Enhanced photoelectric conversion efficiency of dye-sensitized solar cells by the synergetic effect of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{g-C}_3\text{N}_4$

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ABSTRACT $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite photoanodes were successfully designed for the first time. The photoelectric conversion efficiency of $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell can result an efficiency of 7.37%, which is higher than those of pure TiO_2 cell and $\text{TiO}_2\text{-C}_3\text{N}_4$ composite cell. The enhancement of the efficiency can be attributed to the synergetic effect of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and C_3N_4 . Electrochemical impedance spectroscopy analysis revealed that the interfacial resistance of the $\text{TiO}_2\text{-dye}/\text{I}_3^-/\text{I}^-$ electrolyte interface of $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composites cell was much smaller than that of pure TiO_2 cell. In addition, the $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell had longer electron recombination time and shorter electron transport time than that of pure TiO_2 cell.

Keywords: $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$, synergetic effect, luminescence, dye-sensitized solar cells.

INTRODUCTION

With the increasingly serious energy crisis, more and more people begin to explore new alternative energy. Dye-sensitized solar cells (DSSCs) have received tremendous attention for the development of next-generation solar cells because of their high power conversion, low-cost and environment-friendliness [1–3]. It is well known that the amount of dye adsorption, light harvesting efficiency, and the ability of charge separation and transport are three important factors to improve the photoelectric conversion efficiency of DSSCs [4–8]. In particular, the properties of materials such as excellent light scattering, fast electron transport and large specific surface area play an important role in enhancing the light conversion efficiency of DSSCs [9,10]. In order to enhance the photoelectric conversion efficiency

of a DSSC, researchers have designed different architectures of TiO_2 nanocrystalline films, such as doping of metal and nonmetal elements, surface modifications, and combination with narrow band gap semiconductors [11–13]. In addition, the conduction and valence bands of the rare earth (RE) ion modified TiO_2 nanoparticles have higher potentials than those of unmodified TiO_2 nanoparticles due to the participation of RE ions in the hybridization orbital of TiO_2 , which can reduce the probability of recombination of excited electrons and holes to increase the short-circuit current during the operation of the DSSCs.

RE ions doped luminescent materials usually show unique down-conversion (DC) and up-conversion (UC) properties, which offer the opportunity to improve light harvesting and thereby the efficiency of the solar cells [14–16]. To date, there have been a number of reports on luminescence materials. Among them, fluorides doped with RE ions have low photon energies and high quantum efficiencies, which give them the potential for widespread applications in optical communication, display devices, and solid-state lasers. Especially, NaYF_4 is acknowledged as the most efficient luminescence host material at present. However, the incorporation of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ into DSSCs can lead to poor charge transfer due to the poor electrical conductivity of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ [17–23], which limits the significant enhancement of photoelectric conversion efficiency of DSSCs.

As a new metal-free semiconductor, $\text{g-C}_3\text{N}_4$ has attracted increasing attention owing to its excellent mechanical, electrical, thermal, and optical properties, and outstanding potential for energy conversion and storage. Some efforts

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Scheme 1 Mechanism of light harvesting in $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cells.

have been devoted to combining C_3N_4 with a metal or oxide to form heterojunctions because composite materials could present complementary properties. It could be used as a photoanode material in DSSC due to its ability to absorb a large part of visible light. More importantly, g- C_3N_4 has more negative conduction band position than that of TiO_2 , which may effectively prevent the migration of electrons from TiO_2 to the electrolyte [24–26].

As a result, if one can design dual-mode luminescent $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite photoanodes, the efficiency of the solar cells can be enhanced due to the synergetic effect of $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ and g- C_3N_4 .

Based on the above consideration, we prepared a $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite by combining the hydrothermal with chemisorption method, which have the ability to improve the efficiency of the solar cells. The high photovoltaic activity of the $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite photoanode is superior to the most reported photoanodes [27–30]. The significantly improved photoelectric conversion efficiency of DSSC is related to the synergetic effect of $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ nanoparticles and C_3N_4 (Scheme 1). The electron transport and interfacial recombination kinetics were investigated by the

electrochemical impedance spectroscopy (EIS) and intensity-modulated photocurrent/photovoltage spectroscopy.

EXPERIMENTAL SECTION

Preparation of $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ nanoparticles

All chemicals used in this paper were analytical grade and used as received without further purification. In a typical synthesis, 0.5 g polyvinyl pyrrolidone was added to 10 mL deionized water, and the solution was thoroughly stirred. An aqueous solution of 1.6 mL $\text{Y}(\text{NO}_3)_3$, 0.4 mL $\text{Yb}(\text{NO}_3)_3$ and 0.04 mL $\text{Er}(\text{NO}_3)_3$ was added into the above solution under stirring at room temperature for 10 min. Then, 0.212 g NaF was added to the above mixture under stirring. Subsequently, the milky colloidal solution was transferred to a 50 mL Teflon-lined autoclave, and heated at 140°C for 10 h. The systems were then allowed to cool to room temperature. The final products were collected by means of centrifugation, washed with deionized water and ethanol, and dried at 80°C .

Preparation of $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ nanocomposites

The C_3N_4 was first prepared by heating melamine to 550°C

for 2 h in N_2 atmosphere. An appropriate amount of C_3N_4 was added into methanol then the beaker was placed in a sonifier cell disrupter for 2 h to completely disperse the C_3N_4 . The $NaYF_4:Er^{3+}/Yb^{3+}$ powder was added into the above solution and stirred in a fume hood for 24 h. After volatilization of the methanol, an opaque powder was obtained after drying at $100^\circ C$ in N_2 atmosphere.

Materials characterization

The crystal structure was analyzed by X-ray powder diffraction (XRD) patterns obtained by Bruker D8 Advance diffractometer by using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA). The size and morphology of the final products were investigated by transmission electron microscopy (TEM, JEOL, JEM-2100) and scanning electron microscopy (SEM). Nitrogen adsorption-desorption isotherms were collected using a Tristar II 3020 surface area and porosity analyzer (Micromeritics). Thermogravimetry (TG) measurements were carried out on a thermal analyzer (TGA-7, Perkin-Elmer, USA) using a 2-mm internal diameter Teflon tube with a heating rate of $10^\circ C$ per minute under a flow of air. Fourier transform infrared (FTIR) spectra of the samples were recorded at room temperature with a Perkin-Elmer Spectrum one FTIR spectrometer using the KBr pellet method. UV-vis absorption spectra were determined by a UV-vis spectrophotometer (Shimadzu UV-2550, Tokyo, Japan). The photoluminescence spectra were recorded with a Hitachi F-4600 fluorescence spectrophotometer at room temperature. The UC luminescence spectra were recorded using a Hitachi F-4600 fluorescence spectrophotometer with an adjustable laser (980 nm) as the excitation source with a fiber-optic accessory. For comparison of the luminescence properties of different samples, the luminescence spectra were measured with the same instrument parameters (2.5 nm for spectral resolution (FWHM) of the spectrophotometer and 400 V for PMT voltage).

Fabrication of photoelectrodes

Fabrication of photoelectrode and the assembly of DSSCs: several pastes, from homogeneously mixing $NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ and TiO_2 (Degussa P25) into 1.5 mL of TiO_2 colloid, were prepared. The TiO_2 colloid was prepared following the previously published synthesis procedure [31]. A screen-printed double layer of $TiO_2-NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ was used as the photoanode. The first layer of $TiO_2-NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ was prepared by a doctor-blade method on the fluorine doped tin oxide (FTO) substrate and then sintered

at $450^\circ C$ for 30 min. Subsequently, the second layer of $TiO_2-NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ was covered on the first $TiO_2-NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ film and then sintered at $450^\circ C$ for 30 min again. The sensitization of the photoelectrodes was achieved by immersing them into 0.5 mmol L^{-1} $((C_4H_9)_4N)_2[Ru(4\text{-carboxy-4'-carboxylate-2,2' bipyrindine})_2(NCS)_2]$ dye (N719, Solaronix SA, Switzerland) in acetonitrile and *tert*-butanol (volume ratio, 1:1) for 48 h at room temperature. The Pt counter electrodes were prepared following the previous literature [32]. The dye-sensitized photoanode was assembled with a Pt counter electrode into a sandwich-type cell. The sandwich-type cell was further fixed together with epoxy resin. The space between the electrodes was filled with the electrolyte, which comprised 0.6 mol L^{-1} 1-propyl-2,3-dimethyl-imidazolium iodide, 0.05 mol L^{-1} I_2 , 0.1 mol L^{-1} LiI, and 0.5 mol L^{-1} *tert*-butylpyridine (TBP) in 3-methoxypropionitrile (3-MPN), by capillary action.

Photovoltaic properties

Photovoltaic measurements were carried out with a solar simulator (Oriel, USA) equipped with an AM 1.5G radiation (one sun conditions, 100 $mW\ cm^{-2}$) filter as the light source. The irradiation area of DSSCs was 0.09 cm^2 . The EIS were performed with a computer-controlled IM6 impedance measurement unit (Zahner Elektrik, Germany) and carried out by applying sinusoidal perturbations of 10 mV with a bias of $-0.8\ V$ at a frequency ranging from 10 mHz to 1 MHz. The obtained spectra were fitted with ZsimpWin software in terms of appropriate equivalent circuits. The electron transport and recombination properties were measured by intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) (Zahner Elektrik, Germany). The DSSCs were probed through the photoanode side by a frequency response analyzer using a white light emitting diode (wlr-01) as the light source. The frequency range was 0.1–1000 Hz. The irradiated intensity was varied from 30 to 150 $W\ m^{-2}$.

RESULTS AND DISCUSSION

Crystal structures and morphologies of samples

The crystal structure, particle size and morphologies of the products were obtained by XRD, TEM and SEM images. Fig. 1 shows the XRD patterns for the prepared $NaYF_4:Er^{3+}/Yb^{3+}$, g- C_3N_4 , and $NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ nanocomposites. As shown in curve 1 of Fig. 1a, the positions of the diffraction peaks for the pure $NaYF_4:Er^{3+}/Yb^{3+}$

Figure 1 (a) XRD patterns of (1) NaYF₄:Er³⁺/Yb³⁺, (2) C₃N₄, (3) NaYF₄:Er³⁺/Yb³⁺-C₃N₄ nanocomposites, and (b) EDX analysis of the NaYF₄:Er³⁺/Yb³⁺-C₃N₄ nanocomposites.

nanocrystals could be easily indexed as a pure cubic phase NaYF₄:Er³⁺/Yb³⁺ (JCPDS No. 39-0724). No other impurity peaks were detected. Curve 2 in Fig. 1a shows the XRD pattern of g-C₃N₄. The pure g-C₃N₄ sample has distinct peaks at 13.0° and 27.3°, which were indexed as (100) and (002) diffraction planes. Curve 3 in Fig. 1a shows the XRD pattern of the NaYF₄:Er³⁺/Yb³⁺-C₃N₄ nanocomposites. The results indicated that NaYF₄:Er³⁺/Yb³⁺ and C₃N₄ coexisted in the NaYF₄:Er³⁺/Yb³⁺-C₃N₄ nanocomposites. The crystal phase of NaYF₄:Er³⁺/Yb³⁺ remained unchanged after compositing with g-C₃N₄. In order to further investigate the NaYF₄:Er³⁺/Yb³⁺-C₃N₄ nanocomposites, we measured the compositions by using energy dispersive X-ray analysis

(EDX), as shown in Fig. 1b. The results indicated that the elemental components were C, N, Na, F, Y, Yb and Er, indicating that the NaYF₄:Er³⁺/Yb³⁺ and C₃N₄ coexisted in the nanocomposites.

The TEM image of C₃N₄ is shown in Fig. 2a. Obviously, C₃N₄ exhibits a sheet like morphology. The corresponding TEM images of NaYF₄:Er³⁺/Yb³⁺ and NaYF₄:Er³⁺/Yb³⁺-C₃N₄ nanocomposites are shown in Fig. 2b–f. The results of TEM images indicated that the NaYF₄:Er³⁺/Yb³⁺ nanocrystals tended to aggregate. A large amount of NaYF₄:Er³⁺/Yb³⁺ nanocrystals were on the surface of C₃N₄ sheets.

Fig. 3a shows the FTIR spectra of C₃N₄, NaYF₄:Er³⁺/Yb³⁺,

Figure 2 The TEM and HRTEM images of (a) C₃N₄, (b, c) NaYF₄:Er³⁺/Yb³⁺, and (d–f) NaYF₄:Er³⁺/Yb³⁺-C₃N₄ nanocomposites.

and $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ nanocomposites. The peaks at 1638 and 1238 cm^{-1} were attributed to the C=N and C-N stretching vibrations, respectively. It is noted that the C=N and C-N stretching vibration peaks moved to a higher wavenumber after compositing with $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, suggesting the formation of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ nanocomposites. The amount of C_3N_4 could be obtained by thermogravimetric analysis (TGA), as shown in Fig. 3b. The amount of C_3N_4 in all $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ nanocomposites could be calculated from the second weight loss, and the results indicated that the amount of C_3N_4 was nearly consistent to the dosage of C_3N_4 added.

The optical absorption of the $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, C_3N_4 and $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ nanocomposites was conducted with a UV-vis absorption spectrometer, as shown in Fig. 4a. The UV-vis absorption band increases with increasing the amount of C_3N_4 , which is benefit for the absorption of excitation light.

It is well known that the photoelectric performance of DSSCs was closely related to the specific surface areas of

the samples. N_2 adsorption-desorption isotherms of the as-obtained C_3N_4 and $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ nanocomposites with different C_3N_4 contents were performed to determine the surface area of the samples, as shown in Fig. 4b. The Brunauer-Emmett-Teller (BET) surface areas are 6.1291, 7.1199, and 9.2241 $\text{m}^2 \text{g}^{-1}$ for $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ (1:0.25), $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ (1:0.5), and C_3N_4 , respectively.

UC luminescence of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$

The UC luminescent spectra of the cubic phase $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ were measured, as shown in Fig. 5. The emissions centered at 379, 409, 520, 539, and 651 nm originated from the $^4\text{G}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$, $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ of Er^{3+} ions, respectively. For comparison, the absorption spectrum of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ was also shown in Fig. 5. We can find the absorption band of C_3N_4 overlaps very well with the 379 and 409 nm emission peaks of $\text{NaYF}_4:\text{Er}^{3+}/$

Figure 3 (a) FT-IR spectra and (b) TGA curves of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, C_3N_4 and $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ nanocomposites.

Figure 4 (a) UV-vis absorption spectra and (b) N_2 adsorption-desorption isotherm curves of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, C_3N_4 , and $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}-\text{C}_3\text{N}_4$ nanocomposites.

Figure 5 UC luminescence spectra of (a) NaYF₄:Er³⁺/Yb³⁺ (black curve) and (b) NaYF₄:Er³⁺/Yb³⁺-C₃N₄ (red curve) under 980 nm excitation. The blue curve shows the absorption spectrum of NaYF₄:Er³⁺/Yb³⁺-C₃N₄. (c) CIE diagram of NaYF₄:Er³⁺/Yb³⁺ and NaYF₄:Er³⁺/Yb³⁺-C₃N₄ nanocomposites.

Yb³⁺ nanocrystals. And thus, the 379 and 409 nm emission can be highly quenched due to being absorbed of C₃N₄. As expected, the $^4G_{11/2} \rightarrow ^4I_{15/2}$ and $^2H_{9/2} \rightarrow ^4I_{15/2}$ emissions of NaYF₄:Er³⁺/Yb³⁺-C₃N₄ almost disappeared. The CIE coordinates of the UC luminescence were (0.322, 0.545) and (0.327, 0.462) for the NaYF₄:Er³⁺/Yb³⁺ and NaYF₄:Er³⁺/Yb³⁺-C₃N₄, respectively.

To investigate the fundamental UC mechanism of NaYF₄:Er³⁺/Yb³⁺-C₃N₄, the pumping power dependence of the fluorescent intensity was investigated. Fig. 6 shows

the logarithmic plots of the emission intensity as a function of excitation power for the $^4F_{7/2}/^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ emissions. For an unsaturated UC process, the emission intensity is proportional to the n^{th} power of the excitation intensity, and the integer n is the number of the laser photons absorbed per upconverted photon emitted. Obviously, the values of n for NaYF₄:Er³⁺/Yb³⁺-C₃N₄ nanocomposites are smaller than those for NaYF₄:Er³⁺/Yb³⁺, which can be attributed to the energy transfer from NaYF₄:Er³⁺/Yb³⁺ to C₃N₄.

Figure 6 Plots (log-log) of emission intensity versus excitation power in (a) NaYF₄:Er³⁺/Yb³⁺-C₃N₄ and (b) NaYF₄:Er³⁺/Yb³⁺.

Fig. S1 in Supplementary information shows the emission spectrum of the $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ excited at 495 nm. The $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions were observed. Figs S2 and S3 show the excitation spectra of the $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ monitored at 522 and 550 nm, respectively.

Photoelectrochemical properties of $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite DSSCs

In order to investigate the effects of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ on the photoelectric properties of DSSCs, the DSSC prototype devices were fabricated using N719-sensitized $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite as electrodes. Here, the mass ratio of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}:\text{C}_3\text{N}_4$ was 1:2. Fig. 7a shows the photocurrent density-voltage (J - V) curves of pure TiO_2 , $\text{TiO}_2\text{-C}_3\text{N}_4$, and $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ cells. The corresponding values of the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and overall conversion efficiency (η), obtained from the curves of solar cells, are shown in Table 1. It was found that the performance of $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ cell was not only higher than that of pure TiO_2 cell, but also higher than those of $\text{TiO}_2\text{-C}_3\text{N}_4$ cell. It is noted that the photoelectric conversion efficiencies of the DSSCs were also enhanced by the incorporation of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ with different mass ratio of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}:\text{C}_3\text{N}_4$. Detailed information on the light harvesting of the DSSCs can be ob-

tained from the incident-photon-to-current conversion efficiency (IPCE) spectra in Fig. 7b. Obviously, the photoelectric conversion efficiency of the $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ cell was higher than that of pure TiO_2 cell.

Presumably, several mechanisms might be responsible for the enhancement of the efficiency of the $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell. First, the improvement of the efficiency of the $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell was related to the luminescence of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$. However, the results of the IPCE spectra indicate that the luminescence of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ only has a little effect on the performance improvement. Second, it is well known that the conduction and valence bands of the RE ion modified TiO_2 nanoparticles have higher potentials than those of unmodified TiO_2 nanoparticles due to the participation of RE ions in the hybridization orbital of TiO_2 , which can reduce the probability of recombination of excited electrons and holes to increase the short-circuit current during the operation of the DSSCs. Finally, the UV-vis absorption band of $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ increases with increasing the amount of C_3N_4 , which is beneficial for the absorption of visible light (Fig. 4). More importantly, C_3N_4 has more negative conduction band position than that of TiO_2 , which may effectively prevent the migration of electrons from TiO_2 to the electrolyte. And thus, the $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ cell performance was improved by introducing $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$.

Figure 7 (a) J - V curves of pure TiO_2 , $\text{TiO}_2\text{-C}_3\text{N}_4$, and $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ cells. (b) IPCE of pure TiO_2 and $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ cells.

Table 1 Solar cell parameters of pure TiO_2 cell, $\text{TiO}_2\text{-C}_3\text{N}_4$, and $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cells under simulated solar light radiation

DSSCs	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
Pure TiO_2	0.72	15.6	0.60	6.82
$\text{TiO}_2\text{-C}_3\text{N}_4$	0.73	16.7	0.59	7.22
$\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$	0.74	17.1	0.58	7.37

EIS is a powerful method to investigate internal resistances in the charge-transfer process of DSSCs. The wide frequency range of EIS means that it can measure wide-scale internal resistances of each electrochemical step at the same time. DSSCs are complex systems which are composed of several interfaces. A high level of electron accumulation must occur because photogenerated electrons are not extracted immediately at the electrode contact under illumination. Generally, the impedance at low frequency (0.05–1 Hz) refers to the Nernst diffusion of I_3^-/I^- within the electrolyte. The impedance at high frequency (1–100 kHz) corresponds to the capacitance and charge-transfer resistance at the $Pt|I_3^-/I^-$ electrolyte interface. The medium-frequency response at 1–100 Hz is related to the photoelectrode-dye/ I_3^-/I^- electrolyte interface, where the accumulation of photoelectrons and redox shuttles is expected. Fig. 8a shows the EIS of pure TiO_2 cell and $TiO_2-NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ cell. It can be seen that the interfacial resistance of the TiO_2 -dye/ I_3^-/I^- electrolyte interface of $TiO_2-NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ cell is much smaller than that of pure TiO_2 cell.

The inset of Fig. 8a shows the equivalent circuit fitting of the impedance spectra, $R_s[C_1(R_1O_1)](R_2CPE)$, which was used for all the DSSCs. R_s is the series resistance, corresponding to the sheet resistance of the FTO glass, the contact resistance and the wire resistance. R_2 represents the charge transfer resistance between the photoelectrode-dye/ I_3^-/I^- electrolyte interface. Z_{Dif} represents the finite-length Warburg impedance. The impedance of the finite-length Warburg diffusion is expressed as

$$Z_{Dif} = R_{Dif} \frac{\tanh(j\omega\tau)^{1/2}}{(j\omega\tau)^{1/2}}, \quad (1)$$

where $R_{Dif} = B/Y_0$, and $\tau = B^2$. B is a constant phase element. According to the equivalent circuit, the EIS data obtained by fitting the impedance spectra of composite DSSCs are listed in Table 2. It can be seen that R_2 , representing the interfacial resistance of the TiO_2 -dye/ I_3^-/I^- electrolyte interface, is 10.27 Ω for pure TiO_2 cell and 8.473 Ω for $TiO_2-NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ composite cell. In addition, the series resistance (R_s) for pure TiO_2 cell and $TiO_2-NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ cell are 33.91 and 33.61 Ω ,

Figure 8 (a) Nyquist plots of DSSCs comprised of pure TiO_2 cell and $TiO_2-NaYF_4:Er^{3+}/Yb^{3+}-C_3N_4$ composite cell. (b) Transport time constant and (c) recombination time constant for DSSCs as a function of applied voltage (or quasi-Fermi energy). (d) Comparison of charge collection efficiency for DSSCs as a function of applied voltage (or quasi-Fermi energy).

Table 2 Parameters obtained by fitting the impedance spectra of composite solar cells using the equivalent circuit in the inset in Fig. 8a

DSSCs	R_s (Ω)	C_1 (F)	R_1 (Ω)	Y_{01} (S)	B ($s^{1/2}$)	R_2 (Ω)	CPE
Pure TiO_2	33.91	1.988×10^{-5}	2.299	0.006722	0.2179	10.27	1.546×10^{-5}
$\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$	33.61	2.575×10^{-5}	2.14	0.004464	0.4035	8.473	1.996×10^{-5}

respectively, indicating that the incorporation of $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ is beneficial for the interfacial electron transfer of $\text{FTO}|\text{TiO}_2$.

In DSSCs, the electron recombination time (τ_n), the electron transport time (τ_d), and the charge collection efficiency (η_{cc}) are important factors for the performance of DSSCs. IMPS and IMVS are conventional methods to investigate the electron transfer and recombination process. The IMPS response plots and IMVS response plots of pure TiO_2 cell and $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell are shown in Fig. 8b, c. Compared with pure TiO_2 cell, the $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell had longer electron recombination time and shorter electron transport time. It noted that shorter transport time and longer recombination time is beneficial for enhancing photoelectric properties.

The charge collection efficiencies (η_{cc}) of DSSCs are determined by the relation: $\eta_{cc} = 1 - \tau_d/\tau_n$. Where, τ_d is the charge transport time and τ_n is the charge recombination lifetime. Fig. 8d shows the charge collection efficiencies of pure TiO_2 cell and $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ cell. The $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell has a higher charge collection efficiency than pure TiO_2 cell.

It is well known that the photoelectric conversion efficiencies of DSSCs are also related to the amount of dye adsorption on the $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ photoanodes. Obviously, the amount of desorption dye of $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ photoanode is larger than that of $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ photoanode, as shown in the Fig. S4, which consistent with the result of BET surface areas (Fig. 4).

CONCLUSIONS

In summary, we successfully synthesized $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ nanocomposites by combining hydrothermal with chemisorption method, which not only exhibited enhanced bright UC luminescence under 980 nm excitation but also could be chosen to design $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite photoanodes. The results indicated that the photoelectric conversion efficiency was enhanced greatly by the incorporation of $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$. Especially, the photoelectric conversion efficiency of $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell was also

higher than that of $\text{TiO}_2\text{-C}_3\text{N}_4$ composite cell. The result of EIS analysis revealed that the interfacial resistance of the $\text{TiO}_2\text{-dye}|I_3^-/I^-$ electrolyte interface of $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell was much smaller than that of pure TiO_2 cell. In addition, the $\text{TiO}_2\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ composite cell has longer electron recombination time and shorter electron transport time than that of pure TiO_2 cell. Overall, the significantly improved photoelectric conversion efficiency of DSSC is ascribed to the synergetic effect of $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ and C_3N_4 .

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of this article.

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利用 $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ 和 $\text{g-C}_3\text{N}_4$ 的协同效应提高染料敏化太阳电池的光电转化效率

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摘要 本文首次成功设计并得到以 $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ 复合材料作为光阳极的染料敏化太阳电池. 与纯 TiO_2 和 $\text{TiO}_2\text{-C}_3\text{N}_4$ 电池相比, $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ 复合电池的效率明显提高. 研究表明, $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ 复合电池的 $\text{TiO}_2\text{-dye}|\text{I}_3^-/\text{I}^-$ 界面阻抗小于纯 TiO_2 电池. 此外 $\text{TiO}_2\text{-NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}\text{-C}_3\text{N}_4$ 电池具有更长的复合时间和更短的传输时间. 电池效率的提高归结于 $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ 和 $\text{g-C}_3\text{N}_4$ 的协同效应.