Enhanced photoelectric conversion efficiency of dye-sensitized solar cells by the incorporation of flower-like Bi$_2$S$_3$:Eu$^{3+}$ sub-microspheres

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In this paper, TiO$_2$-Bi$_2$S$_3$ and TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite photoanodes were successfully designed, which not only fully absorb visible light but also transfer the electron from Bi$_2$S$_3$ to TiO$_2$ conduction band due to the narrow band gap and high conduction band of Bi$_2$S$_3$. Compared to pure TiO$_2$ cell, the photoelectric conversion efficiencies of TiO$_2$-Bi$_2$S$_3$ and TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite cells were increased significantly. In addition, the efficiency of TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite cells were higher than that of TiO$_2$-Bi$_2$S$_3$ cell which could be attributed to the larger BET surface area of Bi$_2$S$_3$:Eu$^{3+}$. The electron transport and interfacial recombination kinetics were investigated by the electrochemical impedance spectroscopy and intensity-modulated photocurrent/photovoltage spectroscopy. The results indicated that the interfacial resistance of the TiO$_2$-dye$I_3^-$/I$^-$/electrolyte interface of TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite cell was much bigger than that of pure TiO$_2$ cell. In addition, the TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ cell has longer electron recombination time and longer electron transport time than pure TiO$_2$ cell. The charge collection efficiency of TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite cell was higher than that of pure TiO$_2$ cell.

In the past decade, dye-sensitized solar cells (DSSCs) have attracted extensive attention due to their easy fabrication, lowcost and relatively high conversion efficiency$^{1,2}$. A typical DSSC consists of a dye-sensitized semiconductor photoanode, an electrolyte with the dissolved iodide/triiodide (I$_3^-$/I$^-$) redox couple between the electrodes and a catalytic counter electrode$^{3-6}$. Especially, an advanced photoelectrode is one of the most important prerequisites for highly efficient DSSCs. A variety of materials have been used as photoelectrodes and show good electrocatalytic activity. In general, TiO$_2$ has been widely used as for DSSCs owing to its large surface area for loading more dye molecules, the sensitizer of the DSSC is mainly N719 dye, and the DSSC consists of TiO$_2$ film sensitized by a dye for absorbing incident light. Recently, extensive studies on the individual components of DSSCs have been performed to further reduce production costs and to achieve better cell performance$^{7-9}$. Many attempts have been made to enhance the performances of DSSCs by controlling the size, shape and morphologies of the semiconductors, utilizing low band gap organic materials, introducing buffer layers, and so on. Among them, one facile and efficient approach is to introduce foreign ions into organic semiconductors$^{10,11}$. Some metal oxides$^{12-13}$, nitrides$^{14}$, carbides$^{15}$ and sulfides$^{16-19}$ have also been investigated as CEs due to their preferentially electrocatalytic activity. However, the application of sulfides as photoanode has been seldom reported. Metal sulfides gained more attention due to their facile preparation conditions and relatively low toxicity. As a well-known semiconductor, bismuth sulfide (Bi$_2$S$_3$) has the potential to improve the photocatalytic activity due to its narrow bandgap (~1.4 eV)$^{20,21}$. It could has been used as a photoanode materials in DSSC due to its ability to absorb a large part of visible light up to 800 nm and transfer the electron from Bi$_2$S$_3$ to TiO$_2$ conduction band. So far, there are many classic preparation methods for Bi$_2$S$_3$, such as hydrothermal method, solvothermal method, electrochemical deposition, microwave refluxing, organometallic complex decomposition and chemical vapor deposition$^{22-28}$.

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As a result, if one can design down-conversion luminescent TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite photoanodes, not only the utilization of visible light can be improved but also the electron can transfer from Bi$_2$S$_3$ to TiO$_2$ conduction band (see Fig. 1). And thus, the efficiency of the solar cells can be enhanced. In addition, metal ions doping semiconductor is also an effective strategy to improve the photocatalytic performance. Based on the consideration above, we report the synthesis of flower-like Bi$_2$S$_3$:Eu$^{3+}$ through a hydrothermal route, and introduce Bi$_2$S$_3$:Eu$^{3+}$ to the dye-sensitized solar photoanodes. The BET surface areas increased with increasing Eu$^{3+}$ concentration. The photoelectric conversion efficiencies of TiO$_2$-Bi$_2$S$_3$ and TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite cells were significantly increased compared to pure TiO$_2$ cell. The electron transport and interfacial recombination kinetics of cells were investigated in detail.

**Discussion**

Figure 2(a–d) represent the typical SEM images of the Bi$_2$S$_3$ products with different Eu$^{3+}$ concentrations, which show that the products are composed of flower-like nanostructures. The average diameter of these superstructures is about 500 nm. The TEM and HRTEM images are presented in Fig. 2(e,f). The HRTEM image reveals that the interplanar spacing of 0.36 nm corresponds to the (130) plane of Bi$_2$S$_3$.

Figure 3 shows the XRD patterns of Bi$_2$S$_3$ nanocrystals (without annealing) with different reaction time, which are in good agreement with the standard data of orthorhombic phase Bi$_2$S$_3$ (JCPDS 17-0320). No other impurity peaks were detected. Figure 4 shows the XRD patterns of Bi$_2$S$_3$ nanocrystals after annealing at different temperatures. It can be seen crystalline size increases with increasing the annealing temperature. The peaks in Fig. 4 marked by asterisk (*) arise from cubic phase Bi particles (JCPDS 44-1256). The other diffraction peaks can be indexed to the orthorhombic phase Bi$_2$S$_3$. Figure 5 shows the XRD pattern of Bi$_2$S$_3$:Eu$^{3+}$ nanocrystals (without
annealing) with different Eu$^{3+}$ concentrations. Obviously, no other impurity peaks were detected with increasing Eu$^{3+}$ concentration.

Figure 6 shows the Raman spectra of Bi$_2$S$_3$:Eu$^{3+}$ with different Eu$^{3+}$ concentrations. The typical features in Raman spectra were located at 129 cm$^{-1}$, 610 cm$^{-1}$ and 965 cm$^{-1}$. The 610 and 965 cm$^{-1}$ bands are assigned to the Bi-S stretching vibrations. The 129 cm$^{-1}$ is attributed to the surface of the optical phonon modes.
Figure 6. Raman spectra of Bi$_2$S$_3$:Eu$^{3+}$ nanocrystals prepared at 180 °C for 12h with different Eu$^{3+}$ concentrations.

Figure 7 shows the UV-vis diffuse reflectance spectrum of Bi$_2$S$_3$ nanocrystals prepared at 180 °C for 12h.

Figure 7 shows the UV-vis diffuse reflectance spectrum of Bi$_2$S$_3$ nanocrystals. The inset displays the plot of the transformed Kubelka-Munk function versus energy of light. The Kubelka-Munk function, $F(R)$, allows the optical absorbance of a sample to be approximated from its reflectance: $F(R) = (1 - R)^2/2R$. For a semiconductor sample this allows the construction of a Tauc Plot-(F(R).h$^n$) vs hv. For a direct band gap semiconductor the plot $n = 1/2$ will show a linear Tauc Region just above the optical absorption edge. Extrapolation of this line to the photon energy axis yields the semiconductor band gap. The calculated value of the band gap is about 1.22 eV for Bi$_2$S$_3$ nanocrystals.

In order to investigate the effects of TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ on the photoelectric properties of DSSCs, the DSSC prototype devices were fabricated by using N719-sensitised TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite electrodes. Figure 8(a) shows the photocurrent-voltage (I–V) curves of pure TiO$_2$ cell, TiO$_2$-Bi$_2$S$_3$ composite cell, and TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ cells. The mass concentrations of Bi$_2$S$_3$:Eu$^{3+}$ in the TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ cells are 1%, 3%, and 5%, respectively. The corresponding values of the open-circuit voltage (Voc), short-circuit current (Jsc), fillfactor (FF), and overall conversion efficiency ($\eta$), obtained from the curves of solar cells, are shown in Table 1. The result indicated that the photoelectric conversion efficiencies of the TiO$_2$-Bi$_2$S$_3$ and TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite cells were higher than that of pure TiO$_2$ cell. The best photoelectric conversion performance was observed when the mass concentration of Bi$_2$S$_3$:Eu$^{3+}$ was 3%. The high Voc of the TiO$_2$-Bi$_2$S$_3$ could be attributed to heavy doping effects. Heavy impurity doping makes the conduction and valence bands shift, and brings about the so-called Band Gap Narrowing that resulting in the decrease of open circuit voltage. Figure 8(b) shows the incident photon to current (IPCE) spectra of pure TiO$_2$, TiO$_2$-Bi$_2$S$_3$, and TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ composite cells. The results indicated that the photon-to-current conversion efficiency obviously increases by the incorporation of Bi$_2$S$_3$:Eu$^{3+}$. With the increase of the proportion of Bi$_2$S$_3$:Eu$^{3+}$ in TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ cell, the efficiency increases first, and then decreases. At low concentrations of Bi$_2$S$_3$:Eu$^{3+}$, the increase of the efficiency with the proportion of Bi$_2$S$_3$:Eu$^{3+}$ could be attributed to the narrow band-gap and higher conduction band of Bi$_2$S$_3$, which not only improve the utilization of visible light but also transfer the electron from Bi$_2$S$_3$ to the conduction band of TiO$_2$. However, the incorporation of Bi$_2$S$_3$:Eu$^{3+}$ can influence the electrical conductivity of TiO$_2$ and lead to a decrease in photocurrent. In addition, the effects of pure Bi$_2$S$_3$ on the photoelectric properties of DSSC were also studied. The results indicated that the photoelectric conversion efficiency of TiO$_2$-Bi$_2$S$_3$ cell was lower than that of TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ cell.
It is well known that the photoelectric performance was closely related to the ratios of the surface areas of samples. N$_2$ adsorption-desorption isotherms and the corresponding BJH pore size distribution plots of the as-obtained Bi$_2$S$_3$:Eu$^{3+}$ with different Eu$^{3+}$ concentrations were performed to determine the surface area of the samples, as shown in Fig. 9. The BET surface areas are 4.8435, 5.4181, 6.6296, and 7.1739 m$^2$/g for 0%, 10%, 15%, and 20% Eu$^{3+}$, respectively.

EIS is a powerful method to investigate internal resistances for 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 Hz–100 Hz is related to the photoelectrode–dye|I$_3^-$/$I^-$ electrolyte interface, where the accumulation of photoelectrons and redox shuttles is expected. Figure 10 shows the EIS of pure TiO$_2$ cell and TiO$_2$-Bi$_2$S$_3$:Eu$^{3+}$ cell. It can be seen...
The interfacial resistance of the TiO₂-dye|I₃⁻ electrolyte interface of TiO₂-Bi₂S₃:Eu³⁺ cell is much bigger than that of pure TiO₂ cell. All these results indicated that the performance of the solar cells can be improved by adding Bi₂S₃:Eu³⁺.

The inset in Fig. 10 shows the equivalent circuit fitting of the impedance spectra, R s[C 1(R 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|I₃⁻ 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 tanh(\(j\omega\tau)^{1/2}\) where R Dif = B/Y₀ 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 R2, representing the interfacial resistance of the TiO₂-dye|I₃⁻ electrolyte interface, is 30.31 Ω for pure TiO₂ cell and 41.30 Ω for TiO₂-Bi₂S₃:Eu³⁺ composite cell. It is noted that the lower interfacial resistance can result in higher interfacial electron transfer, which is a beneficial factor for enhanced photoelectric conversion efficiency. In addition, the series resistance (R s) for pure TiO₂ cell and TiO₂-Bi₂S₃:Eu³⁺ cell are separately 31.53 Ω and 41.26 Ω, indicating that the incorporation of Bi₂S₃:Eu³⁺ is not beneficial for the interfacial electron transfer of FTO|TiO₂.

In DSSCs, the electron recombination time (\(\tau_n\)), the electron transport time (\(\tau_d\)), and the charge collection efficiency (\(\eta_{cc}\)) are important factors for the performance of DSSCs. Time-resolved photoluminescence spectrum can be used as an effective method to characterize the interface electron transport and electron recombination of the solar cell[34,35]. But restricted by the conditions, we can not test Time-resolved photoluminescence spectrum. However, the IMVS and IMPS are also a kind of effective characterization methods, which can be used to characterize the transmission life, charge separation and recombination of interface electrons. The IMPS response plots and IMVS response plots of pure TiO₂ cell and TiO₂-Bi₂S₃:Eu³⁺ composite cell are shown in Fig. 11. Compared with pure TiO₂ cell, the TiO₂-Bi₂S₃:Eu³⁺ composite cell has longer electron recombination time and longer electron transport time. It noted that longer transport time can result in poorer photoelectric properties, while longer recombination time is beneficial for enhancing photoelectric properties.

The charge collection efficiencies (\(\eta_{cc}\)) of DSSCs are determined by the relation: \(\eta_{cc} = 1 - \tau_d/\tau_n\). Where, \(\tau_d\) is a charge transport time and \(\tau_n\) is a charge recombination lifetime. Figure 12 shows the charge collection efficiencies of pure TiO₂ cell and TiO₂-Bi₂S₃:Eu³⁺ cell. TiO₂-Bi₂S₃:Eu³⁺ composite cell has a higher charge collection efficiency than pure TiO₂ cell. All these results indicated that the performance of the solar cells can be improved by adding Bi₂S₃:Eu³⁺.

In summary, flower-like Bi₂S₃:Eu³⁺ was successfully prepared by a facial solvothermal method. The obtained Bi₂S₃:Eu³⁺ was chosen to design TiO₂-Bi₂S₃:Eu³⁺ composite photoanodes. The result indicated that the photoelectric conversion efficiency were enhanced greatly by the incorporation of Bi₂S₃:Eu³⁺. The best photoelectric conversion performance was observed when the mass concentration of Bi₂S₃:Eu³⁺ was 3 wt%. The result of EIS analysis revealed that the interfacial resistance of the TiO₂-dye|I₃⁻ electrolyte interface of TiO₂-Bi₂S₃:Eu³⁺ composite cell was much bigger than that of pure TiO₂ cell. In addition, the TiO₂-Bi₂S₃:Eu³⁺ composite cell exhibited longer electron recombination time, longer electron transport time, and higher charge collection efficiency than pure TiO₂ cell.

### Table 2. Parameters obtained by fitting the impedance spectra of composite solar cells using the equivalent circuit in the inset of Fig. 9.

| DSSCs          | R₂/Ω | Z₁/F | Rₛ/Ω | Y₀/S | B/Y₀ | η₁/Ω | CPE       |
|----------------|------|------|------|------|------|-------|-----------|
| Pure TiO₂      | 31.53| 9.378 × 10⁻⁴ | 12.00 | 0.01077 | 0.387 | 30.31 | 0.0005914 |
| TiO₂-Bi₂S₃:3%Eu³⁺ | 41.26| 7.789 × 10⁻⁴ | 12.30 | 0.00641 | 0.252 | 41.30 | 0.00217   |

**Figure 10.** Nyquist plots of DSSCs comprised of pure TiO₂ cell and TiO₂-Bi₂S₃:Eu³⁺ cell. Inset is the equivalent circuit used to represent interfaces in composite solar cells composed of FTO|TiO₂-dye|I₃⁻||Pt|FTO.
those of pure TiO2 cell. Of course, the enhancement of the efficiency of the TiO2-Bi2S3:Eu3+ composite cells was also related to the larger BET surface areas of Bi2S3:Eu3+.

**Methods**

**Synthesis of flower-like Bi2S3 nanocrystals.** In a typical experiment, Bi(NO3)3, CH3N2S and Eu(NO3)3 were separated add to ethylene glycol (10 ml), and the solution was thoroughly stirred. Subsequently, the solution was transferred to a 50 ml Teflon-lined autoclave for 12 h at 180 °C. After cooling to room temperature, the final products were collected by means of centrifugation, washed with ethanol, dried at 80 °C in air and then annealed at different temperature.

**Fabrication of photoelectrodes.** Fabrication of photoelectrode and the assembly of DSSCs: several pastes, from homogeneously mixing Bi2S3:Eu3+ and TiO2 (Degussa P25) into 3 mL of TiO2 colloid, were prepared with different mass concentrations of Bi2S3:Eu3+. The TiO2 colloid was prepared following the previously published synthesis procedure. A screen-printed double layer of TiO2-Bi2S3:Eu3+ was used as the photoanode. The first layer of TiO2-Bi2S3:Eu3+ was prepared by a doctor-blade method on the FTO substrate and then sintered at 450 °C for 1 h. Subsequently, the second layer of TiO2-Bi2S3:Eu3+ was covered on the first TiO2-Bi2S3:Eu3+ film and then sintered at 450 °C for 30 min again. The sensitization of the photoelectrodes was achieved by immersing them into 0.5 mM [(C4H9)4N][Ru(4-carboxy-4′-carboxylate-2,2′-bipyridine)2(NCS)2] dye (N719, Solaronix SA, Switzerland) in acetonitrile and tertbutanol (volume ratio, 1:1) for 48 h at room temperature. The Pt counter electrodes were prepared following the previous literature. The dye-sensitized photoanode was assembled with a Pt counter electrode into a sandwichtype 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 M 1-propyl-2,3-dimethyl-imidazolium iodide, 0.05 M I2, 0.1 M LiI, and 0.5 M tert-butylpyridine (TBP) in 3-methoxypropionitrile (3-MPN), by capillary action.

**Materials Characterizations.** The composition of the materials was determined by a Rigaku (Japan) DMAX-rA X-ray diffraction meter (XRD) equipped with graphite monochromatized Cu Kα radiation.
(γ = 1.541874 Å), keeping the operating voltage and current at 40 kV and 40 mA. The size and morphology of the final products were investigated by scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL, JEM-3010). UV-Vis absorption spectrum were determined by a UV–Vis spectrophotometer (Shimadzu UV-2550, Tokyo, Japan). The Raman spectra were measured by a HORIBA JOBIN YVON LabRam-HR 800 micro-Raman spectrometer.

**Photovoltaic properties study.** Photovoltaic measurements were carried out with a solar simulator (Oriel, USA) equipped with an AM 1.5G radiation (1 sun conditions, 100 mW cm−2) filter was used as the light source. Current-voltage (J–V) curves were measured with a BAS100B electrochemical analyzer (Zahnier Elektrik, Germany). The area of DSSCs is 1.5 cm² and the irradiation area is 0.09 cm² with a light intensity meter. The photoanode of Bi₂S₃:Eu³⁺ films were fabricated in the same condition. To make the data strictly and scientifically, all the cells was test for at least 5 times then obtained an average value. The EIS were performed with a computer-controlled IM6e impedance measurement unit (Zahnier Elektrik, Germany) and carried out by applying sinusoidal perturbations of 10 mV with a bias of ~0.8 V at a frequency ranges 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) (Zahnier 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 mW cm⁻².

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Author Contributions
B.Y.X. performed synthesis experiments, G.F.W. and H.G.F. designed the experiment. G.F.W. carried out photoelectrochemical evaluation and discussion. B.Y.X. and G.F.W. wrote the manuscript.

Additional Information
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