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Multifunctional photon conversion materials for enhancing silicon solar cells

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Abstract

A type of multifunctional erbium (Er³⁺) and ytterbium (Yb³⁺) codoped NaY(WO₄)₂ phosphors, with simultaneous photon upconversion, photon quantum cutting, and luminescence ratiometric temperature sensing abilities, have been developed, opening up new possibilities for high-performance silicon solar cells.

As traditional fuel sources (coal, oil, and natural gas) continue to deplete on a global scale, there is a surging demand for renewable energies. The Sun irradiates Earth with 120,000 terawatts of power, while humans consume only 15 terawatts globally. Solar cells have demonstrated significant potential by converting sunlight into electricity through the photovoltaic effect.

Silicon solar cells (SSCs), based on crystalline or polycrystalline silicon, dominate the world photovoltaic market, constituting ~95% of the total global production in 2022¹. Despite their market dominance, the power conversion efficiency of industrially produced solar modules is within a marginally acceptable range of 18–22% under standard test conditions (Air Mass 1.5). The theoretical maximum efficiency for single-junction SSCs, with a bandgap (E_g) of 1.1 eV, is ~30% according to the Shockley-Queisser limitation². The primary challenge lies in the significant loss of 70% of Sun energy irradiated to the photovoltaic device, which is attributed to the spectral mismatch between the solar terrestrial spectrum and the absorption spectrum of silicon semiconductor. This mismatch involves thermalization relaxation of photoexcited 'hot' charge carriers (electron/hole) to the band edges (both the conduction band (for the electron) and the valence band (for the hole)) (thermalization loss) and the transmission of photons with energies below the bandgap

of the silicon (transmission loss). In other words, spectral mismatch results in the under-utilization of harvested ultraviolet light (<530 nm, ~149 W m⁻²) as well as the non-utilization of transmitted infrared light (>1100 nm, ~164 W m⁻²)³. Advances in SSCs are urgently needed to increase the performance and reduce the cost of harvesting solar power.

Photon upconversion and quantum-cutting materials present a promising solution to address the spectral mismatch challenge in SSCs by effectively managing the solar spectrum. Upconversion involves the conversion of two or more sub-bandgap infrared photons into a single above-bandgap photon, generating useful photoexcited electron-hole pairs. A detailed balance model, as proposed by Trupke et al., predicts the efficiency limits of a solar cell with an upconverter placed beneath a bifacial solar cell and a perfect reflector at the upconverter's rear surface. The calculated maximum efficiency reaches 50.69% at a bandgap (E_g) of 2 eV and 40.2% at $E_g = 1.1$ eV (silicon bandgap) under unconcentrated terrestrial Air Mass 1.5 incident light, surpassing the Shockley-Queisser limitation⁴.

On the flip side, quantum cutting is a reverse process to upconversion, in which a high-energy photon is split into two (or more) lower-energy photons. The photoluminescence quantum yields of quantum cutting materials theoretically can exceed 200%, showcasing promise for applications in light-emitting diodes and solar cells^{5–8}. For solar cells, this implies that one ultraviolet photon can produce two electron-hole pairs, thereby enhancing

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power conversion efficiency. Predictions indicate that mounting a photon quantum cutting layer on the front surface of a conventional single-junction SSCs could achieve a maximum power conversion efficiency of up to 38.6%, exceeding the Shockley-Queisser limitation^{9,10}. Importantly, the application of spectral converting layers does not necessitate alterations to the existing solar cell device structure. As a result, there is a growing demand for phosphors with both upconversion and quantum cutting capabilities to address the spectral mismatch problem in current SSCs.

Furthermore, the in-situ temperature measurement of operating SSCs is imperative. This is particularly true due to the potential temperature escalation caused by high-intensity sunlight exposure, which may result in decreased photovoltaic output or even module failure¹¹. Luminescence nanothermometry, especially the one based on the sharp luminescence of lanthanides, provides a means for precise monitoring of local heat dissipation. This monitoring occurs at high spatial resolution, reaching down to the nanoscale, and allows for remote detection without the need for physical contact between probes and detectors¹².

The development of phosphors with upconversion and quantum cutting abilities, along with effective temperature probing, is therefore on demand to significantly enhance the performance of SSCs. This need was not successfully addressed until recently in a study published in *Light: Science & Applications* by Gao et al. where they introduced a multifunctional phosphor, erbium (Er³⁺), and ytterbium (Yb³⁺) doped NaY(WO₄)₂¹³.

Intense and nearly-pure emission from Yb³⁺ under 378 nm excitation was observed due to a concentration-dependent quantum cutting process, as depicted in Fig. 1. A set of singly Er³⁺-doped NaY(WO₄)₂ phosphors experiments illustrated that photoexcitation at 378 nm, matching the ground state absorption of ²I_{15/2} → ⁴G_{11/2}, exclusively produced intense 530/552 nm emissions at the ²H_{11/2}/⁴S_{3/2} energy levels, respectively, with negligible emissions from the lower-lying ⁴F_{9/2} energy level. This observation indicates that the energy of absorbed photons within the energy levels between ²H_{11/2}/⁴S_{3/2} and ⁴G_{11/2} can all be entirely accumulated to the ²H_{11/2}/⁴S_{3/2} reservoir through multiphonon-assisted nonradiative relaxations. The cumulative addition of harvested ultraviolet photons to the appropriate energy level is a crucial step in maximizing the effectiveness of the photon quantum-cutting process. When fixing Er³⁺ dopant concentration at the optimized one (5%), codoping Yb³⁺ ions (from 0% to 50%) results a continuous increase of Yb³⁺ infrared luminescence at 1000 nm (²F_{7/2} → ²F_{5/2}), coinciding with a progressive decrease of 530/552 nm luminescence from the ²H_{11/2}/⁴S_{3/2} reservoir energy levels. In contrast, the emission from the ²H_{9/2} → ⁴I_{9/2} transition of Er³⁺, while

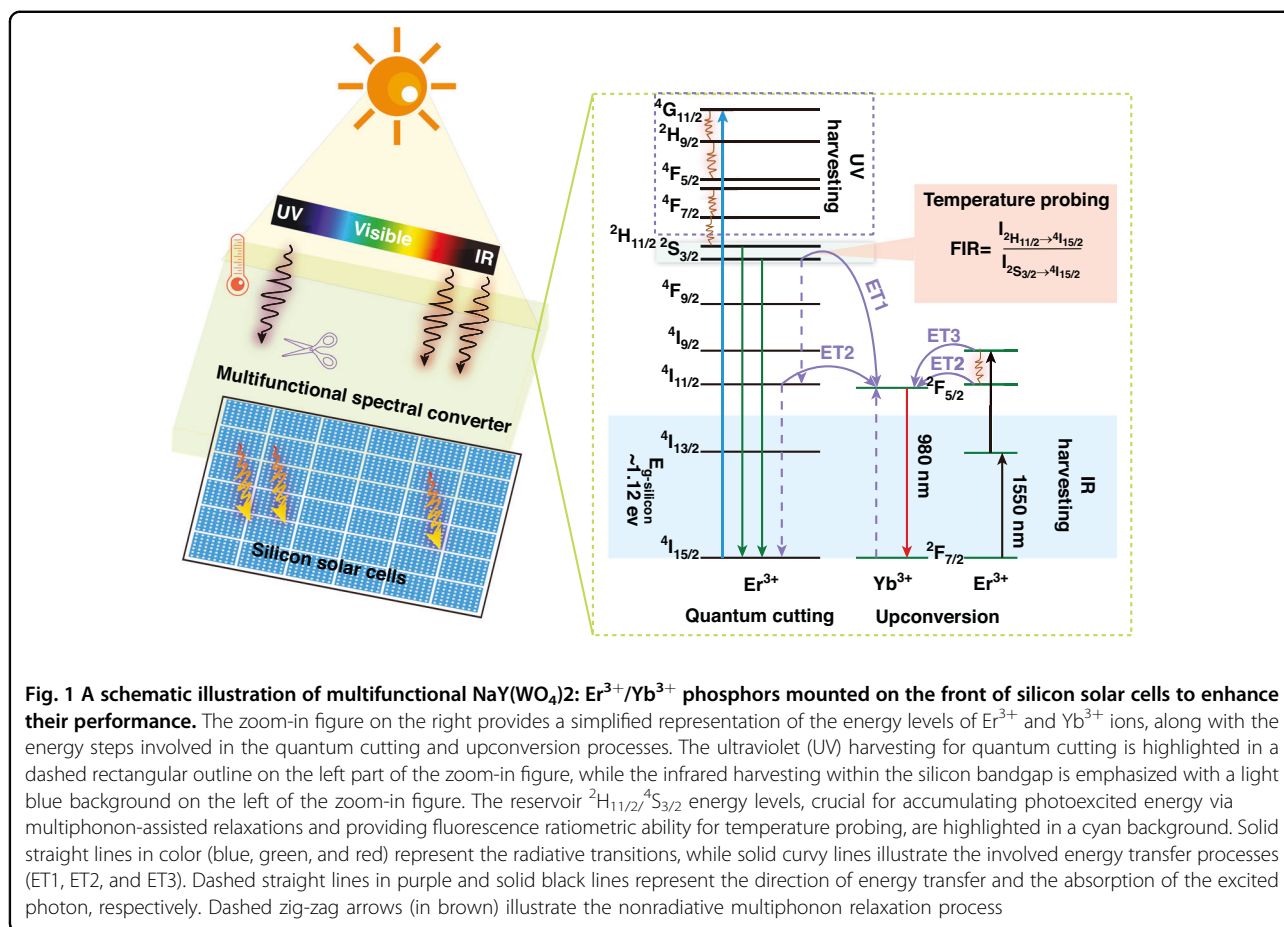
weak, remains constant. These results validate the presence of efficient energy transfer (ET1) process, which depopulates the ²H_{11/2}/⁴S_{3/2} energy levels of Er³⁺ and results in the simultaneous population of the ²F_{5/2} energy level of Yb³⁺ ions and the ⁴I_{11/2} energy level of Er³⁺ ions (Fig. 1). Radiative and nonradiative relaxations from the ⁴I_{11/2} energy level are expected to populate the ⁴I_{13/2} energy level, leading to amplified infrared emission at 1550 nm due to the ET1 process. However, a decrease in luminescence intensity at 1550 nm was observed, indicating the presence of the ET2 process. In this process, the Er³⁺ at the ⁴I_{11/2} energy level will transfer its excited energy to the ground state ²F_{7/2} of Yb³⁺, promoting the Yb³⁺ dopant to its excited ²F_{7/2} energy level. Judd-Ofelt calculations and experimental luminescence decay measurements were employed to elucidate the radiative rates, nonradiative rates, and energy transfer rates of all significant energy levels in Er³⁺ ions. These analyses unveiled an ultrahigh quantum cutting efficiency of 173%.

It has been established that, under 1550 nm excitation, singly Er³⁺-doped materials exhibit upconversion luminescence at 1000 nm, originating from the ⁴I_{11/2} → ⁴I_{15/2} transition. The ⁴I_{11/2} energy level is populated through a two-photon upconversion process, wherein a ground state absorption of the excitation photon populates the ⁴I_{13/2} energy level. Subsequently, energy transfer from another Er³⁺ ion at the ⁴I_{13/2} energy level can further elevate the Er³⁺ ion from the ⁴I_{13/2} energy level to the ⁴I_{9/2} energy level. This is followed by multiphonon-assisted relaxation, ultimately leading to the population of the ⁴I_{11/2} energy level. The efficient ET2 process found in quantum cutting process results in the intense emission of Yb³⁺ at 1000 nm through the ²F_{5/2} → ²F_{7/2} radiative relaxation. This is substantiated by the observation that the presence of Yb³⁺ ions results in 20-fold increase at 1000 nm, in comparison to the singly Er³⁺-doped NaY(WO₄)₂ phosphors. Note that while the ET3 process is not explicitly mentioned, it cannot be ruled out as a contributor to the population of Yb³⁺ ions at the ²F_{5/2} energy level.

The intensity ratio of luminescence at 530/552 nm for the ²H_{11/2}/⁴S_{3/2} reservoir energy levels has been well established to be very sensitive to local temperature change. The fluorescence intensity ratio (FIR) of $I_{2H_{11/2} \rightarrow 4I_{15/2}} / I_{4S_{3/2} \rightarrow 4I_{15/2}}$ can be expressed as¹⁴:

$$FIR = \frac{I_{2H_{11/2} \rightarrow 4I_{15/2}}}{I_{4S_{3/2} \rightarrow 4I_{15/2}}} = N \exp\left(\frac{-\Delta E}{kT}\right) \quad (1)$$

where $I_{2H_{11/2} \rightarrow 4I_{15/2}}$ and $I_{4S_{3/2} \rightarrow 4I_{15/2}}$ are the integrated intensities of emission bands centered at 530 and 552 nm, respectively; N is a constant, ΔE is the energy gap between the thermally coupled energy levels ²H_{11/2} and ⁴S_{3/2}, k is Boltzmann's constant, and T is the absolute temperature. Precise temperature measurements were conducted within



the range of 300–720 K, revealing a maximum absolute temperature sensitivity of $\sim 0.01 \text{ K}^{-1}$ at 443 K and maximum relative temperature sensitivity of 0.01 K^{-1} at 300 K. Given that solar cells typically operate at temperatures lower than 573 K (300 °C) to prevent damage, the developed $\text{NaY}(\text{WO}_4)_2:\text{Er}^{3+}/\text{Yb}^{3+}$ runs within this temperature range (300–573 K), exhibiting absolute and relative sensitivities approximating their maximum values. This observation aligns with the limited thermal quenching of the overall intensity of the ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2}$, decreasing by only 25.8% when elevating temperature from 300 K to 720 K.

While various upconverting, quantum-cutting materials, and temperature sensors have been individually explored to enhance the performance of SSCs^{15–19}, this study marks the first introduction of a multifunctional photon conversion material, $\text{NaY}(\text{WO}_4)_2:\text{Er}^{3+}/\text{Yb}^{3+}$, combining all three modalities. This innovative approach holds the potential for synergistic effects to maximize the efficiency of industrially produced SSC modules without altering their existing structures. The exceptionally high quantum cutting efficiency (173%) of ultraviolet light, impressive upconversion of sub-bandgap photons, and high-temperature sensitivity are attributed to the

appropriate lattice phonon energy of the host material (900 cm^{-1}). This phonon energy is sufficiently high to facilitate effective accumulation of harvested ultraviolet energy to the ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2}$ reservoir energy level for quantum cutting and temperature sensing through multiphonon-assisted relaxations. Simultaneously, the lattice phonon energy is small enough (compared to the large energy gap of 3091 cm^{-1}) between the ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2}$ energy levels and the ${}^4\text{F}_{9/2}$ energy level to prevent further nonradiative relaxations at the reservoir energy levels. Importantly, the relatively large lattice phonon energy, compared to hexagonal sodium yttrium fluoride (350 cm^{-1}), plays a pivotal role in bridging an energy mismatch of $\sim 2200 \text{ cm}^{-1}$ in the first step ET 1 process to entail an efficient quantum cutting process.

Despite the significant progress made in this work, certain challenges still require further exploration. Firstly, there is a need for experimental confirmation or measurement of efficiencies for quantum cutting and upconversion processes, but quantifying the absorbance of lanthanide phosphors presents a challenge. Experimental determination of luminescence quantum efficiency will provide a solid basis for comparison among different

luminescent materials and evaluation for practical applications. Secondly, lanthanides have narrow and limited absorption properties in both the infrared and ultraviolet ranges, ~10-fold narrower and 10,000 times lower than those of organic dye molecules²⁰. This limitation poses a significant challenge for the practical application of lanthanide-based luminescent materials as spectral converters to enhance SSCs performance. However, coupling these phosphors with both infrared dyes to harvest light above 1100 nm and ultraviolet dyes to harvest light below 530 nm for sensitizing the upconversion and quantum-cutting processes holds great promise. This approach could potentially make these multifunctional phosphors more practical for bolstering the power conversion efficiency of SSCs beyond the Shockley-Queisser limit.

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References

- Razzaq, A., Allen, T. G., Liu, W. Z. & Wolf, S. D. Silicon heterojunction solar cells: Techno-economic assessment and opportunities. *Joule* **6**, 514–542 (2022).
- Shockley, W. & Queisser, H. J. Detailed balance limit of efficiency of p-n junction solar cells. *J. Appl. Phys.* **32**, 510–519 (1961).
- van der Ende, B. M., Aarts, L. & Meijerink, A. Lanthanide ions as spectral converters for solar cells. *Phys. Chem. Chem. Phys.* **11**, 11081–11095 (2009).
- Trupke, T., Green, M. & Würfel, P. Improving solar cell efficiencies by up-conversion of sub-band-gap light. *J. Appl. Phys.* **92**, 4117–4122 (2002).
- Wu, K., Li, H. & Klimov, V. I. Tandem luminescent solar concentrators based on engineered quantum dots. *Nat. Photon.* **12**, 105–110 (2018).
- Wei, M. et al. Ultrafast narrowband exciton routing within layered perovskite nanoplatelets enables low-loss luminescent solar concentrators. *Nat. Energy* **4**, 197–205 (2019).
- Cai, T. et al. Mn²⁺/Yb³⁺ codoped CsPbCl₃ perovskite nanocrystals with triple-wavelength emission for luminescent solar concentrators. *Adv. Sci.* **7**, 2001317 (2020).
- Lee, H. J. et al. Coherent heteroepitaxial growth of III-VI₂ Ag(In,Ga)S₂ colloidal nanocrystals with near-unity quantum yield for use in luminescent solar concentrators. *Nat. Commun.* **14**, 3779 (2023).
- Richards, B. S. Luminescent layers for enhanced silicon solar cell performance: Down-conversion. *Sol. Energy Mater. Sol. Cells* **90**, 1189–1207 (2006).
- Trupke, T., Green, M. A. & Würfel, P. Improving solar cell efficiencies by down-conversion of high-energy photons. *J. Appl. Phys.* **92**, 1668–1674 (2002).
- Dhimish, M. & Hu, Y. H. Rapid testing on the effect of cracks on solar cells output power performance and thermal operation. *Sci. Rep.* **12**, 12168 (2022).
- Jia, M. C. et al. Lanthanide-based ratiometric luminescence nanothermometry. *Nano Res.* **16**, 2949–2967 (2023).
- Gao, D. et al. Near infrared emissions from both high efficient quantum cutting (173%) and nearly-pure-color upconversion in NaY(WO₄)₂:Er³⁺/Yb³⁺ with thermal management capability for silicon-based solar cells. *Light Sci. Appl.* **13**, 17 (2024).
- Balabhadra, S., Debasu, M. L., Brites, C. D. S., Ferreira, R. A. S. & Carlos, L. D. Upconverting nanoparticles working as primary thermometers in different media. *J. Phys. Chem. C* **121**, 13962–13968 (2017).
- Richter, A., Hermle, M. & Glunz, S. W. Reassessment of the limiting efficiency for crystalline silicon solar cells. *IEEE J. Photovolt.* **3**, 1184–1191 (2013).
- Savin, H. et al. Black silicon solar cells with interdigitated back-contacts achieve 22.1% efficiency. *Nat. Nanotechnol.* **10**, 624–628 (2015).
- Battaglia, C., Cuevas, A. & De Wolf, S. High-efficiency crystalline silicon solar cells: status and perspectives. *Energy Environ. Sci.* **9**, 1552–1576 (2016).
- Yoshikawa, K. et al. Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%. *Nat. Energy* **2**, 17032 (2017).
- Cariou, R. et al. III-V-on-silicon solar cells reaching 33% photoconversion efficiency in two-terminal configuration. *Nat. Energy* **3**, 326–333 (2018).
- Wang, X. D. et al. Dye-sensitized lanthanide-doped upconversion nanoparticles. *Chem. Soc. Rev.* **46**, 4150–4167 (2017).