

## Article

# Bi-Function $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$ -Assisted Double-Layered Photoanodes for Improving Efficiency of Dye-Sensitized Solar Cells

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**Abstract:** A bi-function  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$ -assisted double-layered photoanode was designed to improve the efficiency of dye-sensitized solar cells (DSSCs). The scanning electron microscopy (SEM) results show that the introduction of  $\text{Mn}^{2+}$  ions leads to smaller-sized  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  nanospheres, which is changed from nanosheet-shaped  $\text{TiO}_2$  and  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}$ . Based on Scherrer's formula from the X-ray diffraction (XRD) peak (101), the crystallite sizes decrease due to the introduction of  $\text{Mn}^{2+}$  ions. By utilizing screen-printing techniques, DSSCs fabricated by bi-function  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$ -assisted double-layered photoanodes exhibit the short-circuit current density ( $J_{sc}$ ) of 15.68 mA/cm<sup>2</sup>, open-circuit voltage ( $V_{oc}$ ) of 0.67 V, fill factor ( $FF$ ) of 0.71 and the power conversion efficiency (PCE) of 7.41%. The PCE of our designed DSSC is higher than that of DSSCs with a  $\text{TiO}_2/\text{TiO}_2$  photoanode (6.84%), which is attributed to the bi-function effects of  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  including the conversion of NIR into visible light and improved light scattering. An increased charge transfer resistance of the photoanode/electrolyte interface indicates the suppressed charge recombination of electrons with the electrolyte redox couple ( $\text{I}^-/\text{I}_3^-$ ) in DSSCs with a  $\text{TiO}_2/\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  double-layered photoanode, which also contributes to the enhanced performance of DSSCs. The double-layered photoanode fabricated by bi-function  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  nanospheres will provide a promising avenue for moving DSSCs forward to meet practical applications.

**Keywords:** dye-sensitized solar cells; double-layered photoanodes;  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$ ; light-harvesting efficiency



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## 1. Introduction

Dye-sensitized solar cells (DSSCs) have been attracting extensive research interest due to their large-scale fabrication and low cost, as well as being environmentally friendly and having potential flexibility [1]. To our knowledge, although the conventional single silicon solar cells have been applied in industrial production, the high cost and difficult purification technology of the single crystal growth process, and non-flexibility of single silicon semiconductor, seriously suppress the further application of silicon solar cells. Moreover, the unit size of single silicon solar cells is also limited by the size of single silicon crystals. In the case of a new generation of perovskite solar cells, the toxic lead ( $\text{Pb}^{2+}$ ) ions, expensive hole transport layer and the harsh fabrication condition impede their commercialization application. Therefore, the large-scale and flexible application of DSSCs still needs to be explored. The typical sandwich structure of DSSCs is fabricated with metal oxide semiconductor/organic dye molecules/redox electrolyte/counter electrode/conductive substrates, in which metal oxide semiconductors including  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{ZnO}$  are used as the photoanode. Compared to other DSSC photoanodes,  $\text{TiO}_2$  is

the most preferred one due to its low cost, that it is eco-friendly and non-toxic, and its larger specific surface area, chemical stability and photo-stability [2]. On the other hand,  $\text{TiO}_2$  can be used as a component of gamma radiation shielding, reducing the thermal energy of DSSCs [3]. There are two roles of the  $\text{TiO}_2$  photoanode in DSSCs. One is used to absorb organic dye molecules for the utilization of sunlight. The other is electron collection and transport. However, owing to the high transparency and weak light scattering of conventional nanocrystalline  $\text{TiO}_2$  photoanodes, the light-harvesting efficiency of DSSCs is limited [4]. Double-layer structured photoanodes consisting of a dye-loading layer and a light-scattering layer could suppress the optical loss and increase the optical path of the  $\text{TiO}_2$  photoanode, boosting the efficiency of DSSCs [5]. L. Zhao prepared a double-layered photoanode mixing an  $\text{NaLuF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$  upconverter with commercial P25 to obtain high efficiency of DSSCs [6]. It has been reported by R. Mitty that the utilization of a bi-function  $\text{CeO}_2:\text{Er}^{3+}/\text{Yb}^{3+}$ -assisted photoanode of DSSCs achieved high PCE, exceeding 9.5% [7]. Therefore, it is necessary to explore the studies on the combination of upconversion (UC) technology with double-layered photoanodes for improving the efficiency of DSSCs.

In the typical sandwich structure of DSSCs, the roles of organic dyes (such as N3 and N719) are the absorption of sunlight and the generation of photoelectrons. Although N719 is a highly efficient organic dye and exhibits a suitable gap-band of 1.80 eV, N719 can only absorb the visible sunlight, which limits the solar spectral response range and further reduces the photovoltage efficiency of DSSCs [8]. Therefore, the UC technology, converting NIR sunlight into visible UC light utilized by organic dyes, is introduced to settle this problem. Lanthanide-ion-doped UC materials have been certified as a useful strategy for improving the photovoltaic efficiency of solar cells [9]. For example, J.H. Hu utilized  $\text{NaYbF}_4:\text{Ho}^{3+}$  UC materials to extend the spectral response range and achieve a high PCE of 7.52% [10]. A.K. Narula synthesized the double-layer down/upconverter composed of  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}@\text{ZnO}$  and  $\text{Nd}^{3+}$ , with  $\text{Yb}^{3+}@\text{ZnO}$  to suppress the dark current and charge recombination, improving the photovoltaic properties of DSSCs [11]. Among many lanthanide ions, the  $\text{Yb}^{3+}/\text{Tm}^{3+}$  co-doped system is one of the most promising candidates, since it not only efficiently absorbs the NIR light of  $\text{Yb}^{3+}$  ions but also emits the absorbable blue and red UC emissions [12,13]. Moreover, the  $\text{Yb}^{3+}$  ion has a large absorption cross section, around 980 nm, and transfers energy to  $\text{Tm}^{3+}$  ions [14]. However, the insufficient efficiency of UC emissions still constitutes the main limitations for practical applications in DSSCs. It is proposed that transition metal ions ( $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^{+}$  and  $\text{Au}^{+}$ ) could efficiently enhance the intensities of UC emissions. Through increasing crystal lattice structure asymmetry by  $\text{Mg}^{2+}$  ions, Q.M. Huang increased the brightness of blue and red emissions over 20 times in cubic  $\text{Y}_{3.2}\text{Yb}_{0.4}\text{Er}_{0.08}\text{Al}_{0.32}\text{F}_{12}$  UC materials [15]. In comparison with other UC host materials,  $\text{TiO}_2$  with the low phonon energy and high thermal stability is an ideal host material, which can be used as a photoanode applied in DSSCs. Accordingly,  $\text{TiO}_2/\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  double-layered photoanodes not only can enhance the light harvesting but also can shorten the distance between the UC materials and the organic dye N719. Furthermore,  $\text{TiO}_2$  also possesses excellent luminescence properties, such as UV-induced transition  $\text{Ti}^{4+} \leftrightarrow \text{Ti}^{3+}$  [16] and the light conversion of near-infrared light into stronger UV light emission [17], which is favorable for enhancing the efficiency of DSSCs.

By utilizing HF as the  $\text{F}^{-}$  source in the hydrothermal synthesis process, HF plays a key role in controlling the morphology of  $\text{TiO}_2$  samples [18], including nanosheets and nanospheres. For example, Q.J. Zhang and Y.F. Wu reported that lanthanide-doped anatase  $\text{TiO}_2$  nanosheet films were obtained through the exfoliation erosion phenomena of HF etching [19]. X.S. Zhao synthesized F-doped  $\text{TiO}_2$  microspheres by Ostwald ripening and found the effect of HF species on the formation of  $\text{TiO}_2$  hollow spheres [20]. Moreover, although  $\text{Yb}^{3+}/\text{Er}^{3+}$  co-doped  $\text{TiO}_2$  spheres possessed a smaller specific area, applied in the electrode they enhanced the light-scattering effect, resulting in a higher efficiency of DSSCs [21].

In this work,  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  nanospheres synthesized by a simple hydrothermal method were fabricated into double-layered photoanodes of DSSCs.  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/$

$\text{Mn}^{2+}$  nanospheres could increase the light-harvesting range and the light-scattering ability. According to our previously reported works [22], the intensities of blue and red UC emissions increase with the increased concentration of  $\text{Mn}^{2+}$  ions. Therefore, the high concentration of 3 mol%  $\text{Mn}^{2+}$  ions was chosen here.  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  nanospheres emit strong blue and red UC emissions under 980 nm excitation. The effect of bi-function  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$ -assisted double-layered photoanodes on photovoltaic performance of DSSCs is discussed.

## 2. Materials and Methods

### 2.1. Synthesis of $\text{TiO}_2$ Nanosheets and $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$ Nanospheres

$\text{TiO}_2$  nanosheets and  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  nanospheres (denoted as  $\text{TiO}_2$  and  $\text{TiO}_2:\text{YTM}$ ) were synthesized by a simple hydrothermal method. Titanium isopropoxide (TTIP, 99.99%) solution was slowly dropped into 0.6 mL HF solution to obtain the mixture solution.  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (99.99%),  $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (99.99%) and  $\text{MnO}_2$  with molar ratio of 2 mol%:0.3 mol%:3 mol% were dissolved in the above mixture solution under stirring. Subsequently, the mixture solutions were transferred into the autoclave and heated at 200 °C for 24 h. Finally, the white products of  $\text{TiO}_2:\text{YTM}$  were collected by washing with DI and ethanol several times and dried at 60 °C for 12 h. For comparative study, the undoped  $\text{TiO}_2$  nanosheets were produced by hydrothermal method at 200 °C for 24 h.

### 2.2. Device Fabrication

FTO glasses patterned by laser were cleaned by sonicated in detergent, DI, acetone and ethanol for 30 min successively and then dried. We designed a double-layered photoanode consisting of a  $\text{TiO}_2$  (Dyesol 18NR-T) layer and as-prepared  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  layer. A dense  $\text{TiO}_2$  layer (Dyesol 18NR-T) was deposited on FTO by utilizing a scraper method under sintering successively at 80 °C for 30 min and 500 °C for 30 min to remove the residual organics. The  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  pastes were obtained by the following processes: Firstly, 0.05 g ethyl cellulose was added into 5 mL absolute ethyl alcohol under stirring at 80 °C. Secondly, 400  $\mu\text{L}$  terpinenol, 4  $\mu\text{L}$  OP emulsifier, 30  $\mu\text{L}$  acetylacetone and 0.1 g  $\text{TiO}_2$  were added into the above solutions to volatilize completely the absolute ethyl alcohol. Subsequently, the  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  pastes were deposited on FTO/ $\text{TiO}_2$  by screen-printing technique, followed by sintering at 500 °C for 30 min. The sintered FTO/ $\text{TiO}_2$ / $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  were treated in a fresh aqueous  $\text{TiCl}_4$  solution (0.04 M) at 80 °C for 1 h and then washed by DI and ethanol several times to eliminate redundant  $\text{TiCl}_4$ . After sintering at 80 °C for 30 min, the as-treated FTO/ $\text{TiO}_2$ / $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  were immersed into N719 solutions under dark condition for 24 h. Finally, the FTO/ $\text{TiO}_2$ / $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  double-layered photoanodes with N719 dye were washed by ethanol several times and sintered at 80 °C for 2 h, which was named as  $\text{TiO}_2/\text{TiO}_2:\text{YTM}$ . The Pt electrode was used as counter electrode. The electrolyte was injected into the gap between the photoanode and Pt electrode to fabricate DSSC with device structure of FTO/ $\text{TiO}_2$ / $\text{TiO}_2:\text{YTM}$ /Pt electrode, which was denoted as  $\text{TiO}_2:\text{YTM}$ -DSSC. As for comparative study,  $\text{TiO}_2$ -DSSC and  $\text{TiO}_2:\text{YT}$ -DSSC based on  $\text{TiO}_2/\text{TiO}_2$  and  $\text{TiO}_2/\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}$  double-layered photoanodes were also produced, respectively.

### 2.3. Characterizations

The surface morphology was evaluated by scanning electron microscopy (SEM, SU8010, Hitachi, Ltd., Tokyo, Japan). The phase structures were obtained using X-ray diffraction (Ultima-IV, Rigaku, Ltd., The Woodlands, TX, USA) with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). The UC PL spectra and decay curves were excited by a continuous 980 nm diode laser and recorded by the spectrometer and photomultiplier (MDL-III-980/ZolixScanBasic, Zolix Instruments Co., Ltd., Beijing, China). Absorption spectra were recorded on a Shimadzu ultraviolet (UV)-3600 UV-visible spectrophotometer (Shimadzu, Kyoto, Japan). The scanning wavelength range was 400–750 nm, and the scanning step

was fixed at 1 nm. In order to minimize the measurement error, the  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  nanospheres were pressed into wafer with the radius of 1 cm and the thickness of 1 mm, which could reduce the light path length. The current density–voltage  $J$ - $V$  curves of PSCs were measured using a solar simulator equipped (SCS 100, Zolix Instruments Co., Ltd., Beijing, China) along with AM 1.5 G,  $100 \text{ mW cm}^{-2}$  simulated solar illumination (previously calibrated by a standard silicon solar cell). The active cell area was controlled in a black metal mask ( $0.09 \text{ cm}^2$ ).

### 3. Results

The SEM images of the as-synthesized undoped  $\text{TiO}_2$ ,  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}$  [22] and  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  are shown in Figure 1, displaying that the undoped  $\text{TiO}_2$  has the sheet-shaped rectangle with a side length of  $\sim 50 \text{ nm}$  (Figure 1a). Bigger-sized  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}$  nanosheets are observed in Figure 1b, which were synthesized in our previous work [22]. The introduction of  $\text{Yb}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Mn}^{2+}$  ions into the  $\text{TiO}_2$  crystal lattice leads to the sphere-like shapes in smaller size for  $\text{TiO}_2:\text{YTM}$  (Figure 1c). The formation of  $\text{TiO}_2$  and  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}$  nanosheets is caused by the lower surface free energy because  $\text{F}^-$  ions are adsorbed and accumulated on the surfaces. When  $\text{Mn}^{2+}$  ions are introduced,  $\text{Mn}^{2+}$  ions consume the concentration of  $\text{F}^-$  ions due to the reaction between  $\text{F}^-$  and  $\text{Mn}^{2+}$  ions. Consequently, the lower concentrations of  $\text{F}^-$  ions cannot stabilize crystal planes, resulting in the spheres of  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$ . Similar to the morphology-dependent properties of nanocrystalline Bi films [23], the morphology plays a key role in the efficiency of DSSCs, which is discussed in the next section.

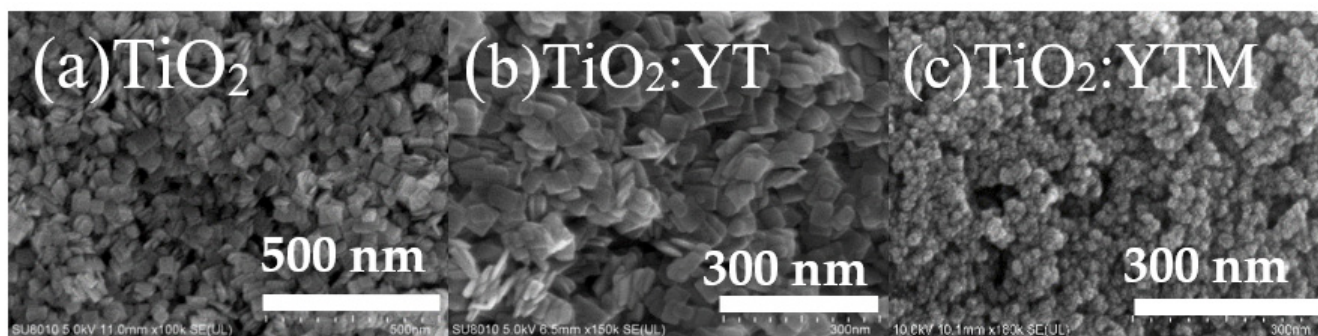


**Figure 1.** SEM images of (a) undoped  $\text{TiO}_2$ , (b)  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}$  [22] (Date from reference [22]) and (c)  $\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$ .

XRD patterns of undoped  $\text{TiO}_2$ ,  $\text{TiO}_2:\text{YT}$  [22] nanosheets and  $\text{TiO}_2:\text{YTM}$  nanospheres, as shown in Figure 2, were used to verify the crystal structure. The XRD diffraction peaks of  $\text{TiO}_2$ ,  $\text{TiO}_2:\text{YT}$  and  $\text{TiO}_2:\text{YTM}$  can be attributed to the standard anatase phase of  $\text{TiO}_2$  (JCPDS no. 21-1272). Moreover, XRD peaks at  $2\theta = 25.2^\circ$ ,  $36.9^\circ$ ,  $37.8^\circ$ ,  $38.6^\circ$ ,  $48.8^\circ$ ,  $53.9^\circ$ ,  $55.1^\circ$ ,  $62.7^\circ$ ,  $68.8^\circ$ ,  $70.4^\circ$  and  $75.2^\circ$  are ascribed to (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) reflection planes, respectively. However, a small amount of impurity  $\text{YbF}_3$  phase indexed at  $2\theta = 27.8^\circ$  and  $31.7^\circ$  (JCPDS No. 49-1805) is observed for  $\text{TiO}_2:\text{YTM}$  nanospheres, which may be due to the reaction between  $\text{Yb}^{3+}/\text{Tm}^{3+}$  and  $\text{F}^-$  ions. The crystallite sizes of  $\text{TiO}_2$ ,  $\text{TiO}_2:\text{YT}$  and  $\text{TiO}_2:\text{YTM}$  were calculated by using Scherrer's formula from the major diffraction peak (101), which were found to be 17.3, 177 and 12.4 nm, respectively, in agreement with Figure 1a–c.

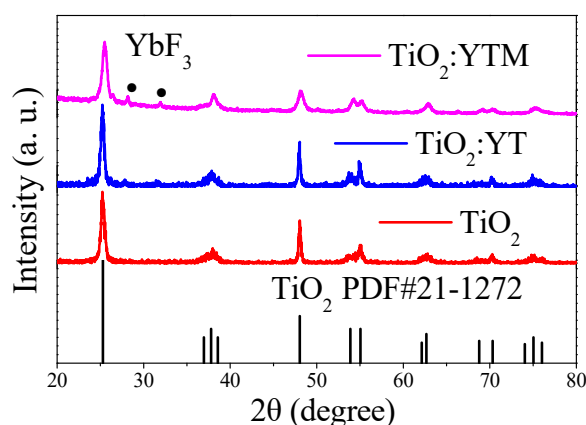


**Figure 2.** XRD patterns of  $\text{TiO}_2$ ,  $\text{TiO}_2\text{:YT}$  nanosheets [22] (Date from reference [22]) and  $\text{TiO}_2\text{:YTM}$  nanospheres.

The UC emission spectra of  $\text{TiO}_2\text{:YT}$  nanosheets and  $\text{TiO}_2\text{:YTM}$  nanospheres under 980 nm excitation are shown in Figure 3a. It can be seen that a strong blue UC emission centered at 478 nm is attributed to the  $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transition of  $\text{Tm}^{3+}$  ions, and two red UC emissions at 647 nm/695 nm are corresponding to the  $^1\text{G}_4 \rightarrow ^3\text{F}_4$  and  $^3\text{F}_3 \rightarrow ^3\text{H}_6$  transitions of  $\text{Tm}^{3+}$  ions, respectively [24–26]. Compared to  $\text{TiO}_2\text{:YT}$  nanosheets, the drastically increased blue and red UC emissions are observed in  $\text{TiO}_2\text{:YTM}$  nanospheres. Consequently,  $\text{TiO}_2\text{:YTM}$  nanospheres used as a part of the double-layered photoanode of DSSCs could effectively broaden the sunlight spectral response because the blue and red visible emissions are easily absorbed by the N719 dye.

The mechanism for the enhanced blue and red UC emissions caused by  $\text{Mn}^{2+}$  ions can be understood by the bidirectional energy transfer processes between the  $\text{Tm}^{3+}$  and  $\text{Mn}^{2+}\text{-Yb}^{3+}$  dimer [22]. As shown in Figure 3b, the blue emission at 478 nm, red emission at 647 nm and red emission at 695 nm are yielded by the radiatively relaxing processes of  $^1\text{G}_4 \rightarrow ^3\text{H}_6$ ,  $^1\text{G}_4 \rightarrow ^3\text{F}_4$  and  $^3\text{F}_3 \rightarrow ^3\text{H}_6$ , respectively. The increased population of the  $^3\text{F}_{2,3}$  states of  $\text{Tm}^{3+}$  ions arises from the back energy transition (BET) process of  $^3\text{H}_6 (\text{Tm}^{3+}) + ^1\text{F}_7/2, ^4\text{T}_{1g} > (\text{Mn}^{2+}\text{-Yb}^{3+} \text{ dimer}) \rightarrow ^3\text{F}_2 (\text{Tm}^{3+}) + ^1\text{F}_7/2, ^6\text{A}_{1g} > (\text{Mn}^{2+}\text{-Yb}^{3+} \text{ dimer})$ , contributing to an enhancement of red UC emission at 695 nm. Moreover, the enhanced population of the  $^1\text{G}_4$  state ( $\text{Tm}^{3+}$ ), which is responsible for the stronger blue emission at 478 nm and red one at 647 nm, is resulted from the BET process and the energy transition (ET3) process of  $^3\text{H}_4 (\text{Tm}^{3+}) + ^2\text{F}_{5/2} (\text{Yb}^{3+}) \rightarrow ^1\text{G}_4 (\text{Tm}^{3+}) + ^2\text{F}_{7/2} (\text{Yb}^{3+})$ . Here, the ET4 process of  $^1\text{G}_4 (\text{Tm}^{3+}) + ^1\text{F}_7/2, ^6\text{A}_{1g} > (\text{Mn}^{2+}\text{-Yb}^{3+} \text{ dimer}) \rightarrow ^3\text{H}_6 (\text{Tm}^{3+}) + ^1\text{F}_7/2, ^4\text{T}_{1g} > (\text{Mn}^{2+}\text{-Yb}^{3+} \text{ dimer})$ , which reduces the population of the  $^1\text{G}_4$  state of  $\text{Tm}^{3+}$  ions, is neglected.

Figure 4a,b display the UV-vis spectra of the  $\text{TiO}_2/\text{TiO}_2$ ,  $\text{TiO}_2/\text{TiO}_2\text{:YT}$  and  $\text{TiO}_2/\text{TiO}_2\text{:YTM}$  double-layered photoanodes including absorptivity and transmittance, respectively, which are used to demonstrate the influence of the  $\text{TiO}_2/\text{TiO}_2\text{:YTM}$  double-layered photoanode on the photovoltage performance of DSSCs. As seen in Figure 4a, the  $\text{TiO}_2/\text{TiO}_2\text{:YTM}$  double-layered photoanode exhibits the strongest light absorption intensity among three photoanodes, providing evidence for enhancing NIR light harvesting. In contrast, the transmittance intensities exhibit the opposite trend for undoped  $\text{TiO}_2/\text{TiO}_2$ ,  $\text{TiO}_2/\text{TiO}_2\text{:YT}$  and  $\text{TiO}_2/\text{TiO}_2\text{:YTM}$  double-layered photoanodes (Figure 4b). The dye-loading capacity for DSSCs is investigated by the absorption spectra of the N719 dye desorbed from  $\text{TiO}_2/\text{TiO}_2$ ,  $\text{TiO}_2/\text{TiO}_2\text{:YT}$  and  $\text{TiO}_2/\text{TiO}_2\text{:YTM}$  double-layered photoanodes, as shown in Figure 4c. It can be seen that the two absorption peaks located at 380 nm and 512 nm belong to the N719 dye molecules. The absorption intensities decrease significantly in bi-function  $\text{TiO}_2/\text{TiO}_2\text{:YTM}$  double-layered photoanodes in comparison to  $\text{TiO}_2/\text{TiO}_2$  and  $\text{TiO}_2/\text{TiO}_2\text{:YT}$  photoanodes.

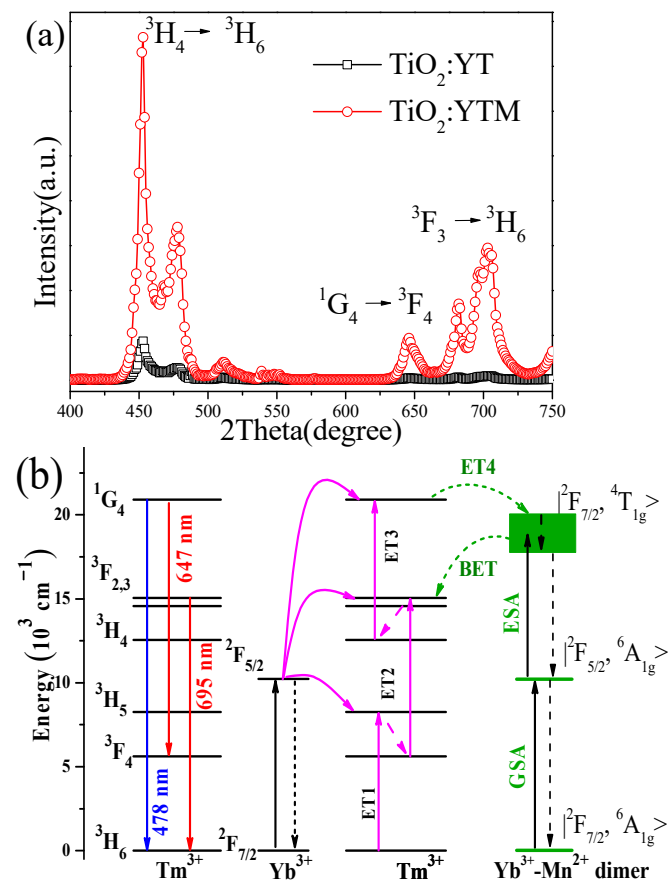


**Figure 3.** (a) The UC emission spectra of  $\text{TiO}_2\text{:YT}$  [22] and  $\text{TiO}_2\text{:YTM}$  nanospheres under 980 nm excitation; (b) the UC mechanism of  $\text{TiO}_2\text{:YTM}$ .

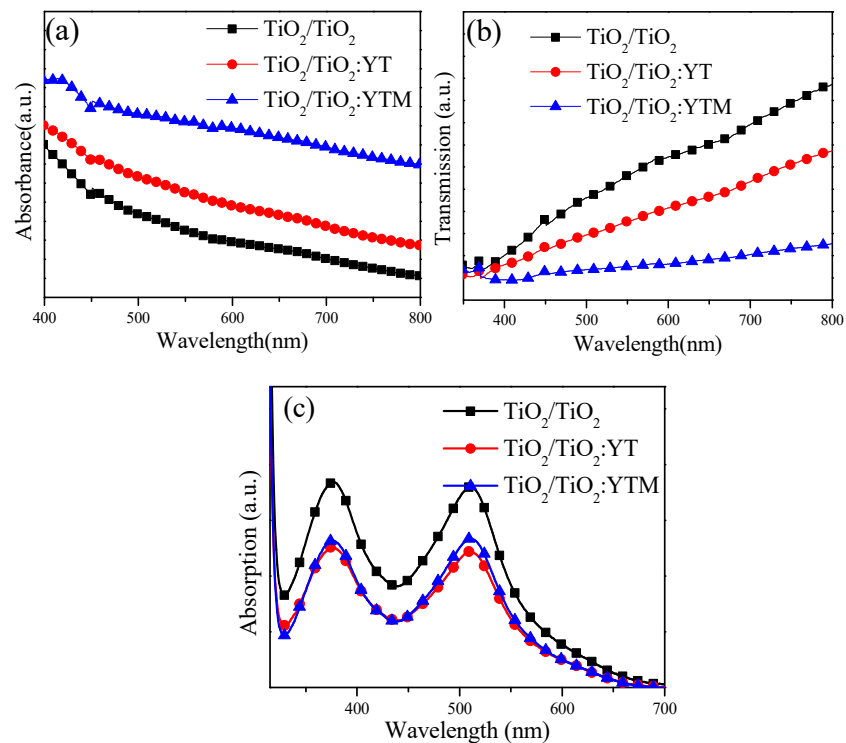


**Figure 4.** UV-vis spectra of  $\text{TiO}_2/\text{TiO}_2$ ,  $\text{TiO}_2/\text{TiO}_2\text{:YT}$  and  $\text{TiO}_2/\text{TiO}_2\text{:YTM}$  photoanodes: (a) Absorptivity; (b) Transmittance; (c) UV-vis spectra of N719 dye desorbed from photoanodes.

The bi-function  $\text{TiO}_2/\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  double-layered photoanode is used to improve the light absorption and performance of DSSCs, and a schematic design of the double-layered DSSC structure is shown in Figure 5a. The photocurrent density–photovoltage ( $J$ - $V$ ) plots of  $\text{TiO}_2$ -DSSC,  $\text{TiO}_2:\text{YT}$ -DSSC and  $\text{TiO}_2:\text{YTM}$ -DSSC are shown in Figure 5b, and the corresponding photovoltaic parameters including open-circuit voltage ( $V_{oc}$ ), short-circuit photocurrent density ( $J_{sc}$ ), fill factor (FF) and power conversion efficiency (PCE) are listed in Table 1.  $\text{TiO}_2$ -DSSC,  $\text{TiO}_2:\text{YT}$ -DSSC and  $\text{TiO}_2:\text{YTM}$ -DSSC display  $J_{sc}$  of 0.63, 0.66 and 0.67  $\text{mA cm}^{-2}$ ,  $V_{oc}$  of 14.84, 15.37 and 15.68 V, FF of 0.73, 0.70 and 0.71, and PCE of 6.84%, 7.12% and 7.41%, respectively. The enhanced PCE of 7.41% in  $\text{TiO}_2:\text{YTM}$ -DSSC is due to the broadened solar spectral response range and the increased light-scattering ability, as proved by effective UC of  $\text{TiO}_2:\text{YTM}$  nanospheres (Figure 3a). Moreover, the N719 dye molecules could absorb more visible light with the help of  $\text{TiO}_2:\text{YTM}$  nanospheres, yielding the increase in photogenerated electrons. The enlarging electrons contribute to the enhancement of  $J_{sc}$ ,  $V_{oc}$  and PCE for  $\text{TiO}_2:\text{YTM}$ -DSSC. On the other hand,  $\text{TiO}_2:\text{YTM}$ , acting as scattering centers, could increase the light travel path in the  $\text{TiO}_2/\text{TiO}_2:\text{YTM}$  double-layered photoanodes, which is also responsible for the increased PCE of  $\text{TiO}_2:\text{YTM}$ -DSSC. Due to the matching absorption band of the N719 dye with the visible emissions, the upconverted blue and red emissions resulted from  $\text{TiO}_2/\text{TiO}_2:\text{YTM}$  double-layered photoanodes make N719 dye molecules become easily injected into the electrons of  $\text{TiO}_2$ , resulting in larger photocurrent densities and an enhanced PCE of  $\text{TiO}_2:\text{YTM}$ -DSSC. The combination of the increased UV-vis absorption intensity of  $\text{TiO}_2:\text{YTM}$  nanospheres (Figure 4a) and the decreased absorption intensity of N719 dye desorbed from the  $\text{TiO}_2/\text{TiO}_2:\text{YTM}$  photoanode (Figure 4c) suggests that the improved PCE of  $\text{TiO}_2:\text{YTM}$ -DSSC is mainly attributed to the enhancement of light-harvesting efficiency caused by UC technology rather than the dye-loading capacity of N719 dye molecules.

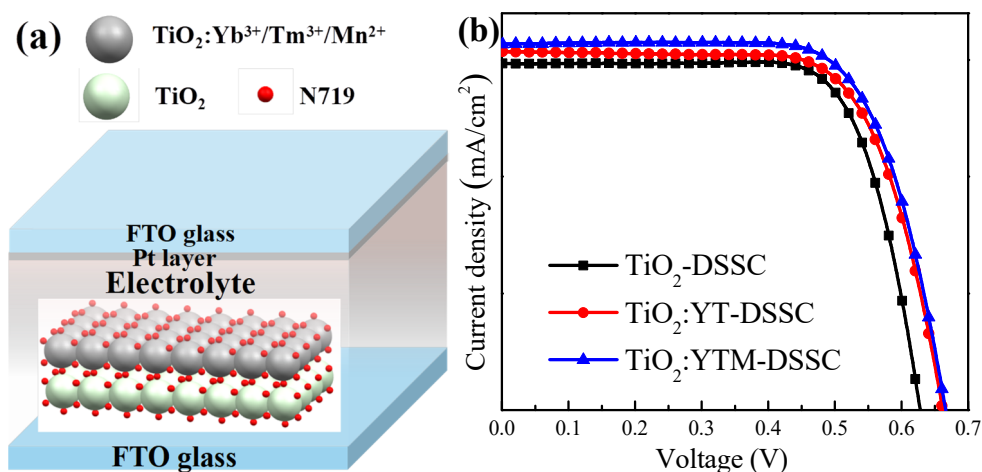


**Figure 5.** (a) A schematic design of the double-layered DSSC structure; (b) I- $V$  curves of  $\text{TiO}_2$ -DSSC,  $\text{TiO}_2:\text{YT}$ -DSSC and  $\text{TiO}_2:\text{YTM}$ -DSSC.

As is well known, DSSCs possess four interfaces including FTO/ $\text{TiO}_2$ ,  $\text{TiO}_2$ /dye, dye/electrolyte and electrolyte/electrode. The transfer of interface electrons and the kinetic recombination process of  $\text{TiO}_2$ -DSSC,  $\text{TiO}_2:\text{YT}$ -DSSC and  $\text{TiO}_2:\text{YTM}$ -DSSC are investigated by Nyquist plots obtained by electrical impedance spectroscopy (EIS). Figure 6 shows that there are two semicircles in Nyquist plots, including a small semicircle in the high frequency region and a large semicircle in the intermediate frequency region. Here, it may be possible that the ion migration resistance of the liquid electrolyte is too small to form an electrochemical interface, resulting in no semicircular arc being found in the low-frequency region [6]. The small semicircle is corresponding to the charge transfer resistance ( $R_{ct1}$ ) of the electrolyte/counter electrode interface, and the large semicircle means the charge transfer resistance ( $R_{ct2}$ ) of the  $\text{TiO}_2$  photoanode/electrolyte interface. The almost similar

small semicircle is due to the double-layered photoanodes. At the intermediate frequency region, the increased radii of the large semicircle obviously observed in  $\text{TiO}_2\text{:YTM-DSSC}$  is because electrons are suppressed to recombine with the electrolyte redox couple ( $\text{I}^-/\text{I}_3^-$ ) in  $\text{TiO}_2/\text{TiO}_2\text{:YTM}$  double-layered photoanodes. The decreased recombination process corresponds to the reduced transmission resistance of photogenerated electrons in DSSC, improving the performance of DSSCs.

**Table 1.** The performances of  $\text{TiO}_2$ -DSSC,  $\text{TiO}_2\text{:YT-DSSC}$  and  $\text{TiO}_2\text{:YTM-DSSC}$ , and the performances of DSSCs with double-layered photoanodes and DSSCs with UC layers.

| Double-Layered Photoanodes                                 | $V_{oc}$ (V) | $J_{sc}$ ( $\text{mA}/\text{cm}^2$ ) | FF     | PCE (%) | Ref.      |
|------------------------------------------------------------|--------------|--------------------------------------|--------|---------|-----------|
| $\text{TiO}_2$ -DSSC                                       | 0.63         | 14.84                                | 0.73   | 6.84    | This work |
| $\text{TiO}_2\text{:YT-DSSC}$                              | 0.66         | 15.37                                | 0.70   | 7.12    | This work |
| $\text{TiO}_2\text{:YTM-DSSC}$                             | 0.67         | 15.68                                | 0.71   | 7.41    | This work |
| $\text{ZnO}/\text{TiO}_2/\text{TiO}_2$                     | 0.727        | 16.63                                | 0.59   | 6.84    | [5]       |
| $\text{NaLuF}_4\text{:Yb/Er/P25/flower-like}$              | 0.69         | 21.19                                | 0.56   | 8.14    | [6]       |
| $\text{TiO}_2/\text{Ag}$                                   |              |                                      |        |         |           |
| $\text{CeO}_2\text{:Fe/Yb/Er/TiO}_2$                       | 0.744        | 16.704                               | 0.61   | 7.30    | [9]       |
| $\text{YbF}_4\text{:Ho/TiO}_2$                             | 0.693        | 15.62                                | 0.696  | 7.52    | [10]      |
| $\text{NaYF}_4\text{:Yb, Er@BiOCl/TiO}_2$                  | 0.74         | 13.06                                | 0.7119 | 6.88    | [27]      |
| $\text{TiO}_2\text{:Er}^{3+}, \text{Yb}^{3+}/\text{TiO}_2$ | 0.68         | 15.30                                | 0.68   | 7.18    | [8]       |

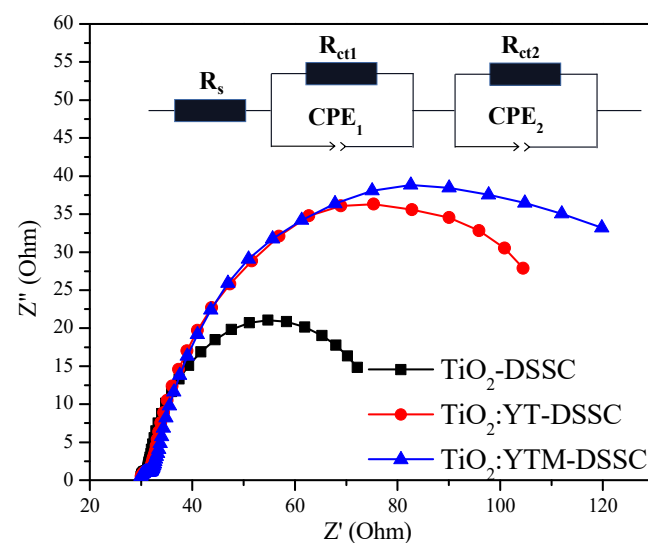


**Figure 6.** Nyquist curve of  $\text{TiO}_2$ -DSSC and  $\text{TiO}_2\text{:YTM-DSSC}$ .

#### 4. Conclusions

In summary, we designed bi-function  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$ -assisted double-layered photoanodes to achieve a high PCE of 7.41% for DSSCs. Bi-function  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  nanospheres synthesized by a simple hydrothermal method not only upconvert NIR light into blue and red UC emissions absorbed by N719 dye but also act as a scattering layer for DSSCs. By adding  $\text{Mn}^{2+}$  ions, the smaller-sized  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  nanospheres are obtained, which is calculated to be 12.4 nm based on Scherrer's formula. Under 980 nm excitation,  $\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  nanospheres exhibit obvious enhancement of blue and red UC emissions, which is attributed to the BET process of  $^3\text{H}_6 (\text{Tm}^{3+}) + |^2\text{F}_{7/2}, ^4\text{T}_{1g} > (\text{Mn}^{2+}\text{-Yb}^{3+} \text{ dimer}) \rightarrow ^3\text{F}_2 (\text{Tm}^{3+}) + |^2\text{F}_{7/2}, ^6\text{A}_{1g} > (\text{Mn}^{2+}\text{-Yb}^{3+} \text{ dimer})$  and ET3 process of  $^3\text{H}_4 (\text{Tm}^{3+}) + ^2\text{F}_{5/2} (\text{Yb}^{3+}) \rightarrow ^1\text{G}_4 (\text{Tm}^{3+}) + ^2\text{F}_{7/2} (\text{Yb}^{3+})$ . Compared to the  $\text{TiO}_2/\text{TiO}_2$  and  $\text{TiO}_2/\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}$  photoanodes, the  $\text{TiO}_2/\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  double-layered photoanode exhibits the strongest absorptance, indicating an enhancement of NIR light harvesting. DSSC based on the  $\text{TiO}_2/\text{TiO}_2\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  double-layered photoanode

possesses an increased  $J_{sc}$  of 0.67,  $V_{oc}$  of 15.68 V, FF of 0.71 and PCE of 7.41%, which is attributed to the effectively increased solar spectrum response caused by the UC technology of  $\text{Yb}^{3+}/\text{Tm}^{3+}$  co-doped system. By analyzing Nyquist plots obtained by EIS measurement, the bi-function  $\text{TiO}_2/\text{TiO}_2:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Mn}^{2+}$  double-layered photoanode hinders the charge recombination between electrons and electrolyte redox couple ( $\text{I}^-/\text{I}_3^-$ ), enhancing the PCE of DSSCs.

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