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Integrating up-conversion nanoparticle films to maximize photovoltaic power output

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Article Open Access Published	ABSTRACT
	Silicon-based photovoltaic (PV) panels are key technologies

Keywords

- Clean energy
- Sustainable technology
- Photovoltaic system
- Nanoparticle thin film
- Solar energy efficiency

technologies in the pursuit of sustainable energy solutions, yet enhancing their efficiency remains a significant challenge. The mismatch between the solar irradiance spectrum and the absorption spectrum of silicon results in a considerable loss of useful solar energy. In addition, the absorption of infrared radiation by PV panels leads to thermal buildup, which further reduces the power output over time. This study proposes the development of a lightconversion film incorporating up-conversion nanoparticles (UCNPs) to enhance the efficiency of PV panels. Lanthanide-based UCNP, NaYF4³⁺/Er³⁺, were selected for their ability to convert near-infrared (NIR) light into visible light, thereby converting otherwise wasted thermal energy into usable electrical energy. UCNPs convert energy through their intrinsic material properties, exhibiting good photostability, which is critical for long-term applications, thereby potentially reducing the overall cost of solar energy production. As a proof of concept, the UCNPs were incorporated into a fluoropolymer matrix (FEVE) and applied to transparent 3M films, which were subsequently tested across different days on silicon-based PV panels at the roof of the campus building at SIT@Dover between the period of May to July 2024. The matrix and films were chosen for their optical transparency and ease of application onto PV panels. Material characterization of the UCNP-coated films showed an optimal intersection between optical transparency and upconverted emission intensity at a 10% concentration of UCNP. From empirical testing, the mixture of blue and green-emitting UCNPs delivered the best performance in terms of consistent power generation. Notably, the 10% green-emitting UCNP film outperformed the other configurations during peak sunlight, yielding power increases of 3.52% and 3.48%, respectively. When the UCNP-coated film's performance was isolated from the substrate film, improvements were more pronounced, with gains of 9.74% and 9.69%, suggesting that better performance can be achieved if the UCNP is directly incorporated into the PV panel. Assuming that a 9% increment in power generation can be achieved on a large scale, the estimated levelized cost of electricity (LCOE) can be reduced from SGD\$1.31 to SGD\$1.16. As part of future work, the UCNPs will be incorporated directly into the glass of PV panels or as an additional coating layer above the Silicon cells. This study contributes to the ongoing development of photovoltaic technologies, providing a practical solution to improve panel performance and support the global transition toward more efficient and sustainable energy systems.

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1. Introduction

Renewable energy sources, especially solar power, have become increasingly critical in the global pursuit of sustainable energy solutions and the mitigation of climate change. Solar energy, which is both abundant and renewable, offers a potential pathway for reducing dependence on non-renewable energy sources like fossil fuels and limiting the environmental damage associated with their consumption. Among the different available solar technologies, photovoltaic (PV) technology, which directly converts light energy into electricity, has seen substantial advancements over the past few decades [1].

Silicon-based solar cells, in particular, dominate the market due to their well-understood physics, relatively low production cost, and high efficiency when compared to other materials. However, silicon solar cells face inherent limitations in their efficiency, and various strategies have been explored to enhance their performance. Current state-of-the-art silicon solar cells have made notable progress in terms of light energy conversion efficiency, with laboratory cells achieving efficiencies exceeding 26% and commercial PV modules typically reaching between 15% to 22% efficiency under standard test conditions. This marks a substantial improvement over earlier generations. However, silicon solar cells, like all single-junction solar cells, are limited by a phenomenon known as the Shockley-Queisser limit, which defines the theoretical maximum efficiency of a single-junction photovoltaic device under ideal conditions.

For silicon with a bandgap of approximately 1.1 eV, the upper limit of efficiency is around 33% under direct sunlight. This limit arises from the fundamental physics of energy conversion, where only photons with energy equal to or greater than the material's bandgap can be absorbed, and excess energy is lost as heat.



Additionally, the limit accounts for losses due to the recombination of charge carriers and the inability to fully utilize lower-energy photons, particularly in the infrared spectrum [2].

Furthermore, there is a mismatch between the absorption spectrum of silicon and the solar emission spectrum [3]. Silicon absorbs photons primarily in the visible to near-infrared (NIR) range, but it does not efficiently absorb lower-energy photons in the infrared region because their energy is insufficient to promote the electrons across the bandgap.

Conversely, high-energy photons like ultraviolet light can be absorbed, but the excess energy beyond the bandgap of silicon is lost as heat through the thermalization process, where photogenerated charge carriers relax to the conduction band. This loss of excess energy reduces the overall efficiency of the solar cell, as it cannot be converted into useful electrical power.

One promising approach to overcoming these limitations is to broaden the effective absorption spectrum of silicon solar cells. Upconversion, an anti-Stokes process, where low-energy photons (typically in the NIR or infrared region) are absorbed by a material and, through a series of excited-state transitions, are re-emitted as higherenergy photons (usually in the visible or ultraviolet range). This phenomenon allows previously unutilized infrared photons to be converted into higher-energy visible light, which can then be absorbed by silicon.

Upconversion nanoparticles (UCNPs), which are typically doped with rare-earth elements such as lanthanides (e.g., erbium, ytterbium, or thulium), are characterized by their ability to absorb multiple low-energy photons and re-emit them as a single, higher-energy photon.

The unique optical properties of these nanoparticles, such as their ability to selectively absorb and emit light at different wavelengths, make them well-suited for enhancing the performance of silicon solar cells [4].

UCNPs consist of a host matrix, typically NaYF₄ doped with lanthanide ions, chosen for its stability and crystal structure. The key feature of these nanoparticles is their ability to undergo multiphoton absorption, where two or more low-energy photons are absorbed and subsequently upconverted into a single higher-energy photon.

For example, a combination of NIR photons might excite the UCNPs to an energy level that allows them to emit visible light. This process is facilitated by the unique electronic properties of the lanthanide ions, which can absorb and re-emit light at specific wavelengths due to the unique 4f-4f transitions inherent to lanthanide elements [5].

These UCNPs can be integrated into photovoltaic devices in various ways. By converting infrared or near-infrared photons, which silicon cannot efficiently absorb, into higher-energy visible or near-ultraviolet photons, UCNPs enable silicon solar cells to capture a broader range of the solar spectrum. This effectively reduces the

energy loss due to the spectral mismatch between the solar spectrum and silicon's absorption properties. UCNPs can also serve as a light-trapping layer in silicon solar cells. Due to their nanoscale size, UCNPs can scatter light within the solar cell, increasing the effective optical path length. This enables more light to interact with the silicon material, improving the probability of photon absorption and enhancing the overall performance of the solar cell [6]. UCNPs are known for their exceptional photostability, with the capability to withstand prolonged exposure to sunlight without significant degradation in their ability to absorb and emit light.

This property makes them ideal for long-term use in outdoor solar energy applications, where durability and longevity are crucial [7]. UCNPs can be synthesized in a variety of shapes and sizes, providing flexibility in how they are integrated into existing solar cell architectures. They can serve as filler particles in the Ethylene-vinyl acetate (EVA) matrix, which normally serves as the encapsulant in the silicon solar module to bind the different layers together and protect the solar cells from overstressing, cracking, and environmental effects.

Alternatively, they can be spray coated onto solar cells with solvent such as Polyvinyl Alcohol (PVA) before encapsulation with EVA. The addition of UCNPs to solar cells does not require significant alterations the manufacturing process, therefore potentially cutting down the cost of producing electrical energy.

The integration of UCNPs into silicon-based solar cells holds the potential to significantly enhance their efficiency, potentially pushing their performance beyond the traditional Shockley-Queisser limit for single-junction cells. This could have profound implications for the future of solar energy, offering a pathway to more efficient, costeffective, and scalable solar technologies.

Moreover, as UCNPs are composed of abundant and non-toxic materials (such as lanthanides), their use in solar cells aligns with the broader goal of developing environmentally friendly and sustainable energy solutions. The ability to harness a larger portion of the solar spectrum would also contribute to reducing the amount of silicon material required to achieve a given power output, potentially lowering production costs and further driving the adoption of solar power.

In summary, the application of upconversion nanoparticles represents a promising strategy for improving the efficiency of silicon-based solar cells. By addressing the spectral mismatch and thermalization losses inherent in traditional photovoltaic systems, UCNPs can significantly broaden the range of wavelengths that contribute to power generation, thereby increasing the overall energy conversion efficiency.

As research into UCNPs continues and new manufacturing techniques are developed, their integration into nextgeneration solar technologies could play a critical role in meeting the world's growing energy demands while mitigating climate change. This work seeks to develop a simple method to apply UCNPs to commercial solar PV panels as a proof of concept to demonstrate the ability of UCNPs to enhance solar power generation efficiency.

2. Materials and methods

2.1. UCNP synthesis

99% purity lanthanide oxides Ytterbium (Yb2O3) and Erbium (Er2O3) were obtained from Jiayuan Advanced Materials and reacted with 1 M Hydrochloric Acid (HCl) to convert them to chlorides. High-purity lanthanide chloride hexahydrates of Yttrium (YCl3·6H2O) and Thulium (TmCl3·6H2O) were obtained from Sigma-Aldrich and Shanghai Aladdin Biochemical Technology Co. Ltd., respectively. Reagent grade >99.0% Sodium Chloride (NaCl) from Sigma-Aldrich, Ammonium Fluoride (NH4F) from Fisher Chemicals and Polyethyleneimine, branched (PEI) from Acros Organics were also used in the synthesis. These chemicals were used without further treatment or purification.

The synthesis of NaYF4:Yb3+/Er3+ was modified from the methods published in literature [8]. NaYF₄: Yb,Er upconversion nanoparticles were synthesized using a hydrothermal method. In this process, the appropriate molar concentrations of the constituent lanthanide chlorides were introduced into a precursor solution.

The solution was subsequently transferred to a hydrothermal autoclave, which was sealed and heated in an oven at 200°C for 2 hours to facilitate nanoparticle formation. After the reaction, the UCNPs were retrieved, thoroughly washed several times with water and ethanol to remove impurities, and then dried. The final nanoparticles were collected for further characterization and testing.

The synthesized UCNPs are named based on their dominant upconverted emission wavelengths. Specifically, UCNPs exhibiting red emission are labeled as R-UCNPs, those emitting green are designated as G-UCNPs, and those with blue emission are referred to as B-UCNPs, and so on.

2.2. Characterization

The synthesized upconversion nanoparticles (UCNPs) were characterized using a JEOL JSM IT300LV Scanning Electron Microscope (SEM) to examine the morphology of the crystalline structure. UCNP films were then fabricated for further analysis, with their optical transmittance measured using a UV-Vis spectrophotometer across the wavelength range of 300 nm to 2000 nm.

Additionally, the same films were subjected to infrared (IR) laser illumination, and the upconverted emission spectral intensity was recorded using an Ocean Insight QEPro High-Performance Spectrometer. This comprehensive characterization approach allowed for a detailed assessment of both the structural and optical properties of the UCNP films.

2.3. Film coating

The upconversion nanoparticles (UCNPs) were incorporated into a Fluoroethylene vinyl ether (FEVE) resin and subsequently roll-coated onto transparent polyethylene terephthalate (PET) films. Both the FEVE resin and the PET film substrates were selected for their high optical transmittance and superior durability, ensuring the stability and effectiveness of the UCNP-coated films under various environmental conditions.

2.4. PV testing setup

Three 60W silicon solar panels were prepared for outdoor testing, with each panel incorporated into a test setup consisting of a photovoltaic (PV) panel, a charge controller, a 12V lead-acid battery, and an LED floodlight. The current drawn by the LED floodlight was intentionally chosen to exceed the output of the solar panel, thereby maintaining the system in bulk charging mode.

This configuration was designed to ensure maximum charging current, irrespective of weather conditions, and to prevent the solar panel from transitioning into absorption or float mode, conditions under which the current collected would be limited. Two of the test setups were coated with upconversion nanoparticle (UCNP) thin films and placed outdoors on the roof of the SIT@Dover campus for the duration of the study.

The testing period lasted from May to July 2024, during which samples were replaced after triplicate data sets were collected for each configuration. Testing data was primarily logged during peak sun conditions between 11.30 am to 1.30 pm. To ensure consistency and facilitate comparison across different testing days, one panel was designated as the reference, and all subsequent data were normalized relative to this reference panel.

3. Results and discussion

The lanthanide-based upconversion nanoparticles (UCNPs) were synthesized using the procedures outlined previously. The as-synthesized UCNPs were characterized by Scanning Electron Microscopy (SEM) to assess their morphology and size distribution, as depicted in Figure 1(a).

Analysis of the SEM image revealed that the nanoparticles exhibit an average length of $1.622 \mu m$ and an average width of 439.89 nm. The particles show a predominantly uniform shape with a relatively narrow size distribution, indicating that the synthesis method yields well-defined and homogeneous nanoparticles.

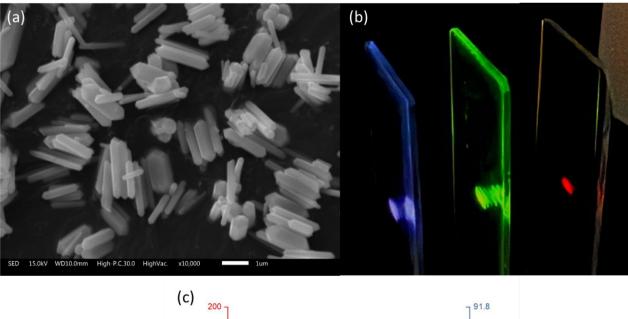
The UCNPs were incorporated into FEVE resin and irradiated with an infrared (IR) laser powered by a 0.8 A current source. Although the IR light is not visible to the naked eye, the UCNP-coated films effectively converted the IR light into visible emission. By varying the concentrations of the lanthanide ions during synthesis, red, green, and blue emissions were achieved, as shown in Figure 1(b).

This demonstrates that the upconverted emission can be tuned across the visible spectrum, indicating that, with further optimization, it may be possible to finely adjust the upconverted wavelengths to match the absorption spectrum of silicon, potentially enhancing the efficiency of silicon-based photovoltaic systems.

UCNP film samples were prepared with concentrations of 5, 10, and 15 wt% of UCNPs in FEVE resin and characterized using a UV-Vis spectrophotometer to measure the optical transmittance of light through the films across the wavelength range of 300 nm to 2000 nm. The same films were subsequently irradiated with an IR laser, and the intensity of their upconverted emission was recorded under identical laser power conditions. The transmittance in the visible region was then averaged and tabulated according to UCNP concentration and compared with the intensity of the upconverted emission.

The intersection of the average visible transmittance and the upconverted emission intensity, as shown in Figure 1(c), was used to determine the optimal concentration of UCNPs in the film for maximizing performance.

Based on the optimal concentration derived from these characterization tests, the subsequent films that were prepared for outdoor testing are all made with 11 wt% concentration of UCNPs in FEVE.



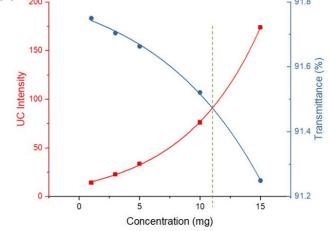


Figure 1. (a) SEM of the synthesized UCNPs (b) Upconverted emission photographs of the synthesized UCNPs, showing red, green, and blue visible emission when irradiated by an IR laser (c) Comparison of the upconverted photoemission intensity and the average transmittance in the visible range of light.

Figure 2(a) illustrates a photograph of the UCNP film, demonstrating its high optical transparency. Films of up to 1.5m in length have been fabricated in the lab, with excess

being made for characterization purposes. Figure 2(b) depicts the actual test setup located on the roof of SIT@Dover, comprising three identical configurations as detailed in the materials and methods section. The experimental setup includes a Fluke NORMA 6004 Portable Power Analyzer, a 4-channel device utilized for recording voltage and current data. Voltage and current probes are directly attached for measurements, and a current clamp sensor, calibrated prior to each test, is connected to each solar panel setup to accurately measure current flow. Figure 2(c) provides a schematic of the connections and components used in the physical setup. Each of the solar PV panels is connected to the Maximum Power Point Tracking (MPPT) controller, a storage battery, and an LED flood light, which serves as a load to discharge the stored power (to avoid saturation of battery storage). Additionally, two TanD

MCR-4TC Thermocouple Loggers, each with a 4-channel temperature logging capacity, were employed to monitor the surface temperatures of all three setups concurrently. Simultaneously, a HOBO MX1101 Temperature/Relative Humidity Data Logger was deployed to record ambient temperature and relative humidity conditions. Before the commencement of each experimental run, all three photovoltaic panels were configured to measure the temperature and power generated without the application of any films or coatings. This control test was essential to minimize any variations in hardware performance or external environmental factors, ensuring the accuracy of subsequent measurements.

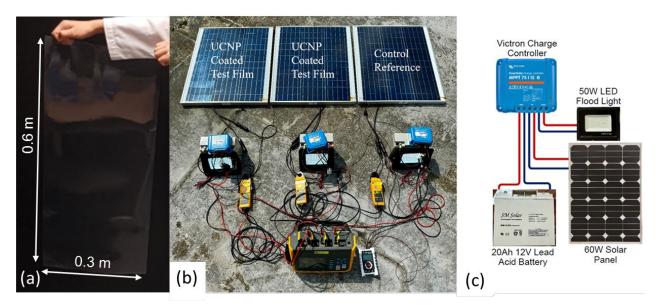


Figure 2. (a) Photo of UCNP film demonstrating high optical transparency (b) Physical testing setup (c) Test setup components used and electrical connections.

Three UCNP samples were synthesized based on their upconverted emission wavelengths, with two mixtures prepared for further analysis. The first mixture, composed of R-UCNP and G-UCNP in a 1:1 ratio, is designated as RG-UCNP. The second mixture, consisting of G-UCNP and B-UCNP in a 1:1 ratio, is labeled as GB-UCNP.

These mixtures were designed with the aim of maximizing the upconverted emission spectrum to better match the absorption range of silicon solar cells, thereby converting unused infrared wavelengths into useful visible light that can be absorbed by the cells.

Table 1:	Average power	generated	by eacl	n PV setup.
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			Change Com-
	Average	Change Cor	n- pared to Un-
Setup	Power	pared to Co	ntrol coated Film
Control	40.68 W	-	6.01 %
Uncoated Film	38.38 W	-5.66 %	-
G-UCNP Film	42.10 W	3.48 %	9.69 %
GB-UCNP Film	42.11 W	3.52 %	9.74 %
RG-UCNP Film	39.17 W	-3.72 %	2.07 %

The UCNP mixtures were then incorporated into FEVE resin and coated onto PET films as 50 μ m thin layers. As

shown in Figure 3(a), the UCNP films exhibit characteristic emission peaks corresponding to the lanthanide concentration used during their synthesis. The G-UCNP film displays prominent peaks at 650 nm and 540 nm, which correspond to red and green light, respectively. In contrast, the GB-UCNP films exhibit an additional peak at 470 nm, corresponding to blue visible emission.

The RG-UCNP film shows relatively weaker emissions at 650 nm and 540 nm compared to the G-UCNP film. This attenuation in emission intensity can be attributed to the non-synergistic interaction between the R-UCNP and G-UCNP components, which both emit at similar wavelengths, leading to mutual suppression of the overall emission intensity.

In terms of photovoltaic performance, the GB-UCNP and G-UCNP films demonstrated power increases of 3.52% and 3.48%, respectively, compared to the control, and 9.74% and 9.69%, respectively, compared to the uncoated film. Conversely, the RG-UCNP film resulted in a decrease in power generation.

This can be explained by the photoemission spectra presented in Figure 3(a). While the GB-UCNP film

exhibited a synergistic combination of upconverted emissions, leading to an expanded emission spectrum, the RG-UCNP mixture did not show such a synergistic effect. The lack of spectral expansion in the RG-UCNP film is directly reflected in the observed decrease in power generation, highlighting a clear correlation between the composition of UCNPs in the film and the resultant power enhancement for the photovoltaic panels.

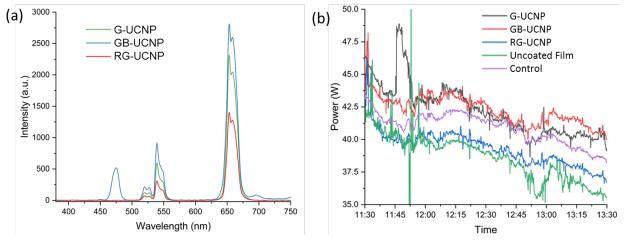


Figure 3. (a) Upconverted emission spectrums of the mixed films (b) Normalized power generated by PV panels coated with various UCNP films.

4. Feasibility of commercial application

As demonstrated in this work, the incorporation of UCNP into photovoltaic setups can be as simple as mixing UCNP (in powder form) directly into a transparent resin material that can be coated directly onto any applicable surface. Using mechanical mixing, the UCNP was incorporated into FEVE resin in desired quantities and roll coated onto PET films for ease of handling.

The use of substrate films was selected to facilitate sample changes throughout the experimental period. Once the optimal concentration and composition of UCNPs are determined, the UCNP-infused resin can be directly applied to the surfaces of photovoltaic panels. This method effectively minimizes any potential heat-trapping effects that could result from air gaps between the coating films and the PV surface.

Alternatively, UCNPs can be integrated during the PV panel production process. Potential approaches include incorporating the UCNPs directly into the glass of the PV panel or applying a thin layer of UCNPs above the silicon layer prior to panel sealing.

Integrating UCNPs at the production stage offers the potential to further enhance photovoltaic efficiency by amplifying both the upconversion and light scattering effects. This approach could mitigate the thermalization effect and increase the likelihood of light absorption by the silicon cells, thereby improving overall power generation performance.

A critical factor for the commercialization of this technology is its cost-effectiveness, which can be assessed using the Levelized Cost of Electricity (LCOE). The LCOE is a key metric that quantifies the per-unit cost (typically expressed in \$/kWh) of electricity generated by a particular energy source over its operational lifetime. It accounts for all associated costs, including those related to the construction, operation, maintenance, and decommissioning of the system, as well as any capital or financing costs. The LCOE is calculated by dividing the total lifetime costs of the energy project by the total amount of electricity expected to be generated during the system's lifespan. A lower LCOE signifies a more cost-efficient energy generation system, making it an essential parameter for comparing the economic viability of different energy technologies, such as solar, wind, or fossil fuels.

Based on the findings of this study, if a 9% improvement in power generation efficiency is realized, the LCOE is estimated to decrease from SGD\$1.31 to SGD\$1.16, indicating a potential reduction in the cost of solar energy production [9]. Further cost reductions can potentially be achieved if the UCNPs can be directly incorporated into the PV production process.

5. Conclusion

This study investigated the UCNPs to enhance the efficiency of silicon-based photovoltaic (PV) panels by converting near-infrared (NIR) light into visible light, thereby reducing energy loss and thermal buildup. Lanthanide-based $NaYF_4^{3+}/Er^{3+}$ UCNPs were incorporated into a fluoropolymer matrix (FEVE) and applied to transparent 3M films, which were tested on PV panels at SIT@Dover between May and July 2024. The UCNP-coated films demonstrated optimal performance at a 10% concentration, showing power increases up to 9.74%, suggesting that directly incorporating UCNPs into PV panels could further improve efficiency.

Assuming a potential 9% increase in power generation, the levelized cost of electricity (LCOE) can be decreased

from SGD\$1.31 to SGD\$1.16. Future work will explore integrating UCNPs directly into PV glass or as a coating layer, offering a promising solution for more efficient and cost-effective solar energy production.

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