Nanoparticle enhanced spectral filtration of insolation from trough concentrators

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Abstract

A nanoparticle fluid filter consisting of gold nanoparticles and indium tin oxide nanocrystals was fabricated and the optical properties were assessed. Results were integrated against the AM 1.5 solar spectrum to determine solar weighted efficiency of the filter for light energies transmitted above the bandgap to a photovoltaic cell for direct electrical generation while absorbing light below the bandgap that is converted to heat for thermal storage or processing. Temperature dependent bandgaps for both GaAs and cSi were used for optimization of the filter design. GaAs is preferred based upon its higher IR reflectivity, lower temperature coefficient, and greater high-temperature efficiency. However, cSi is significantly cheaper than current and projected GaAs costs. It was found that the experimental filter efficiency was 62% for GaAs and 56% for cSi which was within 6% of previous theoretical predictions.

Keywords: Spectral Filtration, Concentrating, Nanoparticles, thermal, photovoltaic

1. Introduction

Efficient conversion of insolation into dispatchable electrical energy requires utilization of the entire solar spectrum. This requires either multi-junction photovoltaic (PV) cells with chemical battery storage, concentrating solar power with no PV, or hybrid solar-thermal collectors utilizing PV with thermal storage. Existing utility scale solar systems (non-PV) use concentrating solar power to convert heat into thermal energy. This energy can be stored more cheaply than storage of electric or chemical energy in the form of batteries using PV. However, conversion of solar energy into electricity can be more efficient and is more cost-effective in PV systems. A hybrid design could allow advantages of both systems through the generation of dispatchable energy with a larger system efficiency and reduced system cost [1]. Hybrid solar-thermal systems work by selectively filtering the wavelengths of light that would otherwise be unused or underutilized by the PV cell and converting that energy into heat [2–4]. The challenge is designing a system that optimizes electrical and thermal generation at low cost and operates at high enough temperatures to allow for generation of electricity from the production of heat.

Metal and highly doped semiconducting nanoparticles exhibit size and shape-dependent surface plasmon resonance modes, arising due to the collective oscillation of free electrons within the particle in response to incident electromagnetic fields. Excited plasmons have been utilized in heat generation or light trapping in thin films [5,6], tunable metamaterials and frequency selective surfaces [7–9], colloidal suspensions in a medium of various shapes,

sizes, and composition [10–13], and for selective catalysis through plasmon decay into hot electrons [14,15]. Because the plasmon modes strongly couple with light, many metal nanoparticles possess narrow band resonances that selectively absorb or scatter particular energies of incident photons, giving rise to vivid colors when dispersed in solutions or thin films, an effect that has been unknowingly used for centuries in dichroic and stained glass. Nanoparticles used as color filters include both size and shape controlled colloidal nanoparticles along with planar metamaterials which utilize geometric coupling analogous to Bragg diffraction [16,17]. However, while tunable filters using a colloidal nanoparticle fluid matrix have been researched [18–20], they have not been readily utilized in the industry or experimentally demonstrated with any high degree of spectral filtration.

This work presents a spectral filter design for a parabolic trough solar concentrator which is designed to use the heat transfer fluid as the filter itself. To make the filter customizable to each unique system with primary dependency on operating temperature and PV band gap, the optical properties of the fluid must be controllable. This is achieved by integration of suspended plasmonic nanoparticles (NP) with tunable absorption properties into the fluid. This paper investigates both GaAs and cSi as the working PV cells and discusses the NP mixture and sensitivity on the PV operating temperature which will shift the semiconductor band gap. Filter design allowed for 80% (80%) of the sub bandgap light to be absorbed while transmitting 82% (76%) of the energy above the bandgap when the GaAs (cSi) PV cell is operating between 90 and 200° C realizing that this ratio can be adjusted to increase above bandgap transmission if desired. This suggests that the filter can be utilized in both small scale commercial and residential markets as well as lower temperature utility scale designs. Utilization of thermal energy could be used for either dispatchable energy or for markets where heat could be used for other applications such as water heating or industrial processes.

2. Materials and methods

2.1. Modeling

The model used to calculate filter optical properties was based on individual nanoparticles properties using the radiative transport equation (RTE). The RTE can model the transfer of energy from a photon as it moves through a particular medium [19,21–23]. Absorbance of light in the fluid was calculated by solving the integral equation

$$\mu \frac{\partial I_\lambda}{\partial \tau_\lambda} + I_\lambda = \frac{\omega_\lambda^{\text{tr}}}{2} \int_{-1}^1 I_\lambda d\mu + 2\pi n_\lambda^2 (1 - \omega_\lambda^{\text{tr}}) B_\lambda(T) \quad (1)$$

where I_λ is the spectral radiation intensity, B_λ is the spectral blackbody intensity, and μ is the cosine of the angle measured between the direction of light and the normal to the medium. Variables τ_λ and $\omega_\lambda^{\text{tr}}$ are the spectral optical depth and transport scattering albedo of the medium respectively. The optical depth and transport scattering coefficients can be determine from the polarizability model calculations with the following relations:

$$\tau_{\text{tr}} = \int_0^z (\alpha_\lambda + \sigma_\lambda) dz \quad (2)$$

$$\omega_\lambda^{\text{tr}} = \frac{\sigma_\lambda}{(\alpha_\lambda + \sigma_\lambda)} \quad (3)$$

Where

$$\alpha_\lambda = \frac{3f_v Q_a}{4r} + K \quad (4)$$

$$\sigma_\lambda = \frac{3f_v Q_s}{4r} \quad (5)$$

where f_v is the volume fraction of the particles in the host medium, K the spectral extinction coefficient of the base fluid, r is the particle radius, and Q_a and Q_s are the absorption and scattering coefficients, respectively, which are discussed in detail below.

The boundary conditions for the RTE are given as:

$$I_\lambda(0, \mu) = R_{\lambda, \text{top}} I_\lambda(0, -\mu) + (1 - R_{\lambda, \text{top}}) I_\lambda \delta(1 - \mu) \quad (6)$$

$$I_\lambda(\tau_0, -\mu) = R_{\lambda, \text{bottom}} I_\lambda(\tau_0, \mu) \quad (7)$$

where $R_{\lambda, \text{top}}$ is the spectral reflectance of the top surface, $R_{\lambda, \text{bottom}}$ is the spectral reflectance at the bottom, and τ_0 corresponds to the position at the bottom of the layer. Transmission, absorption, and reflection were determined based upon combination of scattering and extinction properties of each individual nanoparticle and the base fluid [24].

Nanoparticle optical properties were calculated using the Clausius-Mossotti polarizability (α_{CM}) with a correction to account for spheroidal particles. This relation is given by

$$\alpha_{CM}(\omega) = \frac{abc}{3} \frac{m^2 - 1}{1 + L_i(m^2 - 1)} \quad (8)$$

where a , b , and c are the spheroid radii along the x , y , and z axes, $m = \epsilon_{NP}^2 / \epsilon_{medium}^2$ is the ratio of refractive indices inside to outside the particle, and L_i is a shape parameter with i being the direction of incident polarization [25,26]. For the case of sphere, L_i is equal to 1/3 and Eq. (8) reduces to the well-known Clausius-Mossotti (CM) polarizability for spheres. A prolate spheroid (with $a > b = c$) model was used to determine the optical properties of gold nanorods as a function of aspect ratio. For prolate spheres, the shape parameter has an analytic expression in the form [27]

$$L_a = \frac{1 - e^2}{2e^3} \left[\ln \frac{1 + e}{1 - e} - 2e \right], \quad (9)$$

with orthogonal polarization given by

$$L_b = L_c = 1/2 (1 - L_a), \quad (10)$$

where eccentricity is defined as

$$e = \left(1 - \frac{b^2}{a^2} \right)^{-1/2}. \quad (11)$$

Increased scattering and radiation is accounted for mathematically by modification of the polarizability model using the modified long wavelength approximation (MLWA). The MLWA is an extension to the Clausius-Mossotti relation and is given by

$$\alpha_{MLWA} = \frac{1}{(\alpha_{CM})^{-1} - \frac{2}{3}ik^3 - \frac{k^2}{R}} \quad (12)$$

with k being the medium wavenumber and R the semi-radius of the particle in the direction of polarization [14,28]. The MLWA and CM polarizabilities are indistinguishable for particles much smaller than the incident wavelength of light where absorption is the primary contributor to plasmon decay.

Scattering and absorption coefficients can be directly calculated using the previously described polarizability models. Total extinction and scattering cross section of light are given by the expressions

$$C_{ext} = k \text{Im}(\alpha) \quad (13)$$

$$C_{sca} = \frac{k^4}{6\pi} |\alpha|^2 \quad (14)$$

with absorption cross section being found by subtraction, $C_{abs} = C_{ext} - C_{sca}$ [28,29]. Extinction, scattering, and absorption efficiencies are determined by taking the calculated cross sections and dividing by the cross sectional area.

Reflection of the top and bottom surface of the flow channel was obtained by extrapolating experimental data from commercially available solar glass (www.daglass.pl). In Fig. 1, transmission spectra are shown for float glass (dotted) and low iron glass including an anti-reflective (AR) coating on both sides (solid). Spectral reflection for AR coated glass was used in the model to determine spectral absorbed and transmitted solar energy in/through the designed filter.

Fig 1. Comparison of transmission through float glass (dash-blue) and through the low iron solar glass with an anti-reflective (AR) coating (solid-red).

2.2. Synthesis

The heat transfer fluid used in the experiments was Duratherm S. Duratherm S is a polydimethyl siloxane based oil and was chosen based on its optical properties relative to the cell bandgap, long term thermal stability of the optical properties, and chemical similarity to the nanoparticle surfactant for stabilization purposes [30]. Optical properties of the fluid were measured and assessed as a heat transfer fluid in the nanoparticle fluid filter. The solar fluid filter

proposed here is a combination of gold nanospheres and nanorods and indium tin oxide (ITO) nanocrystals. Both bare and silica encapsulated gold nanorods along with silica coated nanospheres were provided by nanoComposix and characterized to determine optimized fluid design utilizing experimental spectra. Spectra of nanospheres are shown in Fig. 2 Silica coating is required for thermal stability of rods even at moderate temperatures above 60 °C otherwise ripening will occur resulting in the rod shape changing to a sphere [31]. Non-coated rods were acquired for parametric testing while the coated rods were obtained for the final mixture due to the increased complexities of silica encapsulation. Silica coated nanorods were 26 nm wide and 122 nm long with a 45 nm thick silica coating. Transmission electron micrographs of the starting gold nanorod sample and the silica coated nanorods, revealing some silica sphere impurities are shown in Fig. 3.

Fig 2. Measured absorbance of 50 nm Au spheres with 45 nm silica coating.

Figure 3. TEM image of gold nanorods prior to silica coating (top) and after coating with amorphous silica (bottom).

In-house synthesis of indium tin oxide nanoparticles (ITO) was performed to have greater control over the optical properties in the infra-red (IR) spectral region. Synthetic procedures for ITO was performed by following the works of Garcia et al. [32] and Gilstrap et al. [33]. One mmol of indium acetylacetonate was mixed with 0.2 mmol of tin acetylacetonate and 3 mmol of myristic acid. Twenty milliliters of octadecene (solvent) was added to the mixture and the whole mixture was purged with argon gas. Purging was done five consecutive times each followed by degassing at zero atmospheric pressure. After the completion of the purging and degassing, the reaction mixture was finally maintained at a vacuum set point of 15 atm and the temperature of the reaction increased to 110 °C and was stirred for two hours. The temperature was increased to 295 °C and 10 ml of a previously degassed and heated solution of oleyamine in octadecene was added to the mixture. The temperature of the reaction was reduced to 240 °C and maintained for an additional one hour. Contrary to previous works where addition of oleyamine solution resulted in rapid color change; orange to dark green, the color of the solution in this case did not immediately turn to dark green. However, when 10 ml of chloroform was added to the mixture it immediately turned green showing the presence of ITO nanoparticles. Particles were precipitated out of the solution by adding absolute ethanol.

Combination of dynamic light scattering (DLS) measurements (data not shown) and transmission electron microscopy (TEM) revealed the size of the ITO crystals to be on the order of 6-11 nm in diameter as seen in Fig. 4.

Figure 4. TEM image of synthesized ITO nanocrystals.

Spectra of the nanoparticles were acquired over the wavelength range from 300 to 4,000 nm using both UV-Vis and Fourier Transform IR (FTIR) spectroscopy. Spectra were measured in the UV-Vis from 300 to 1400 nm using a Shimadzu UV-Vis 2600 and FTIR spectra were measured from 855 to 4,000 nm with a Perkin Elmer Spectrum Two. Spectra for individual nanoparticle types were extracted by subtracting a baseline consisting of a quartz cuvette and the suspending fluid (water for nanorods and hexane for ITO). Indium tin oxide nanocrystals were synthesized to have a tin doping concentration of 16% based upon recent studies on control of ITO plasmon resonance [32]. Tuning of the plasmon resonance in ITO nanoparticles can be done by adjusting both tin doping concentration and nanocrystal diameter [32,34]. Synthetic procedures were chosen based upon the desired plasmon resonance locations. Measured spectra revealed the ITO plasmon peak was centered around 2,200 nm.

3. Results and Discussion

3.1. Nanoparticle Optical Properties

Optimization of the fluid filter requires several simulations of varying nanoparticle aspect ratio to determine which particle combination provides the highest filter efficiency. Previous results have shown theoretical models of nanoparticle types and the effect of filter optimization [19,24]. Here, experimental results were compared to theoretical models to perform optimizations that more closely represent a real system. Since it was previously determined that a combination of gold nanorods and ITO provide the best filter for GaAs using theoretical models, experimental analysis was performed for the same particle types.

Bare nanorods were acquired from nanoComposix suspended in water and optical properties measured. Simulations were performed for nanorods using Eqs. (8-12) of varying aspect ratio ranging from 1:4 to 1:8 so that the plasmon wavelength was matched in both theory and experiment. Spectra for each simulation and experiment were normalized for comparison and results are shown in Fig. 5.

Fig 5. Comparison of (a) experimentally measured spectra and (b) theoretical bare nanorod spectra. Dashed vertical lines indicate the experimental and theoretical spectra have peaks centered at the same wavelength.

Two important differences were observed between the theoretical and experiment data. First, it was observed that the experimental spectra had a larger full width at half maximum (FWHM) than the theoretical nanorods. There are several reasons for the broadening. A larger bandwidth can signify increased plasmon decay [14,35] and some broadening is expected in experimental spectra due to imperfections of the nanoparticle surface leading to increased decay routes for the excited plasmon. In addition, while the modelled spectra are from only a single size of nanorod, the experimental spectra arise from a sample containing a narrow but non-negligible size distribution, hence it is expected that inhomogeneous broadening is the primary contribution to the observed differences. Second, it was observed that a larger secondary plasmon peak (~ 515 nm) was present in the experimental data. This secondary peak has two primary sources. Nanorods are anisotropic and have two primary dimensions. The length dimension is responsible for the primary plasmon peak while the width dimension produces a smaller peak in the 500-530 nm range. This effect was included in the modeling by adding contributions from polarization along the primary and secondary dimensions of the rod. However, magnitude of the primary resonance is significantly higher than the secondary resonance due to the large size difference in the dimensions. Dispersion in the experimental rod lengths is also expected to contribute to a smaller primary peak in relation to the secondary peak. In addition, the synthesis procedure creates some spherical impurities in addition to rods. These spheres resonate around 500-530 nm as well. The increased secondary plasmon peak in the experimental spectra is expected to be a contribution of the nanorods and unwanted spheres in the solution (See Fig. 3).

The variety of nanorod aspect ratios provided a wide range of spectra which was interpolated to perform optimization of the fluid filter using real data. Spectra of measured nanorods revealed that each rod could be broken down into three parts: Dipole resonance, secondary resonance, UV absorption. The primary dipole resonance is a result of light polarization along the long axis of the nanorod and shifts with aspect ratio [36]. The secondary resonance which is mainly static for each rod aspect ratio is a combination of light polarized along the short axis of the rod and small gold spheres in the solution as a result of the synthesis. The UV absorption is a combination of gold properties and surfactant for colloidal stabilization.

The interpolation was performed by fitting Lorentzian peaks to the primary dipole and secondary resonances and an empirical fit for the UV region. The Lorentzian fits were performed by first converting the absorbance data from wavelength-dependent to energy-dependent since the plasmon peaks are approximately Lorentzian in frequency-space. Peak location (ω_{peak}), bandwidth (Γ), and experimental peak height (H_{exp}) were extracted for each peak and the Lorentzian fit was made using

$$LP = H_{LP} \frac{\frac{1}{2}\Gamma}{(\omega - \omega_{peak})^2 + \left(\frac{1}{2}\Gamma\right)^2} \quad (15)$$

where $H_{LP} = (H_{exp})(\Gamma/2)$ is the Lorentzian height scaling factor. The additional factor $\Gamma/2$ in H_{LP} is required to match the peak heights of the Lorentzian to experimental data. Both primary dipole and the secondary resonance peaks were fit using Eq. (15) above. Amplitude of the secondary resonance Lorentzian fit was matched to experimental data by subtracting the value of the dipole Lorentzian fit from H_{exp} of the secondary peak.

The UV portion of the data was empirically fit using an inverted parabola with vertex located at the smallest wavelength data point and x-intercept located at the secondary peak location. Order of the parabola was found by running simulations to find which parabola gave the smallest error revealing a 3rd order ($-x^3$) as the best fit. Each component of the peak fits and their collective sum are given in Fig. 6.

Fig 6. Comparison of Lorentzian fit (dotted) and experimental (solid) normalized extinction spectra for bare nanorods of increasing aspect ratio.

Simulations for ITO were compared to experimental spectral results. The Drude model was used to calculate particle dielectric including a term to account for electron scattering off the surface of the particle [37] in conjunction with the polarizability model using Eq. (8) for a sphere. Surface scattering of electrons in nanoparticles is only applicable for particles in the 5 to 20 nm diameter size range. Below 5 nm diameter, nonlocal effects start to dominate, which is outside the scope of this work. Free carrier density was varied to approximate the spectral shifting due to changes in tin doping [32,38]. Two primary properties affect optical properties of ITO nanoparticles. First, increasing nanoparticle diameter causes the plasmon peak to redshift as illustrated in Fig. 7 (a) [16]. Redshifting is a result of changes in scattering off the nanoparticle surface. In (a), simulation results are for a tin doping of approximately 16% for particle diameters of 5 and 50 nm. It is noted that non-local effects observed for small particles (<5 nm) are not taken into effect in (a). Second, tin doping has previously been shown to shift plasmon resonance [39]. A tin concentration of 16% was chosen here since resonance is blue shifted more compared to other tin concentration

levels. Figure 7 (b) illustrates the comparison between modeled ITO nanoparticles with 7 nm diameter using the Drude model with particle polarizability (dotted) fitted to experimentally measured spectra (solid). Magnitude of the theoretical spectra was scaled to match experimental for comparison.

Figure 7. Optical properties of ITO showing effects of (a) increasing nanoparticle diameter in the model and (b) comparison of theory (dotted) to experiment (solid) of approximately 7 nm diameter ITO.

3.2. Angle dependence on fluid absorption

Angle dependence of reflection was incorporated into the model by consideration of a parabolic trough geometry. For a typical parabolic trough with 15 to 20 times concentration, reflected angles into the collector are between 0 and 60 degrees. Here, we include collector shading for normal incidence reducing the angle spread to approximately 6 to 60 degrees. Effects of angle of incidence include a modification to the reflection off the top and bottom surfaces and an increased pathlength through the fluid filter. Since the refractive index of the fluid (1.47) is almost identical to the glass (1.5), glass/fluid interfaces were neglected.

Reflection off the two surfaces as a function of incident angle are taken into account by weighting the normal incidence reflection. Graph for the weighted reflection is given in Fig. 8. Spectral reflection as a function of incident wavelength is weighted across the entire spectra using the values in Fig. 8.

Fig 8. Angle dependent reflection off AR coated low-iron solar glass at 800 nm as reported at (www.daglass.pl).

The increased pathlength can be calculated for a given incidence angle using Snell's law. A typical glass panel thickness is 3.2 mm and the fluid flow channel is 10 mm thick. As a function of angle, the path of the light through the fluid in units of mm is given by

$$Path = \frac{10}{\cos(\alpha)}, \quad (16)$$

where $\alpha = \sin^{-1}(\sin(\theta)/1.5)$ and θ is the angle of incidence. Neglecting the glass/fluid interface gives results that are independent of the glass thickness, which can be variable. The pathlength through the fluid varies from 10.03 to 12.25 mm over the angles 6 to 60 degrees. Interplay between increased reflection and increased path length must be evaluated to optimize the volume fraction of nanoparticles in the fluid to achieve the best possible spectral filter.

To get a clearer understanding of the flux as a function of angle, a ray tracing simulation was performed. Concentrator, support bars, and the receiver were modeled using the open source program SolTrace from the National Renewable Energy Laboratory (NREL). A schematic of the concentrating system is shown in Fig. 9. Flux was calculated by counting the number of rays that hit the receiver at particular ranges of angles divided by the total number of rays that hit the receiver. Angles were discretized from 0 to 60 degrees in increments of 5 degrees with a total of 450,389 rays. Results of the simulation are given in Table 1. Angle dependence into the optical model for the solar filter was incorporated by weighting the results of each angle range by the total flux using a weighted average. The incident angles in the model were also discretized in 5 degree segments and chosen to be at the center of each range given in Table 1.

Fig 9. Schematic on the concentrator system including the PV receiver and fluid filter in the path of the concentrated light.

Table 1. Average ratio of rays (weighted flux) to hit the receiver per angle range.

Angle	0-5	5-10	10-15	15-20	20-25	25-30	30-35	35-40	40-45	45-50	50-55	55-60
Flux	0	0.101	0.103	0.081	0.101	0.096	0.066	0.077	0.097	0.092	0.088	0.099

3.3. PV reflection

Placement of the fluid filter directly in front of the PV receiver has the advantage of being able to recollect light that passes through the filter and reflects off the PV cell. Two commercial GaAs cells were acquired from Alta

Devices and the spectral reflectance was measured using UV-Vis from 300-1400 nm and FTIR from 1200-4000 nm at room temperature. Results of the measurements are given in Fig. 10. Results showed thin film interference patterns across the spectral range particularly evident in the sub-bandgap region. Measurements of a second GaAs PV cell showed the same reflection behavior, but a slightly longer period of oscillation due to thickness variations from one sample to the next (data not shown). To incorporate GaAs reflection in the model, temperature dependence of the band gap had to be accounted for. The room temperature bandgap of GaAs is approximately 850 nm. The bandgap shifts to between 900 and 920 nm for temperatures between 80 and 190 °C. Exact bandgap values were calculated using the model from Ref. [40]. To do this, measured reflection data was used up to a wavelength of 600 nm. From 600 nm to the band gap, a reflection value of 5.5% was used corresponding to the average value of reflection over that range for the room temperature measurements. Then, reflection for wavelength above the bandgap were set to 95% based upon the average of the thin film interference. In this way, the band gap could be shifted and the corresponding reflection off the cell could be approximated for temperature dependence. Reflection from the cSi cell was set to 50% for wavelengths longer than the temperature dependent bandgap.

Fig. 10 Measured reflection off the commercial GaAs Alta PV cell.

Due to physical placement of the fluid filter directly in front of the PV receiver, back reflected light off the PV receiver was incorporated into the calculation to determine increased filter efficiency by a second pass through the fluid. The back reflected light was included by modifying the pathlength from the value L to

$$L * (1 + PV_{ref}(\lambda) * Glass_{trans}(\lambda)) \quad (17)$$

where L is the angle dependent length through the filter, $PV_{ref}(\lambda)$ is the measured spectral reflectance off the PV receiver, and $Glass_{trans}(\lambda)$ is the transmission through the anti-reflection coated glass.

3.4. Optimization of Experimental Data

Optical properties of synthesized nanoparticles were collected and used in the RTE to determine efficiency of the solar filter using measured data. Measured absorbance (A) spectra of each nanoparticle was converted into extinction efficiency using the expression

$$Ext = \frac{lC}{A} \quad (18)$$

where l is the cell pathlength and C is the nanoparticle concentration [41]. Experimental extinction was used in the RTE the same way modeled nanoparticles were to determine transmission, reflection, and absorption of the fluid filter. Simulations were run using the Lorentzian fit for measured gold nanorod absorption properties. Parametric sweeps over varying nanorod aspect ratios for two distinct rods in the fluid with the synthesized ITO spectral data were performed to determine the optimal nanoparticle combination for filter performance with a GaAs cell.

It is noted that splits between absorption and scattering are not readily measurable experimentally. This is due to the difficulty in capturing scattered light to discern what portion of extinction is due to scattering. Modeling the nanoparticles can give an indication of the split in magnitude between scattering and absorption. For 50 nm diameter spheres and 5 to 10 nm diameter ITO, nearly all the contribution from extinction is due to absorption. For nanorods simulated with the same experimental dimensions, the absorption to scattering ratio is approximately 35:1 calculated using polarizability models [17]. It is noted, that the scattering takes place exclusively at the primary plasmon peak with the secondary plasmon peak being absorption. Even though the scattering is non-zero, previous works have shown that this effect is not large for smaller scattering magnitudes in the RTE [19]. This is a result of scattered light having a large probability of being reabsorbed by a different nanoparticle in the fluid. For this reason, experimental data was assumed to be composed entirely of absorption and scattering effects were neglected. Particles with higher scattering percentages contribute to the overall filter performance through an increase in reflection and a decrease in absorption [19].

The performance metric of the nanoparticle filter is based upon maximizing total energy absorbed below the temperature dependent bandgap while simultaneously minimizing above-bandgap absorption. The percent of energy absorbed was obtained by integrating the absorbance spectra against the solar spectrum using

$$\int_a^b Abs(\lambda) * S_{energy}(\lambda) d\lambda \quad (19)$$

where λ is the wavelength in nanometers, S_{energy} is the spectral AM 1.5 solar energy, and $Abs(\lambda)$ is the theoretical/measured percent spectral absorption in the fluid. Absorption estimates were determined by scaling the measured absorbance (A) to account for the 1 cm thick path length filter using Beer's law ($A = \epsilon CL$). In Beer's law, ϵ is the material extinction coefficient, C is the concentration, and L is the path length. It is noted that scaling the path length is identical to scaling the concentration. Scaled absorbance was converted to transmission (T) using

$$A = -\log_{10}(T) \quad (20)$$

Percent of energy absorbed above (below) the bandgap was obtained by integrating from 350 nm to the bandgap wavelength (λ_{BG}) (from λ_{BG} to 4000 nm) for GaAs as a function of PV temperature. Energy absorbed and transmitted for a filter designed for cSi was performed the same way but by considering a bandpass filter from 600 to the temperature dependent bandgap of approximately 1150 nm. Temperature values were varied from 90 to 190° C in 10° C increments and the energy absorbed above and below the gap was averaged. Energy absorbed was divided by the total temperature-averaged energy in each above and below gap wavelength ranges to get the percent absorbed in the fluid filter. The same process was applied to the spectral transmission to obtain percent transmission through the fluid filter.

Optimization of filter performance was based on maximizing below bandgap absorption while simultaneously maximizing above bandgap transmission. For a GaAs PV cell, ITO nanocrystals mixed with nanorod pairs were simulated with plasmon absorbance peaks varied from 900 to 1200 nm and 1000 to 1400 nm in 10 nm increments for each of the nanorods by interpolating and extrapolating the Lorentzian fits to the experimental data. The same simulations were performed but with a single nanorod varying from 900 to 1400 nm. It was found that a combination of a single nanorod with ITO and two nanorods with ITO gave equally as good results. The optimized nanorod supported a resonance at 1100 nm with ITO resonating at 1800 nm based on synthesis targeting 16% tin doping. This combination gave a sub-bandgap absorption of 80% and an above-bandgap transmission of 85% when back reflection off the PV cell was included. Volume fractions for the nanorods and ITO were 1.62×10^{-8} and 6.51×10^{-6} , respectively. Having two nanorods in the mixture resonating at 1080 and 1200 nm gave the best result for a nanorods pairs by absorbing 80% of the sub-bandgap light and transmitting 85% of the above bandgap light. Volume fractions for the shorter wavelength nanorod, longer wavelength nanorod, and ITO were 7.43×10^{-7} , 1.50×10^{-8} , and 2.99×10^{-6} . The reason the two nanorod solution performed just as well as a single nanorod is due to the secondary peak in the visible range. Increased IR absorption from the second rod was offset by increased visible absorption as well.

Optimization for cSi was performed based upon a bandpass filter set up. Since cSi has a lower energy bandgap and does not efficiently convert high energy photon into electrons, a filter that passes light from 600 nm to the bandgap and absorbing all other wavelengths was chosen. Optimization of nanoparticles for this filter involved ITO doping concentration for IR absorbance and choice of nanospheres for absorbance of wavelengths less than 600 nm. It was found that a combination of a 50 nm diameter gold sphere and 16% doped ITO [38]. Volume fractions for the gold spheres and ITO were found to be 1.65×10^{-7} and 1.39×10^{-5} , respectively.

3.5. Synthesized Nanofluids

Based upon the optimization results, silica coated gold nanorods and ITO nanocrystals with selected sizes and doping levels were combined together in Duratherm S to create a fluid filter with the desired optical properties for a GaAs based design. Volume fractions for each nanoparticle type were estimated to be on the order of 10^{-8} for the Au nanorod and 10^{-6} for the ITO. These values were based upon yield estimates for the synthetic procedure and Beer-Lambert's law. Measurements were performed using a 1 mm path length quartz cuvette.

Measured optical data from the mixture was integrated with respect to the solar spectrum to determine the amount of energy absorbed and transmitted in the fluid. Absorbance was measured using a combination of UV-Vis and FTIR to obtain the values over the entire spectrum from 350 to 2400 nm as shown in Fig. 9. Above 2400 nm little solar energy is present. Figure 11 (a) shows the measured spectra with the blank quartz cuvette background removed and (b) shows the same spectra with the quartz and Duratherm S subtracted out. In (b), contributions from the silica coated nanorod and ITO are labeled. High absorbance below 400 is a result of absorption off both nanorods and scattering off the ITO nanocrystals. While effects of scattering from the ITO is most likely itself non-negligible in the UV, wavelengths below 400 nm do not contribute significantly to the overall performance of the filter due to decreasing glass transmission and significantly reduced solar energy.

Fig 11. Measured absorbance spectra of nanorods and ITO mixed in Duratherm S optimized for GaAs. (a) Shows AuNR, ITO, and Duratherm. (b) Shows only AuNR and ITO with Duratherm subtracted out.

Measured optical properties of the nanoparticle fluid were consistent with expectations. The double peak appeared for the nanorod with the primary dipole oscillation at 1040 nm and the secondary short axis oscillation at 514 nm. The ITO exhibited a plasmon peak at 2150 nm. Based upon the morphology of the nanorods and ITO, these peaks were in line with theoretical expectations and previous experimental reports [32,39,42,43].

The created nanoparticle fluid is expected to absorb 80% of the sub-bandgap light and pass through 72% of the above-bandgap light based off the RTE model. These values do not include reflection off the PV cell. Performance of a fluid filter can be compared to other filter designed using a common metric. The filter efficiency is defined as the percent absorbed below the bandgap minus the percent absorbed above the bandgap. This is given as

$$Eff = \%Subgap_{absorbed} - \%Above_{gap}_{absorbed} \quad (21)$$

In a perfect filter, the efficiency would be 100% sub bandgap absorbed and 0% above bandgap absorbed giving a filter efficiency of 100%. For the filter design described here, the efficiency is 80%-28% or 52%. This value includes losses from reflection off the glass containing the nanoparticle fluid and accounts for bandgap variations due to temperature fluctuations along the PV receiver.

Inclusion of back reflection off the PV into the model improved the filter to have 80% sub-bandgap absorption with an improved 82% above-bandgap transmission. Particle concentration was reduced in the model to account for the increased pathlength from back reflection in order to maximize transmission of above bandgap light to the PV. This resulted in an increased filter efficiency of 62%. This is only 3% less than the predicted filter performance using the theoretical and Lorentzian model. Resulting absorption, transmission, and reflection of the filter at a temperature of 80 ° C are given in Fig. 12 (a) with the absorbed solar spectrum given in (b). The increased IR absorption from back reflection is observed by the jump in the absorption spectra at the bandgap at 894 nm. It is noted, that increased visible absorption in the fluid is not necessarily detrimental to the hybrid CPV/T system. Since this light is converted

into heat, the energy is not lost, but is rather used as dispatchable energy instead of immediate electrical energy from PV.

Fig 12. Measured fluid mixture spectral (a) absorption, transmission, and reflection and (b) solar absorbance optimized for a GaAs PV cell.

For the cSi cell, the spectra from the gold nanospheres and ITO particles were inserted into the RTE model to determine absorbed and transmitted solar energy. It was found that the particle combination was capable of absorbing 80% of the energy for wavelengths shorter than 600 nm and longer than the bandgap while transmitting 76% of light between 600 nm and the bandgap when including back reflection off the cSi. Results of the RTE model are shown in Fig. 13 giving spectral absorption, reflection, and transmission (a) and plotting the solar spectrum along with the absorbed spectrum (b). This analysis showed that the filter efficiency was 56%. This is lower than the GaAs designed filter due to the lower back reflection off the cSi module and the lack of a particle absorbing between the temperature dependent band edge at approximately 1,150 nm and the ITO absorbance. However, simulations showed that adding a nanorod to this region did not improve filter efficiency (data not shown).

Figure 13. Measured fluid mixture spectral (a) absorption, transmission, and reflection and (b) solar absorbance optimized for a cSi PV cell.

Comparison was made between performances of this filter against other designs present in the literature. While limited experimental data exists in the literature for direct comparison, a few theoretical works have been published using nanoparticle fluid filters. One work reported theoretical nanoparticle fluids for various PV materials. While GaAs was not optimized for in Ref. [44], the best case was found for Ge with a theoretical filter efficiency of 67.1% [44]. Other PV materials in Ref. [44] were found to have theoretical efficiencies between 55% and 65%. However, theoretical results in Ref [44] depend on the use of core-shell particles, which can be difficult to achieve experimentally with shell thicknesses below approximately 10 nm as required to achieve theoretical filters [45] and did not include all of the optical loss terms included here. This work uses nanorods as opposed to nanoshells owing to the higher consistency in size distribution and ability to experimentally control optical properties. Theoretical work for idealized nanorods and ITO in Duratherm S optimized for GaAs previously showed a theoretical filter efficiency of 68% [19]. This work has shown that experimentally created fluid filters have an efficiency that is only 6% less than optimized and idealized theoretical nanoparticles.

Conclusion

A nanoparticle fluid filter for solar filtration was built and characterized. Modeling of experimental spectra allowed calculation of reflection, absorption, and transmission through the synthesized nanoparticle fluid mixture. It was observed that a filter efficiency of 62% was obtained for nanoparticles optimized for GaAs for a low wavelength pass design. The nanoparticle filter optimized for cSi for a bandpass scenario was observed to have an efficiency of 56%. These values are comparable to previous theoretical works and are among the first experimentally measured value for solar filtration using nanoparticles, especially considering the realities of the incoming solar flux being distributed angularly and the reflection from the

glass channels. The filter is designed for trough concentrators, but can be utilized in many systems requiring selective filtration of light.

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