Application of upconversion luminescence in dye-sensitized solar cells

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An upconversion luminescence powder TiO$_2$(Er$^{3+}$, Yb$^{3+}$) is prepared by a hydrothermal method and used to fabricate dye-sensitized solar cell (DSSC). The TiO$_2$(Er$^{3+}$, Yb$^{3+}$) powder undergoes upconversion luminescence, converting infrared light which the dye can not absorb into visible light with wavelengths of 510–700 nm which the dye can absorb, increasing the photocurrent of the DSSC. TiO$_2$(Er$^{3+}$, Yb$^{3+}$) also acts as a p-type dopant, heightening the Fermi level of the oxide film, which increases the photovoltage of the DSSC. The best performance of the DSSC is found when the ratio of TiO$_2$/luminescence powder is 1/3 in the luminescence layer. Under simulated solar irradiation of 100 mW cm$^{-2}$ (AM 1.5), the DSSC containing TiO$_2$(Er$^{3+}$, Yb$^{3+}$) doping achieves a light-to-electricity energy conversion efficiency of 7.28% compared with 6.41% for the undoped DSSC.

dye-sensitized solar cell, upconversion luminescence, p-type doping

In 1991, Gratzel’s group [1] reported a dye-sensitized solar cell with simple preparation procedure, low-cost, high efficiency and good stability, this new kinds of solar cell bring a revolutionary innovation for photoelectrical solar cell, and blaze a development direction for new generation’s solar cells. The conversion efficiency of DSSC can reach up to 11% [2]. In DSSC, dyes N3 and N-719 often are used as photosensitized agents, and photoanodes together with TiO$_2$ [1–5], therefore the solar light can be absorbed and transferred into electrical energy. The dye molecules can be regarded as an “electron pump”, the driving energy of the pump comes from the solar light. The mainly absorption wavelength ranges for dyes N3 and N-719 are 290–700 nm [3–5]. About 43% of the radiant energy from the sun in the infrared region is not absorbed, which limits the sun energy conversion efficiency of DSSC. It is significant for transferring infrared light to visible light which the dye can absorb and enhancing the light-to-electricity conversion efficiency of DSSC.

Rare-earth-doped compounds have aroused extensive research as conversion luminescent mediums with potential applications in phosphors, display monitors, X-ray imaging, scintillators and solid-state lasers [6–10] because of their unique properties arising from their 4f electrons. However, using rare-earth-doped compounds for upconversion luminescence in DSSC has not been attempted so far.

In this paper, a luminescent TiO$_2$(Er$^{3+}$, Yb$^{3+}$) powder is prepared by a hydrothermal method and used to fabricate a DSSC. TiO$_2$(Er$^{3+}$, Yb$^{3+}$) behaves as an upconversion luminescence medium, transferring infrared light to visible light which the dye can absorb, enhancing the light-to-electricity conversion efficiency of the DSSC.

1 Materials and methods

1.1 Materials and apparatus

TiO$_2$ nanoparticles (P25), butyl titanate, isopropanol, iodine,
solution of nitric acid (0.1 mol L\(^{-1}\)) of distilled water. The precipitate was added to an aqueous water (150 mL), immediately forming a white precipitate. Tetrabutyl titanate (10 mL) was rapidly added to distilled water. The system was stirred at 80°C until a translucent blue-white liquid formed. The resultant colloid was prepared by the following procedure \[11\] - \[14\]. Using tetrabutyl titanate as precursor, a TiO\(_2\) nanocrystal colloid was prepared by the following procedure \[11\] - \[14\]. Tetrabutyl titanate (10 mL) was rapidly added to distilled water (150 mL), immediately forming a white precipitate. The system was stirred for 30 min. The precipitate was filtered using a glass frit and washed three times. The resulted precipitate was added into the nitrate solution, the pH of the mixed solution with a sheet resistance of 15 \(\Omega\) cm\(^2\) was purchased from Hartford Glass Co. This was used as a substrate for precipitation of a TiO\(_2\) porous film and was cut into rectangles with a size of 2 cm \(\times\) 1.5 cm. The main apparatus include in a stabilized power supply Xe/Hg arc lamp (CHF-XM-500W, Changtuo Scientific Ltd, Beijing, China) an electrochemical workstation (CHI660C, Shanghai Chenhua Device Company, China), an X-ray diffractometer (Bruker D8 Advance, Germany), an UV-Vis 2550 spectrophotometer and a Spectrofluorometer (FSP920, Edinburgh Instruments).

1.2 Preparation of TiO\(_2\) nanocrystal colloid

Using tetrabutyl titanate as precursor, a TiO\(_2\) nanocrystal colloid was prepared by the following procedure \[11\] - \[14\]. Tetrabutyl titanate (10 mL) was rapidly added to distilled water (150 mL), immediately forming a white precipitate. The system was stirred for 30 min. The precipitate was filtered using a glass frit and washed three times with 100 mL of distilled water. The precipitate was added to an aqueous solution of nitric acid (0.1 mol L\(^{-1}\), 100 mL) and stirred vigorously at 80°C until the slurry became a translucent blue-white liquid. Thereinto 70 mL resultant colloidal suspension was autoclaved at 200°C for 12 h to form a white, milky slurry. The autoclaved 70 mL slurry was added to original blue-white liquid, adding 0.2 g TiO\(_2\) powder (P25), stirring 30 min, and then the second time hydrothermal treatment was conducted. The resultant slurry was concentrated to 1/5 of its original volume, then PEG-20,000 (20 wt%-30 wt% slurry) and a few drops of emulsification reagent Triton X-100 \[12\] were added to form a stable TiO\(_2\) nanocrystal colloid.

1.3 Preparation of upconversion luminescence colloid

A TiO\(_2\):(Er\(^{3+}\), Yb\(^{3+}\)) powder was prepared by the following process. Some of Er\(_2\)O\(_3\), Yb\(_2\)O\(_3\), and LiOH (as melt reagent) \[15\] were first dissolved in nitric acid (10 wt%) to form a nitrate solution. Meanwhile, 10 mL of tetrabutyl titanate was added to 150 mL of vigorously stirred distilled water, immediately forming a white precipitate. The system was stirred for 30 min. The precipitate was filtered using a glass frit and washed three times. The resulted precipitate was added into the nitrate solution, the pH of the mixed solution was adjusted to 1 by adding acetic acid (10 mL) and distilled water. The system was stirred at 80°C until a translucent blue-white colloid formed. The resultant colloid was autoclaved (filled less than 80%) at 200°C for 12 h to form a white precipitate containing Er\(^{3+}\) and Yb\(^{3+}\). After the precipitate was vacuum dried at 100°C, ground, calcined at 800°C for 2.5 h and cooled to room temperature, an upconversion luminescence powder was obtained.

The upconversion luminescence powder was added to the TiO\(_2\) colloid in different ratios and concentrated at 80°C. then PEG-20000 (20 wt%-30 wt% slurry) and a few drops of Triton X-100 were added to form a stable upconversion luminescence colloid.

1.4 Preparation of upconversion luminescence electrode

Plastic adhesive tape was fixed on the four sides of the cleaned FTO conducting glass plate to restrict \[13\] the thickness of 10 \(\mu\)m and the area of 1 cm \(\times\) 1 cm for the oxide film. The TiO\(_2\) colloid was dropped on the FTO glass plate using a scalpel. The resulting films were sintered at 450°C in air for 30 min to solidify the TiO\(_2\) film and delete organic impurity on the film, after cooling down to 80°C, a normal TiO\(_2\) film was obtained. By using the same method, an upconversion luminescence layer with thickness of 4 \(\mu\)m was covered on the TiO\(_2\) film. The resultant film was immersed in a 3\(\times\)10\(^{-3}\) mol L\(^{-1}\) solution of N-719 in absolute ethanol for 24 h to adequately absorb the dye. The dye-sensitized oxide film was washed with anhydrous ethanol and dried in moisture-free air in dark to give a dye-sensitized upconversion luminescence electrode.

1.5 Characterization

The phase and crystal structure of TiO\(_2\):(Er\(^{3+}\), Yb\(^{3+}\)) upconversion luminescence powders were checked with an X-ray diffractometer (Bruker D8 Advance, Germany) using Cu K\(_\alpha\) radiation (\(\lambda = 1.5405\) Å) under 40 kV, 40 mA, and scan rate: 3°/min, scan range: 10°-80°. UV-Vis absorption spectrum of dye was measured using a UV-Vis 2500 spectrophotometer (Shimadzu Corporation, Japan). The photoluminescence (emission and excitation) spectra of the upconversion luminescence powders were checked with an X-ray diffractometer (Bruker D8 Advance, Germany) using Cu K\(_\alpha\) radiation (\(\lambda = 1.5405\) Å) under 40 kV, 40 mA, and scan rate: 3°/min, scan range: 10°-80°. UV-Vis absorption spectrum of dye was measured using a UV-Vis 2500 spectrophotometer (Shimadzu Corporation, Japan). The photoluminescence (emission and excitation) spectra of the upconversion luminescence powders were measured on a spectrofluorometer (FSP920, Edinburgh Instruments).

Photoelectric properties of the DSSCs were measured with an electrochemical workstation (CHI660C, Shanghai Chenhua Device Company, China) and a stabilized power supply Xe/Hg arc lamp (CHF-XM-500W, Changtuo Scientific Ltd, Beijing, China).

1.6 DSSC assemblage and photoelectric measurements

A DSSC was assembled by injecting an electrolyte into the aperture between the TiO\(_2\) film electrode (anode electrode) and a Pt-coated counter electrode \[14\]. The electrolyte was consisted of 0.60 mol L\(^{-1}\) tetrabutyl ammonium iodide, 0.10 mol L\(^{-1}\) I\(_3\), and 0.50 mol L\(^{-1}\) 4-tert-butyl-pyridine in acetonitrile.

Using the stabilized power supply Xe/Hg arc lamp as a solar light simulator, controlling the incident light intensity...
(P<sub>m</sub>) of 100 mW cm<sup>-2</sup>, the short circuit density (J<sub>SC</sub>, mA cm<sup>-2</sup>) and open circuit voltage (V<sub>OC</sub>, V) were measured using the electrochemical workstation (CHI660C, Shanghai Chenhua Device Company, China). The fill factor (FF) and the light-to-electricity conversion efficiency (η) of the DSSC were calculated according to the following equations [16]:

\[
\eta(\%) = \frac{V_{\text{max}} \times J_{\text{max}}}{P_m} \times 100\% = \frac{V_{\text{OC}} \times J_{\text{SC}} \times FF}{P_m} \times 100\%,
\]

\[
FF = \frac{V_{\text{max}} \times J_{\text{max}}}{V_{\text{OC}} \times J_{\text{SC}}},
\]

where \(J_{\text{max}}\) (mA cm<sup>-2</sup>) and \(V_{\text{max}}\) (V) are the current density and voltage at the point of maximum power output on the \(J-V\) curves, respectively.

2 Results and discussion

2.1 XRD patterns

The XRD patterns of the TiO<sub>2</sub> and TiO<sub>2</sub>:(Er<sup>3+</sup>, Yb<sup>3+</sup>) powders are shown in Figure 1. Figure 1(a) shows that nearly all of the peaks correspond to the anatase phase (PDF No. 21-1272). Some of the rutile phase present in P25 is also observed. The anatase XRD peaks in Figure 1(a) are intense and well resolved, suggesting that the resultant TiO<sub>2</sub> nanocrystals are highly crystalline. Nearly all of the anatase TiO<sub>2</sub> changes to the rutile phase after calcination at 800°C for 2.5 h (Figure 1(b)), because the signals after calcination are consistent with PDF card No. 65-0192. Figure 1(c) shows peaks resulting from the rutile phase of TiO<sub>2</sub> in the TiO<sub>2</sub>:(Er<sup>3+</sup>, Yb<sup>3+</sup>) powder as well as some pyrochlore phases from Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (marked with p).

The average diameters (\(D_{hkl}\)) of the particles can be calculated by the Scherrer formula [17]:

\[
D_{hkl} = \frac{k \lambda}{\beta \cos \theta},
\]

where \(D_{hkl}\) is the particle size in the normal direction for \((h k l)\) crystal face. Here, the constant \(K\) (depends on the particle shape, face index, \(\beta\) and \(D_{hkl}\)) adopts 0.9 [14]. \(\lambda\) (0.1540 nm) is the wavelength of the Cu-Kα radiation, \(\theta\) is the diffraction angle and \(\beta\) is the full width at half-maximum (FWHM in radians).

According to Figure 1 and eq. (3), the apparent size \(D\) of the TiO<sub>2</sub> nanocrystals in Figure 1(a) and the upconversion luminescence powders in Figure 1(c) are 19 nm and 68 nm, respectively. Compared with the diffraction peaks in curves (a) and (b), the intensity of diffraction peaks in curve (c) increase, indicating that the conversion luminescence powder has a higher crystallization and larger size, which the larger particles as light scattering points extend the light diffuse path, and enhance the incident photons capture efficiency [18]. Meanwhile, it is known that the refractive index of the anatase phase is lower than that of the rutile phase (anatase: 2.5; rutile: 2.7). Thus TiO<sub>2</sub>:(Er<sup>3+</sup>, Yb<sup>3+</sup>) layer show a higher refractive index than undoped TiO<sub>2</sub>, which should help to increase light-to-electricity conversion efficiency of the DSSC.

2.2 Excitation and emission spectra of TiO<sub>2</sub>:(Er<sup>3+</sup>, Yb<sup>3+</sup>)

Figure 2(a) shows the excitation spectra of the TiO<sub>2</sub>:(Er<sup>3+</sup>, Yb<sup>3+</sup>) powder. A strong, broad peak at 978 nm is observed. The band centered at 978 nm can be identified as the transition of Yb<sup>3+</sup> from 2F<sub>7/2</sub> to 2F<sub>5/2</sub>, indicating that the upconversion luminescence powder can effectively absorb the infrared light.

The luminescence spectra of the TiO<sub>2</sub>:(Er<sup>3+</sup>, Yb<sup>3+</sup>) powder exhibits peaks in the green region from 510–570 nm and in the red region from 610–700 nm as shown in Figure 2(b). Upconversion fluorescence excitation can be readily observed with a 978 nm laser. The peaks centered at 978 nm can be identified as the transition of Yb<sup>3+</sup> from \(^2\)F<sub>7/2</sub> to \(^2\)F<sub>5/2</sub>, indicating that the upconversion luminescence powder can effectively absorb the infrared light.

The luminescence spectra of the TiO<sub>2</sub>:(Er<sup>3+</sup>, Yb<sup>3+</sup>) powder are shown in Figure 2(b). Upconversion luminescence powder exhibits peaks in the green region from 510–570 nm and in the red region from 610–700 nm as shown in Figure 2(b). Upconversion luminescence can be readily observed with a 978 nm laser. The peaks centered at 521, 544 and 650 nm correspond to the Er<sup>3+</sup> transitions, \(^4\)I<sub>11/2</sub> \(\rightarrow\) \(^4\)I<sub>15/2</sub>, \(^4\)S<sub>3/2</sub> \(\rightarrow\) \(^4\)I<sub>15/2</sub>, and \(^4\)F<sub>9/2</sub> \(\rightarrow\) \(^4\)I<sub>15/2</sub> [19–22] transitions, respectively. These upconversion luminescences, especially in 544 nm, are accorded with the absorption wavelength of the N-719. When doping the TiO<sub>2</sub>:(Er<sup>3+</sup>, Yb<sup>3+</sup>) powder in the photoanode of DSSC, it will effectively enhance the light-to-electricity efficiency of DSSC.

Figure 3 shows the energy level diagram for Er<sup>3+</sup> and Yb<sup>3+</sup> codoped systems and upconversion luminescence process. The upconversion luminescence mechanism is shown as [20,22]: Yb<sup>3+</sup> ions have a much larger absorption cross-section relative to that of Er<sup>3+</sup> ions around 978 nm, so Yb<sup>3+</sup> ions are excited preferentially. An Er<sup>3+</sup> ion can then be excited from the \(^4\)I<sub>11/2</sub> ground state to the \(^4\)I<sub>15/2</sub> excited state by energy transfer from an excited Yb<sup>3+</sup> ion. The Er<sup>3+</sup> ion is...
Figure 2  Excitation (a) and luminescence (b) spectra of TiO_2:(Er^{3+}, Yb^{3+}) powders excited with a laser at 978 nm.

subsequently excited to the \(^2F_{13/2}\) state by absorbing energy from another Yb\(^{3+}\) ion. The Er\(^{3+}\) ion then decays nonradiatively to the \(^3H_{11/2}, ^4S_{3/2}\) and \(^4F_{9/2}\) levels. In addition, Er\(^{3+}\) ions in the \(^1I_{13/2}\) excited state can decay nonradiatively to the \(^1I_{15/2}\) level and be excited to the \(^4F_{9/2}\) level by absorbing a second photon, resulting in green light emission (521 nm and 544 nm; \(^2H_{11/2} \rightarrow ^2I_{15/2}\) and \(^4S_{3/2} \rightarrow ^4I_{15/2}\), respectively). Alternatively, the Er\(^{3+}\) can further relax and populate the \(^4F_{9/2}\) level leading to the red emission at 650 nm from the transition \(^4F_{9/2} \rightarrow ^4I_{15/2}\).

2.3 UV-Vis absorption spectrum

The UV-Vis absorption spectrum of the dye-sensitized TiO_2 electrode is shown in Figure 4. A strong, broad absorption band occurs from 290 to 700 nm with a maximum at about 385 nm and a shoulder at 528 nm. It should be noted that the dye-sensitized TiO_2 electrode cannot absorb light with wavelengths higher than 700 nm. According to the discussion on excitation and luminescence spectra, addition of TiO_2:

(Er\(^{3+}, Yb^{3+}\)) powder into the TiO_2 electrode should allow the infrared light with wavelength about 978 nm which the dye cannot absorb transfers to the green light and the red light which the dye has a high absorption. Therefore, the more solar irradiation is absorbed by DSSC and the light-to-electricity conversion efficiency of the DSSC is increased.

2.4 Influence of upconversion luminescence on the photoelectric properties of DSSC

To investigate the effect of infrared irradiation on DSSCs,
we used a filter stop to remove the light of wavelength less than 720 nm. Figure 5 shows the photovoltaic characterization of the DSSCs with and without the upconversion luminescence powder under infrared irradiation of 60 mW cm\(^{-2}\). The DSSC lacking the upconversion luminescence powder possessed the photovoltaic parameters: \(J_{SC} = 0.105\) mA cm\(^{-2}\), \(V_{OC} = 401\) mV, \(FF = 0.560\) and \(\eta = 0.04\%\). The DSSC containing the upconversion luminescence powder displays enhanced photovoltaic parameters: \(J_{SC} = 0.248\) mA cm\(^{-2}\), \(V_{OC} = 561\) mV, \(FF = 0.631\) and \(\eta = 0.146\%\). The enhancement indicates that the upconversion luminescence layer can transfer infrared light to visible light which the N-719 dye can absorb effectively, increasing the harvested sunlight and improving the efficiency of the DSSC.

The photocurrent-voltage curves of the DSSCs with and without an upconversion luminescence powder under simulated solar light irradiation of 100 mW cm\(^{-2}\) (AM 1.5) are shown in Figure 6. Table 1 shows the influence of the amount of the luminescence powder on the photoelectric properties of the DSSCs. As the amount of the luminescence powder in the DSSC increases, \(J_{SC}\) increases and then decreases, and \(V_{OC}\) increases. The maximum efficiency of the DSSC is achieved when the mass ratio of TiO\(_2\)/luminescence powder is 1/3 in the luminescence layer.

The increase in \(J_{SC}\) with the amount of the luminescence powder at low concentrations is because the luminescence powder absorbs infrared light (978 nm) which it transfers to visible light (510–700 nm), resulting in an increase in incident light harvest, photoinduced electrons in unit area, and \(J_{SC}\) in the DSSC. On the other hand, larger particle sizes in the upconversion luminescence layer extend the light transmission distance, improving the incident light harvest [23], and increasing the photocurrent. However, when Er\(^{3+}\) and Yb\(^{3+}\) are doped in TiO\(_2\), some crystal defects are present. The defects can capture photoinduced electrons and holes, leading to a decrease in photocurrent, especially in higher Er\(^{3+}\) and Yb\(^{3+}\) concentration. This explains why \(J_{SC}\) increases and then decreases as the amount of TiO\(_2\):(Er\(^{3+}\), Yb\(^{3+}\)) in the DSSC increases.

According to Gratzel, \(V_{OC}\) corresponds to the potential difference between the Fermi level of the electrons in the oxide film and the redox potential of the electrolyte [1,2]. When Er\(^{3+}\) and Yb\(^{3+}\) ions substitute Ti\(^{4+}\) ion lattice sites in TiO\(_2\), similar to Si semiconductors, i.e., p-type doping, the energy level of the oxide film is elevated, resulting in an increase of \(V_{OC}\). In our experiments, the electrolyte is the same so it is unsurprising that \(V_{OC}\) increases as the amount of Er\(^{3+}\) and Yb\(^{3+}\) ions increase. When the mass ratio of TiO\(_2\)/TiO\(_2\):(Er\(^{3+}\), Yb\(^{3+}\)) is 1/5 in the luminescence layer, \(V_{OC}\) reaches 0.817 V. This value is higher than that of other DSSCs with the same structure, showing significance of p-type doping for enhancing the photovoltage of DSSCs.

Comprising \(J_{SC}\), \(V_{OC}\), \(FF\) and \(\eta\), when the mass ratio of TiO\(_2\)/TiO\(_2\):(Er\(^{3+}\), Yb\(^{3+}\)) is 1/3 in the upconversion luminescence layer, the light-to-electricity conversion efficiency of the DSSC reaches 7.28%, which is an improvement of 13.6% compared with the DSSC not doped with rare-earth ions.

### 3 Conclusions

In summary, a TiO\(_2\):(Er\(^{3+}\), Yb\(^{3+}\)) powder was synthesized using a hydrothermal method. The powder was used to fabricate an oxide film in the DSSCs. The rare-earth oxide undergoes upconversion luminescence, transferring infrared light (DSSC can not absorb) into visible light with wave-
lengths of 510–700 nm (DSSC can absorb), enhancing the photocurrent of the DSSC. As a p-type dopant, the rare-earth oxide increases the Fermi level of the oxide film and the photovoltage of DSSC. The highest efficiency of the DSSC is reached when the mass ratio of TiO$_2$/TiO$_2$(Er$^{3+}$, Yb$^{3+}$) is 1/3 in the upconversion luminescence layer. Under a simulated solar light irradiation of 100 mW cm$^{-2}$ (AM 1.5), the DSSC containing TiO$_2$/TiO$_2$(Er$^{3+}$, Yb$^{3+}$) doping achieved a short-circuit current density of 15.45 mA cm$^{-2}$, an open-circuit voltage of 0.748 V and a photocurrent of the DSSC. As a p-type dopant, the rare-earth doping in DSSCs for providing an effective way to improve their sunlight conversion efficiency.

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