Final Report for the GCEP Project:
Ultra High Efficiency Thermo-Photovoltaic Solar Cells Using Metallic Photonic Crystals As Intermediate Absorber and Emitter

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Abstract
We have achieved significant accomplishments on the developments of nanophotonic absorber and emitter structures for solar thermal photovoltaic applications. The highlight include:

(1) The first computational design of a realistic nanophotonic absorber and emitter structures that enable system efficiency beyond the Shockley-Queisser limit. We have provided the first computational design of a Tungsten photonic structures that enable all-angle, near-unity absorption for the entire solar spectrum. We have also designed the first Tungsten emitter structure that possesses sufficient spectral selectivity in order to achieve system efficiency beyond the Shockley-Queisser limit.

(2) Experimental demonstrations of photonic crystal thermal emitters that operate at record high temperatures. To achieve high efficiency solar TPV system requires the absorber and emitter to operate at a high temperature (~2000K). This places severe constraint on the materials and structures that can be used in the intermediate. For example, while Tungsten nanostructures have been very widely used to tailor thermal emission, there has been substantial concern regarding the stability of such structures at high temperatures. We have discovered several template-based synthetic methodologies for forming materials with high thermal stabilities into three-dimensional photonic crystals. Using these methodologies, we have demonstrated photonic crystal thermal emitters that can withstand a record-high temperature of 1800K without structural degradation. This is an important milestone towards overcoming one of the fundamental challenges that have prevented the success of solar TPV in the past.

(3) The establishment of an emissometer at Stanford that enables accurate and absolute characterization of emissivity at elevated temperatures. This system provides absolute emissivity measurements at elevated temperature with high accuracy. We have established excellent consistency satisfying Kirkhoff’s law
between the emissivity measurement obtained on this system, and direct measurement of the absorptivity. Obtaining such a high quality data at elevated temperature is important as it directly allows us to assess the feasibility of nanophotonic structures at the challenging conditions of solar thermophotovoltaic systems.

(4) **Theoretical proposal and experimental demonstration of the thermal extraction scheme.** We show that the thermal emission of a finite-size blackbody emitter can be enhanced in a thermal extraction scheme, where one places the emitter in thermal contact with an extraction device consists of a transparent object. Our result indicates that one can get far more thermal emission from an emitter of a given size than previously anticipated, while staying within the constraints of the second law of thermodynamics. Our work points to the design of a new generation of thermal emitter with power output significantly beyond what has been previously thought to be possible.

**Introduction**

When a single-junction solar cell is illuminated by sunlight, its efficiency is subject to the Shockley-Queisser limit, which sets a fundamental upper bound on the efficiency. This limit arises from several intrinsic loss mechanisms: Solar photons below the band gap do not contribute to electrical current. For each photon above the band gap, the difference between the photon energy, and the output energy at approximately the band gap energy minus approximately 0.5eV (biased at the maximum power point), is dissipated as heat. As a result, the theoretical maximum efficiency of an ideal single junction cell maintained at a room temperature of 300K cannot exceed 41% under solar illumination and maximum concentration. In the absence of concentration, this limit is 31%\(^1\).

![Image of solar cell and emitter](image)

**Figure 1.** The concept of solar thermophotovoltaics.

In thermo-photovoltaic (TPV) solar energy conversion\(^2\), the solar cell is not directly exposed to solar radiation. Instead, an intermediate element is heated by absorbing solar radiation (Figure 1). The emitted thermal radiation from the intermediary, whose spectrum can be very different from that of sunlight, is then converted into electrical energy by a solar cell.

The TPV solar cell concept can be highly efficient, because the intermediate absorber/emitter tailors the spectrum of the light incident on the solar cell. The ideal
intermediary should provide broadband absorption of sunlight, as well as a narrow band emission with a wavelength tuned to the band gap of the solar cell. When exposed to such a narrow band emission, the performance of a single junction solar cell approaches the thermodynamic limit of the Carnot efficiency. Taking into account the radiative thermal transfer between the sun and the intermediate absorber, the overall maximum efficiency of a TPV cell is \( \eta = (1 - T_s^4 / T_i^4) \times (1 - T_i / T_c) \), where \( T_s \) and \( T_i \) are the temperatures of the sun and the solar cell, at 6000K and 300K, respectively\(^3\). The maximum efficiency of the TPV cell is 85.4% when the temperature of the intermediary is maintained at \( T_i = 2544K \). This efficiency is very close to the thermodynamic limit (86.8%) in any reciprocal system. With a single-junction solar cell, a solar TPV system therefore has a theoretical efficiency limit that is more than double that of the case where the same single-junction cell is directly exposed to sunlight.

In spite of its conceptual appeal, there has not been any experimental demonstration of a solar TPV system with efficiencies beyond standard solar cells. The objective of our project is to systematically remove some of these basic roadblocks that prevents the demonstration of high-efficiency solar TPV systems. In particular:

(1) Prior to our work, there has never been an actual design of a nanophotonic structure that enables system efficiency beyond the Shockley-Queisser limit. Instead, the experimental demonstration has focused on flat tungsten surface, which we know from theoretical analysis can never enable superior performance. We have computationally designed realistic absorbers and emitters that can improve solar TPV system efficiency beyond Shockley-Queisser limit, and moreover developed a novel thermal extraction scheme that can significantly improve the output power of thermal emitters.

(2) While nanostructured narrow-band thermal emitters have been widely studied in the past decade, the material systems of these emitters are such that the nanostructure does not survive at the kind of temperature (>2000K) required in a solar TPV system. Also, these nanostructure emitters have not been optimized for solar TPV system. In fact, our own system analysis indicates that the existing emitters are inadequate to enable high efficiency performance. A significant accomplishment of our project is the development of photonic crystal emitter structures that are stable at high temperature relevant for solar TPV applications.

The accomplishments of our project will be discussed in more details in the Results Section.

**Background**

The control of thermal radiation through nanophotonic structures represents a very active direction within the general area of nanophotonics. Within the period while our project is on-going, significant progresses have been made on the design of new nanophotonic structures to tailor thermal emission. Control of the spectral properties of thermal emission has been demonstrated using arrays of metallic thermal antennas\(^4\). Spatial shaping of thermal emission has also been demonstrated in a metallic surface with concentric metallic grating\(^5\). There has also been significant works exploring single
thermal emitters\textsuperscript{6}, where absorption cross-section beyond its geometric cross-section has been demonstrated. Since the Kirkhoff law relates the absorption and the thermal emission properties of any object, such a demonstration then indicates the possibilities of these structures for enhancing total thermal emission power. Finally, a group at MIT has demonstrated the integration of miniaturized thermophotovoltaic systems integrating TPV emitters with solar cells\textsuperscript{7}. However, very few of these works have directly tackled the significant challenges that are inherent in the solar thermophotovoltaic systems.

Most high temperature TPV studies have focused on tungsten-based structures. Tungsten is both refractory (melting point of 3422 °C) and it exhibits an intrinsically preferential thermal emission for TPV applications (higher emissivity at optical frequencies, and lower emissivity in the IR). While other materials have been considered, the vast majority of the reports focus on tungsten due to these advantageous properties. High quality 2D structured thermal emitters, formed via conventional lithography tools, have been of interest for TPV applications for some time\textsuperscript{7}. 3D structured emitters offer the potential to manipulate emission to a level not possible via a 2D structured surface\textsuperscript{8}. However, patterning tungsten at the small length scales into thermally stable structures, which are required to effectively manipulate emission at wavelengths matching high efficiency PV cells, remains challenging. Previous reports of 3D tungsten structures include those formed by chemical vapor deposition\textsuperscript{9,10,11}, sol gel processing\textsuperscript{12,13}, and electrodeposition\textsuperscript{14}. While these methods were able to form tungsten-based structures with the appropriate characteristic length scales for TPV emitters, their thermal stability was limited, at least in part by the quality and density of the infilled material. Through our work, many of these limitations have now been overcome.

**Results:**

*Computational design of a solar TPV system with realistic absorbers and emitters*

As the theoretical basis for our project, we provided the first computational design of a solar TPV system with realistic absorbers and emitters that have system efficiency beyond the Shockley-Queisser limit. For the absorber, we design a structure as shown in Figure 2a, which consists of a periodic array of Tungsten nano-pyramids\textsuperscript{15}. The shape of the pyramid provides a gradual impedance transformation, which minimizes reflection that otherwise would have occurred due to the large electromagnetic impedance mismatch between Tungsten and air. The absorption spectra of this structure shows near perfect absorption over the entire solar wavelength range (Figure 2a). We also observe similar strong absorption for a wide range of angles of incidence up to 60 degrees, which is important in order for such a system to operate at high solar concentration. Finally, the absorption of the structure decreases in the longer wavelength range, which is beneficial in reducing the thermal radiation loss from the absorber.

For the emitter, we design a multi-layer structure as shown in Figure 2b, where a flat Tungsten surface is separated from a multi-layer dielectric film\textsuperscript{16}. Unlike traditional filter structure, which relies upon far-field incoherent coupling between the Tungsten layer and the film, here the distance between the Tungsten layer and the film is judiciously chosen (in the range of a few microns) to create an emissivity peak at the wavelength of 0.7 eV, and a very strong suppression of emissivity below 0.7 eV (Figure 2b).
Starting with these realistic absorber and emitter spectra as obtained by direct full-field electromagnetic simulations, and by performing a detailed-balance analysis of a 0.7eV solar cell, we obtain the efficiency of the overall system, as shown in Figure 2c. Here we assume an area ratio of absorber and emitter of 50, which is experimentally realistic. The system reaches efficiency close to 50\%, significantly above the Shockely-Queisser limit for the optimal 1.1eV cell. Here we do not assume photon recycling between the cell and the emitter, which may further enhance the efficiency of the cell. The analysis here indicates that one can indeed use a nanophotonic design to create absorber and emitter structures that will result in overall efficiency enhancement in solar cells significantly beyond conventional limit.

Figure 2. Analysis of a solar TPV system incorporating nanophotonic absorbers and emitters, and a 0.7eV solar cell. (a) Absorber. The structure, shown in the inset, consists of an array of Tungsten pyramids. The periodicity is 250nm. The black and red curves are the spectra of absorptivity and AM 1.5 sunlight, respectively. (b) Emitter. The structure, shown in the inset consists of a flat Tungsten surface separated from a multilayer dielectric stack. The red curve is the emissivity spectrum for this structure. The gray curve is the spectrum for an optimized nano-structured Tungsten surface. (c) Red curve: TPV System efficiency as a function of concentration. Blue solid and dashed curve: Shockley-Queisser limit for 1.1 and 0.7eV solar cells respectively.

Nanophotonic thermal emitters operating at record-high temperatures

Over the past 4 years, we discovered several template-based synthetic methodologies for forming materials with high thermal stabilities into three-dimensional photonic crystals, and investigated both the thermal stabilities and high temperature optical properties of photonic structures fabricated using these materials. Three specific material systems were investigated in depth: chemical vapor deposition (CVD) grown HfB$_2$\textsuperscript{17}, electrodeposited tungsten\textsuperscript{18}, and atomic layer deposition (ALD) grown tungsten\textsuperscript{17}. All three systems exhibited powerful optical properties and significant thermal stabilities as described here. For all systems, the templates consisted of three-dimensional colloidal crystals. While such templates may not provide the ideal symmetry and structure for TPV applications, they enable efficient development of three-dimensionally structured high temperature materials, and are among the simplest structures to model. We now have the capability to form considerably more complex optically optimized structures via holographic patterning strategies\textsuperscript{19}. 
Figure 3a-d outline the fabrication procedure and Figure 3e provides an image of an electrodeposited Tungsten structure *after* annealing at 1400 °C for 12 hours\(^{18}\). The key finding here was that by coating the structure with a thin (15 nm) layer of HfO\(_2\), the high temperature stability could be increased by over 200 °C. Further improvement of temperature stability requires fully dense tungsten (something not provided by electrodeposition). Conformal deposition of dense tungsten on silica colloidal crystal templates was achieved by ALD using SiH\(_4\) and WF\(_6\) via a fluorosilane elimination reaction. The result was a very high quality tungsten inverse opal (Figure 4) which could withstand up to 1500 °C, an unprecedented thermal stability. In very recent work, we have created HfB\(_2\) 3D photonic crystals by CVD, which appear structurally very similar to the images in Figure 4. HfB\(_2\) is rather ‘special’. The electrical and optical properties of HfB\(_2\) are similar to metals (resistivity two times that of tungsten at room temperature), however it is a highly covalent ceramic with an exceptionally high melting point (3290 °C). This material, or composites of this material with tungsten, may provide a level of optical tunability not provided by simple metals.

**Figure 3.** (a-d) 3D template directed electrodeposition. a) A silica colloidal crystal was grown on a tungsten foil. b) W was electrodeposited inside the 3D template. c) W inverse opal obtained after template removal by HF etching. d) The W inverse opal was coated with HfO\(_2\) by ALD to enhance the thermal stability. e) SEM cross-sectional image after annealing at 1400 °C for 12 hours.

**Figure 4.** Top (a) and side (b) SEM micrographs of tungsten photonic crystals deposited by ALD after removal of the silica colloidal crystal template. (c) protected with HfO\(_2\) and annealed at 1500 °C.

*Establishment of an emissivity measurement system*

We have established a high-temperature emissometer measurement system (Figure 5). This emissivity system, initially constructed by Peumans, is now located at and
maintained by Fan’s lab at Stanford. The sample holder is based on a 1” diameter high temperature heater in an ultrahigh vacuum chamber (Figure 5). Samples are mounted on the heater. A feed through mechanism allows rotation of the heater in vacuum, in order to measure the angular dependence of the spectral radiance. External imaging and collimating optics are used to guide the spectral radiance into the entry port of FTIR spectrometer (Figure 5).

This system provides absolute emissivity measurements at elevated temperature with high accuracy. The ALD grown tungsten samples were first annealed at 1400 °C to simulate the effect of higher temperatures on the structure, and then measured at 600-900 °C. We observe an exceptional correlation between the optical reflectometry measurements taken at Illinois, and the emissivity measurements obtained at Stanford (Figure 6). While Kirchhoff’s law requires correlation between the emissivity and optical reflectance, in practice this is often not observed due to temperature dependent material parameters, complications with obtaining high quality emissivity measurements, and that fact the reflectance measurements require much smaller spot sizes than emissivity measurements, and thus are often not representative of the actual sample. The strong correlation observed here thus provides direct evidence of both the quality of the sample, and the quality of the measurement system.

Figure 5. (a) and (b) Schematic of Stanford high-temperature emissometer. (a) Collecting thermal emission from a heated sample. (b) Collecting thermal emission from the black body reference. PM=parabolic mirror; APT=aperture. (c) Photograph of the emissometer. (d) Photograph of the inside of the vacuum chamber.
Figure 6. Emissivity (Stanford), and Reflectance (Illinois) from the HfO$_2$ protected tungsten 3D photonic crystal shown in Figure 4. The photonic crystal was annealed at 1400 °C prior to measurement. Note the exceptional correlation between emissivity and reflectance, which almost perfectly matches that required by Kirchhoff's law. The emissivity of a flat tungsten film is ~0.25 over this entire range.

Demonstration of Thermal Extraction

As an important step towards new capabilities for controlling thermal emission, we have recently theoretically proposed and experimentally demonstrated that far-field thermal emission of a finite-size blackbody emitter can be significantly enhanced through the concept of thermal extraction.$^{20}$

An ideal blackbody emitter of an area $S$ at a temperature $T$, in direct contact with free space (Figure 7a), has a total emission to far-field of $\sigma T^4 S$ in vacuum, where $\sigma$ is the Stefan-Boltzmann constant. Any actual macroscopic thermal body cannot emit more thermal radiation than a blackbody. The Stefan-Boltzmann law is derived using the properties of vacuum only, and the upper bound here is independent of the physical characteristics of the emitter. An emitter with a refractive index higher than vacuum does have higher internal thermal radiation intensity. However, the high refractive index also leads to total internal reflection, which prevents significant portion of the internal radiation from leaving the emitter. Only the part of the internal radiation that is not totally internal reflected can contribute to far-field emission.

Thermal extraction exploits the portion of the trapped internal radiation and makes it contribute to far field emission. The total emission enhancement can reach up to $n^2 \sigma T^4 S$, where $n$ is the refractive index of the emitter. As an example of the thermal extraction scheme, Figure 7d shows an extraction medium made from a ZnSe dome in optical contact with the emitter, which in this case is a carbon dot (black). ZnSe is transparent in the infrared frequency regime and thus does not absorb or emit thermal radiation. It has a refractive index similar to that of the carbon emitter. At the interface between the carbon emitter and the dome, there is no total internal reflection. Therefore, all internal radiation in the emitter can enter the dome. Once inside the dome, the radiation propagates toward the dome surface where they leave to the far field vacuum. Since the dome has a radius and also surface area larger than the emitter, there is no total internal reflection at the dome surface.
We have used the emissometer setup, as shown in Figure 5, to demonstrate the thermal extraction effect. The sample is placed on a temperature-controlled heater, which then is placed in the vacuum chamber. The thermal emission is measured using both a FTIR spectrometer and IR camera. The enhanced emission is observed in all angles (Figure 7f). Figure 7g shows the emission spectra measured at normal direction. The spectral density from an ideal blackbody of the same size as the carbon black dot is plotted as reference (black lines). As expected, the bare carbon dot (blue lines) emits less than the ideal blackbody, with an emissivity of 0.85 in the normal direction. In the presence of the dome, the emitted power in the normal direction from the same carbon black dot is enhanced by 4.46 fold. The total power integrated over all angles is 7.6mW for the bare carbon dot, and 31.3mW for the carbon dot with the dome. It is important to note that the total emission is only 10.4mW for an ideal thermal body of the same size of the carbon dot.

Figure 7. Experimental demonstration of thermal extraction. a,b) Emission source made of carbon dot is coated on an aluminum plate placed on a temperature controlled heater. Carbon refractive index around 2.3 and an emissivity around 0.85. The dot has a radius $r = 1.025\text{mm}$. d,e) Thermal extraction device made of ZnSe hemisphere is placed in close contact with carbon dot. Dome has a diameter of 6mm and refractive index 2.4. c) and f) Infrared images of the thermal sources maintained at a temperature of 553K. Images are taken at 0, 30 and 60 degrees. All images have the same color scale. Values on the color scale bar are linearly proportional to the photon counts of detectors in the camera. g) Emitted power spectra measured at 553K for collection angles of normal direction. Red and blue lines are for the carbon dot with and without the hemispherical dome, respectively. Black lines are emission power from an ideal blackbody of the same area as the carbon dot at the same temperature.

The concept of thermal extraction as demonstrated above, which combines thermal emitter with a transparent dielectric, opens many important opportunities for thermal emitter design. In the conventional TPV emitter design, the spectral narrowing of the emission is achieved through structuring of a metallic emitter. Since the emitting area necessarily needs to be larger than the absorber area, conventional TPV intermediate design requires one to maintain a high temperature over a relatively large area, which
places additional complexity on the thermal design of the system. In contrast, with the thermal extraction scheme, the area of the metallic thermal emitter is decoupled from the actual emitter area. As a result, one only needs to maintain high temperature over a much smaller area, which simplifies the thermal design. Also, with thermal extraction, the spectrum of the thermal emission can be designed by controlling the extraction dielectric medium. Thus, this alleviates the need to maintain nanostructures in metal at high temperature. Many dielectric materials have better thermal stability compared with refractive metals. Moreover, to achieve thermal extraction the dielectric structure in fact needs not be in direct physical contact with the emitter, and also there is no need to maintain the dielectric structure itself at high temperature since it is largely transparent. Therefore, we anticipate that thermal extraction will significantly reduce the requirement to create structures that are stable at high temperature.

Conclusions

In this project, we have very significantly advanced the state-of-the-art in solar thermophovoltatics, by providing a solid theoretical basis, by overcoming some of the fundamental material challenges, and by demonstrating a new route towards better thermal emitter design through thermal extraction. These works are certainly important for the ultimate demonstration of a solar TPV system that has much higher efficiency compared with the Shockley-Queisser limit. The works will also be important for the general capabilities of manipulating thermal radiation, which is important for a wide range of energy technologies including solar thermal technology and radiative cooling.

Publications and Patents

Publications:


Plenary and Keynote Talks


10. S. Fan, Distinguished Speaker, “Nanophotonics for energy and information applications”, Department of Electrical and Computational Engineering, Purdue University, December 13, 2012.


Invited Talks:


4. P. V. Braun, “3D Photonic Crystals with Embedded Dielectric, Metallic and Emissive Features for Controlling the Generation and Harvesting of Photons”, META ’10, Cairo, Egypt, February 2010


Patents


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