A New Up-conversion Material of Ho$^{3+}$-Yb$^{3+}$-Mg$^{2+}$ Tri-doped TiO$_2$ and Its Applications to Perovskite Solar Cells

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Abstract

A new up-conversion nanomaterial of Ho$^{3+}$-Yb$^{3+}$-Mg$^{2+}$ tri-doped TiO$_2$ (UC-Mg-TiO$_2$) was designed and synthesized with a sol-gel method. The UC-Mg-TiO$_2$ presented enhanced up-conversion fluorescence by an addition of Mg$^{2+}$. The UC-Mg-TiO$_2$ was utilized to fabricate perovskite solar cells by forming a thin layer on the electron transfer layer. The results display that the power conversion efficiency of the solar cells based on the electron transfer layer with UC-Mg-TiO$_2$ is improved to 16.3 from 15.2% for those without UC-Mg-TiO$_2$. It is demonstrated that the synthesized UC-Mg-TiO$_2$ can convert the near-infrared light to visible light that perovskite film can absorb to improve the power conversion efficiency of the devices.

Keywords: Ho$^{3+}$-Yb$^{3+}$-Mg$^{2+}$ tri-doped TiO$_2$, Up-conversion nanomaterial, Perovskite solar cells

Background

More attentions have been paid to the perovskite solar cells (PSCs) in the field of solar cells [1–5]. The power conversion efficiency (PCE) of the PSCs has been exceeding 22% within a few years [6]. However, the perovskite materials usually absorb the visible light whose wavelength is less than 800 nm, and more than half of the solar energy is not be utilized, especially in the region of near-infrared (NIR). To solve the issues, one of the effective methods is to apply the up-conversion nanomaterial to perovskite solar cells by converting the NIR light to visible light that the perovskite can utilize [7–9]. The beta-phase sodium yttrium fluoride ($\beta$-NaYF$_4$) is commonly used as the host lattice for rare earth ions to prepare the up-conversion materials. While the $\beta$-NaYF$_4$-based up-conversion materials are insulators, which is not beneficial for the electron transfer [ETL] [10].

Titanium dioxide (TiO$_2$) nanocrystal with anatase phase is commonly used as the electron transfer material in the perovskite solar cells due to its suitable energy band structure, low cost, and long stability [11–13]. However, the energy band gap of TiO$_2$ is large (3.2 eV), which hampers its applications. To improve the applications of TiO$_2$ in visible light and near-infrared region, some methods were explored. One of the effective methods is doping TiO$_2$ with metal or non-metal [14–16]. Yu et al. [17] demonstrated that Ho$^{3+}$-Yb$^{3+}$-F$^{-}$ doped TiO$_2$ could convert NIR light to visible light that can be absorbed by the dye-sensitized solar cells (DSSCs). Zhang and co-authors [18] proved that Mg-doped TiO$_2$ can change the Fermi energy level of TiO$_2$ to enhance the performance of perovskite solar cells.

In this work, we are preferred to combine the rare earth ions (Ho$^{3+}$ and Yb$^{3+}$) and the metal ion (Mg$^{2+}$) doped TiO$_2$ together to synthesize a new material with enhanced up-conversion fluorescence. Our purpose is to explore how the addition of Mg$^{2+}$ affect the up-conversion fluorescence of TiO$_2$ and to apply the up-conversion nanomaterial of Ho$^{3+}$-Yb$^{3+}$-Mg$^{2+}$ tri-doped TiO$_2$ to perovskite solar cells. The results display that the addition of Mg$^{2+}$ enhanced the up-conversion emission of TiO$_2$, and the application of Ho$^{3+}$-Yb$^{3+}$-Mg$^{2+}$ tri-doped TiO$_2$ improved the PCE of PSCs to 16.3% from 15.2%.
Methods/Experimental

Materials

Formamidinium iodide (FAI), Methylamium bromide (MABr), Lead diiodide (PbI₂), 2,2′,7,7′-Tetrakis-(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD), and lead dibromide (PbBr₂) were purchased from Xi’an Polymer Light Technology Corp. (China). The SnO₂ colloid solution was purchased from Alfa Aesar (tin (IV) oxide). Dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), 4-tert-butylpyridine (TBP), and lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD (China).

Synthesis of Ho³⁺-Yb³⁺-Mg²⁺ Tri-doped TiO₂

The up-conversion material of Ho³⁺-Yb³⁺-Mg²⁺ tri-doped TiO₂ was synthesized with a reported method [19] with some modifications. Firstly, a Titanium tetra-butanolate was obtained by mixing acetylacetone (AcAc) and Titanium tetrabutanolate (Ti(OBu)₄) for 1 h under stirring at 25 °C, and then the isopropyl alcohol (IPA) was added to prepare the (Ti(OBu)₄) solution. A mixed solution of IPA, HNO₃, and H₂O was dropped into the solution slowly. After stirring for 6 h, a TiO₂ sol with a color of light yellow was obtained. In a typical synthesis, the molar ratio of AcAc, HNO₃, and H₂O to Ti(OBu)₄ was 1:0.3:2:1. For the synthesis of Ho³⁺-Yb³⁺ co-doped TiO₂, Ho(NO₃)₃·5H₂O and Yb(NO₃)₃·5H₂O were used as the elemental sources and added into the solution. Typically, the molar ratio of Ho³⁺:Yb³⁺:Ti = 1:x:100 (x = 2, 3, 4, 5). For the synthesis of Ho³⁺-Yb³⁺-Mg²⁺ tri-doped TiO₂, Ho(NO₃)₃·5H₂O, Yb(NO₃)₃·5H₂O, and Mg(NO₃)₂·6H₂O as the elemental sources were added into the solution, and the molar ratio of Ho³⁺:Yb³⁺:Mg²⁺:Ti = 1:4:4x:100 (x = 0, 1, 1.5, 2, 2.5). The obtained solution was referred to as Ho³⁺-Yb³⁺-Mg²⁺ tri-doped TiO₂ (UC-Mg-TiO₂) sol. The solvent in the solution was removed by heating at 100 °C for 10 h. Then, the material powders were heated for 30 min at 500 °C.

Preparation of PSCs

The FTO was washed in detergent, acetone, and isopropanol, and then treated for 15 min with UV-O₃. A blocking layer was prepared by a spin-coating method using a solution of titanium disopropoxide bis (acetylacetone) in 1-butanol with the concentration of 1 M and then heated for 30 min at 500 °C. An electron transfer layer (ETL) prepared by a spin-coating method using TiO₂ sol which is obtained by diluting TiO₂ (30NR-D) using ethanol (1:6, mass ratio), and then heated for 10 min at 100 °C and 30 min at 450 °C. The UC-Mg-TiO₂ was used to fabricate the solar cells by spin-coating a mixed solution of UC-Mg-TiO₂ sol and TiO₂ sol (UC-Mg-TiO₂:TiO₂ = x:(100 − x), v/v, x = 0, 20, 40, 60, 80, and 100) on the ETL and heating for 30 min at 500 °C. A perovskite film was fabricated according to the reported method [20]. In brief, the precursor solution of perovskite was prepared by dissolving FAI (1 M), PbI₂ (1.1 M), MABr (0.2 M), and PbBr₂ (0.22 M) in the
mixture of DMF/DMSO (4:1 v:v), and a stock solution of CsI (1.5 M) in DMSO was added. The perovskite film was obtained by spin-coating method with 1000 rpm for 10 s and 4000 rpm for 30 s, and 200 μL chlorobenzene was dropped on the sample before the end of 20 s. A hole transfer layer (HTL) was obtained by the spin-coating method using a spiro-MeOTAD solution at 4000 rpm for 30 s. The spiro-OMeTAD solution was prepared by dissolving 72.3 mg spiro-MeOTAD in 1 mL chlorobenzene and by adding 28.8 μL TBP, 17.5 μL Li-TFSI solution (520 mg/ml in acetonitrile). Finally, an Au anode was made on the hole transfer layer by thermal evaporation.

Characterization
Photoluminescence (PL) spectra were acquired using a fluorometer of FLS 980 E. A diffractometer of DX-2700 was used to obtain the X-ray diffraction (XRD) patterns. X-ray photoelectron spectra were measured with a spectrometer of XPS THS-103. Absorption spectra were obtained with a spectrophotometer of Varian Cary 5000.

![Fig. 3 X-ray photoelectron spectra of UC-Mg-TiO₂.](image)

**Fig. 3** X-ray photoelectron spectra of UC-Mg-TiO₂. a Ti 2p, b Ho 4d, c Yb 4d, and d Mg 2p

![Fig. 4 a Absorption spectra of TiO₂ (30NR-D) and UC-Mg-TiO₂. b Tauc plots](image)

**Fig. 4** a Absorption spectra of TiO₂ (30NR-D) and UC-Mg-TiO₂. b Tauc plots
Scanning electron microscope (SEM) images were performed using a microscope of JSM-7001F. A Keithley 2440 Sourcemeter was applied to measure the photocurrent-voltage (I-V) curves of the solar cells under an illumination of AM 1.5. An electrochemical workstation of CHI660e was utilized to get the electrochemical impedance spectroscopy (EIS). The incident photon-to-current conversion efficiency (IPCE) was measured with a solar cell IPCE recording system (Crowntech Qtest Station 500ADX).

Results and Discussion

The up-conversion fluorescence of the materials was optimized by varying the molar ratio of Ho³⁺ and Yb³⁺. The up-conversion emission of Ho³⁺-Yb³⁺ co-doped TiO₂ with varying molar ratio of Ho³⁺ and Yb³⁺ (Ho:Yb:Ti = 1:x:100) was shown in Fig. 1a, which were excited with an 980 nm NIR light. Two strong up-conversion emission peaks were observed at 547 nm and 663 nm. Additional file 1: Figure S1 shows the up-conversion mechanisms of the Ho³⁺-Yb³⁺ co-doped TiO₂. The fluorescence peaks at 663 nm and 547 nm could correspond to the 5F₅ → 5I₈ and (5S₂, 5F₄) → 5I₈ transitions of Ho³⁺, respectively [21]. It can be seen that the intensity of the up-conversion fluorescence is the largest when the molar ratio of Ho³⁺ and Yb³⁺ is 1:4. Figure 1b presents the up-conversion photofluorescence of Ho³⁺-Yb³⁺-Mg²⁺ tri-doped TiO₂ with different doping contents of Mg²⁺ (Ho:Yb:Ti:Mg = 1:4:x:100, molar ratio). The up-conversion fluorescence was enhanced by the addition of Mg²⁺. When the doping content of Ho³⁺:Yb³⁺:Mg²⁺ = 1:4:2, the up-conversion emission is the strongest for Ho³⁺-Yb³⁺-Mg²⁺ tri-doped TiO₂. Hereinafter, the UC-Mg-TiO₂ with the molar ratio of Ho³⁺:Yb³⁺:Mg²⁺ :Ti = 1:4:2:100 was applied.

Figure 2 shows the X-ray diffraction of TiO₂ (30NR-D) and UC-Mg-TiO₂. According to the PDF card (JCPDS card no.21–1272), the peaks located at 2θ = 25.6 °, 37.7 °, 48.1 °, and 53.7 ° in the patterns could belong to the (101), (004), (200), (105), (211), and (204) crystal planes, respectively. This displays the phase of UC-Mg-TiO₂ is anatase.

To demonstrate the doping of Ho, Yb, and Mg into TiO₂, the X-ray photoelectron spectra of UC-Mg-TiO₂ were obtained. The XPS survey spectrum of UC-Mg-TiO₂ was presented in Additional file 1: Figure S2. Figure 3a shows the high-resolution photoelectron spectra of Ti 2p, which had two peaks of Ti 2p₁/₂ and Ti 2p₃/₂ located at 458.2 eV and 458.2 eV, respectively. Figure 3b, c shows the high-resolution photoelectron peaks of Ti 2p, which had two peaks of Ti 2p₁/₂ and Ti 2p₃/₂ located at 463.7 eV and 458.2 eV, respectively.
parameters were abstracted. The experiments were performed, and from which the photovoltaic partition of Ho$^{3+}$ and Yb$^{3+}$. It can be seen that the doping of V solar cells mesoporous layers with and without UC-Mg-TiO$_2$. There are five absorption peaks of Ho, Yb, and Mg atoms were incorporated into TiO$_2$.

Figure 4a shows the absorption spectra of TiO$_2$ (30NR-D) and UC-Mg-TiO$_2$. There are five absorption peaks appear in the absorption spectrum of UC-Mg-TiO$_2$, which are corresponding to characteristic absorption of Ho$^{3+}$ and Yb$^{3+}$. It can be seen that the doping of Ho, Yb, and Mg improves the absorption of TiO$_2$ in visible light region and expands its absorption to NIR range. The Tauc plot can be used to estimate the energy band gap of material [24]. The Tauc plots from the absorption spectra were presented in Fig. 4b. The energy band gap values can be calculated to be 3.09 eV and 3.18 eV for UC-Mg-TiO$_2$ and TiO$_2$ (30NR-D), respectively. The UC-Mg-TiO$_2$ presents a smaller band gap than TiO$_2$.

Figure 5 shows the SEM photograph of TiO$_2$ (30NR-D) and UC-Mg-TiO$_2$ films. The size of the nanoparticle is about 25 nm for 30 NR-D, and particle size is about 28 nm for UC-Mg-TiO$_2$. The two films are uniform. Thus, the UC-Mg-TiO$_2$ displays a similar morphology and particle size to TiO$_2$ (30NR-D).

The PSCs were fabricated based on the electron transfer layers with and without UC-Mg-TiO$_2$. The electron transfer layer with UC-Mg-TiO$_2$ was prepared by spin-coating the mixed solution of UC-Mg-TiO$_2$ sol and TiO$_2$ sol (UC-Mg-TiO$_2$:TiO$_2$ = x:(100 − x), x = 0, 20, 40, 60, 80, and 100, $\nu$/($\nu$). I-V measurements of the solar cells were performed, and from which the photovoltaic parameters were abstracted. The $J_{sc}$, $V_{oc}$, FF, and PCE of the solar cells in this work were obtained by an average of the values of 20 samples. The relation of PCE with the contents of UC-Mg-TiO$_2$ was displayed in Fig. 6a. Firstly, the PCE of the solar cells becomes large, and after that becomes small with the increase of the UC-Mg-TiO$_2$ contents, which reaches the maximum value at the content of 60% (UC-Mg-TiO$_2$:TiO$_2$ = 60:40, $\nu$/($\nu$). Table 1 presents the photovoltaic parameters of solar cells based on the electron transfer layers with and without UC-Mg-TiO$_2$. The open-circuit voltage ($V_{oc}$) and short-circuit current ($I_{sc}$) of the solar cells with UC-Mg-TiO$_2$ were increased to 1.05 V and 22.6 mA/cm$^2$ from 1.03 V and 21.2 mA/cm$^2$ for the solar cells without UC-Mg-TiO$_2$, respectively. Thus, the PCE of the devices based on the electron transfer layer with UC-Mg-TiO$_2$ was improved to 16.3% from 15.2% for those without UC-Mg-TiO$_2$. The typical I-V curves of the devices are shown in Fig. 6b. The PCE histograms of the solar cell performance of 20 samples with and without UC-Mg-TiO$_2$ are presented in Additional file 1: Figure S3.

Some experiments were carried out to explain the improvement. Figure 7 displays the energy band structures of the materials contained in the solar cells based on some reports [25, 26], and the energy band gap from the Tauc plots is shown in Fig. 4b. The conduction band difference between perovskite and TiO$_2$ becomes larger for UC-Mg-TiO$_2$ compared with that of TiO$_2$ (30NR-D), since the UC-Mg-TiO$_2$ has a smaller band gap than TiO$_2$ (30NR-D). This may be one of the reasons to give a larger $V_{oc}$ for the devices based on the electron transfer layer with UC-Mg-TiO$_2$ [27, 28].

Figure 8a shows the steady-state photoluminescence (PL) of the perovskite films on the electron transfer layers with and without UC-Mg-TiO$_2$. The PL peak located at 760 nm is originated from the perovskite film [29]. The PL intensity of the perovskite film on electron transfer layer with UC-Mg-TiO$_2$ decreased compared with that of perovskite film on electron transfer layer without UC-Mg-TiO$_2$. This implies that the electron transport and extraction of UC-Mg-TiO$_2$ from the perovskite film is more efficient than that of TiO$_2$ (30NR-D). This can be further demonstrated by the time-resolved photoluminescence (TRPL) of the samples shown in Fig. 8b. It can be seen that the decay time of TRPL for the perovskite film on electron transfer layer with UC-Mg-TiO$_2$ is faster than that of perovskite film on electron transfer layer without UC-Mg-TiO$_2$. This indicates that the charge transfer for the former is faster than the latter [30, 31].

### Table 1 Photovoltaic parameters of the solar cells based on the mesoporous layers with and without UC-Mg-TiO$_2$

| Solar cells          | $V_{oc}$ (V) | $I_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|----------------------|-------------|----------------------|--------|---------|
| Without UC-Mg-TiO$_2$| 1.03 ± 0.04 | 21.2 ± 0.7           | 69.6 ± 1.2 | 15.2 ± 0.5 |
| With UC-Mg-TiO$_2$  | 1.05 ± 0.03 | 22.6 ± 0.6           | 68.7 ± 1.3 | 16.3 ± 0.3 |

Fig. 7 Energy band structures of the materials contained in the solar cells.

Zhang et al. Nanoscale Research Letters (2018) 13:262
Figure 9a shows the Nyquist plots obtained from the electrochemical impedance spectroscopy (EIS) of the solar cells based on the electron transfer layer with and without UC-Mg-TiO₂. The Nyquist plots can be fitted by an equivalent circuit which is schematically shown in Fig. 9b. The $R_s$, $R_{rec}$, and $C_μ$ are the series resistance, recombination resistance, and the capacitance of the device [32, 33]. The detailed fitting values are presented in Table 2. The $R_s$ value of the devices based on the electron transfer layers with UC-Mg-TiO₂ is nearly the same with that of those without UC-Mg-TiO₂. While the $R_{rec}$ value of the devices based on electron transfer layer with UC-Mg-TiO₂ is larger than that of those without UC-Mg-TiO₂. This implies that UC-Mg-TiO₂ could effectively decrease the charge recombination.

To confirm the contributions of the up-conversion material UC-Mg-TiO₂ to the photocurrent of the solar cells, the I-V measurements were carried out under the simulated solar radiation filtered with a band-pass NIR filter (980 ± 10 nm). Figure 10a displays the I-V curves of the solar cells based on the electron transfer layers with and without UC-Mg-TiO₂. The short-circuit current ($I_{sc}$) of the solar cells with UC-Mg-TiO₂ is obviously larger than that of those without UC-Mg-TiO₂. This demonstrates the effect of UC-Mg-TiO₂ on the photocurrent of the solar cells, because UC-Mg-TiO₂ converts the near-infrared photons into visible photons, which the solar cells can absorb to produce additional photocurrent [7, 17]. Figure 10b shows the IPCE spectra of the solar cells with and without UC-Mg-TiO₂. The IPCE of the solar cells with UC-Mg-TiO₂ is increased, especially at the range of 400~650 nm, compared with that of those without UC-Mg-TiO₂. This could be caused by the up-conversion effect of UC-Mg-TiO₂ [7, 17].

Conclusions
The up-conversion nanomaterial of Ho³⁺-Yb³⁺-Mg²⁺ tri-doped TiO₂ (UC-Mg-TiO₂) was synthesized successfully. The up-conversion emissions of the UC-Mg-TiO₂ were enhanced with an addition of Mg²⁺. We applied the UC-Mg-TiO₂ to the PSCs, in which the UC-Mg-TiO₂ was used to modify the electron transfer

| Solar cells | $R_s/Ω$ | $R_{rec}/Ω$ | $C_μ$/$T/F$ | $C_μ/P$ |
|------------|--------|------------|----------|--------|
| With UC-Mg-TiO₂ | 23.4   | 489.2      | 9.9E-8   | 0.8    |
| Without UC-Mg-TiO₂ | 23.1   | 837.5      | 13.1E-8  | 0.8    |
layer. The $V_{oc}$ and $I_{sc}$ of the devices with UC-Mg-TiO$_2$ were improved to 1.05 V and 22.6 mA/cm$^2$ from 1.03 V and 21.2 mA/cm$^2$ for those without UC-Mg-TiO$_2$, respectively. And the PCE of the devices with UC-Mg-TiO$_2$ was increased to 16.3% from 15.2% for those without UC-Mg-TiO$_2$.

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### Additional file

Additional file 1: Figure S1. Up-conversion mechanisms of the Ho$^{3+}$-Yb$^{3+}$ co-doped TiO$_2$. Figure S2. XPS survey of UC TiO$_2$. Figure S3 PCE histograms of the solar cell performance of 20 samples with and without UC-Mg-TiO$_2$. (DOCX 77 kb)

### Abbreviations

EIS: Electrochemical impedance spectroscopy; NIR: Near-infrared; PCE: Power conversion efficiency; PL: Photoluminescence; PSCs: Perovskite solar cells; TRPL: Time-resolved photoluminescence

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### Availability of Data and Materials

All data are fully available without restriction.

### Authors’ Contributions

YLM and ZLZ performed the experiments and prepared the manuscript. All other authors contributed to the measurements, data analysis, and the manuscript modification. All authors read and approved the final manuscript.

### Competing Interests

The authors declare that they have no competing interests.

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