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Engineered nanomaterials for solar energy conversion

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Abstract
Understanding how to engineer nanomaterials for targeted solar-cell applications is the key to improving their efficiency and could lead to breakthroughs in their design. Proposed mechanisms for the conversion of solar energy to electricity are those exploiting the particle nature of light in conventional photovoltaic cells, and those using the collective electromagnetic nature, where light is captured by antennas and rectified. In both cases, engineered nanomaterials form the crucial components. Examples include arrays of semiconductor nanostructures as an intermediate band (so called intermediate band solar cells), semiconductor nanocrystals for multiple exciton generation, or, in antenna–rectifier cells, nanomaterials for effective optical frequency rectification. Here, we discuss the state of the art in p–n junction, intermediate band, multiple exciton generation, and antenna–rectifier solar cells. We provide a summary of how engineered nanomaterials have been used in these systems and a discussion of the open questions.

1. Introduction
The proposed mechanisms for the conversion of solar energy to electricity include those exploiting the particle nature of light in conventional photovoltaic cells, where absorbed photons generate electron–hole pairs, and those using the collective electromagnetic nature of the light, where sunlight is captured by antennas and rectified. In recent years, there has been immense progress in solar-cell technologies and a dramatic decrease in their cost. For example, the efficiency of solid-state photovoltaic (PV) cells started with values of ∼5% [1], but now there are routinely achievable values of >20% in Si-based systems and >30% in GaAs-based systems [2].

Perhaps the best way to track the technological progress is by examining the three generations of PV, defined by the increase of efficiency versus the reduction in cost [2]. First generation PV includes solar cells made of semiconducting p–n junctions, such as single crystal Si and poly-grain Si. Second generation PV reduced cost by introducing the thin-film technologies. Examples include amorphous Si, thin-film Si, CuInSe₂, CdTe, and dye-sensitized photochemical cells. Current, third generation, PV should lead to an increase in efficiency. Proposed improved solar cells include e.g., high efficiency multi-gap tandem cells, multiple exciton generation solar cells, intermediate band solar cells (IBSCs), hot carrier converters, thermophotovoltaics/thermophotonics, etc. Furthermore, it has been proposed that sunlight could be captured by (nano)antennas and rectified using a diode by exploiting the wave nature of the light [3–5, 2].

Engineered nanomaterials are the key building blocks of the current generation solar cells. For example, the idea behind the IBSCs is to introduce one or more energy levels within the bandgap so that they absorb photons in parallel with the normal operation of a single-bandgap cell [6]. The search for optimal sub-bandgap absorbers has been focused on highly mismatched semiconductor alloys that naturally exhibit an intermediate band (IB) [7, 8, 6], and on nanostructures, in particular arrays of quantum dots that form an IB [9–11, 8, 6].
Other examples include the potential usage of semiconducting nanocrystals in multiple exciton generation solar cells, where excitation of a semiconductor nanocrystal by a single, high-energy photon may result in a few electron–hole pairs [2, 12–19], or nanomaterials for the design of optical antennas with a typical dimension of ~100–1000 nm, supporting modes which exhibit extremely short wavelengths and strong confinement of the electromagnetic field on the nanometer scale [5, 2, 20].

A new playground has opened for engineered nanomaterials, and at this point it is simply not sufficient to focus only on technological improvements. Further technological breakthroughs depend strongly on an improved fundamental understanding of electronic, optical, and transport properties of nanomaterials and finding an efficient way to transfer technology from research laboratories to industry. Recent advances in computational nanoscience, combined with state-of-the-art experiments, could potentially enable such breakthroughs.

Quantum mechanical models have become sophisticated enough to handle nanosystems of a few tens or a few thousands up to hundreds of thousands of atoms, including excitations and many-body effects. They are able to handle realistic structural information obtained from the structural characterization measurements and take into account all the relevant effects, including the strain and piezoelectric effects, and external magnetic and electric fields [21]. Using these models we can, at least in principle, connect structure and physical properties of a nanomaterial.

Furthermore, combining the quantum methods with machine learning algorithms has opened new pathways for the design and engineering of nanomaterials with targeted properties [21]. Once a targeted physical property has been defined, the quantum mechanical models and search/machine learning algorithms are employed to deduce one or a few best candidate nanomaterials. It was suggested that, for technological applications, the same method could be used to optimize the nanomaterials with respect to the targeted physical property, avoiding a long and costly process that includes nanomaterials’ fabrication and characterization [21]. However, before even considering the application of the predictive-theory-guided design to solar cells, we need to understand the current fundamental and practical problems with the solar cells. Only then can we discuss how realistic and potentially useful the predictive-theory-guided design could be.

Here, we discuss the state of the art in p–n junctions, IB, multiple exciton generation, and antenna–rectifier solar cells. We provide a summary of how engineered nanomaterials have been used in these systems and a discussion of the open questions. For example, we address recent findings on how to exceed the thermodynamical limit on light trapping [22], or very recently reported multiple exciton generation enhancement of photocurrent in PbSe nanocrystal-based solar cells [19]. Understanding how to engineer nanomaterials for targeted solar-cell applications is the key to improving their efficiency and could lead to breakthroughs in the design.

2. p–n junction solar cells

The solar spectrum contains photons with energies ranging from about 0.5 eV to 3.5 eV. Conventional solar-cell technology is based on a single p–n junction, benefiting from one electron–hole pair for each absorbed photon, as shown in figure 1(a). When light quanta are absorbed, electron–hole pairs are generated, and if their recombination is prevented they can reach the junction, where they are separated by an electric field.

Current photovoltaic technologies utilize semiconductors, such as large crystals of silicon, or thin films of amorphous silicon, cadmium telluride (CdTe), or copper indium gallium selenide (CIS). The semiconductor material has to be able to absorb a large part of the solar spectrum, which is determined by its bandgap, as illustrated by examples in figure 1(b). For example, amorphous silicon has a higher bandgap (1.7 eV) than crystalline silicon (1.1 eV), which means that it absorbs the visible part of the solar spectrum more strongly than the infrared portion of the spectrum.

The p–n junction solar cells based on crystalline silicon now routinely achieve an efficiency of ~22% [23, 2]. The maximum thermodynamic efficiency for single-bandgap devices, assuming detailed balance, is 31%, the Shockley–Queisser limit [24]. It is obvious from figure 1(b) that by layering materials with different bandgaps one can improve the efficiency. This is the underlying idea of the multi-layer (‘tandem’) cells, which are highly efficient, but also expensive [2].

The energy conversion efficiency of solar cells based on thin-film silicon is typically lower than that of bulk silicon [23]. These limitations have been overcome by employing light-trapping schemes. The incoming light is obliquely coupled into the silicon and the light traverses the film several times, enhancing the absorption in the films [23]. The minimum thickness of the material is defined by the thermodynamical limit on light trapping [25]. However, recent findings demonstrate that, in principle, any semiconductor material can exceed the light-trapping limit when the local density of optical states (LDOS) of its absorbing layer exceeds the LDOS of the bulk semiconductor material [22]. This could potentially allow for the design of novel solar cells that can absorb light from the entire solar spectrum, but are ~10 nm thick [22].

Another way of creating the p–n junctions in semiconductors is by utilizing the electric field effect, where the concentration of charge carriers in a semiconductor is altered by the application of an electric field. Very recently, it has been proposed to exploit this effect to induce a p–n junction, enabling, at least in principle, a high quality p–n junction to be made of basically any arbitrary semiconductor [26]. The idea is to carefully design the top electrode so the gate electric field can sufficiently penetrate the electrode and more uniformly modulate the semiconductor carrier concentration and type. The method is illustrated on the example of silicon and copper oxide, where in the case of silicon, the top contact is made of a single layer of graphene across the surface [26].

The major factors limiting the conversion efficiency are the inability to absorb photons with energy less than the
bandgap, thermalization of photon energies exceeding the bandgap, and radiative recombination losses [23, 2]; see figure 1(a). When a photon is absorbed with energy greater than the bandgap of a semiconductor, the resultant carrier undergoes fast cooling via phonon scattering and emission.

Three approaches have been put forward to address this loss of efficiency [2]: (i) increasing the number of energy levels, typically by using a stack of multiple p–n junctions in different semiconductor materials (figure 1(b)); in this way higher-energy photons are absorbed in the higher-bandgap semiconductors and lower-energy photons in the lower-bandgap semiconductor; (ii) capturing carriers before thermalization, yielding a higher photovoltage; and (iii) multiple-carrier-pair generation per high-energy photon or single-carrier-pair generation with multiple low-energy photons, leading to the enhancement of the photocurrent.

3. Intermediate band solar cells

The main idea behind IBSCs is to introduce one or more energy levels within the bandgap such that they absorb photons in parallel with the normal operation of a single-bandgap cell [6, 8, 2, 27, 28]. A band diagram of an IBSC is shown in figure 2(a). Sub-bandgap energy photons are absorbed through transitions from the valence band (VB) to the intermediate band (IB) and from the IB to the conduction band (CB), enabling, at least in principle, IBSCs to achieve both high current and high voltage.

The IB has to be partially occupied to enable absorption from the VB into the empty states of the IB, and from occupied states of the IB to the CB. Splitting the Fermi level into three separate quasi-Fermi levels preserves the high output voltage of the cell [6]. Of course, VB to IB and IB to CB transitions must be optically allowed and strong, and the IB needs to be electronically isolated from both the CB and the VB, so VB to IB and IB to CB absorption spectra do not have spectral overlaps with each other [8, 11, 27]. The theoretical limiting efficiency of IBSC is 63% [27], derived at isotropic sunlight illumination and assuming the Sun and Earth temperatures to be 6000 K and 300 K, respectively. Under the same conditions, the maximum efficiency of a single-gap solar cell was 41%. Variation of the efficiency with the IB–VB gap $E_1$ is shown in figure 2(b), where we used data from Laque and Marti [27].

The quest for finding optimal sub-bandgap absorbers has been focused on (i) alloys that naturally exhibit an IB [7, 8, 6] and (ii) nanostructures, in particular arrays of quantum dots (QDs) that form an IB [9–11, 8, 6].

**Bulk IBSCs.** The electronic band structure of highly mismatched semiconductor alloys can be tuned both experimentally and theoretically to exhibit three electronically isolated energy bands [8]. In highly mismatched alloys this
can be achieved by the substitution of a relatively small fraction of host atoms with an element of very different electronegativity. Examples include III–V and II–VI alloys, in which group V and VI anions are replaced with the isovalent N and O, respectively, see e.g., [29, 30]. The electronic structure of such alloys is determined by the interaction between localized states associated with N or O atoms and the extended states of the host semiconductor matrix. As a result the conduction band splits into two subbands with distinctly nonparabolic dispersion relations [29], affecting the optical and electrical properties of these alloys. A narrow lower band can be formed only if the localized states lie well below the conduction band edge. Consequently, the absorption spectrum is modified by adding two new absorption edges, which can be tuned, at least in principle, to fall within the solar energy spectrum [30]. Experimental examples include the formation of an IB within the bandgap of highly mismatched semiconductor alloys such as Zn$_{1-x}$Mn$_x$Te$_{1-y}$ and Ga$_x$As$_{1-x}$P$_y$ [29, 30]. The IB was detected by spectral photoreflectance measurements, and its formation was attributed to band anticrossing. In order to obstruct electron tunneling between the IB and CB, and consequently maintain a high open-circuit voltage, blocking layers were introduced. This was successfully demonstrated on an example of GaN$_{0.024}$As$_{0.976}$ [28, 8].

From theoretical and computational viewpoints, few ab initio calculations have been performed in the quest for optimal IB materials. The most promising of these has been V$_{0.25}$In$_{0.75}$S$_3$, which has strong sub-bandgap absorption and an inherently partially filled IB [7]. This is important because it means that the IB is already partially filled without having to rely on impurity doping, which reduces densities and therefore lowers absorption levels.

Bulk IBSCs have so far exhibited efficiencies far below their potential, and the issue of finding the best candidate materials for this technology is essential if IBSC research is to succeed.

**Quantum dot IBSCs.** An IB can also be formed from the confined states of QDs situated within the bandgap of a host semiconductor. QDs should be closely spaced and with high quality interfaces, which would enable the strong wavefunction overlap and the formation of minibands. To achieve strong absorption to and from the IB, a high concentration of QDs is required. By engineering the parameters such as QD geometry (size and shape), inter-dot separation, and dot arrangement, one can optimize IB position and width to achieve the maximum efficiency [31, 32]. Typically, self-assembled (In, Ga)As QDs embedded in a GaAs matrix have been used as an IB (see, e.g., [6]). Other examples include InAs QDs in a GaAs/(Al, Ga)As matrix [33], or GaSb QDs in GaAs [34]. Interestingly, some of these devices have demonstrated features of IBSC operation, and achieved efficiencies over 18% [10, 6].

Self-assembled QDs consist of $10^4$–$10^6$ atoms of a semiconductor such as (In, Ga)As embedded in another semiconductor matrix, e.g., GaAs. They are fabricated by the Stranski–Krasstanov (SK) growth mode, which uses the natural lattice mismatch between the substrate and the deposited material [35, 36]. The shape and average size of these QD islands depend mainly on factors such as the strain intensity in the layer as related to the misfit of the lattice constants, the temperature at which the growth occurs, and the growth rate. The islands evolve to the state of quasi-equilibrium in which they assume the shape of pyramids or lenses formed on a thin wetting layer, that are then capped by the barrier material. The main advantages of the SK growth mode are fabrication of defect-free QDs of small sizes, homogeneity in sizes and shapes of QDs, formation of ordered arrays of 3D coherent islands, and fairly convenient growth processes [35, 36]. Indeed, their structural perfectness (no impurities, dislocations, and defects), the excellent isolation from the environment, and the ability to charge the system with a few electrons or holes (multiexcitons), have made them essential in studying many-particle physics in confined spaces [37, 38]. Unlike colloidal QDs, where nonradiative decay channels rapidly destroy multiexcitons and, e.g., cause blinking in photoluminescence (commonly interpreted as being caused by the presence of extra charges that enhance nonradiative decay rate) [39, 40], in self-assembled QDs the multiexcitons ‘survive’ (and decay radiatively). Also, the photocorrosion and photostability [41] of colloidal QDs, where QDs stability depends on the solution (e.g., it was found that CdS QDs in nonpolar solvent were remarkably stable even under UV light irradiation) [41], do not influence self-assembled QDs.

In order to create a mini-band, some measure of homogeneity must exist between the successive quantum dot layers. However, the strain may accumulate so that layers of coherent quantum dots may no longer be formed, thus limiting the number of QD layers [42–44]. The strain-induced limit of the number of QD layers can be lifted by employing systems with the strain symmetrization within the structure, such as the (In, Ga)As/Ga(As, P) system [11]. It was found that, whereas the number of QD layers was indeed increased, the intensity of absorption between QD-confined electron states and the host CB was weak (because of their localized-to-delocalized character) and the position of the IB within the matrix bandgap did not satisfy suitable energetic locations for the IB [11].

Furthermore, one of the challenges in the QD IBSC design has been the loss of output voltage at room temperature compared to reference solar cells without an IB [6]. The loss of voltage at room temperature is caused by the thermal escape of electrons from the IB to the CB (in addition to tunneling of electrons from the IB to the CB) [6, 8].

Thus, from a fundamental viewpoint, there is a need for better understanding of the nature of the IB (localized versus extended), and carrier relaxation processes. From a purely technological viewpoint, the quest for improved fabrication techniques and more suitable materials (strain symmetrization and strong absorption between the IB and CB) has only just begun. As an illustration of the sensitivity of the problem, careful fabrication of InAs/GaAs IBSCs led to a significant elimination of output-voltage reduction [45], potentially opening pathways for room temperature IBSCs.
Figure 3. The single photon generation of multiple excitons (electron–hole pairs). (a) Bulk and (b) nanocrystal.

Figure 4. (a) The ideal profiles for carrier multiplication efficiency $\eta$, the number of excitons generated by absorption of a photon, for bulk PbSe (green), nanocrystals NC1 (blue) and NC2 (red). The shaded region represents the AM1.5G solar spectrum [49]. (b) Quantum yield versus photon energy for PbSe [13, 50, 15, 47] and PbS [13, 17, 47] nanocrystals (NCs) and bulk; data from various groups illustrate wide variations of reported MEG QYs. The quantum yield represents the averaged number of excitons per absorbed photon. QY = 200% means all dots have two excitons.

4. Multiple exciton generation solar cells

Multiple exciton generation (MEG), or carrier multiplication, is the generation of more than one electron–hole pair (exciton) by absorption of one photon [46–48]. High-energy photons, at least twice the bandgap energy, absorbed in a bulk semiconductor can generate one or more additional electron–hole pairs close to the bandgap energy through a scattering process, known as impact ionization (the inverse of Auger recombination) (figure 3(a)) [2, 47, 48, 46]. The impact ionization was previously observed in bulk Si, PbS, PbSe, Ge, InSb, etc. This effect is inefficient in bulk because the rate of impact ionization is much slower than the rate of radiative recombination at low electron energies (in visible and near IR spectrum) and the need to conserve momentum. In addition, the impact ionization in bulk is not useful for energy conversion purposes because the required photon energies lie outside the solar spectrum (3.5 eV); e.g., it requires $\sim$7 eV photons to produce one extra carrier in silicon [19, 46, 2].

Thus, it was proposed that MEG can be more efficient in semiconducting nanocrystals [12, 15]. Given the unique electronic structure properties of nanocrystals–atomic-like electronic structure and size-dependent bandgap energies [15, 38], it was suggested that the relaxation dynamics of photogenerated carriers may be affected by quantization effects, and lead to more efficient solar cells (figure 3(b)). For example, hot carrier cooling rates of impact ionization could become competitive with the rate of carrier cooling [2, 13].

Numerous experiments have confirmed the existence of MEG in nanocrystals (although not without controversy, as discussed below) by showing that excitation of a semiconductor nanocrystal by a single, high-energy photon may result in a few electron–hole pairs (figure 3(b)) [2, 12–19]. The single photon generation of multiple excitons occurs on a very short time scale following photon absorption, where the efficiency increases with the energy of the photon.

Figure 4(a) shows the ideal profiles for multiple exciton generation efficiency $\eta$ [48, 46] in bulk PbSe $E_g = 0.27$ eV (green), nanocrystal NC1 with $E_g = 0.72$ eV (1722.2 nm) (blue) and nanocrystal NC2 with $E_g = 1.3$ eV (954 nm) (red). The efficiency $\eta$ is defined as the number of excitons generated by absorption of a photon. It was calculated using the detailed balance model under the assumptions that all photons with energies above the bandgap were absorbed and those with energies less than the bandgap were not, that the only loss is the radiative recombination, and that all photogenerated carriers are collected [48]. The calculations also give the maximum efficiency depending on the bandgap,
defined as $\eta_{\text{max}}(E_g) = 4/E_g$ [48]. In our case this gives, e.g., $\eta_{\text{max}}(E_g = 0.72) = 5$ and $\eta_{\text{max}}(E_g = 1.3) = 3$.

Figure 4(b) shows quantum yield (QY) versus photon energy for PbSe [13, 50, 15, 47] and PbS [13, 17, 47] nanocrystals and bulk. The quantum yield represents the averaged number of excitons per absorbed photon. Data from various groups illustrate wide variations of reported MEG QYs [13–19, 50]. This caused controversies, especially at the beginning, because the reported experimental probes of MEG have relied only on indirect evidence of the existence and efficiency of MEG (signature of Auger recombination within the exciton population decay traces) [16, 46, 18, 2].

In a typical MEG experiment, ultrafast transient absorption spectroscopy is used to infer the number of electron–hole pairs produced per absorbed photon. Samples are illuminated with a low-intensity beam of high-energy photons, and the ensuing dynamics of multiexciton decay versus single exciton decay are measured. If a fast component with a lifetime similar to multiexciton lifetimes is observed in addition to exciton decay, it is attributed to multiexcitons. However, MEG artifacts exist and can give ‘false positive’ signatures of MEG. For example, the single exciton decay can acquire a fast component due to opening of nonradiative channels, e.g., electron or hole traps in a nanocrystal surface [46]. Detailed discussion of the measurement of MEG versus its artifacts, and the proposed ways to minimize chances of overestimating MEG QY, is given in [46].

Furthermore, disagreements have arisen over the role of quantum confinement for MEG. Interpretations range from those showing that the MEG efficiency of the PbSe nanocrystal is about twice the efficiency observed in bulk PbSe [19, 48] to those stating that the advantage of nanocrystal MEG is merely due to a possibly larger photovoltage owing to quantum confinement [46]. Finally, there is the issue of the impact the MEG can have on solar energy conversion, demonstrating that MEG can occur in a working solar cell.

Very recently, MEG-induced enhancement of photocurrent in PbSe nanocrystal-based solar cells was demonstrated [19]. For the best device measured, the external quantum efficiency, defined as the spectrally resolved ratio of collected charge carriers to incident photons, peaked at 114 ± 1%. The associated internal quantum efficiency, corrected for reflection and absorption losses, was 130% [19]. The solar-cell architecture incorporated arrays of QD layers in p–n planar heterojunctions. Special attention was paid to the chemistry of PbSe QD surfaces, including removing long-chain organic ligands (such as oleic acid) while controlling electrical properties, and using four distinct chemical treatments (1,2-ethanediol, which showed reduced MEG, and hydrazine, methylamine, and ethanol, which preserved MEG). Furthermore, the beneficial aging effect on the solar cell performance was observed under oxygen and water-free nitrogen storage conditions [19].

Theoretical studies regarding the basic mechanisms of MEG give confusing results. Models offering explanations of MEG range from those that consider a coherent superposition of single and multiple exciton states; to excitations of a virtual multiexciton state that is strongly coupled to a real multiexciton state; to incoherent impact ionization, analogous to bulk impact ionization with appropriate modifications of the electronic states [16, 51, 2]. In order to distinguish between different interpretations, one would need additional constraints on the set of initial parameters. The set of initial parameters includes the coupling strength between excitons and multiexcitons, decay rates, and/or density of states. This is still an open issue.

Theoretical/computational models should link structure (typically extracted from structural characterization measurements) and predict or explain experiment. They should also predict any size dependence, explain how MEG is influenced by the coupling of the nanocrystal to its environment, and provide understanding of how MEG is influenced by coupling of nanocrystals. However, structural information about nanocrystal systems is not complete. For example, it is difficult to extract information about the surface of a nanocrystal, so it is not clear whether a charge carrier can reside at the nanocrystal surface in deep-trap energy states or not. One could, e.g., analyze different nonradiative decay channels for an assumed nanocrystal structure and then discuss the plausibility of the constructed scenarios.

From a more pragmatic (but not necessarily recommended) viewpoint, whereas understanding of the underlying physics is unquestionably important, the primary interest should lie in demonstrating that MEG can occur in a working solar cell. MEG-induced enhancement of photocurrent in PbSe nanocrystal-based solar cells has been very recently achieved [19], so the practical challenge is how to improve the MEG-enhanced quantum efficiency and search for different or new candidate nanomaterials for MEG, e.g., PbSe nanorods, carbon-based nanostructures, etc [19, 2]. Usage of simple empirical models that heavily rely on experiment can be more useful than employment of detailed many-body atomistic methods. Also, although not the most elegant approach, it is not uncommon in materials science to use linear regression or neural networks to interpret experimental data when physical models do not exist or are difficult to implement; see, e.g., [52]. The underlying equations do not have to be physically justified and the parameter set is determined by fitting the equations to a large set of experimental data [21, 52].

5. Antenna–rectifier system for solar energy conversion

Solar energy can be converted to electricity by exploiting the wave nature of light instead of its particle nature: sunlight is captured by (nano)antennas and then rectified [3–5, 2]. The fact that this approach had been previously successfully applied at longer wavelengths in radio and microwave frequency bands [53] opened the possibility, at least initially, for high efficiency conversion of solar energy. The uses of rectennas in the microwave region have been investigated over the past half century for power transmission and detection. Applications have included long-distance power beaming, signal detection, and wireless control systems [53, 4].
Conventional rectennas consist of two distinct elements [53, 4, 5], a dipole antenna plus a separate rectifying diode such as an MIM or Schottky diode, as illustrated in figure 5(a).

In the case of solar energy conversion to electricity, a rectenna device should collect and rectify electromagnetic radiation distributed over a wide range of submicron wavelengths (from the infrared (IR) through the visible portion of the spectrum, extending the range to $10^{14}$ Hz and higher), which, in contrast to monochromatic microwave radiation, is also incoherent and unpolarized. Schottky diodes are generally limited to frequencies less than 5 THz [54] and conventional MIM diodes have been used up to frequencies of about 100 THz [54–56, 5]. So, it is not obvious if an antenna–rectifier system, as used for monochromatic radio and microwave radiation, can be simply applied for solar energy conversion, for example, how to design an antenna to collect sunlight, or how to obtain efficient optical frequency rectification.

The conversion efficiency for the rectenna system in the case of monochromatic radio and microwave radiation is more than 80% [53]. Estimates for the theoretical limiting conversion efficiency of the antenna–rectifier solar cells range from 48% [2, 57, 58] to 95% [58], depending on how the antenna–rectifier solar cells were modeled.

In one model [2, 4, 57, 58], electrical noise power received through an antenna is replaced by a resistor at a temperature $T_R$, whose resistance is equal to the radiation resistance of the antenna. If the antenna can be replaced by the resistor at a given temperature, the rectification occurs only if the diode is at a lower temperature $T_D$ ($T_D < T_R$). There is no rectification for $T_R = T_D$, otherwise the second law of thermodynamics is violated, the so called Brillouin paradox [59]. Note that the equivalent arguments can be found in Feynman analysis of the ratchet as an engine [60], where it was shown that the engine cannot work if the vanes and the ratchet are at the same temperature. In both cases the efficiency is less than the Carnot efficiency because of the unavoidable heat exchange between the two thermal reservoirs [61]. It was shown that, if the antenna was replaced by a resistor at the temperature $T_R = 6000$ K, the maximum efficiency was $\sim 48\%$ [57, 58, 2, 4]. Obviously, this is a disappointing low value and casts doubt on the usefulness of the approach.

Other reported values of the theoretical limiting conversion efficiency of the rectenna system are higher than 85%, and are based on rather elementary considerations. For example, the model Sun–space–absorber–solar cell gives the efficiency of $\sim 85\%$ [4], whereas the model Sun–space–solar cell, which included entropy losses, led to the value of $\sim 93\%$ [62, 4].

Unfortunately, it is not clear which one of these methods applies to the rectenna system. Whereas the simple models, which give overly optimistic values of efficiency, do not include specific features of the antenna–rectifier solar cells, the model based on replacing the antenna by a resistor is as good as the initial assumption that the antenna can be replaced by a resistor at the temperature $T_R$. This assumption is valid for lower frequencies (up to the near IR) [4, 53], but it is not clear to what degree the resistor replacement can be used in the optical frequency range. Thus, the question of determining the theoretical limiting conversion efficiency of the rectenna solar cell (that includes all the characteristics of the system) is still open.

From a (more important) practical viewpoint, the design of antennas and rectifiers operating at optical frequencies represents a significant challenge due to the required size and frequency of operation (see, e.g., [5, 20]). We are in a situation in which we need to, on one hand, improve our understanding of the behavior of materials used for antennas, e.g. metals, in the optical regime, which differs from that at frequencies below the IR, and on the other hand improve the ability to fabricate optical antennas with nanometer dimensions. For example, the common requirement for an antenna structure is that its size is comparable to the wavelength of the collected light. For optical antennas this gives a typical dimension of $\sim 100$–$1000$ nm. Such (nano)antennas support localized plasmon polaritons, which exhibit extremely short wavelengths and strong confinement of the electromagnetic field on the nanometer scale [20]. In addition to the size requirements, to produce an effective output signal, the antenna must be coupled to a device that can respond in a time $t \sim 1/f$, which for optical frequencies corresponds to times of $10^{-15}$–$10^{-13}$ s [5].

So far, optical antennas have been produced in a variety of sizes and shapes [63, 5], including, e.g., thin wire or whisker, dipole, bow-tie, etc. For example, figure 5(b) shows a thin wire antenna consisting of arrays of vertically aligned nanowires, where the tips of the nanowires and surface create rectifying tunneling junctions [5, 64, 55]. For a review and

![Figure 5. (a) Block diagram of antenna and rectifier system and load; (b) proposed realization of rectenna system using nanowires.](image-url)
recent developments on antenna issues in rectenna solar cells see, e.g., [5, 20, 65, 66].

In order to get an efficient rectification at optical frequencies, the diode will have to respond fast enough to operate at optical frequencies, and have a relatively low turn-on voltage. It will also require sufficiently small capacitance to minimize its time constant [5].

Quantum point-contact (QPC) devices, e.g. whisker diodes, have been used in measurements of absolute frequencies up to the green portion of the visible spectrum, demonstrating a response time of the order of femtoseconds [5].

One way to realize QPCs is in a break junction by pulling apart a piece of conductor until broken, or, in a more controlled way, in a two-dimensional electron gas (2DEG), e.g. in GaAs/AlGaAs heterostructures [67]. Rectification of the terahertz field has been discussed both experimentally and theoretically, in terms of its coupling to the source–drain bias, or in terms of modulating the QPC gate voltage [68]. Theoretically, one can model, e.g., current fluctuations in a ballistic QPC biased by applied voltage and irradiated by external field, where the external field could be considered to be either coherent (e.g. microwave radiation) or incoherent (e.g. representing the environment at high enough temperature or a heat phonon pulse) [69].

QPCs can also be created by positioning the tip of a scanning tunneling microscope close to the surface of a conductor [70, 71]. The tunneling phenomenon in these QPC devices is such that the current passes predominantly through the sharp protrusion closest to the planar sample surface. The rectification properties of tunneling junctions at fixed gap width originate from material, geometrical, and/or thermal asymmetry, and photo-stimulated changes in the electron flux distribution [5, 72, 64, 55].

Material asymmetry is expected when the electrodes have different work functions: the barrier shape will be asymmetric at zero bias. Thermal asymmetry will occur when there is a temperature difference between the two electrodes causing different electron occupations of the states involved in tunneling. Geometrical asymmetry represents asymmetry of the electrodes comprising the tunnel junctions. Examples include the geometrical asymmetry effect in STM [70], or optical rectification caused by the nonlinear tunneling conduction between gold electrodes separated by a subnanometer gap [71]. The asymmetrical, nonplanar geometry of the pointed whisker in conjunction with the flat anode is an essential requirement for increasing the cut-off frequency of the diode, but inconsistent with the planar geometry [5].

There have been many innovative proposals on how to achieve efficient optical frequency rectification. For example, very recently, Sabou et al [73] theoretically investigated idealized junctions between oppositely doped Mott insulators, modeling them as one-dimensional chains of interacting spin-polarized fermions. They predicted efficient rectification at very high frequencies. For practical realizations, Sabou et al [73] recommended transition metal oxides, which, although often predicted to be conductors by band theory, can be found to be Mott insulators. Also, such oxides can show interesting behavior when driven by high frequency fields.

To summarize, whereas the entire rectenna concept for solar energy conversion may be very difficult to realize in practice, the problems such as understanding the materials behavior at optical frequencies, design and fabrication of antennas with a typical dimension of ~100–1000 nm, or the issue of efficient optical frequency rectification and how to engineer nanomaterials to rectify on such high frequencies, represent challenges that need to be addressed. As to the solar energy conversion using rectennas, at this point only a proof-of-concept device will provide convincing evidence regarding this approach.

6. Discussion and summary

Engineered nanomaterials are the key building blocks of solar cells, irrespective of the mechanisms for the conversion of solar energy to electricity—those exploiting the particle nature of light and those using the collective electromagnetic nature, where light is captured by antennas and rectified. Understanding how to engineer nanomaterials for targeted solar-cell applications is the key to improving their efficiency and could lead to breakthroughs in the design.

The design of nanomaterial-based solar cells is far from being straightforward. Traditional approaches for the improvement of the design of solar cells, or the design of solar cells based on new mechanisms, have relied on the intuition of researchers, focusing on trial-and-error search and accidental discovery.

Alternatively, predictive-theory-guided design combines quantum mechanical methods and search/machine learning algorithms, such as genetic algorithms, data mining, or neural networks, to design optimized nanomaterials with targeted physical properties [21]: we define a targeted physical property and then employ the quantum mechanical and search/machine learning algorithms to deduce the structure. Of course, this sounds very appealing, especially because the computer-generated nanomaterials could be counterintuitive and difficult to discover otherwise, and the actual fabrication of a large number of structures and their processing could be avoided. The main premise behind this approach is that theory is able to correctly link the structure and the property.

The real test for all those predictive methods would be to fabricate nanomaterials using information from the theoretically predicted structure, and then check how their measured physical properties correspond to the targeted ones. Let us analyze and discuss the solar-cell design from the viewpoints of traditional versus predictive-theory-guided design.

In the ‘simplest case’ where the underlying physical processes are well understood, solar-cell design includes a search for optimal constituent nanomaterials and geometries. For example, a thermodynamical limit on the light trapping within a semiconductor can be overcome by using subwavelength nanomaterial-based solar absorbers, such as nanowires that have elevated local density of optical states [22]. Thus, the design reduces to the search for optimal
of nanocrystals. However, structural information about understanding of how MEG is influenced by coupling of the nanocrystal to its environment, and impart dependence, explain how MEG is influenced by the experiment. They should also predict any size structural characterization measurements) and predict or mechanisms of MEG [16, 51, 2]. Theoretical/computational Furthermore, theoretical studies disagree on the basic advantage of nanocrystal MEG is merely in a possibly efficiency observed in bulk PbSe [19, 48] to those stating that MEG efficiency of the PbSe nanocrystal is about twice the where interpretations range from those showing that the MEG efficiency of the PbSe nanocrystal is about twice the expected in bulk PbSe [19, 48] to those stating that the advantage of nanocrystal MEG is merely in a possibly larger photovoltage owing to quantum confinement [46]. Furthermore, theoretical studies disagree on the basic mechanisms of MEG [16, 51, 2]. Theoretical/computational models should link structure (typically extracted from structural characterization measurements) and predict or explain experiment. They should also predict any size dependence, explain how MEG is influenced by the coupling of the nanocrystal to its environment, and impart understanding of how MEG is influenced by coupling of nanocrystals. However, structural information about nanocrystal systems is not complete. For example, it is difficult to extract information about the surface of a nanocrystal, so it is not clear whether a charge carrier can reside at the nanocrystal surface in deep-trap energy states or not. One could, e.g., analyze different nonradiative decay channels for an assumed nanocrystal structure and then discuss the plausibility of the constructed scenarios. From a more pragmatic viewpoint, whereas understanding of the underlying physics is unquestionably important, the primary interest lies in demonstrating that MEG can occur in a working solar cell. This has been very recently achieved [19], so the practical challenge is how to improve the MEG-enhanced quantum efficiency and search for different or new candidate materials for MEG, e.g., PbSe nanorods, carbon-based nanostructures, etc. The recent advances in computational design could enable such a search for optimal materials and geometries, as discussed in [21].

Application of the rectenna system for energy conversion has been present in the literature for quite some time [3–5, 2], discussing theoretical efficiency [4, 2] and proposing various antenna–rectifier realizations [3–5, 65, 66, 71, 2]. At this point only a proof-of-concept device will provide convincing evidence regarding this approach. However, regardless of how difficult it may be to realize the whole rectenna concept for solar energy in practice, the problems such as understanding the materials behavior at optical frequencies, design and fabrication of antennas with a typical dimension of ~100–1000 nm, or the issue of efficient optical frequency rectification and how to engineer nanomaterials to rectify at such high frequencies represent challenges that need to be addressed.

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