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# A simple modification of near-infrared photon-to-electron response with fluorescence resonance energy transfer for dye-sensitized solar cells

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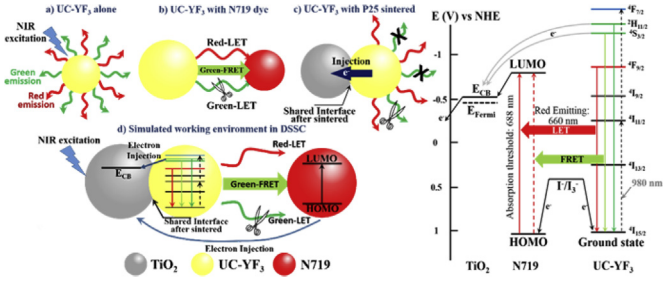
## HIGHLIGHTS

- UC-$YF_3$ is utilized as an attachment layer in DSSC.
- UC-$YF_3$ as light scattering layer achieve a higher power-conversion efficiency.
- FRET and FRET-like process are found in the modified DSSC.
- The NIR-photon to electron process is confirmed by SPS and IPCE.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Upconversion (UC) Er, Yb-$YF_3$ is introduced into dye-sensitized solar cells (DSSC) through a simple method to investigate the effect of UC particles in photoanode. The utilization of UC phosphor can significantly improve the photocurrent of the cells under both infrared irradiation and sunlight. Fluorescence resonance energy transfer (FRET) and luminescence-mediated energy transfer between UC-$YF_3$ and N719 dye are explored as the main contribution that UC-$YF_3$ made to DSSC. With the multi-efforts of UC-$YF_3$, power conversion efficiency (PCE) of DSSC is improved from 5.18% to 6.22%. Besides, Electron transfer between UC-$YF_3$ and $TiO_2$ is found after sintered at 450 °C, and the PCE value of DSSC is improved further (5.34% → 6.76%). In addition, we explore that UC-$YF_3$ can serve as a scattering material to increase the light absorption capability of the cells and increase the photocurrent of the cells under simulated sunlight irradiation.



## 1. Introduction

As a clean and sustainable energy, solar energy has been the most active research area in the energy field in recent years. Owning to their low cost, environmental friendliness, simple production processes, and high efficiency, dye sensitized solar cells (DSSCs) have brought a revolutionary innovation for photoelectrochemical solar cell, and blazed a direction for new-generation solar cells since it was first reported in 1991 by Gratzel's group [1–3]. However, absorption spectra of dyes N3 and N719 which is usually used as standard photosensitized agents do not perfectly match the solar spectrum [4–6]. Photons with lower

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energy (such as NIR light) transmit through the DSSC without any contribution to the electrical output, because these photons are transparent to the dye. Most of the NIR radiations are in the shorter NIR wavelength regions. Of the 52% total solar energy delivered in the NIR region (700–2500 nm), 50% is within the wavelength of 700–1000 nm; 30% lies within the wavelength of 1000–1500 nm; and 20% lies within the wavelength of 1500–2500 nm [7,8]. Although many novel dyes with wide absorption spectra have been reported in the literature [9,10], high cost, complicated production process, as well as low yield limited further improvement of the power conversion efficiency (PCE) of DSSC. A useful method for reducing the transmission loss of photons with lower energy (especially NIR light) is upconverting the low-energy photons into higher-energy-photons, which can be help increase the efficiency of DSSCs [11].

Upconversion materials can generate one high-energy-photon by absorbing two or more low-energy-photons, which is called anti-stokes emission [12,13]. Efficient upconversion photoluminescence from nanoparticles has tremendous potential in application as sunlight-modifier for enhancing efficiency of DSSCs [14]. Typical DSSC systems with upconversion materials are illustrated in Fig. 1, in which rare earth-doped upconversion materials are used for photovoltaic applications. As structured in Fig. 1a, the UC-layer could modify the incident solar spectrum directly. However, there was an intensity loss from the incoming sunlight due to absorption caused by the UC-layer. To overcome this problem, UC particles were used in the reflecting layer or between the reflecting layer and the counter electrode (CE). Sunlight went through the photoanode and then excited the UC-layer [15,16]. The visible light emitted by the UC-layer was reflected back into the DSSC (Fig. 1b). In this case, the light which is transparent to DSSC (major in NIR region) can excite the UC particles and partial lost energy can be recovered. In addition, a combination of UC particles and normal photoanode material as a single-layer or double-layer photoanode has been reported (Fig. 1c) [17–20]. In this design, external loss can be avoided. However, as an addition, appropriate UC particles that can efficiently work with the normal photoanode material but does not interfere with favorable conduction of the photoanode can hardly be found. Besides, UC-particles as a reflector and energy relay material can effectively enhanced the light harvesting and efficiency of the cells. Recently, GY Chen extend the use of the energy relay process for harvesting light in the NIR region with NIR absorption and radiate visible upconverted emission, and the energy of which can then be radiative or nonradiative transferred to the dye sensitizer [11]. However, in their paper, Z907 which can absorb the longest wavelength of 750 nm can absorb both the green and red emission, but all the UC-emitting peak decrease. And cubic Er, Yb-$NaYF_4$ with average diameters of about 7 nm was utilized for doping into the 10 nm-pores of the $TiO_2$ film. Here, we report a simple modification with Er, Yb-$YF_3$ for DSSC by attaching it onto the surface of the $TiO_2$ film. And we found that, with N719 (maximum absorption at *ca.* 540 nm), UC-emission of Er, Yb-$YF_3$ occurring interesting changes, which lead to that the green peak decreased significantly with the red emission little changed. This can prove the fluorescence resonance energy transfer in UC-DSSCs with Er, Yb-$YF_3$, directly. After modification, power conversion efficiency (PCE) of 6.76% was achieved with the blank DSSC of 5.18%, which is an increase of 30.50%. It can be directly observed an NIR light-to-electricity property by SPS and IPCE characterizations.

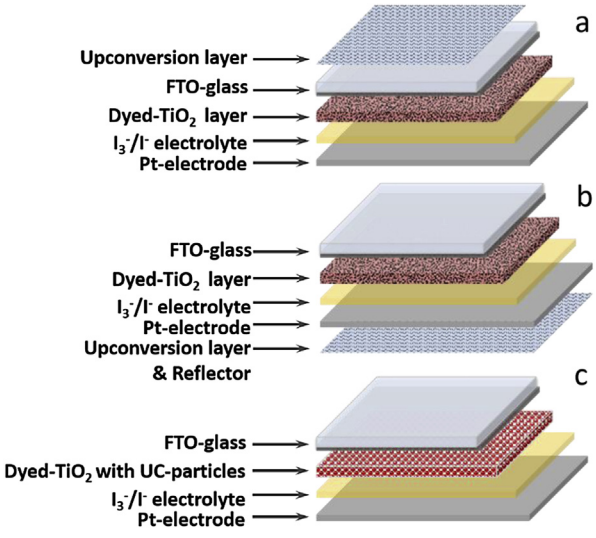


**Fig. 1.** Typical schematic structural diagram of a DSSC with upconversion layers designed and reported before.

## 2. Experimental section

### 2.1. Preparation of Er, Yb-$YF_3$

Er, Yb-$YF_3$ phosphors samples were synthesized by a hydrothermal method similar to the literature [21]. All the chemicals were of analytical grade and used as received without further purification. Stoichiometric $Y_2O_3$, $Yb_2O_3$ and $Er_2O_3$ were firstly dissolved in $HNO_3$ and then transferred into an oven overnight. Then 10 mL distilled water, 0.01 mol NaF and 0.09 mol $NH_4HF_2$ were added into the container. The pH value was adjusted to 3 by adding aqua ammonia dropwise. The suspension was transferred into Teflon-lined stainless steel autoclaves, sealed and maintained at 220 °C for 24 h. After natural cooling, the precipitates were centrifuged several times, washed with distilled water and ethanol to remove the ionic remnants, and dried at 70 °C for 8 h. However, similar process to the literature leads to none $NaYF_4$ but $YF_3$. In our opinion, it is due to the treatment of nitric acid which dissolved the rare earth oxides. In our process, the nitric acid were completely removed by dry the solution in an oven to completely dry. However, in the literature, the nitric acid was retained to the next-step. Thus, the slight difference in the process leads to a different product. To be assembled onto DSSCs, UC-$YF_3$ was dispersed into EtOH, and the solution was dropped onto the photoanode film of $TiO_2$ to form an attachment layer. Finally, the modified photoanodes were sintered in a muffle at 450 °C.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded in the $2\theta$ range of 10–70° using Cu-K$\alpha$ radiation by Shimadzu XRD-6000 X-ray Diffractometer. Luminescence spectra were measured by the Edinburgh FLSP920 combined steady state fluorescence, using a 980 nm laser as the excitation source. The SPS instrument was assembled by Jilin University, monochromatic light was obtained by passing light from a 500 W xenon lamp (CHF-XQ500W, China) through a double-prism monochromator (SBP300, China), and the signals were collected by an SR830 DSP lock-in amplifier (Stanford).

### 2.3. Photoelectrochemical measurements

Optically transparent electrodes were made from an F-doped $SnO_2$-coated glass plate purchased from Acros Organics, Belgium. $TiO_2$ film was fabricated using a screen printing method. The photoanode films of commercial P25 were immersed in a 0.3 mM