar cell can use. Since the upconversion device does not convert with perfect efficiency, it is best to have the solar cell capture all the light it can before upconversion is used. Therefore, the solar cell is located closer to the sun.

Tauc Model of Semiconductor Absorption

To understand what light is available for upconversion after sunlight has passed through a solar cell, it is helpful to know the absorption spectrum of semiconductors. As described in Chap. 1, semiconductors have a band gap. The Tauc model [13, 14] describes the absorption of semiconductors in the energy range just above the band gap. It can be derived from the Fermi Golden Rule.

The Tauc model predicts that the proportion of spectral irradiance at wavelength λ remaining after propagation distance *x* is

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$$T(\lambda, x) = e^{-\alpha(\lambda)x},$$
(10.2)

where α is defined differently depending on the category of the band gap transition *b* [14]:

$$\left(\frac{\alpha hc}{\lambda}\right)^{b} \propto \frac{hc}{\lambda} - E_{g} \text{ where } \begin{cases} b = 2 & \text{direct allowed} \\ b = \frac{2}{3} & \text{direct forbidden} \\ b = \frac{1}{2} & \text{indirect allowed} \\ b = \frac{1}{3} & \text{indirect forbidden} \end{cases}$$
(10.3)

The Tauc model does not account for all semiconductor absorption properties. It assumes that there is only one valence band and one conduction band. Ultimately, there are always additional bands which can absorb higher-energy photons. It does not include absorption caused by exciton states, vibrational (phonon) states, or defects. It is inappropriate for solar cells which are not ordered semiconductors, such as dye solar cells. However, the Tauc model is often adequate.

! Warning

According to the Tauc model, the band gap of a semiconductor cannot be accurately determined by fitting a line to an absorption spectrum.

Experimental Determination

While semiconductor absorption is the mechanism for light capture in solar cells, a variety of other things can reduce the light available for upconversion. The solar cell is partially reflective (Fig. 10.2). There are metal contacts on the solar cell, which may not be homogenous. Solar cells also have protective coatings. The rear of commercial solar cells has a protective backsheet which is opaque [15]. To create upconversion-enhanced solar cells, it is necessary to place the upconversion material between the solar cell and the backsheet.

To accurately determine the light available for upconversion, it is necessary to obtain the associated solar cell and measure its light transmission properties. The angle of incidence of sunlight is variable because the Earth rotates. The reflectivity of the solar cell depends on that angle of incidence. Detailed measurements should account for the angular distributions of sunlight and reflectivity.

To understand the utilization of upconverted light by a solar cell, the absorption spectrum of the solar cell is insufficient. It is necessary to know the external quantum efficiency spectrum of the solar cell under the conditions where it is illuminated by upconversion (typically from the rear). Since the upconversion can be designed to illuminate the solar cell at the wavelength where it is most efficient, the conversion

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Fig. 10.2 Demonstration of the reflectivity of a solar cell



of upconverted light to current can be much more efficient than the conversion of sunlight to current.

10.3 The Beer-Lambert Law

Exponential Decay

The propagation of light through an upconversion material can be predicted with the Beer-Lambert law [16]:

$$T(\lambda, x) = 10^{-x(\epsilon_s(\lambda)C_s + \epsilon_e(\lambda)C_e)}.$$
(10.4)

T is the proportion of spectral irradiance at wavelength λ remaining after propagation distance *x*, $\epsilon(\lambda)$ is the molar absorption coefficient, and *C* is the chemical concentration. The subscript *s* indicates sensitizer properties, and the subscript *e* indicates emitter properties.

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Fig. 10.3 A laser pointer illuminating a uniform, luminescent material. The decay in the luminescence brightness across the material is caused by the Beer-Lambert law



Definition 5 Molar absorption coefficient: $\epsilon(\lambda) = \frac{\log_{10}\left(\frac{I_0}{I_1}\right)}{LC}$ describes the ability of a molecule to capture light. I_0 is the power of the light with wavelength λ illuminating a sample. I_1 is the power transmitted through the sample. L is the length of the path the light takes through the sample. C is the chemical concentration of the molecule in the sample. Molar absorption coefficient is among the most important properties of sensitizers and emitters.

The Beer-Lambert law indicates that light is not absorbed at the surface. Instead, absorption is gradual. The more concentrated the sensitizer, the greater the absorption over a path length. In the Beer-Lambert theory, there is always some light left after passing through a material (Fig. 10.3).

Importance to Efficiency

If the excitation rate of sensitizer is k_{ϕ} at the illuminated surface, then the excitation rate in the interior is $k_{\phi}T(x)$. For the moment, we will consider monochromatic illumination as a simplification. As discussed in Chap. 2, the intensity of upconversion is proportional to

$$k_{\phi}T(x)$$
 at high intensities or (10.5)

$$(k_{\phi}T(x))^2$$
 at low intensities. (10.6)

! Warning

The transition between expressions 10.5 and 10.6 is gradual. Unlike a laser, upconversion does not have an abrupt threshold at which it turns on. Demonstration of the linear behavior of Expression 10.5 is necessary but not sufficient to achieve an efficient device.

Since T(x) decays across a device, the intensity of upconversion also decays. In Regime (10.6), the *efficiency of upconversion also decays* [17]. For any upconversion device which obeys the Beer-Lambert law, a portion of the incident light is absorbed in a region where the device is inefficient. In practice, this is a large portion of the light. Our conclusion is that good device designs have elements which do not obey the Beer-Lambert law.

In addition to attenuating the incident light, the Beer-Lambert law also attenuates the upconversion produced by the emitter. In this case, the Beer-Lambert law distance *x* is not measured from the surface of the device to the point of absorption, but instead is measured from the interior location where the light is emitted to the point where it is absorbed. Unlike sunlight, the upconversion emission propagates in a random direction. The energy captured when emission is absorbed can be recycled as new fluorescence or upconversion, but the recycling is not perfectly efficient. To achieve efficient optical coupling, it is important to select the molar absorption coefficient so that it is small at the wavelength where the emission occurs.

10.4 Scattering

To work around the problems caused by the Beer-Lambert law, the incident light can be scattered. The goal of scattering is to increase the path length traversed by light without increasing the volume of the material. This has the potential to boost efficiency by increasing k_{ϕ} while reducing material cost.

We will assume a device that has planar geometry. The theoretically simplest form of scattering is reflection. Placing a mirror [18] on the opposite side of the upconversion material from the illumination doubles the path length-to-volume ratio.

Random scattering is also an option. For example, Rayleigh or Mie scattering mechanisms distribute light in all directions [19]. Small particles can be placed inside the upconversion material. If these particles have a different index of refraction but no absorption, they will scatter the incident light. A portion of the

scattered light will have reduced path length because scattering can occur near the surface and in the direction of the surface. Most of the light will have increased path length.

Lambertian scattering [20] performs better than isotropic random scattering. It is achieved by placing a white material in the shadow of the upconversion device [18, 21]. Since no scattering occurs until all the sensitizer has been traversed, the path length-to-volume ratio of light with a Lambertian scatterer is always better than with no scatterer. If the illumination is normal to the device surface, then the Lambertian scatterer always increases path length compared to a mirror.

Definition 6 Lambertian: Scattered light intensity proportional to the cosine of the angle measured from the surface normal. Also known as "diffuse."

The ideal scattering material will optimize path length-to-volume ratio by scattering light into the plane of the device. The geometry of this scattering would be similar to Wood's anomaly [22]. Creating such an engineered scattering material is difficult because the illumination is broadband and the angle of incidence is variable.

Scattering is also important to the coupling of upconversion emission to a solar cell. The emission is in a random direction. Scattering can redirect upconversion which is headed away from a solar cell so that it heads toward the solar cell. This can increase performance by up to a factor of 2.

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