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A dual-functional NaLuF₄:Yb³⁺/Er³⁺ material for enhancing photon harvesting in dye-sensitized solar cells

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A new strategy to improve the efficiency of dye-sensitized solar cells by using the external near-infrared light harvesting and light-scattering dual-functional upconversion (UC) material NaLuF₄:Yb³⁺/Er³⁺ is proposed. The photoluminescence spectra of NaLuF₄:Yb³⁺/Er³⁺ showed the emission of green and red light, and these luminescence bands coincided well with the absorption wavelength of N719 dye. A small amount of UC material could serve as a good scattering material in photoelectrodes. The photoelectric conversion efficiency reaches 7.58% at a concentration of 5 wt% of UC (weight ratio of UC to TiO₂), which is 27.18% higher than that of P25 photoanode (5.96%) with similar thickness. This finding may be attributed to the UC luminescence and light scattering properties of the UC material.

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Introduction

Solar energy, an inexhaustible and clean energy source, has been considered as a replacement of non-renewable fossil energy. Dye-sensitized solar cells (DSSCs), which were first reported by Michael Grätzel in 1991,¹ attract considerable attention because of their low cost, possible use in fabricating flexible devices, and relatively good efficiency in photovoltaic conversion of solar energy.^{2–6} A high power conversion efficiency (η) of 14.3% for DSSCs was achieved by using an alkoxysilyl-anchor dye and a carboxy-anchor organic dye.⁷ A sandwich-structured DSSC consists of a transparent conducting oxide glass, such as fluorine-doped tin oxide (FTO) glass; a dye-adsorbed nanocrystalline semiconductor film (most commonly TiO₂); a platinum-coated counter electrode; and an electrolyte containing the I⁻/I³⁻ redox couple. A current is generated when a dye molecule (usually N719) absorbs a photon, enters an excited electronic state, and injects an electron into the conduction band of the metal oxide photoanode. The circuit is completed when the dye is regenerated through electron transfer by a redox system. The electrolyte system is reduced at the counter electrode. Most contemporary research has conducted in-depth related studies on different aspects, such as various morphologies of TiO₂,^{8–10} combining noble metal nanoparticle composite materials,^{11–13} and designing and synthesizing new dyes.^{7,14} Forty-six percent of the total solar energy delivered in the infrared (IR) region (>800 nm)¹⁵ is in the solar spectrum. However, the absorption

range of DSSC electrode with N719 dye as a sensitizer is mainly in the visible region (a maximum absorption range of the solar spectrum is 300–800 nm (ref. 16)), and the absorption of IR light utilization rate of sunlight is low, thereby restricting the power conversion efficiency of DSSC to a certain extent.

An advanced research hotspot improves the absorption of ultraviolet and IR spectrum in DSSCs. Rare earth ions have abundant f-orbital configurations and can exhibit sharp fluorescent emissions *via* intra-4f or 4f–5d transitions. Thus, the ions can absorb low-energy IR light and then emit high-energy visible light in a process called upconversion.¹⁷ Furthermore, the ions can broaden the range of spectral response and increase the utilization rate of light in solar cells.^{18–20} An efficient and stable fluorescent material consists of a host, a sensitizer and an activator. NaREF₄ (RE = rare earth), an important host rare earth fluoride material, has received increasing attention due to its low phonon energy, high chemical and thermal durability, and high efficiency.^{21–23} Moreover, Yb³⁺, which is an excellent sensitizer for the activators, has a high and broad absorption band. Er³⁺ as an activator is the most efficient rare earth ion because of its versatile energy levels in the IR region. The use of NaREF₄:Yb³⁺/Er³⁺ (UC) as a fluoride material is an emerging technique that can increase the efficiency of solar cells. The use of UC (*e.g.*, NaYF₄:Yb³⁺, Er³⁺) in DSSCs has recently been reported to enhance near-infrared (NIR) response. Chunze Yuan *et al.*²⁴ explored the use of colloidal UC nanocrystals as an energy relay material for photovoltaic devices and found that the UC nanocrystals of small size can serve as a scattering material to increase the light absorption capability of cells. Kim *et al.*²⁵ demonstrated enhanced efficiency from 9.02% of reference DSSCs to 10.76% by upconverting β -NaYF₄:Yb³⁺/Er³⁺ phosphor microcrystals as an additional phosphor-reflecting film. β -NaLuF₄ is a very

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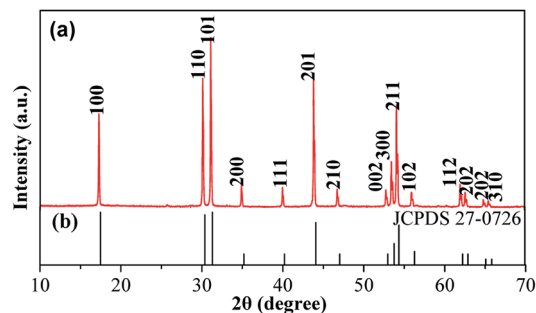


Fig. 1 (a) XRD patterns of the as-prepared NaLuF₄:Yb³⁺/Er³⁺ sample; (b) standard data of hexagonal β -NaLuF₄ (JCPDS 27-0726).

lattice, unit cell becomes larger, so the diffraction angle will decrease.^{28,29} In addition, the diffraction peaks were sharp, thereby suggesting that the prepared samples were highly crystalline. Furthermore, none of impurity peaks were observed, indicating the high purity of the final product, which is the key factor for UC fluorescing.

The as-prepared NaLuF₄:Yb³⁺/Er³⁺ sample of the structure and morphology of the product were observed through SEM and TEM. The SEM image (Fig. 2A and B) clearly indicates that the sizes of the UC materials with a smooth surface are in the range of 200–300 nm. Fig. 2C and D indicate the TEM image of the as-prepared UC materials, which further confirms that the as-

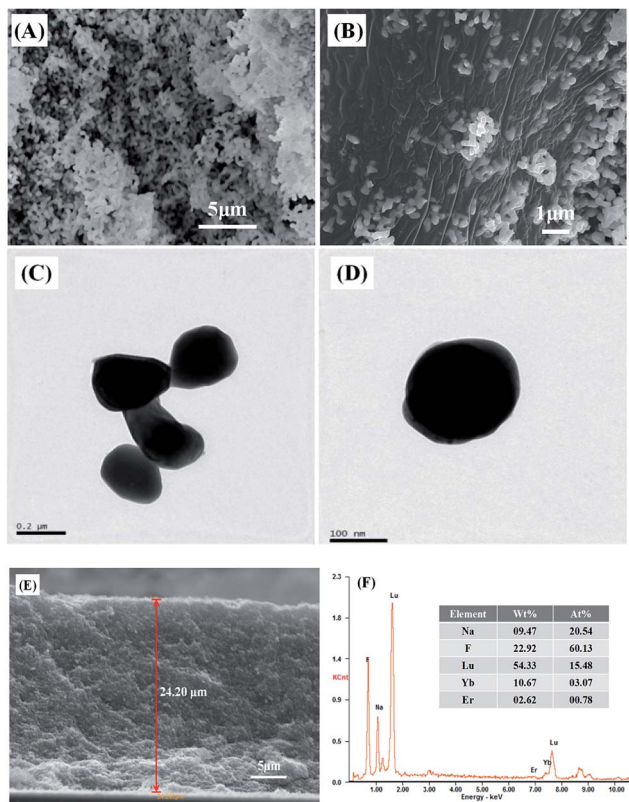


Fig. 2 (A, B) SEM and (C, D) TEM images of the as-prepared NaLuF₄:Yb³⁺/Er³⁺ sample; (E) cross-section image of the composite film; (F) EDX spectrum of NaLuF₄:Yb³⁺/Er³⁺ sample.

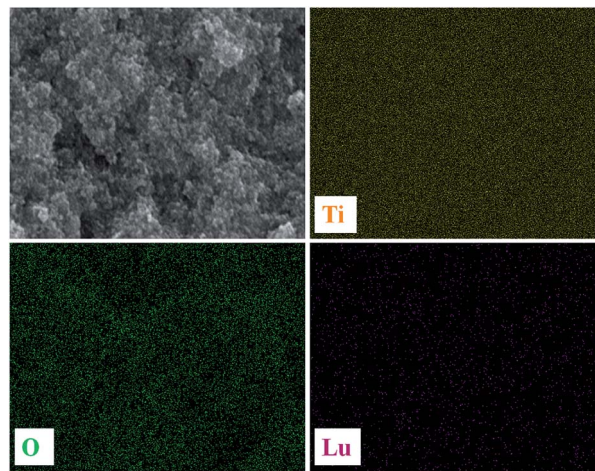


Fig. 3 EDX elemental mapping of the cross-section for Ti, O, and Lu.

prepared samples have an average diameter and a smooth surface relatively. Fig. 2E shows the cross-section image of the composite film with a thickness of approximately 24 μ m, and the UC material was equally embedded in the composite TiO₂ layer. From EDX spectrum (Fig. 2F), peaks of host (Lu) and dopant (Er and Yb) are detected for NaLuF₄:Yb³⁺/Er³⁺, revealing the presence of Er and Yb atoms with a molar ratio of about 4 : 16 : 80 to Lu atoms, which accords with the molar ratio of reactant (2 : 18 : 80), roughly. The chemical mapping of the elements appeared in the EDX is shown in Fig. 3; the Ti, O, and Lu elements are evidently distributed homogeneously in the film.

UC fluorescence

The photoluminescence spectra of the as-prepared NaLuF₄:Yb³⁺/Er³⁺ excited with a $\lambda = 980$ nm laser are shown in Fig. 4. The centered emissions 407, 520, 540, and 654 nm originated from $^2H_{9/2} \rightarrow ^4I_{15/2}$, $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$ of Er³⁺, respectively. In the case of Er³⁺, the most important excitation path is $^4I_{15/2} \rightarrow ^2H_{11/2} \rightarrow ^4F_{7/2}$, which requires two

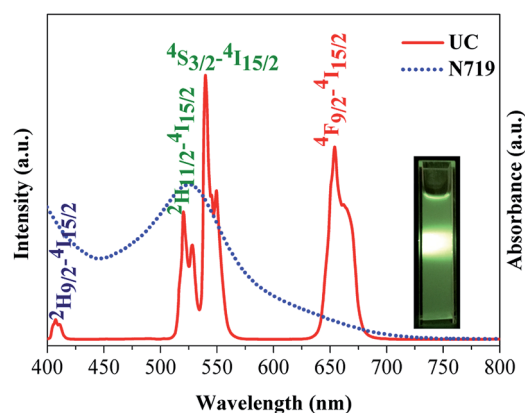
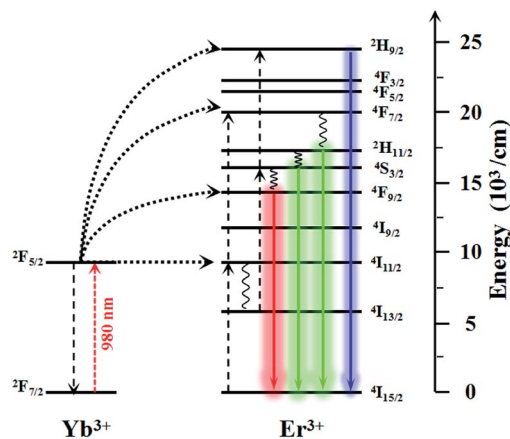


Fig. 4 UC photoluminescence spectrum of NaLuF₄:Yb³⁺/Er³⁺ and UV-vis absorption spectra of N719. The inset shows the photograph of sample under 980 nm laser.





Scheme 2 Schematic of UC populating mechanism for NaLuF₄:Yb³⁺/Er³⁺ under 980 nm excitation.

energy-transfer processes from Yb³⁺. The subsequent multi-photon relaxation populates the emitting ²H_{11/2} and ⁴S_{3/2} states, and the dominant green ²H_{11/2} → ⁴I_{15/2} and ⁴S_{3/2} → ⁴I_{15/2} emissions occur. Alternatively, the electrons can further relax and populate ²H_{9/2} and ⁴F_{9/2} levels, thereby resulting in the occurrence of the blue ²H_{9/2} → ⁴I_{15/2} and red ⁴F_{9/2} → ⁴I_{15/2} emissions. The mechanism responsible for the UC fluorescence of NaLuF₄:Yb³⁺/Er³⁺ is shown in Scheme 2. The luminescence bands coincide perfectly with the absorption wavelength of N719 dye, thereby indicating that the NIR light can be indirectly absorbed by N719 dye through the UC process. In other words, the incorporation of this UC material composite in DSSCs can feasibly enhance sunlight harvesting in the NIR region. Since the light response region extends from the visible light to the infrared region, the light absorption is enhanced and is therefore considered to improve the photoelectric conversion performance of the DSSC device.

UV-vis spectral characterization of photoanodes

To investigate the light-scattering ability of NaLuF₄:Yb³⁺/Er³⁺ UC material, we performed UV-vis DRS of photoanodes over the wavelength range of 350–850 nm as shown in Fig. 5a. In the spectral range of 400–800 nm, the composite photoanodes exhibited higher diffuse reflectance than P25. The UV-vis absorption spectra of photoanodes in Fig. 5b indicates that the photoelectrodes doped with UC increased the absorption of light in 550–1200 nm. According to Mie theory,³⁰ the particles are larger, and the UC materials exhibit effective scattering with a micro-nano size and can act as light scattering centers. On the one hand, UC materials increase the optical path length of the incident light *via* light scattering. On the other hand, UC materials convert the IR light into visible light and broaden the spectral response region. On the basis of these results (Scheme 1), doping with UC will enhance the photocurrent density in the DSSCs.

Photovoltaic performances of DSSCs

The *J*-*V* performance of DSSCs the AM 1.5 sunlight illumination (100 mW cm⁻²) is shown in Fig. 6. The photovoltaic

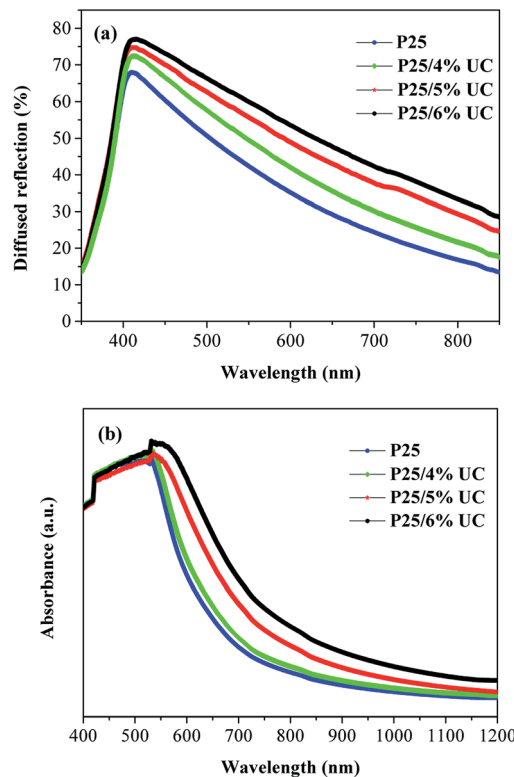


Fig. 5 (a) UV-vis diffuse reflectance and (b) UV-vis absorption spectra of photoanodes with increasing amount of NaLuF₄:Yb³⁺/Er³⁺.

characteristics of these DSSCs, such as short-circuit current density (*J*_{sc}), open-circuit voltage (*V*_{oc}), fill factor (FF), and overall light conversion efficiency (*η*) determined from these measured *J*-*V* curves, are summarized in Table 1. With the increase in UC content, *V*_{oc} increased from 0.725 V to 0.765 V, while *J*_{sc} and *η* increased and then decreased, the highest *J*_{sc} achieved 16.42 mA cm⁻². The highest photoelectric conversion efficiency of 7.58% was achieved at concentration 5 wt% of UC, which is 27.18% higher than that of P25 photoanode (5.96%) with the same thickness. This improvement can be attributed to two reasons. First, the light spectral response range was broadened through UC by doping a small amount of UC

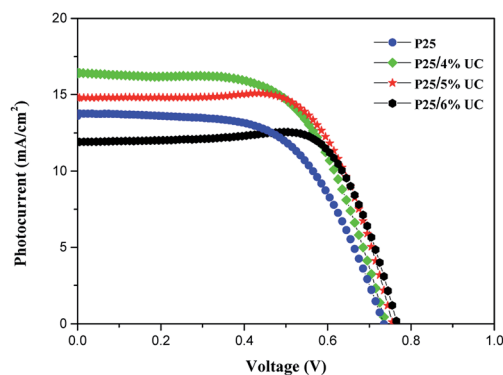


Fig. 6 *J*-*V* curves of DSSCs with increasing amount of NaLuF₄:Yb³⁺/Er³⁺ under simulated AM 1.5 G light.



Table 1 Photovoltaic parameters of DSSCs with increasing amount of NaLuF₄:Yb³⁺/Er³⁺

Samples	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)
P25	13.78	0.725	0.597	5.96
P25/4% UC	16.42	0.735	0.611	7.38
P25/5% UC	14.82	0.755	0.677	7.58
P25/6% UC	11.94	0.765	0.753	6.88

Table 2 Fitted data for the EIS measurement of DSSCs with 5% and without NaLuF₄:Yb³⁺/Er³⁺

Samples	R_s (Ω)	R_{ct} (Ω)	R_w (Ω)	τ_e (ms)
P25	19.26	9.32	22.74	115.3
P25/5% UC	20.18	10.71	31.33	104.7

material into the TiO₂ films. This electrode has more intense absorption in the NIR region compared with the P25 electrode, thereby greatly increasing the utilization rate of solar energy. Second, the enhanced J_{sc} is ascribed to the enhanced light harvesting. Therefore, when there is a small amount of UC, the J_{sc} and η values of the DSSC increase.

EIS was performed to understand the electron transfer process of DSSCs. Fig. 7a shows the EIS Nyquist plots of different devices and equivalent circuit. The impedance at low frequency (0.1–1 Hz) generally refers to the Nernst diffusion process of I⁻/I³⁺ in the electrolyte. The small semicircle at high frequency (1–100 kHz) is related to the electron transfer resistance (R_{ct}) at the Pt|I⁻/I³⁺ electrolyte, and the large semicircle at medium frequency (1 Hz to 1 kHz) corresponds to the transport resistance (R_w) of photoinduced electron at the TiO₂|dye|I⁻/I³⁺ electrolyte interface. R_s is ascribed to the sheet resistance of FTO and the electrical contact resistance between the FTO|TiO₂

film.^{31,32} The EIS data were fitted to the corresponding equivalent circuit model by using ZSimpWin software, and the R_s , R_{ct} , and R_w data are shown in Table 2. R_s and R_{ct} are similar, and R_w increases from 22.74 Ω of P25 photoanode to 31.33 Ω of composite photoanode at concentration 5 wt% of UC, thus implying that the electron transport within the DSSC is weaker. The higher transport resistance may be attributed to the serious charge recombination effect and poor charge transport ability of UC in the photoanodes. Hence, low electron diffusion and collection efficiency in the DSSCs is observed. Fig. 7b shows the EIS Bode phase plots. The electron lifetime (τ_e) in DSSCs is determined by the characteristic frequency peak in the low frequency (f_{max}) according to the following equation: $\tau_e = 1/(2\pi f_{max})$.^{31,32} On the basis of the calculations, minimal changes are obtained with a low doping amount.

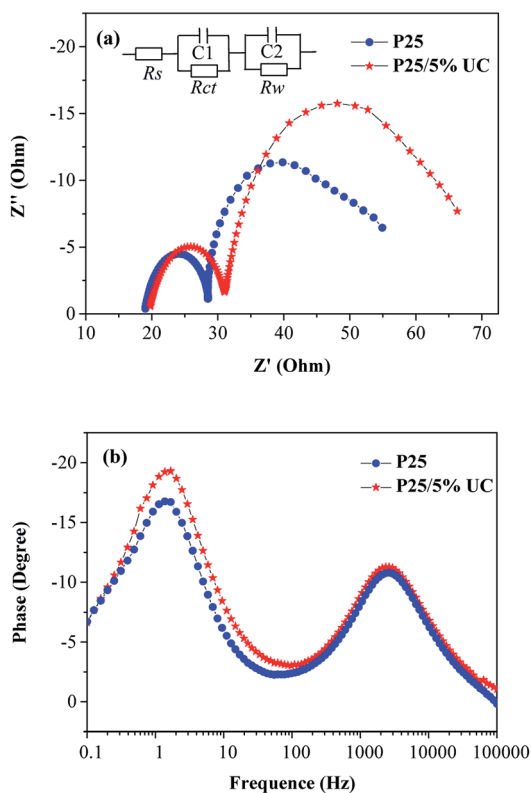
After considering the aforementioned results, we can conclude that NaLuF₄:Yb³⁺/Er³⁺ can enhance power conversion efficiency because of its remarkable light scattering properties and UC luminescence. However, the intrinsic defects of NaLuF₄:Yb³⁺/Er³⁺ materials are not beneficial for electron transfer, thereby reducing the photocurrent. Thus, the optimum doping amount was explored.

Conclusions

In summary, we synthesized a dual-functional material called NaLuF₄:Yb³⁺/Er³⁺ through the co-precipitation method and then introduced the material into DSSCs. As a luminescence medium, the material efficiently converts IR to visible light, and this ability coincides well with the absorption range of N719 dye. With its excellent UC luminescence and light scattering properties of NaLuF₄:Yb³⁺/Er³⁺ achieved 7.58% efficiency at concentration 5 wt%, which is 27.18% better than the efficiency of P25 photoanode (5.96%), and a 19.16% improvement in the photocurrent. This dual-functional NaLuF₄:Yb³⁺/Er³⁺ material will provide a new strategy for enhancing photon harvesting in DSSCs.

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**Fig. 7** (a) EIS Nyquist plots and (b) Bode phase plots for DSSCs with 5% and without NaLuF₄:Yb³⁺/Er³⁺.

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