

Upconverter solar cells: materials and applications

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Spectral conversion of sunlight is a promising route to reduce spectral mismatch losses that are responsible for the major part of the efficiency losses in solar cells. Both upconversion and downconversion materials are presently explored. In an upconversion process, photons with an energy lower than the band gap of the solar cell are converted to higher energy photons. These higher photons are directed back to the solar cell and absorbed, thus increasing the efficiency. Different types of upconverter materials are investigated, based on luminescent ions or organic molecules. Proof of principle experiments with lanthanide ion based upconverters have indicated that the benefit of an upconversion layer is limited by the high light intensities needed to reach high upconversion quantum efficiencies. To address this limitation, upconverter materials may be combined with quantum dots or plasmonic particles to enhance the upconversion efficiency and improve the feasibility of applying upconverters in commercial solar cells.

Introduction

The ever growing energy demand combined with the decreasing resources of fossil fuels makes it evident that there is a need for a transition towards renewable energy supply technologies. Solar cells are projected to make a significant contribution to the future of renewable energy. Solar energy can provide sufficient energy to fill the gap left by fossil fuels using only a limited fraction of the earth surface area.¹ The relatively high efficiency and flexibility allowing for small scale application in rural areas and on roof tops as well as for large grid connected solar energy farms contributes to the rapidly growing solar energy market. To sustain the present market growth, the cost of solar electricity has to decrease further. Cost reduction can be achieved by combining low-cost production technologies, cheaper materials, and increased efficiency of the solar cells. The efficiency of solar cells

is largely determined by the band gap of the semiconductor material. Single junction solar cells suffer from intrinsic efficiency losses. The inability to absorb photons with an energy lower than the band gap and relaxation losses of excess energy of absorbed high energy photons make up ~65% of the total energy loss in single junction solar cells. These spectral mismatch losses are called transmission and thermalization losses, respectively (Fig. 1). Since the sun is a polychromatic light source there is a trade off between these losses, resulting in a fundamentally determined maximum efficiency as a function of band gap energy, as shown in Fig. 2. This maximum energy efficiency of single junction solar cells was already determined by Shockley and Queisser in the 1960's and now is referred to as Shockley–Queisser (SQ) limit.²

The highest efficiencies reported for single junction solar cells such as c-Si and GaAs are presently approaching the maximum efficiency set by the SQ limit.⁴ Further improvement of these high efficiencies becomes increasingly complicated. Expensive techniques are required for incremental efficiency improvements. Clearly, fundamentally different concepts are necessary to

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Broader context

The inability to absorb photons with an energy lower than the band gap and relaxation losses of excess energy of absorbed high energy photons make up ~65% of the total energy loss in single junction solar cells. Spectral conversion of sunlight is a promising route to reduce these spectral mismatch losses. The advantage of spectral conversion is that this can be applied to existing solar cells and that optimization of the solar cell and spectral converter can be done separately. Especially upconversion attracts a lot of attention recently, because it involves low energy photons that are not absorbed by the solar cells. An upconversion layer can be placed at the back of the solar cells and by converting part of the transmitted photons to wavelengths that can be absorbed, it is relatively straightforward to demonstrate a positive contribution from the upconversion layer. In this paper we focus on upconversion materials for solar cells and recent progress in this area is reviewed.

increase the efficiency beyond the SQ limit. Different options are being explored, which can be divided in concepts based on adapting the solar cell and concepts aimed at adapting the solar spectrum. In both cases multiple energy levels are utilized to reduce transmission and thermalization losses.^{5,6} The most common and proven method to overcome the SQ limit is realized in multijunction solar cells, consisting of a stack of solar cells with different band gaps. Each type of solar cell converts a part of the solar spectrum with high efficiencies, resulting in record energy efficiencies above 40%.⁴ Because these cells are electrically connected in series, the solar cell with the lowest current is limiting the efficiency. This makes these types of solar cells sensitive to spectral changes, which are due to seasonal changes,

daily changes, and sky conditions (clear/cloudy).⁷ Other device structures which are investigated to reach higher efficiencies are based on intermediate band solar cells,⁸ hot carrier extraction,⁹ multiple exciton generation, mainly with quantum dots,^{10,11} broadening the absorption spectra in dye sensitised solar cells¹² and other nanostructures.^{13,14} These concepts are still under development at the materials level and the efficiency for some of the effects is controversial.^{15,16}

An alternative approach is spectral conversion aimed at modification of the solar spectrum to achieve a better match with the wavelength dependent conversion efficiency of the solar cell. The advantage of spectral conversion is that this can be applied to existing solar cells and that optimization of the solar cell and



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J.K. Rath

Dr Jatin Rath did his Masters and PhD in Physics at one of the elite institutes of India, I.I.T. Madras. After finishing his PhD in 1986 in solid state physics, he worked at I.A.C.S., Calcutta as scientist in the area of thin film silicon material and solar cells, during which he had visits to Phillips University Marburg, Germany as a United Nations fellow and to Japan on invitation from JEOL Company. From 2000, he has been an Assistant Professor in the research group

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A. Meijerink

Professor Andries Meijerink (47) received his PhD in 1990 at the Utrecht University under supervision of Prof. George Blasse. Afterwards he joined the group of Prof. John Wright at University of Wisconsin in Madison as a post-doctoral fellow. In 1996 he was appointed at the chair of Solid State Chemistry in the Debye Institute of the Utrecht University. He leads an active research group that focuses on the optical spectroscopy of lanthanide ions and of semiconductor quantum dots.

For his research he received several awards, including the DSM Award (1989), Shell Incentive Award (1995), Gold Medal of the Royal Dutch Chemical Society (1999) and ECS Centennial Award (2002). Since 2009 he is a member of the Royal Dutch Academy of Sciences.



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outdoor photovoltaic performance and policy and technology development.

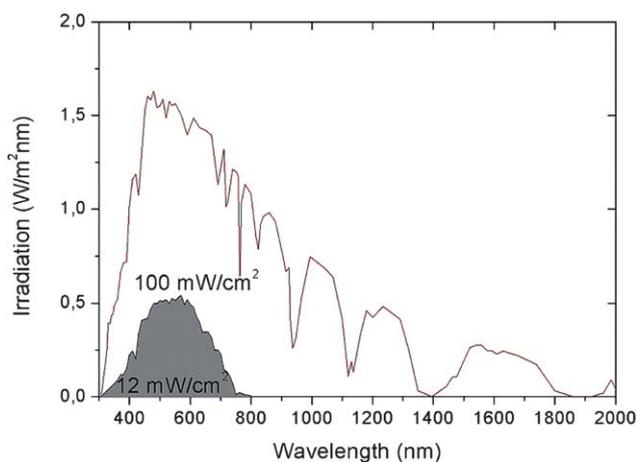


Fig. 1 The standard Air Mass 1.5 solar spectrum and the part of the spectrum (in grey) that is converted into electrical energy by a state of the art a-Si:H solar cell. Lower energy photons are not absorbed by the solar cell. High energy photons are absorbed but lose energy by thermalization. Combined the losses result in an efficiency of 12%, as is indicated by the grey shaded area.

spectral converter can be done separately. Different types of spectral conversion can be distinguished: two low energy (sub-band gap) photons are combined to one high energy photon (upconversion) or one high energy photon is transformed into one (downshifting) or two (downconversion or quantum cutting) lower energy photons. Downshifting can give a marginal



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Ruud Schropp (M'1988) was born in Maastricht (NL) in 1959. He received his MSc in experimental physics from Utrecht University in 1983 and his PhD in mathematics and natural sciences from the University of Groningen in 1987. After that he worked as the Head of R&D at equipment manufacturer Glasstech Solar, Inc., in Colorado, USA on solar cells. In 1989 he joined Utrecht University and in 2000, he was appointed Full Professor in "Physics of Devices". In 2004,

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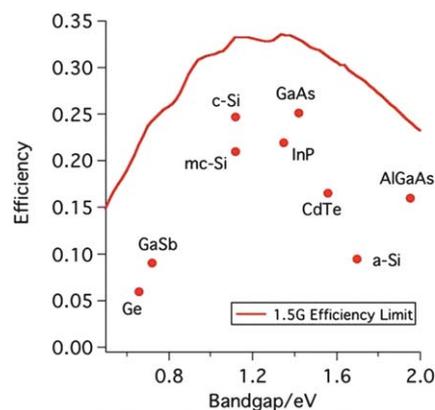


Fig. 2 Maximum theoretical efficiency as a function of the band gap as determined by Shockley and Queisser.¹ The maximum efficiency that has been obtained experimentally for different solar cells is indicated, illustrating that efficiency improvements are possible. Figure copied from ref. 3.

efficiency increase by shifting photons to a spectral region where the solar cell has a higher efficiency. Up- and downconversion however can raise the efficiency above the SQ limit. In Fig. 3 the potential efficiency gain is plotted for c-Si solar cells, with values as published by Richards.¹⁷ Research on spectral conversion is focused on organic dyes and quantum metal ion for up- and downconversion.^{18–20} Especially upconversion attracts a lot of attention recently, because it involves low energy photons that are not absorbed by the solar cells: the transmitted photons. An upconversion layer can be placed at the back of the solar cells and by converting part of the transmitted photons to wavelengths that can be absorbed, it is relatively straightforward to demonstrate a positive contribution from the upconversion layer, even if the upconversion efficiency is low. In contrast, proof-of-principle experiments are complicated for downconverters and downshifters. These spectral converters have to be placed at the front of the solar cell and any efficiency loss will reduce the overall efficiency of the system. Downconversion with close to 200% quantum efficiency has been demonstrated, but the actual quantum efficiency is lower due to concentration quenching and parasitic absorption processes.²¹ Even for

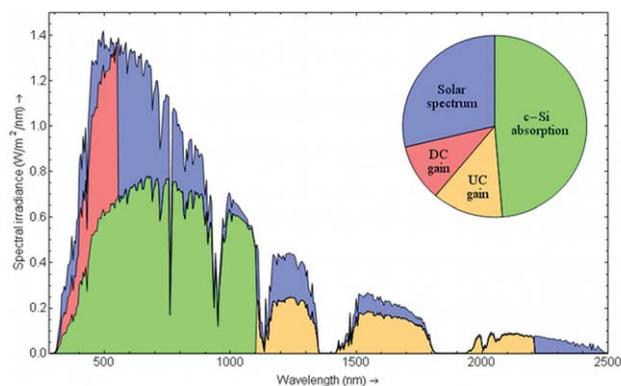


Fig. 3 Potential efficiency gain of down- and 2-photon upconversion for a c-Si solar cell.

a perfect 200% quantum yield system, a higher solar cell response requires a reflective coating to reflect the isotropically emitted photons from the downconversion layer back towards the solar cell. The technology to realize these reflective coatings is available, but so far no proof-of-principle experiments have demonstrated an efficiency gain using downconversion materials. Also an upconverter emits isotropically but since it is placed at the back of the solar cells, the upconversion photons can easily be directed into the solar cell by placing a reflector behind the upconverter layer. In this paper we focus on upconversion materials for solar cells and recent progress in this area is reviewed.

Maximum efficiency

Trupke, Green and Würfel were the first to discuss the potential of increasing the solar cell efficiency through upconversion.²² They considered an upconverter with an intermediate level band at E_{IL} with energy E_1 above the valence band of the solar cell and E_2 below the conduction band of the solar cell, see Fig. 4. In this energy level scheme three energy ranges can be absorbed: energy higher than the band gap and two bands giving rise to upconversion: the first band with energy $E_1 < h\nu < E_2$ and a second band of energy $E_2 < h\nu < E_g$. Following the same approach as Shockley and Queisser the upper limit for energy conversion was calculated to be 63.2% for concentrated sunlight and 47.6% for non-concentrated sunlight assuming the sun to be a 6000 K black body for the optimum combination of E_g and E_{IL} ,²² Fig. 5. When the same calculations are performed for the AM1.5 spectrum, even higher efficiencies can be obtained (for details, see ref. 22 and 23).

It is important to note that the calculations were done for a theoretical upconverter with an infinite lifetime of excited intermediate band state. The intermediate band thus serves as a reservoir for low energy quanta with a 100% upconversion efficiency through subsequent absorption of photons in the energy range of the second band ($E_2 < h\nu < E_g$). In real upconverter materials the lifetime is limited and not all photons are upconverted. The picture is analogous to the principle of the

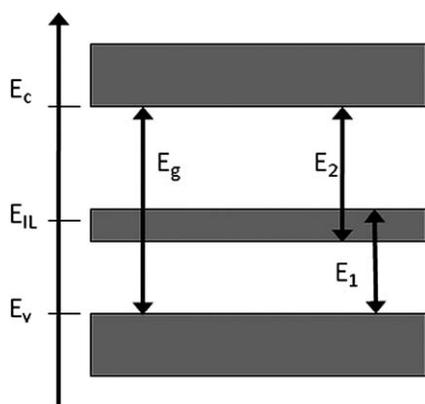


Fig. 4 Energy level structure for a hypothetical upconverter material. Photons with smaller than band-gap energy are absorbed due to the intermediate level band giving rise to a two-step absorption process resulting in the emission of photons with E_g that can be absorbed by the solar cell.

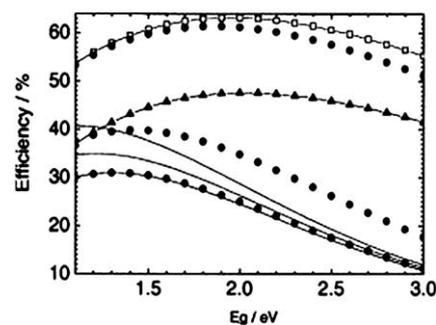


Fig. 5 Maximum efficiencies for an ideal upconverting system. The solid lines represent the SQ limit for 1, 100 and 46 200 suns. The circles represent upconverter system without relaxation in the intermediate bands, with higher efficiencies corresponding to higher concentrations. The triangle symbols give the maximum efficiency under 1 sun when relaxation in the intermediate band is allowed. Reproduced with permission from ref. 22.

intermediate band solar cells, with slightly lower values for the location of the intermediate band,⁹ because there are no restrictions to the maximum photon energy that can be absorbed. In both devices photons are subsequently absorbed by an intermediate band, but in an upconverter this results in emission of a higher energy photon and in an intermediate band solar cell this results in an electron–hole pair. An important difference is that the introduction of an intermediate band in the semiconductor materials affects processes in the solar cell and for high efficiencies it is imperative that the intermediate band levels do not re-trap charge carriers from the valence or conduction band. In the case of upconversion materials, the use of sub-band gap photons by subsequent absorption steps is decoupled from the solar cell and it is theoretically possible to apply upconversion to a variety of solar cells.

Available upconverter materials

Upconverters are materials that are characterized by the fact that the emitted photons are of higher energy than the absorbed photons. This so-called anti-Stokes emission can be achieved in different ways. In second harmonic generation (SHG) birefringent crystals convert highly monochromatic and coherent laser light to higher energies. This process is well known²⁴ and can be very efficient for high laser powers but for conversion of the solar spectrum it is not efficient. To convert the infrared part of the solar spectrum, upconverters are required with an intermediate excited state. A two-step excitation process raises the system from the ground state *via* an intermediate state to a high energy state by absorbing two IR photons. This is followed by emission from the high excited energy state. Generally, two available material classes in which this subsequent absorption of low energy photons to give higher energy emission are considered: (1) metal ions in inorganic host materials, mainly lanthanide ions and transition metal ions^{25,26} and (2) organic chromophores with an extended conjugated π -system.²⁷

Lanthanides

Lanthanides form the group of elements in the periodic table for which the 4f inner shell is filled up to 14 electrons. Lanthanide

ions are typically trivalent (Ln^{3+}) and have a $4f^n5s^25p^6$ electron configuration with $n = 0-14$. The partly filled $4f$ shell is responsible for the unique optical and magnetic properties of lanthanide ions. For n electrons in 14 available orbitals there are 14 over n possible configurations and all configurations can have different energies. This gives rise to a rich energy level structure with energy levels in the NIR, VIS and UV spectral range. Because the outer $5s$ and $5p$ shells shield the $4f$ inner shell, the electronic transitions are independent of the surrounding host materials. The energy levels of the various lanthanide ions are given in the so-called Dieke diagram.²⁸ The trivalent ions may be doped in different host materials, varying from fluorides to oxides, depending on the application.

The transitions between different $4f^n$ states are parity forbidden (no change in dipole moment) and the absorption lines are narrow. The transitions become slightly allowed through admixture of opposite parity states by odd-parity crystal field components or vibrations. The sharpness of the spectral lines results from the weak coupling with the vibrations. There is no Stokes' shift for the optical transitions and this results in the strongly reduced vibrational energy losses. The large variety of absorption and emission wavelengths, the independence on the host materials and the low vibrational energy losses make lanthanides ideal ions for spectral conversion and in almost all artificial light sources, emission originates from lanthanide ions.

Lanthanides are doped in a variety of solids such as crystals, fibers or glass ceramics, to give these materials the desired optical properties. The ions are embedded in hosts preferably with low phonon energy to decrease multi-phonon relaxation between closely spaced energy levels. Low phonon hosts are *e.g.* fluorides, chlorides, iodides, bromides²⁹ and higher phonon energy hosts are usually oxides, such as silicates, borates or phosphates.³⁰ The energy level structure is independent of the host materials, however the phonon energy influences the non-radiative transitions that are possible. Coupling with phonons, albeit weak, provides a non-radiative channel between energy levels that competes with the radiative transitions. As a rule of thumb it holds that when energy levels are separated by less than 5 times the maximum phonon energy of the host, non-radiative multi-phonon relaxation will be dominant, while for energy differences of more than 5 times, radiative decay will dominate.³¹

An extended review on upconverter materials with lanthanides, actinides and transition metals was written by Auzel.²⁶ The most efficient mechanisms behind upconversion with lanthanide ions and transition metals are two-step excitation (excitation to the ground state followed by excited state absorption, GSA/ESA) and upconversion by subsequent energy transfer (ETU) steps of the excited ions. Whereas GSA/ESA is a one-ion process, ETU always involves at least two ions. GSA/ESA is observed for low doping concentration (<1%). The processes are schematically depicted in Fig. 6. In the case of ETU, the upconversion from a lower excited state to a higher excited state is realized by energy transfer between two excited ions, possibly different types of ions.

Different types of energy transfer mechanisms are possible, but mostly non-radiative energy transfer *via* dipole-dipole interaction is the dominant mechanism. Efficient energy transfer requires the ions to be in close proximity³² and thus ETU requires high concentration of the dopants; 20% is not uncommon.

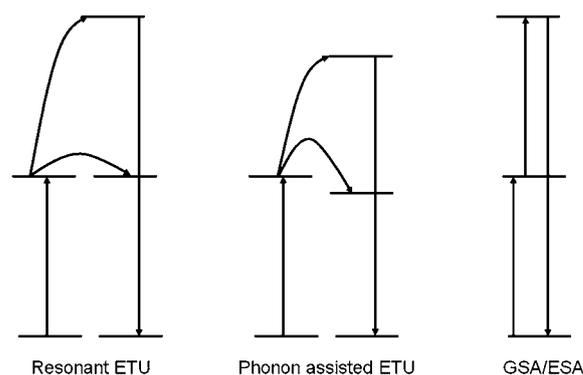


Fig. 6 The most efficient upconversion mechanisms. Energy transfer upconversion (ETU) either resonant or phonon assisted and ground state absorption followed by excited state absorption (GSA/ESA). ETU always requires two ions, whereas GSA/ESA one ion.

The ETU transfer process is generally experimentally determined to be the most efficient process. A powerful technique to determine whether energy transfer or excited state absorption is the main upconversion path, is measuring the luminescence decay curve for the upconverted emission after a short excitation pulse. When GSA/ESA is the main pathway for upconversion, the decay curve is a simple exponential decay from the high state without a rise time. For energy transfer upconversion however, there is first a rise in intensity followed by the decay from the high energy state. The rise results from the slow feeding of the emitting state through the energy transfer step.³³

Some materials are doped with more than one specific metal ion. One ion then acts as a sensitizer and the other ion as activator, depicted in the 2 left diagrams of Fig. 6. A sensitizer ion has preferably a long lifetime, a strong absorption strength and broad absorption spectrum. Sensitized upconverters always involve energy transfer and are therefore in general more efficient than GSA/ESA upconverters. The energy transfer rate is determined by the spectral overlap between the activator absorption and sensitizer emission, the lifetime of the sensitizer emission and the absorption strength of the activator ion. One of the most efficient upconverter materials for NIR to VIS upconversion was found to be $\text{NaYF}_4: \text{Er}^{3+}, \text{Yb}^{3+}$, with Yb^{3+} as sensitizer and Er^{3+} as activator.³⁴ Yb^{3+} has only one energy level around 980 nm ($10\,200\text{ cm}^{-1}$) with a lifetime of ~ 2 ms, making it an ideal sensitizer for near infrared to visible upconversion. Er^{3+} has an energy level around 980 nm and 490 nm ($20\,400\text{ cm}^{-1}$), allowing for two close to resonant energy transfer steps from Yb^{3+} to Er^{3+} . The two-step energy transfer process is depicted in Fig. 7. Er^{3+} emits in the green and red after the upconversion process.

The large spectral overlap between $\text{Yb}^{3+}/\text{Er}^{3+}$ and the efficient ETU for this lanthanide couple, makes $\text{Yb}^{3+}/\text{Er}^{3+}$ a widely investigated NIR-VIS upconversion couple in a variety of host materials.³⁵⁻³⁹ Another well investigated NIR/VIS upconverter couple is $\text{Yb}^{3+}/\text{Tm}^{3+}$, which emits in the blue.^{37,40-42} This requires three-photon absorption and is less efficient.

Next to lanthanides transition metals have also been used for upconversion.^{26,43-48} They have broad absorption bands, which makes them interesting as sensitizer. The broad absorption bands result from a stronger vibronic coupling of the outer d electrons, involved in the optical transitions. Contrary to the lanthanides,

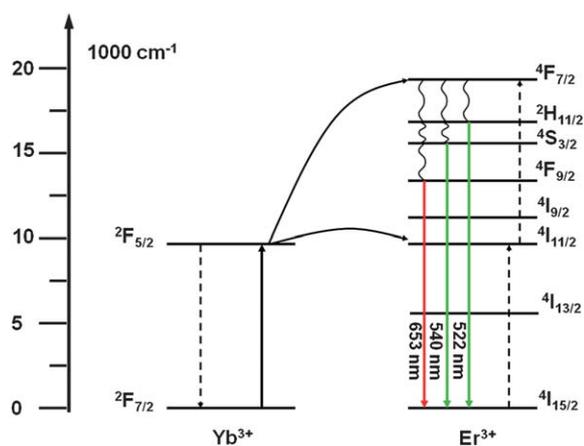


Fig. 7 Schematic energy level scheme for the Yb/Er couple. The Yb^{3+} ion absorbs around 980 nm and transfers the energy from the ${}^2\text{F}_{5/2}$ level to the ${}^4\text{I}_{11/2}$ level of Er^{3+} . Subsequent energy transfer from a second excited Yb^{3+} ion to Er^{3+} (${}^4\text{I}_{11/2}$), excites Er^{3+} ion to the ${}^4\text{F}_{7/2}$ excited state. After multiphonon relaxation to the lower lying ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ states, green and red emissions are observed, as indicated.

the energy level scheme is strongly dependent on the host. The stronger vibronic coupling is responsible for temperature quenching of the emission at elevated temperatures and often only efficient emission is observed at cryogenic temperatures. As a result, most transition metal upconverters only emit upconverted light at cryogenic temperatures. There is one example of room temperature upconversion with transition metals.⁴⁵ An interesting review on upconversion for solar cells including transition metals, lanthanides and organic upconverters is given in ref. 49.

Upconverter efficiency

The feasibility of upconverters to enhance the efficiency of solar cells depends critically on the efficiency of the upconversion process. The efficiency of an upconverter is determined by many variables which influence the radiative, non-radiative and energy transfer rates, *e.g.* phonon energies, spectral overlap between sensitizer emission and activator absorption, temperature, and defects that quench the emission. Very importantly, as upconversion is a non-linear process, the efficiency strongly depends on excitation power. A reported upconversion efficiency value is only valid for a certain excitation light intensity. This makes it difficult to define *the* upconversion efficiency. There is no generally accepted definition on upconversion efficiency. Both power conversion and quantum efficiencies are reported. When the quantum efficiency is determined, it is still not always clear how to interpret the reported values. For example, for one emitted photon at least two photons are absorbed. This means that the maximum internal quantum efficiency is 50%, analogous to the fact that downconversion can have an efficiency of 200%. Still, sometimes this maximum efficiency is reported as 100%.⁵⁰

Another approach is absolute power conversion efficiency. Here the emitted power intensity is compared with the power of the excitation source, P_{in} . The output power can rather easily be determined by integrating the emission spectra with a calibrated detector. Not all emitted wavelengths are to be included, only

those that have an energy higher than the band gap of the solar cell. Typical power efficiencies of NIR-VIS upconverters are of the order of 2% or less.³⁸ As was mentioned above, the most efficient and widely studied upconverter is $\text{NaYF}_4: \text{Er}^{3+}, \text{Yb}^{3+}$ with an absolute power conversion efficiency of 5.5% for the conversion of 980 to 540 nm light,⁵¹ corresponding to an internal quantum efficiency of 23%.³⁷ The values are determined at such high powers that the upconverter efficiency is saturated. At 40 W cm^{-2} , the upconverter efficiency is saturated.³⁸

Clearly, the values reported for upconversion efficiencies are not easily interpreted by just considering the efficiency value reported. The efficiency is dependent on the power density, the efficiency saturates at high power, and the maximum efficiencies are reached at different power densities. The emitted intensity is proportional to P_{in}^n , and the efficiency is therefore proportional to $P_{\text{in}}^n/P_{\text{in}}$ *i.e.* $P_{\text{in}}^{(n-1)}$. Here n is the number of photons (steps) involved in the upconversion process (*e.g.* 2 for the NIR to green/red upconversion in Yb/Er and 3 for the NIR to blue upconversion in Yb/Tm). This only holds in the absence of saturation. Auzel²⁶ listed upconversion efficiencies of NIR-VIS upconverters given in $\text{cm}^{-2} \text{ W}^{-(n-1)}$. The efficiency was defined as (emitted light intensity)/(absorbed radiation intensity) normalized to a power of W cm^{-2} . Vitroceramics and YF_3 were here listed as the most efficient upconverter with a power efficiency of 28%. However, these high values have never been confirmed experimentally at other laboratories and were based on extrapolation of efficiencies measured at much lower intensities.⁵² One problem in the extrapolation of low-power results is that a deviation of the number of 2 or 3 is rather common, leading to much lower values when extrapolating to high intensities. It is important to note that internal efficiencies are reported; *i.e.* the power efficiency of absorbed photons. When dealing with power densities of lasers or sunlight, direct comparison is only possible when the absorption strength of the ion is known for that wavelength or when the output power of the laser is given.

Organic molecules

A second class of materials for which efficient upconversion has been demonstrated are organic and organo-metallic chromophores. Research on upconversion in these chromophores has gained renewed interest recently. The group of Castellano made important contributions to this field, which are included in a recent review.²⁷ The upconverters consists of organic molecules with conjugated π -systems, serving as acceptor, and organo-metallic complexes serving as sensitizer. Some examples of sensitizer and activator molecules used for upconversion are shown in Fig. 8. The sensitizer molecules contain a metal ion center and are characterized by metal-to-ligand charge transfer (MLCT) transitions. The activator molecules are organic molecules, which have a high fluorescence quantum yield.⁵³ The MLCT absorption band of the metal complex sensitizer is usually in the green and red spectral region.

The energy of the MLCT absorption bands varies strongly for different organic molecules and metal-ion complexes, unlike the fixed energy level diagrams for the lanthanides, which makes it harder to find the most efficient combination of sensitizer and activator for upconversion of a specific spectral region. An advantage is the stronger absorption, which leads to lower light

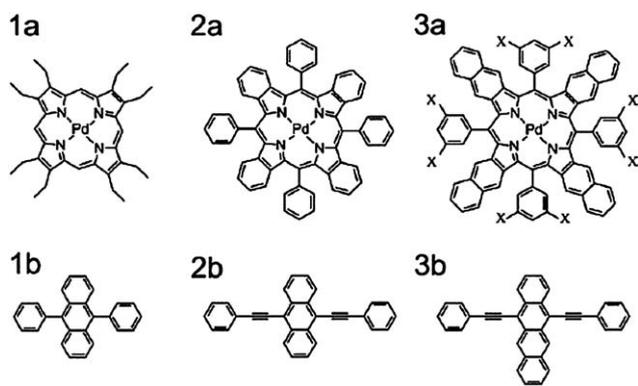


Fig. 8 Examples of organic molecules used for upconversion. The metal complexes 1a (PdOEP), 2a (PdPh₄TBP) and 3a (PdPh₄OMe₈TNP) serve as sensitizer while the molecules 1b (DPA), 2b (BPEA) and 3b (BPEN) are activators. Absorption and emission spectra are given in Fig. 10. Reproduced with permission from ref. 93.

intensities needed for measurable upconversion efficiencies.^{54,55} Therefore, upconversion of non-concentrated transmitted light by organo-metallic chromophores may be feasible.⁵⁶

The photon upconversion in organic molecules is based on triplet–triplet annihilation (TTA),⁵⁷ see Fig. 9. Important requirements are that the triplet and singlet excited state of the sensitizer are nested between the singlet and triplet excited state of the activator. The sensitizer therefore should have a much smaller singlet–triplet splitting than the activator, which is usually the case for MLCT transitions on the sensitizer and an aromatic hydrocarbon activator, which generally has a large singlet–triplet splitting. In the upconversion process, first a sensitizer is excited to the lowest singlet state (strong absorption) and relaxes through intersystem crossing (ISC) to the triplet state. This process is faster than spontaneous emission from the singlet state⁵⁸ and the triplet state is excited efficiently *via* the singlet state. The long lived triplet state of the sensitizer transfers the energy to the long lived activator triplet state. Two activator molecules in the triplet state annihilate yielding one activator in the high energy singlet state and one in the ground state. Upconverted emission is observed from the singlet state of the activator. In the upconversion process several energy relaxation processes take place, which make the blue shift of the upconverted emission with respect to the excitation wavelength smaller than observed for lanthanide upconverters. Typically, blue shifts around 100–200 nm are observed. In Table 1 of ref. 27 an overview of successful sensitizer–activator combinations for upconversion is given, showing that the wavelengths for these upconversion systems range from 780 nm to 560 nm (longest wavelength) up to 442 to 360 nm (shortest wavelength), see Fig. 10. The presently available wavelength ranges limit the applicability to solar cells. Most solar cells (*e.g.* c-Si, GaAs, CIGS, CdTe) have an absorption onset at energies lower than 1.6 eV (~780 nm) and the transmission losses can only be reduced by upconverter systems that absorb and upconvert in the spectral region of wavelengths longer than 800 nm. Though the band tails extend into regions above 800 nm,^{59,60} the upconversion is rather low in these regions because the absorption is so low. The organic molecules are either dissolved in liquids or dispersed in rubber-like polymeric materials. In general the efficiency of the

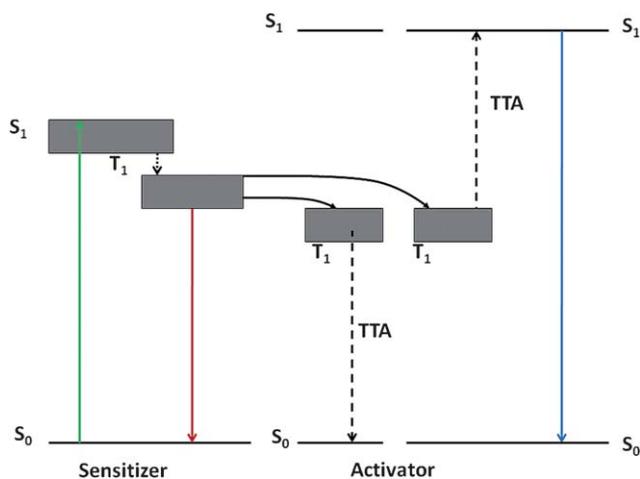


Fig. 9 Energy scheme for upconversion in organic molecules. The singlet state of the sensitizer is excited and relaxes through fast inter-system crossing to the triplet state of the sensitizer. The energy is then transferred to the triplet state of the activator molecules. When two activator molecules come in close proximity, triplet–triplet annihilation results in one activator in the singlet excited state and one in the ground state. The upconversion emission is observed from the singlet state of the activator molecule.

upconverter in a polymeric environment is much lower than the efficiency in solutions, because the energy transfer rate is limited by the diffusion rate of the molecules.⁶¹ For application in most solar cells polymeric hosts are required, however for dye solar cells an upconverter in solution may also be applied.⁶² The intensity of the upconversion emission of polymeric upconverters increases with temperature, because the diffusion of the molecules increases. In recent years, substantial progress has been achieved on the power density needed for measurable upconversion luminescence in rubbery media. Initially, polymeric media in which upconversion was observed required excitation densities of MW cm⁻² and kW cm⁻².⁶³ Recently, upconversion was reported for excitation intensities below 1 mW cm⁻² and under ambient conditions.⁶⁴ The efficiency of upconversion in solid media is still weaker than in inorganic solids.²⁷ Reports on efficiencies are scarce and usually reported efficiencies are internal quantum efficiencies. Theoretical efficiencies of 40% can be achieved with organic upconverters.⁶⁵ They are determined by comparing the emitted upconverted emission with the emission when the band is directly excited. Known quantum yields of the activator molecules are required. Both organic and inorganic upconversion systems have advantages and disadvantages and at present it is hard to predict which type of upconversion will be the system of choice for application in solar cells.

Application of upconverters to solar cells

Until now, only lanthanide upconverters have been applied in solar cells. The upconversion efficiency is low and most demonstrations merely serve as proof of principle showing that an increase in efficiency can in principle be realized by applying an upconversion layer. The absence of proof-of-principle experiments for organic upconverters is related to spectral limitations. Most solar cells have an absorption onset at wavelengths

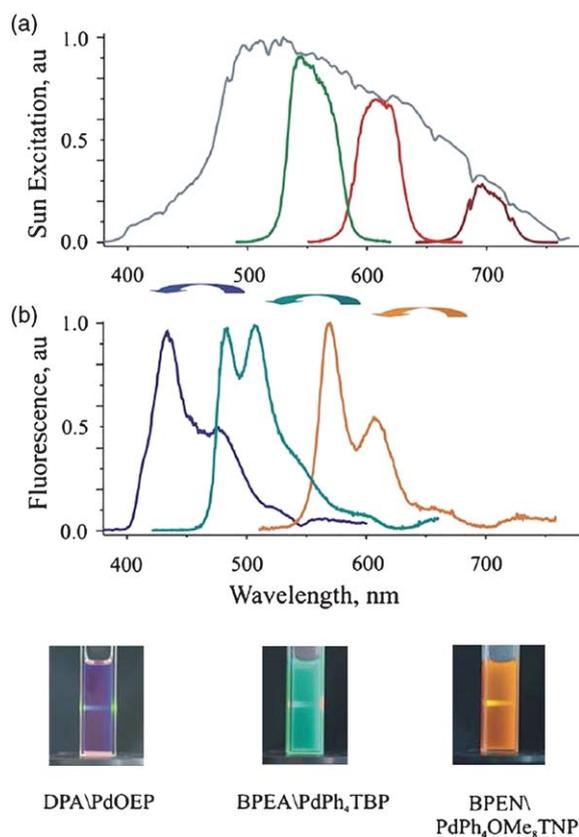


Fig. 10 Illustration of upconversion in three organic upconverter systems. In the top figure the absorption spectra of the sensitizers are shown, together with the solar spectrum, and in the middle figure the upconverted emission spectra from the activators are shown. The sensitizer and activator molecules are given in Fig. 8. In the bottom the upconversion in solutions of the activator/sensitizer systems is demonstrated. Reproduced with permission from ref. 93.

longer than 780 nm, which is the longest wavelength for which organic upconverters have been realized so far. For most solar cells these organic upconverters cannot raise the efficiency since the upconverter has to convert photons that are transmitted by the solar cell. Possibly, organic upconverters in combination with a wide band gap solar cell, like AlGaAs, can be investigated to demonstrate the potential of organic upconverters.

Lanthanide upconverters have been used in combination with GaAs,⁶⁶ c-Si,⁶⁷ a-Si⁶⁸ and dye sensitized solar cells (DSSC)^{69,70} and have been shown to enhance the efficiency by upconversion. In general, the upconverter is applied at the back of a cell as an electrically isolated layer. A back reflector reflects all emitted photons back into the solar cell. Different types of solar cells require different designs for the application of upconverters, as schematically shown in Fig. 11. Except for the design given in ref. 70, where the upconverter is not electrically isolated, the solar cell has to be bifacial, *i.e.* the light also enters from the back, whereas in general, a metal contact is applied at the back to extract the charge carriers generated from the solar cell. With an upconverter the back contact has to be transparent (11c), or cover only a small part of the back area (11a).

The first experiment was done on GaAs solar cells combined with a vitroc ceramic material doped with Yb³⁺ and Er³⁺ for which

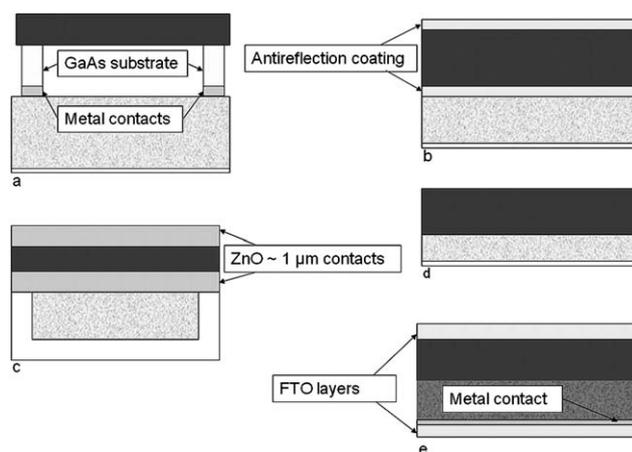


Fig. 11 Schemes for different solar cells used in combination with upconversion layers. The dark areas are the solar cells, (a) GaAs,⁶⁶ (b) c-Si,⁶⁷ (c) a-Si,⁶⁸ (d) DSSC with glass ceramics⁶⁹ and (e) DSSC with upconverter incorporated inside the solar cell.⁷⁰ The shaded areas are the upconverters, darker for (e), indicating that it is part of the solar cell. (a), (b), (d) and (e) have a metallic back reflector and (c) a white back reflector. The light gray areas are the contacts, as shown for GaAs (a) a-Si (c) and DSSC (e). (b) has anti-reflection layers on both sides of the solar cell.

the solar cell characteristics was obtained under extremely high excitation densities. An efficiency of the solar cell of 2.5% was obtained even though the excitation wavelength (891 nm) is not resonant with the absorption peak of Yb³⁺ (~980 nm),³⁰ leading to inefficient upconversion. Secondly the design was such that not all emitted photons were directed to the solar cell, as can be seen from the scheme (Fig. 11a). The upconversion photons are emitted isotropically, in the lateral direction and onto the metal contacts. In 2005 Richards and Shalav^{67,71} showed upconversion under lower excitation density of 2.4 W cm⁻² reaching 3.4%^{67,71} quantum efficiency at 1523 nm in a crystalline silicon solar cell

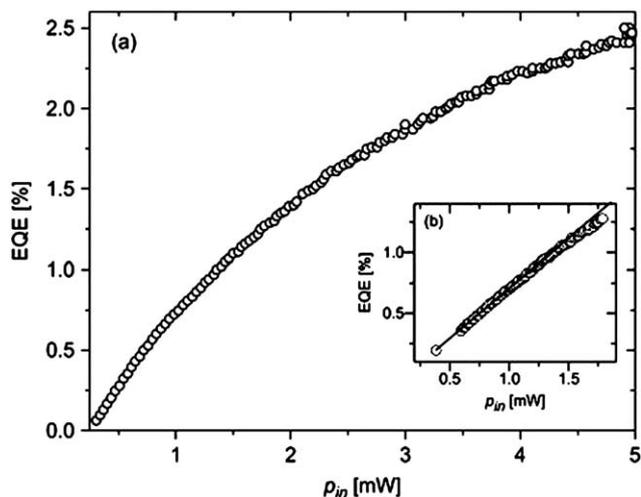


Fig. 12 External quantum efficiency for a c-Si solar cell with NaYF₄:Er³⁺ upconverter after excitation of 1523 nm light. At low power the slope is 1, at high powers the slope is sublinear, implying that the upconverter efficiency is saturating. Reproduced with permission from ref. 81.

with NaYF₄ doped with Er³⁺ as upconverter (Fig. 12). This was for a system optimized for the wavelength of 1523 nm. Intensity dependent measurements showed that the upconversion efficiency was approaching its maximum due to saturation effects.^{71,75}

Since c-Si has a rather small band gap (1.12 eV), transmission losses are not as high as for wider band gap solar cells. Hence, the efficiency gain for larger band gap solar cells can be higher. In 2010, our group showed upconversion of 980 nm infrared radiation in thin film a-Si solar cells.⁶⁸ Due to a high band gap of 1.7 eV, a-Si solar cells can gain more from upconversion. The upconverter host used in this case was also NaYF₄, now doped with both Yb³⁺ and Er³⁺. The synthesis of the upconversion system was not optimized and the upconversion efficiency was well below those reported in ref. 37.

A quantum efficiency of 0.02% was measured under laser excitation of 3 W cm⁻², see Fig. 13. In 2011, upconversion of 980 nm light was also demonstrated in dye sensitized solar cells. No quantum efficiencies were reported, which makes it hard to compare the results. Table 1 summarizes results for upconverter based solar cell devices reported in the past few years. The experiments done on the a-Si solar cells^{68,73} show the variation of

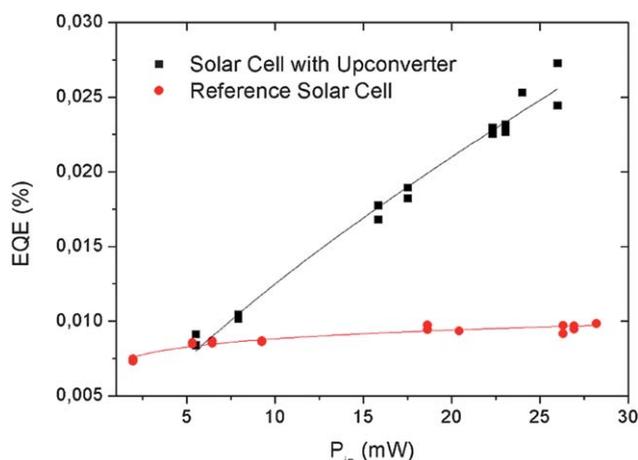


Fig. 13 External quantum efficiency for a-Si solar cells under 980 nm excitation for a reference cell and a cell with an upconverter layer. The efficiency of an upconverter is intensity dependent and the quantum efficiency increases with the intensity of the 980 nm radiation.

Table 1 Overview of experiments on efficiency enhancement in solar cells through upconversion. UC denotes the upconversion material used, SC gives the type of solar cell, EQE is the external quantum efficiency reported for the powers or power densities given in the last column

Ref.	UC	SC	EQE	Wavelength/nm	Power or power density
66	Vitroceraamics	GaAs	2.50% ^b	891	1 W
67	NaYF ₄ : 20% Er ³⁺	c-Si	3.40%	1523	2.4 W cm ⁻²
72	NaYF ₄ : 20% Er ³⁺	c-Si	0.008%	1523	2.3 W cm ⁻²
68	NaYF ₄ : 18% Yb ³⁺ , 2% Er ³⁺	a-Si	0.02%	980	3 W cm ⁻²
73	PTIR545/F ^a	a-Si	0.50%	980	0.6 W cm ⁻²
74	PTIR545/F ^a	c-Si	0.1089%	1500	0.1 mW
69	YAG 3% Yb ³⁺ 0.5% Er ³⁺	DSSC	0.2 mA cm ^{-2c}	980	500 mW
70	UC-TiO ₂	DSSC	0.002%	980	2.5 W

^a Commercial upconversion material from Phosphor Technology Ltd., probably Gd₂O₂S : Yb,Er. ^b Measured solar cell efficiency. ^c Inconsistent values were reported to determine the EQE, thus current is given.

the upconversion efficiency for different UC materials. It seems that Gd₂O₂S: Er³⁺, Yb³⁺ is more efficient than NaYF₄: Er³⁺, Yb³⁺.⁶⁸ This is however largely due to the poor quality of the NaYF₄: Er³⁺, Yb³⁺ material in comparison to the optimized material, which is known to have high upconversion efficiencies.³⁷ At the low intensities used for the experiments, the commercial Gd₂O₂S: Er³⁺, Yb³⁺ was much more efficient than NaYF₄: Er³⁺, Yb³⁺. The efficiency of Gd₂O₂S: Er³⁺, Yb³⁺ started to saturate around 0.6 W cm⁻² with an efficiency still below 1%.⁷³ The highest upconversion efficiencies for optimized NaYF₄: Er³⁺, Yb³⁺ have been reported to be around 10%, saturating at 40 W cm⁻².³⁸ Clearly, optimization of the upconversion material is an important aspect in the route towards a commercial system applying upconversion materials in solar cells.

Increasing the efficiency through device adaptations

The measured quantum efficiencies of the upconverter solar cell devices are rather low. The luminescence quantum efficiency of the upconverter, a parameter that considers only the absorbed photons is much higher.⁶⁷ The quantum efficiencies of solar cells can be determined when taking all carrier collection losses into account. What these losses are depends on the type of solar cell. Generally the losses are optical or electrical in nature. The main optical loss is that not all of the light reaches the upconverter layer. Part of the light is reflected before it enters the cell, incoming light is scattered inside the cell and partly absorbed before it reaches the upconverter layer, see Fig. 14. This results in lower power density of light in the upconverter layer and thus lower upconversion efficiency. The main electrical loss is that the efficiency is lower when light is incident from the rear side and thus the emitted light from the upconverter is not optimally generating the current. The nature of the optical and electrical losses described above and to what extent the losses can be avoided will be discussed for c-Si and a-Si solar cells.

Optical losses

A large part of the incident photons is reflected at the front of a silicon solar cell when there is a large difference in refractive index, *i.e.* at a silicon/air interface. This reflection is minimized by adding an anti-reflection layer. Anti-reflection layers have a thickness chosen such that at the desired absorption wavelength the light is least reflected, due to interference between the

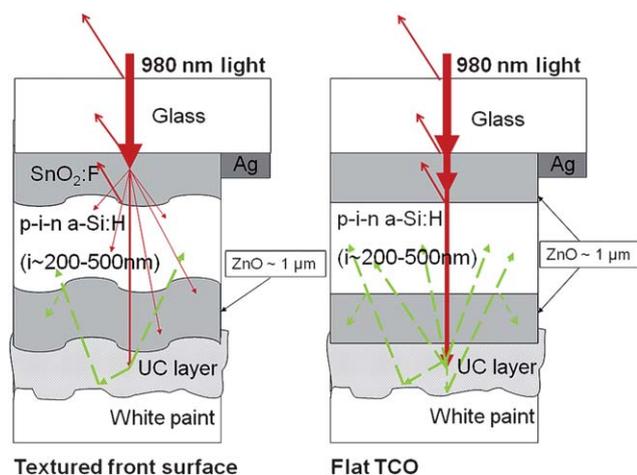


Fig. 14 Optical losses in solar cells; scattering due to texture (left) and reflections at the front and back at the interfaces with large differences in refractive index are shown.

incoming light and the reflected light at the silicon/anti-reflection layer interface. These anti-reflection layers can easily be optimized for the wavelength of choice by adapting the thickness of the anti-reflection layer,⁷⁶ but can only be applied between two media when their refractive indices are respectively lower and higher than that of the AR layer itself *i.e.* at silicon/air or silicon/glass interfaces. Most upconverter layers consist of upconverter species in transparent hosts *i.e.* plastics or glasses. The transparent host materials have a refractive index around 1.5. In the c-Si solar cells this upconverter layer faced the silicon solar cell directly and thus an anti-reflection layer is added between the silicon and the upconverter layer,⁶⁷ Fig. 11b.

For a-Si solar cells, the picture looks a bit different. There is always a TCO layer covering the silicon at the front and the back (Figs. 11c and 14). This TCO layer has a refractive index of around 1.8 and matches closely the refractive index of the upconverter layer (PMMA \sim 1.5). Thus adding an anti-reflection layer between the TCO and upconverter layer is not very meaningful for a-Si solar cells. In fact, the low refractive index of PMMA is beneficial at this location. At the front, the TCO layer may act as anti-reflection layer depending on the type of a-Si solar cells. The light can enter the solar cell through the glass, as depicted in Fig. 14 or the glass can be the substrate and the TCO faces the air. In the first case the TCO layer serves as front contact and thicknesses of 1 μm are required to avoid resistive losses. Anti-reflection layers are merely $1/10^{\text{th}}$ of this thickness. In the latter case the contacts are silver grids and the TCO layer thickness can be adapted to serve as anti-reflection layer for the desired wavelength.

The main advantage of adding an upconverter layer is that a reflector can be applied behind the upconverter layer, reflecting all light back into the solar cell. Because the upconverter is electrically isolated, all kinds of reflectors are possible, like metallic or diffusely reflecting 'white' reflectors. The reflector can also enhance the effect of upconversion, where either the absorption of the emitted light in the solar cell or the excitation light intensity in the upconverter layer is enhanced. When a metallic reflector is applied, the light that is not absorbed by the

upconverter, is specularly reflected back into the upconverter layer. Specular reflection will not decrease the power density of the light and is thus beneficial for the upconverter.⁶⁷ A diffuse reflector increases the absorption of the emitted light due to scattering of the light, resulting in a longer path length of the emitted photons in the solar cell.

Electrical losses

Next to optical losses that influence the performance of the upconverter layer, electrical properties also have substantial influence. These are very difficult to adapt for upconverter solar cells without decreasing the efficiency. First of all is the fact that the cell efficiency for illumination from the rear side is lower. This always results in lower quantum efficiencies for the same wavelengths than that with the illumination at the front surface and thus lower response of the upconverted light. The rear side efficiency is basically lower because the generated electron hole pairs are generated close to the n-side of the p-i-n junction. For a-Si cell the light conventionally enters the solar cells through the p-layer, because the generated holes are limiting the carrier collection due to very low mobility and thus needed to be generated as closely as possible to the side where they are collected. For c-Si solar cell, the pn-junction is not in the middle but at the front. This means that when the solar cell is illuminated from the back, the electron hole pairs generated at the back where most of light is absorbed are far from the depletion region where the holes are separated from the electrons. Thus illumination from the back always results in lower carrier collection and thereby lower efficiency.

The other aspects that influence the upconverter performance negatively are the methods that increase the absorption of incoming light. Light absorption is increased by light trapping effects and scattering.^{77,78} This is detrimental for the upconverter layer, because it homogenizes the light and decreases the light intensity reaching the upconverter layer. Consequently, it has been shown that flat solar cells have higher upconverter performance than solar cells on textured surfaces.^{68,73} For a-Si solar cells, the substrates (TCO) such as Asahi U-type $\text{SnO}_2\text{:F}$ coated glass have their surface textures with feature sizes of \sim 200 nm are optimised for the scattering in the wavelength region where a-Si absorbs (<800 nm) and the light scattering is weaker at the longer wavelengths.⁷⁹ Hence, the light scattering is not considered to be the most dominant reason for the lower upconversion. On the other hand, the textured surface increases the concentration of defects in the silicon layer. Defects play an important role in limiting the performance of a-Si solar cells (due to a high density of dangling bond defects) and less in c-Si solar cells⁸¹ (compare sub-band gap response of c-Si with a-Si Fig. 13 and 15), because defects increase the sub-band gap density of states.⁸⁰⁻⁸² This is manifested by a drop in the V_{oc} , however this drop in V_{oc} outweighs the increase in current due to light scattering, see Table 2. The transparency of sub-band gap light could be increased by a factor of two by using flat solar cells because the sub-band gap response due to midgap defects is reduced, while there is a concomitant increase in V_{oc} . Though, light scattering will be unavoidable, decreasing the midgap defect density in the absorber layer in the solar cell will improve both the upconverter performance and the solar cell.

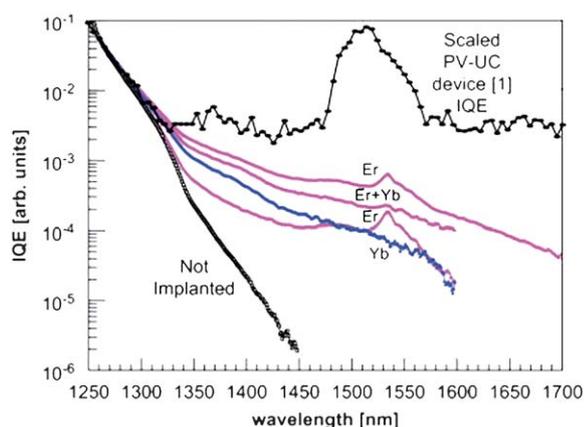


Fig. 15 The sub-band gap response of c-Si solar cells. The response is several orders of magnitude lower than that for a-Si, Fig. 13, implying much less defects. Reproduced with permission from ref. 81.

Light concentration

The light intensities of the lasers used in the experiments discussed above are in the order of a couple of W cm^{-2} . The full solar spectrum has an integrated intensity of 0.1 W cm^{-2} , thus concentrated sunlight is necessary for upconversion. Reasonable concentrations are in the order of a couple of hundred suns applied on multijunction solar cells.⁸³ With a concentrator, the photogenerated current density is proportionally higher, leading to higher V_{oc} for the solar cells and thus higher efficiency. Further, the concentrated light falls perpendicular onto the solar cells, leading to angle-independent absorption of sunlight by the cell, which also contributes to higher efficiencies as well as to higher upconversion efficiencies. The disadvantage is that, in general, with concentrated light the series resistance limits the cell performance. For multijunction solar cells this effect will be less than that for single junction solar cells, because the spectrum is split between the different absorbing layers of subcells, resulting in a net concentration of light for each solar cell less than the total concentration. Moreover, for a-Si cells, there is an additional disadvantage with concentrated light due to light induced midgap defect density which increases with the light intensity to the power of 2/3. This problem demands smart solutions, for example the use of ultrathin cells and local light management around the upconverter, such as plasmonic effect and nano-focusing of light, to be discussed in the next section, instead of exposing the whole cell to high intensity light.

To make upconversion a real possibility for improving infrared response of solar cells, it is important to know how

Table 2 Response of superstrate a-Si solar cells with and without texture in the TCO substrate and with different absorber layer thickness (230 and 500 nm). The flat solar cells had higher upconverter response⁷³ due to decreased sub-band gap absorption

Solar Cell	V_{oc}/V	FF	$J_{sc}/\text{mA cm}^{-2}$	$\text{EQE}_{UC} (\%)$ (at 0.1 W cm^{-2})
Flat 230 nm	0.88	0.67	9.3	0.046
Flat 500 nm	0.86	0.67	10.8	0.052
Textured 230 nm	0.84	0.65	11.7	0.032
Textured 500 nm	0.83	0.69	13.8	0.032

much concentration is necessary. Because, the laser light is monochromatic and the sunlight polychromatic in nature, direct comparison of light power densities is not possible. The best way to compare these intensities, is by multiplying the solar spectrum with the normalized absorption spectrum of the upconverter. The normalized spectrum can be used, when the power density is given and not the absorbed power density. Otherwise the absorbed power density needs to be corrected for the absorbed fraction. Hereby, it is assumed that a higher energy photon contributes to the upconversion in the same way as a lower energy photon. The upconverter materials used with the solar cells^{66–70} have Yb^{3+} (900–1050 nm) and Er^{3+} (1400–1650 nm) as absorber, see Fig. 16. When these normalized absorption bands are multiplied with the solar spectrum the absorbed power densities are then 1.5 mW cm^{-2} for Yb^{3+} absorption and 1.4 mW cm^{-2} for Er^{3+} absorption. Then, from the photon flux of the laser and the solar spectrum the required light concentration can be determined. The concentration varies from 400 suns for 0.6 W cm^{-2} to 2000 suns for 3 W cm^{-2} . One thing that has to be taken into consideration is the effect of the broader band absorption in improving the performance when the two steps of excitations shown in Fig. 4 are not exactly in resonance *i.e.*, 2-color excitation may be more efficient. In Fig. 4, it can be seen that the first energy transfer is optimal when a photon of 1.31 eV is absorbed while for the second transfer step the optimum photon energy is 1.29 eV. This is the advantage of 2-color excitation, as was the assumption when determining the maximum energy improvement possible when the intermediate energy level is not in the middle.²²

Enhancing upconversion

From Table 1 it is clear that the upconversion efficiencies are still rather low and only at high excitation densities, exceeding the solar power density, efficiencies above 1% are reached. As discussed above, concentration of solar light is a viable option. Adaptation of the solar cell design can improve the incoming light intensity by a factor of 2 to $3^{73,80}$ while solar light concentrations of 300–500 times are reasonable for concentrated PV systems.⁸³ Alternative options to enhance the upconversion

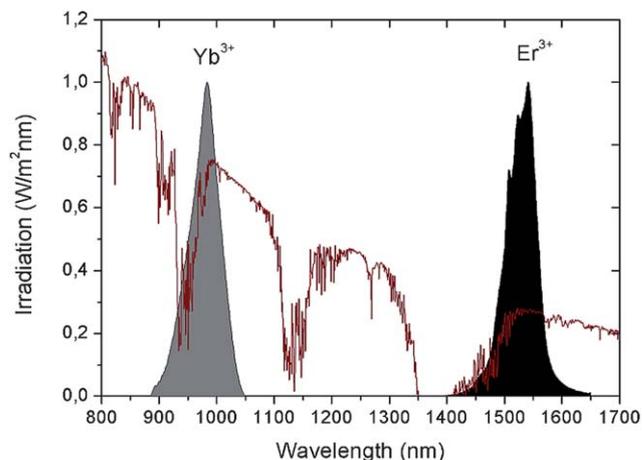


Fig. 16 Near infrared solar spectrum and the normalized absorption spectrum of Yb^{3+} and Er^{3+} .

efficiency exist. The first method is to broaden the absorption spectrum. This is especially necessary for the lanthanide upconverters, for which the upconversion efficiency is limited by the narrow absorption lines and low absorption strengths for the parity forbidden transitions within the $4f^n$ configuration of lanthanide ions. Broadening of the absorption spectrum for lanthanide upconverters can be achieved by using a sensitizer with a broad absorption band and a narrow emission line resonant with the lanthanide absorption line. Sensitization can be achieved by an external sensitizer, *e.g.* quantum dots, or an internal sensitizer, *e.g.* transition metal ions. Quantum dots (QDs) can be incorporated in a concentrator plate where the QDs absorb over a broad spectral range in the IR and emit in a narrow line, *e.g.* around 1520 nm resonant with the Er^{3+} upconversion wavelength. Energy transfer from the QDs to Er^{3+} in this scheme is through radiative energy transfer. The viability of this concept was proven by Pan *et al.*⁸⁴ in c-Si solar cells, where a layer with quantum dots was placed below the upconverter layer. With the quantum dots more light was absorbed and upconverted, which was proven by measuring the excitation spectra for the upconverted emission. The increased upconverted emission resulted in higher currents in the solar cell. Quantum dots may also be used as emitters, by tuning the upconverted emission wavelength to more suitable wavelengths.⁸⁵

Alternatively, transition metal (TM) ions may be used. TM ions have broader and stronger absorption bands than lanthanides. By incorporating TM ions in a host lattice together with a lanthanide upconverter, sensitization of the upconversion process may be achieved if energy transfer from the TM ion to the lanthanide ion occurs. In this case non-radiative (Förster type) energy transfer is the operative mechanism. For example, a Ti^{3+} ion absorbing in the IR range between 700 and 1000 nm due to a d–d transition could transfer its energy to Yb^{3+} and sensitize the Yb–Er upconversion couple. Until now, this sensitization scheme has not been successfully demonstrated, mainly due to the low quenching temperature of the emission from TM ions, which also restricts the use of TM upconverters. The stronger vibronic coupling of d–d transitions causes quenching of the emission well below room temperature for many TM ions.

Even more challenging are options to enhance upconversion efficiencies by manipulating emission and excitation processes through plasmonic coupling.⁸⁶ The use of plasmonic effects with upconverter materials is a new and emerging field, with many possibilities and challenges. In general plasmonic resonance can be used in two ways to increase the upconversion efficiency; either by enhancing the excitation strength or the emission strength.

The first approach uses field enhancement due to plasmonic resonances to increase the absorption strength. When the absorption strength is enhanced, the emission increases with the square of the enhancement in the non-linear regime. In the case of resonance between the plasmon and the optical transition strong enhancement can be achieved. The local field around the metal nanoparticle is enhanced due to local surface plasmon polaritons (collective oscillations of electrons in the metal nanoparticles excited by light). When the upconverter species is situated close to the metal nanoparticles, the field enhancement results in a strong increase in absorption.⁸⁷ A related method is to enhance the absorption strength by nanofocussing of light in

tapered metallic structures.⁸⁸ At the edges enhancement has been reported due to focusing of the light in these areas. Another option is enhancing the emission. In this case, the emission of the upconverter is enhanced by nearby plasmon resonances.⁸⁹

Since the field enhancement decays away exponentially with the distance to metallic nanoparticle, the upconverter species have to be close to the surface of the nanoparticle to benefit from the field enhancement effects. For organic molecules this presents no problem because the molecules are small enough to be placed in the field. For lanthanide upconverters, this is more difficult because the ions are typically contained in materials with grain sizes in the micrometre range. Several groups have managed to make nanosized NaYF_4 particles.^{90,91} This offers the possibility of plasmonic enhancement for these nanosized upconverters. The upconversion efficiency is however lower in nanocrystalline upconverters, probably due to surface quenching effects. Glass ceramics with nanocrystalline upconverters have also been reported.⁹² In these glass ceramics metal nanoparticles can also be incorporated to enhance the upconversion efficiency.

Conclusion

Upconversion for solar cells is an emerging field in photovoltaics. Proof-of-concepts experiments have been reported, demonstrating an increase in efficiency for sub-band gap illumination for different types of solar cells by application of upconverter materials. The challenges are improving the upconversion efficiency, especially for the relatively low excitation densities that are typical for solar illumination, and optimizing the design of the solar cell/upconverter system for maximum efficiency. Besides the well-known lanthanide-based upconversion materials, upconverters based on π – π^* transitions in organic molecules are explored. To enhance the upconversion efficiency and the overall efficiency of the solar cell/upconverter combination, sensitization, light concentration, and design aspects to reduce both optical and electrical losses have been discussed. The use of plasmonic resonance effects may be especially promising to increase the upconversion efficiency. A combination of upconverters with sensitizers to increase absorption and plasmons to enhance the excitation strength, may lead to upconversion efficiencies well above 1% for excitation densities of several mW cm^{-2} .

Acknowledgements

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References

- 1 D. J. C. Mackay, *Sustainable Energy Without Hot Air*, UIT Cambridge, 2008.
- 2 W. Shockley and H. J. Queisser, *J. Appl. Phys.*, 1961, **32**, 510–519.
- 3 <http://www.physics.usyd.edu.au/app/solar/research/pv.html>.
- 4 M. A. Green, E. Keith, H. Yoshihiro and W. Wilhelm, *Prog. Photovoltaics*, 2011, **19**, 84–92.
- 5 G. Conibeer, *Mater. Today*, 2007, **10**, 42–50.

- 6 G. F. Brown and J. Wu, *Laser Photonics Rev.*, 2009, **3**, 394–405.
- 7 R. P. Kenny, A. Ioannides, H. Mülleijans, W. Zaaïman and E. D. Dunlop, *Thin Solid Films*, 2006, **511–512**, 663–672.
- 8 P. Würfel, *Sol. Energy Mater. Sol. Cells*, 1997, **46**, 43–52.
- 9 A. Luque and A. Martí, *Phys. Rev. Lett.*, 1997, **78**, 5014–5017.
- 10 M. C. Hanna and A. J. Nozik, *J. Appl. Phys.*, 2006, **100**, 074510.
- 11 R. D. Schaller and V. I. Klimov, *Phys. Rev. Lett.*, 2004, **92**, 186601.
- 12 J.-H. Yum, E. Baranoff, S. Wenger, M. K. Nazeeruddin and M. Grätzel, *Energy Environ. Sci.*, 2011, **4**, 842–857.
- 13 J. Baxter, Z. Bian, G. Chen, D. Danielson, M. S. Dresselhaus, A. G. Fedorov, T. S. Fisher, C. W. Jones, E. Maginn, U. Kortshagen, A. Manthiram, A. Nozik, D. R. Rolison, T. Sands, L. Shi, D. Sholl and Y. Wu, *Energy Environ. Sci.*, 2009, **2**, 559–588.
- 14 L.-W. Wang, *Energy Environ. Sci.*, 2009, **2**, 944–955.
- 15 R. J. Ellingson, M. C. Beard, J. C. Johnson, P. Yu, O. I. Micic, A. J. Nozik, A. Shabaev and A. L. Efros, *Nano Lett.*, 2005, **5**, 865–871.
- 16 J. J. H. Pijpers, R. Ulbricht, K. J. Tielrooij, A. Osherov, Y. Golan, C. Delerue, G. Allan and M. Bonn, *Nat. Phys.*, 2009, **5**, 811–814.
- 17 B. S. Richards, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 2329–2337.
- 18 W. G. J. H. M. van Sark, A. Meijerink, R. E. I. Schropp, J. A. M. van Roosmalen and E. H. Lysen, *Sol. Energy Mater. Sol. Cells*, 2005, **87**, 395–409.
- 19 B. M. van der Ende, L. Aarts and A. Meijerink, *Phys. Chem. Chem. Phys.*, 2009, **11**, 11081–11096.
- 20 W. G. J. H. M. van Sark, A. Meijerink and R. E. I. Schropp, *Nanoparticles for Solar Spectrum Conversion, Chapter 10 in Nanotechnology for Photovoltaics*, ed. L. Tsakalakos, Taylor&Francis, 2009.
- 21 R. T. Wegh, H. Donker, K. D. Oskam and A. Meijerink, *Science*, 1999, **283**, 663–666.
- 22 T. Trupke, M. A. Green and P. Würfel, *J. Appl. Phys.*, 2002, **92**, 4117–4122.
- 23 T. Trupke, A. Shalav, B. S. Richards, P. Würfel and M. A. Green, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 3327–3338.
- 24 P. Franken, A. Hill, C. Peters and G. Weinreich, *Phys. Rev. Lett.*, 1961, **7**, 118–119.
- 25 G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer, Berlin, 1994.
- 26 F. Auzel, *Chem. Rev.*, 2004, **104**, 139–173.
- 27 T. N. Singh-Rachford and F. N. Castellano, *Coord. Chem. Rev.*, 2010, **254**, 2560–2573.
- 28 G. Dieke and H. Crosswhite, *Appl. Opt.*, 1963, **2**, 675.
- 29 J. Ohwaki and Y. Wang, *Jpn. J. Appl. Phys.*, 1994, **33**, L334–L337.
- 30 F. Auzel, D. Pecile and D. Morin, *J. Electrochem. Soc.*, 1975, **122**, 101–107.
- 31 J. F. Suyver, J. Grimm, K. W. Krämer and H. U. Güdel, *J. Lumin.*, 2005, **114**, 53–59.
- 32 C. Ronda, *Luminescence*, Wiley-VCH, 2007, ch 1, p. 18.
- 33 H. Yersin, *Transition Metals and Rare Earth Compounds II*, Springer Verlag Telos, 2001, vol. 214, ch 1, p. 12.
- 34 N. Menyuk, K. Dwight and J. W. Pierce, *Appl. Phys. Lett.*, 1972, **21**, 159–161.
- 35 K. W. Krämer, D. Biner, G. Frei, H. U. Güdel, M. P. Hehlen and S. R. Lüthi, *Chem. Mater.*, 2004, **16**, 1244–1251.
- 36 J. F. Suyver, A. Aebischer, S. García-Revilla, P. Gerner and H. U. Güdel, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 125123.
- 37 J. F. Suyver, J. Grimm, M. K. van Veen, D. Biner, K. W. Krämer and H. U. Güdel, *J. Lumin.*, 2006, **117**, 1–12.
- 38 R. H. Page, K. I. Schaffers, P. A. Waide, J. B. Tassano, S. A. Payne and W. F. Krupke, *J. Opt. Soc. Am. B*, 1998, **15**, 996–1008.
- 39 A. M. Pires, S. Heer, H. U. Güdel and O. A. Serra, *J. Fluoresc.*, 2006, **16**, 461–468.
- 40 D. C. Hanna, R. M. Percival, I. R. Perry, R. G. Smart, J. E. Townsend and A. C. Tropper, *Opt. Commun.*, 1990, **78**, 187–194.
- 41 X. Wu, J. P. Dennis, G. Özen and F. Pellé, *J. Lumin.*, 1994, **60–61**, 212–215.
- 42 G. Wang, W. Qin, L. Wang, G. Wei, P. Zhy and R. Kim, *Opt. Express*, 2008, **16**, 11907–11914.
- 43 J. F. Suyver, A. Aebischer, D. Biner, P. Gerner, J. Grimm, S. Heer, K. W. Krämer, C. Reinhard and H. U. Güdel, *Opt. Mater.*, 2005, **27**, 1111–1130.
- 44 C. Reinhard, K. Krämer, D. A. Biner and H. U. Güdel, *J. Alloys Compd.*, 2004, **374**, 133–136.
- 45 D. R. Gamelin, M. Wermuth and H. U. Güdel, *J. Lumin.*, 1999, **83–84**, 405–410.
- 46 C. Reinhard, P. Gerner, F. Rodríguez, S. García-Revilla, R. Valiente and H. U. Güdel, *Chem. Phys. Lett.*, 2004, **386**, 132–136.
- 47 D. R. Gamelin and H. U. Güdel, *J. Phys. Chem. B*, 2000, **104**, 10222–10234.
- 48 P. Gerner, K. Krämer and H. U. Güdel, *J. Lumin.*, 2003, **102**, 112–118.
- 49 C. Strümpel, M. McCann, G. Beaucarne, V. Arkhipov, A. Slaoui, V. Švrček, C. del Cañizo and I. Tobias, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 238–249.
- 50 C. Ronda, *Luminescence*, Wiley-VCH, 2007, ch 6, p. 153.
- 51 M. P. Hehlen, M. L. F. Philips, N. J. Cockroft and H. U. Güdel, *Encyclopedia of Materials: Science of Technology*, Pergamon, New York, 2001, 10, 9458.
- 52 F. Auzel and D. Pecile, *J. Lumin.*, 1973, **8**, 32–43.
- 53 R. R. Islangulov, D. V. Kozlov and F. N. Castellano, *Chem. Commun.*, 2005, (30), 3776–3778.
- 54 T. N. Singh-Rachford, A. Haefele, R. Ziessel and F. N. Castellano, *J. Am. Chem. Soc.*, 2008, **130**, 16164–16165.
- 55 R. R. Islangulov, J. Lott, C. Weder and F. N. Castellano, *J. Am. Chem. Soc.*, 2007, **129**, 12652–12653.
- 56 S. Balushev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda and G. Wegner, *Phys. Rev. Lett.*, 2006, **97**, 143903.
- 57 H. Sternlicht, G. C. Niemann and G. W. Robinson, *J. Chem. Phys.*, 1963, **38**, 1326–1335.
- 58 M. Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14–19.
- 59 T. N. Singh-Rachford, A. Nayak, M. L. Muro-Small, S. Goeb, M. J. Therien and F. N. Castellano, *J. Am. Chem. Soc.*, 2010, **132**, 14203–14211.
- 60 V. Yakutkin, S. Aleschenkov, S. Chernov, T. Miteva, G. Nelles, A. Cheprakov and S. Balushev, *Chem.–Eur. J.*, 2008, **14**, 9846–9850.
- 61 J. Mezyk, R. Tubina, A. Monguzzi, A. Mech and F. Meinardi, *Phys. Rev. Lett.*, 2009, **102**, 087404.
- 62 B. E. Hardin, E. T. Hoke, P. B. Armstrong, J.-H. Yum, P. Comte, T. Torres, J. M. J. Fréchet, M. K. Nazeeruddin, M. Grätzel and M. D. McGehee, *Nat. Photonics*, 2009, **3**, 406–411.
- 63 P. E. Keivanidis, S. Balushev, T. Miteva, G. Nelles, U. Scherf, A. Yasuda and G. Wegner, *Adv. Mater.*, 2003, **15**, 2095–2098.
- 64 P. B. Merkel and J. P. Dinnocenzo, *J. Lumin.*, 2009, **129**, 303–306.
- 65 Y. Y. Cheng, B. Fückel, T. Khoury, R. G. C. R. Clady, M. J. Y. Tayebjee, N. J. Ekins-Daukes, M. J. Crossley and T. W. Schmidt, *J. Phys. Chem. Lett.*, 2010, **1**, 1795–1799.
- 66 P. Gibart, F. Auzel, J.-C. Guillaume and K. Zahraman, *Jpn. J. Appl. Phys.*, 1996, **35**, 4401–4402.
- 67 B. S. Richards and A. Shalav, *IEEE Trans. Electron Devices*, 2007, **54**, 2679–2684.
- 68 J. de Wild, A. Meijerink, J. K. Rath, W. G. J. H. M. van Sark and R. E. I. Schropp, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 2395–2398.
- 69 M. Liu, Y. Lu, Z. B. Xie and G. M. Chow, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 800–803.
- 70 G.-B. Shan and G. P. Demopoulos, *Adv. Mater.*, 2010, **22**, 4373–4377.
- 71 A. Shalav, B. S. Richards, T. Trupke, K. W. Krämer and H. U. Güdel, *Appl. Phys. Lett.*, 2005, **86**, 013505.
- 72 B. Ahrens, P. Löper, J. C. Goldschmidt, S. Glunz, B. Henke, P.-T. Miclea and S. Schweizer, *Phys. Status Solidi A*, 2008, **205**, 2822–2830.
- 73 J. de Wild, A. Meijerink, J. K. Rath, W. G. J. H. M. van Sark and R. E. I. Schropp, *Proceedings of the 25th European Photovoltaic Solar Energy Conference*, 2010, pp. 255–259.
- 74 A. C. Pan, C. del Cañizo and A. Luque, *Mater. Sci. Eng., B*, 2009, **159–160**, 212–215.
- 75 S. Fischer, J. C. Goldschmidt, P. Löper, G. H. Bauer, R. Brüggemann, K. Krämer, D. Biner, M. Hermle and S. W. Glunz, *J. Appl. Phys.*, 2010, **108**, 044912.
- 76 J. Zhao and M. A. Green, *IEEE Trans. Electron Devices*, 1991, **38**, 1925–1934.
- 77 J. Müller, B. Rech, J. Springer and M. Vanecek, *Sol. Energy*, 2004, **77**, 917–930.
- 78 P. Campbell and M. A. Green, *J. Appl. Phys.*, 1987, **62**, 243–249.
- 79 J. Springer, A. Poruba and M. Vanecek, *J. Appl. Phys.*, 2004, **96**, 5329–5337.
- 80 L. M. van Dam, W. G. J. H. M. van Sark and R. E. I. Schropp, *Mater. Res. Soc. Symp. Proc.*, 2011, 1321-A01–1321-A04.

- 81 A. Shalav, B. S. Richards and M. A. Green, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 829–842.
- 82 J. de Wild, A. Meijerink, J. K. Rath, W. G. J. H. M. van Sark and R. E. I. Schropp, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 1919–1922.
- 83 H. Cotal, C. Fetzer, J. Boisvert, G. Kinsey, R. King, P. Hebert, H. Yoon and N. Karam, *Energy Environ. Sci.*, 2009, **2**, 174–192.
- 84 A. C. Pan, C. del Cañizo, E. Cánovas, N. M. Santos, J. P. Leitão and A. Luque, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 1923–1926.
- 85 C. Yan, A. Dadvand, F. Rosei and D. F. Perepichka, *J. Am. Chem. Soc.*, 2010, **132**, 8868–8869.
- 86 W. L. Barnes, A. Dereux and T. W. Ebbesen, *Nature*, 2003, **424**, 824–830.
- 87 S. Balushev, F. Yu, T. Miteva, S. Ahl, A. Yasuda, G. Nelles, W. Knoll and G. Wegner, *Nano Lett.*, 2005, **5**, 2482–2484.
- 88 E. Verhagen, L. Kuipers and A. Polman, *Nano Lett.*, 2007, **7**, 334–337.
- 89 J.-C. Boyer, L. A. Cuccia and J. A. Capobianco, *Nano Lett.*, 2007, **7**, 847–852.
- 90 H. Schäfer, P. Ptacek, K. Kömpe and M. Haase, *Chem. Mater.*, 2007, **19**, 1396–1400.
- 91 S. Schietinger, T. Aichele, H.-Q. Wang, T. Nann and O. Benson, *Nano Lett.*, 2010, **10**, 134–138.
- 92 V. K. Tikhomirov, D. Furniss, A. B. Seddon, I. M. Reaney, M. Beggiora, M. Ferrari, M. Montagna and R. Rolli, *Appl. Phys. Lett.*, 2002, **81**, 1937.
- 93 S. Balushev, V. Yakutkin, T. Miteva, G. Wegner, T. Roberts, G. Nelles, A. Yasuda, S. Chernov, S. Aleshchenkov and A. Cheprakov, *New J. Phys.*, 2008, **10**, 013007.