Integrated plasmonic and upconversion starlike Y$_2$O$_3$:Er/Au@TiO$_2$ composite for enhanced photon harvesting in dye-sensitized solar cells

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Abstract

A plasmon-enhanced upconversion composite Y$_2$O$_3$:Er/Au@TiO$_2$ (SYE/A@T) with a three-dimensional starlike morphology is prepared and then mixed with submicron TiO$_2$ (200 nm) to form a multifunctional scattering layer in TiO$_2$-based dye-sensitized solar cells (DSSCs). In such starlike micronsized upconverter, Au nanoparticle-assisted plasmon effect can intensify the upconversion emission of Y$_2$O$_3$:Er, and simultaneously TiO$_2$ coating can improve the charge transport within SYE/A@T. Therefore, the SYE/A@T shows extended light-absorbing range to near-infrared region and improved light-scattering ability, leading to an improved photovoltaic performance of DSSCs. With the optimum mixing ratio, a conversion efficiency of 8.62% is attained, which is a significant improvement of 27.6% compared with the cell without adding SYE/A@T. Our work provides a feasible strategy to prepare an upconversion composite with plasmon-enhanced emission and enable this composite to accommodate the DSSCs system and improve the conversion efficiency of DSSCs.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have drawn considerable attention since their advent in 1991 [1] due to their characteristics of low cost, ease of production, and high conversion efficiency...
2–6]. Typically, a sandwich-structured DSSC device is composed of a dye-sensitized TiO2 film photoanode, a platinum counter electrode, and an I−/I3 redox couple electrolyte [7]. In a DSSC, incident photons are absorbed by dye molecules, and then dye molecules inject electrons into the conduction band of TiO2 upon optical excitation [7]. However, the widely used commercial dye sensitizers, such as N719 and N3, exhibit limited absorption wavelength ranges below 700 nm, owing to their inherent optical bandgaps of over 1.8 eV. Thus, approximately 50% of the total solar energy in infrared light (NIR) could not be harnessed by conventional ruthenium dyes, and hence limit the optoelectronic conversion efficiency of device, leaving plenty of room to improve the performance of DSSCs through dye molecular sensitizers exploitation, as well as composition modification of photoelectrode [8]. One commonly used way to broaden the spectral response of DSSCs to NIR region or even infrared region is to developing panchromatic dye sensitizers [9,10] or cosensitizing by multiple dyes with complementary absorption spectra [5,11–15]. However, most new designed panchromatic dye could not absorb visible light as strongly as conventional ruthenium dyes, and multiple dyes mostly involve complicated cosensitization procedures.

Another feasible strategy to overcome this limitation is to use upconversion (UC) luminescent materials, which can convert light in infrared light (NIR) could not be harnessed by conventional ruthenium dyes, and multiple dyes mostly involve complicated cosensitization procedures.

To overcome this limitation, Shan [38] and Ramasamy [39] proposed to coat an external light-reflecting layer consisting of UC NPs on the back of platinum electrode in DSSCs to avoid the recombination effect, and achieved an increase of efficiency ~10.2%. For internal scattering layer, coating a shell with TiO2 or SiO2 is a conventional way to eliminate surface defects. Liang designed a highly uniform core-double-shell structured β-NaYF4:Yb,Er@SiO2@TiO2 to effectively inhibit negative recombination effect [40]. This paper reports the design and synthesis of a plasmon-enhanced UC composite comprising a core of starlike Y2O3:Er (SYE) attached with Au NPs and a shell of anatase TiO2 NPs. To balance the light scattering, electron transport and mechanical strength, the Y2O3:Er/Au@TiO2 composite was mixed with TiO2 submicron spheres (200 nm in diameter) to form a multifunctional hybrid scattering layer in TiO2-based DSSC devices. The schematic of preparation process and configuration of photoanode film is shown in Fig. 1. The micron-sized three-dimensional (3D) SYE acts as an effective NIR upconversion and light scattering center, resulting in strong and broader absorption [25]. By attaching Au NPs, the NIR light can be more effectively converted to visible light via plasmon-enhanced UC and ultimately absorbed by the dye sensitizer. By coating TiO2, the surface charge recombination on SYE is largely reduced and the dye-loading is increased.

2. Experimental

2.1. Materials

Yttrium nitrate hexahydrate (Y(NO3)3·6H2O), erbium nitrate pentahydrate (Er(NO3)3·5H2O) and 4-tert-butylpyridine (TBP) were obtained from Aladdin. TiO2 (20 nm) paste for the transparent layer and TiO2 (200 nm) paste for scattering layer were purchased from Wuhan Ge’ao Co. Ltd. Iodide (I2), lithium iodide (LiI), 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), chloroplatinic acid (H2PtCl6), chloroauroic acid (HAuCl4) and titanium tetrafluoride (TiF4) were purchased from Sigma-Aldrich Co. Ltd. Dye sensitizer, cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dis-carboxylato)-ruthenium(II)- bis-tetrabutylammonium (N719) was obtained from Solaranix. All other chemicals were purchased from Beijing Chemical Works and were used without further purification. All solutions used in this work were prepared with 18.2 MΩ cm−1 water produced by a reverse osmosis water system (Easy pure II, Barnstead).

2.2. Preparation of 3D starlike Y2O3:Er/Au composite

The 3D starlike Y2O3:Er (denoted as SYE) was prepared with a modified method reported by Lu et al. [25]. For preparation of 3D starlike Y2O3:Er/Au composite (denoted as SYE/A), 100 mg of as-prepared SYE powder was dispersed in 50 ml deionized H2O and sonicated for 30 min at room temperature. Then, 0.1 mL of 1% HAuCl4 solution was added to the mixture, followed by dropwise adding 2 mL of 0.1% NaBH4 solution to react for 10 min with vigorous stirring. The resultant solution was centrifuged, and the precipitate was washed with deionized water several times and then dried at 80 °C in air overnight.

2.3. Preparation of 3D starlike Y2O3:Er/Au@TiO2 composites

To construct core-shell structured 3D starlike Y2O3:Er/Au@TiO2 composites (denoted as SYE/A@T), 100 mg of as-prepared SYE/A powder was dispersed in 60 ml solvent with an equal volume of H2O: ethanol and then sonicated for 30 min at room temperature. Then, 2 mL of 40 mM TiF4 solution was added to the above mixture, followed by being stirred for 30 min. Finally, the mixture was transferred to Teflon-lined autoclaves and heated to 180 °C for 6 h. The resultant solution was centrifuged, and the precipitate was washed with deionized water and anhydrous ethanol several times and then dried at 100 °C in air overnight. Finally, the obtained powder was calcined at 500 °C for 3 h. For comparison, composites without Er doped (denoted as SY/A@T) and without Au NPs attached (denoted as SYE@T) were also prepared with the same procedure.

2.4. DSSC device assembly

In order to obtain the paste for multifunctional scattering layer (denoted as MSL), the as-prepared SYE/A@T corresponding to mass-fraction levels varying from 10% to 25% with respect to the commercial TiO2 (200 nm) were mixed added into the paste. To construct a photoanode, a TiO2-SYE/A@T based MSL was covered on a TiO2 (20 nm) transparent layer (denoted as TL) with a screen-printing method and then dried at 70 °C for 1 h, followed by...
a programmed heating of 500 °C for 30 min. For comparison, SYE-, SYE@T-, and SY/A@T-mixed photoelectrodes together with pure TiO₂ photoelectrode (without adding upconversion species) were also prepared in parallel. The thicknesses of the photoelectrode films were all about 15 μm (11 μm for the TL and 4 μm for the MSL). The resultant photoelectrodes were immersed into a 0.5 mM

![Fig. 1. Schematic diagram of experimental process for SYE/A@T and the photoanode configuration of DSSCs.](image)

![Fig. 2. SEM images of (a, b) SYE, (c) SY, and (d) SYE/A@T. TEM images of (e) SYE and (f) SYE/A@T. (g, h) HRTEM images of SYE/A@T. (i) EDS spectrum of SYE/A@T with measured atom content. (j) XRD patterns of the prepared SYE and SYE/A@T.](images)
N719 dye solution in anhydrous ethanol for 24 h at room temperature. The counter electrodes were prepared by drop-coating a 0.35 mM H2PtCl6 isopropanol solution on the FTO/glass substrate, followed by annealing at 400°C for 15 min. Afterwards, the photoanode and the counter electrode were assembled into a sandwich cell using a surlyn sheet by automatic hot-pressing. Finally, the electrolyte consisting of 0.05 M I2, 0.1 M LiI, 0.5 M DMPB, and 0.5 M TBP in acetonitrile was injected into the space between the counter electrode and the photoanode. The active area of a DSSC device exposed in light was 0.16 cm².

2.5. Characterization

To detect the overall structure and morphology of as-synthesized composites and photoelectrodes, the samples were characterized by scanning electron microscopy (SEM) using a JEOL-6701F microscope equipped with an X-ray energy dispersive spectrometer (EDS). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL 3010 microscope operated at 300 kV. The crystal structures were identified by X-ray powder diffraction (XRD) using an X-ray diffractometer (X’Pert PRO MPD, Panalytical) with a Cu-Kα radiation. The absorption and diffuse reflectance spectra were measured by a UV–vis spectrophotometer (Lambda 950, Perkin Elmer). The upconversion photoluminescence spectra were performed on a spectrophotometer (FLS980, Edinburgh) with a CW NIR laser at 980 nm as the excitation source. Dye loading measurements were conducted by immersing the dye-sensitized photoanode films in 0.1 M NaOH solution and measuring the concentration of the desorbed dye by UV–vis absorption spectrophotometry. Photovoltaic performances of DSSCs were characterized by measuring the current density-voltage (J–V) curves under air mass 1.5 global (AM 1.5G) light using a solar light simulator (Newport 69911, Stratford, CT, USA), and the data were recorded by an electrochemical workstation (CHI660C, Shanghai). The infrared irradiation (λ > 800 nm) was obtained by using an 800 nm highpass optical filter on the path of the simulated solar light. The electrochemical impedance spectroscopy (EIS) was performed on an electrochemical workstation (Zennium Zahner, Germany) under AM 1.5G, and the EIS Nyquist plots were measured at a bias of Voc with ac amplitude of 10 mV under a frequency ranging from
10\(^{-1}\)–10\(^5\) Hz.

3. Results and discussion

3.1. Morphological and structure characterization

Fig. 2a and b are SEM images of as-prepared SYE, showing that the SYE exhibits a 3D starlike structure, and each single petal is apparently stacked with arrays of 1D smooth-faced nanorods. In order to reveal the morphology variation arising from Er doping, and Au NP attachment together with TiO\(_2\) coating, SEM images of SY (Fig. 2c) and SYE/A@T (Fig. 2d) are also provided. One can see that these SY-based samples maintain analogous structure and morphology after introduction of foreign species. However, it is worth noting that upon being attached with Au nanoparticles (Au NPs) and coated with TiO\(_2\), the surface of SYE/A@T become rougher, as shown in Fig. 2d. Such surface roughness variation originating from Au NPs attachment and TiO\(_2\) coating can also be clearly observed by TEM images of SYE/A@T (Fig. 2f). The high resolution TEM (HRTEM) images (Fig. 2g and h) provide more details of the SYE/A@T. From the low magnification HRTEM image (Fig. 2g), both attached Au NPs of ~8 nm and ~30 nm thick TiO\(_2\) shell can be observed on the surface of the SYE. The high magnification HRTEM image (Fig. 2h) of the coating layer of SYE/A@T shows two typical interplanar distances of 0.235 nm and 0.350 nm, which are assigned to the (111) crystal plane of Au and (101) crystal plane of anatase TiO\(_2\), respectively. Additionally, nano-sized internal pores within the shell of TiO\(_2\) grains can be also observed, which is thought to be able to increase the dye-loading amount of photoelectrode. From EDS spectrum (Fig. 2i), peaks of host (Y and O) and dopant (Er) are detected for SYE/A@T composite, revealing the presence of Er atoms with a molar ratio of about 1:10 to Y atoms, which accords with the molar ratio of reactant (1:10). In addition, relatively weak signals of Ti and Au are also discerned for SYE/A@T composite, further verifying the successful attachment of Au NPs and coating of TiO\(_2\) on the SYE surface. Fig. 2j shows the XRD patterns of the SYE and SYE/A@T. The XRD diffraction peaks of both the SYE and SYE/A@T can be readily indexed to the pure cubic-phase Y\(_2\)O\(_3\) (JCPDS 41-1105), indicating that either doping Er\(^{3+}\) or modifying with Au and TiO\(_2\) does not change the crystal structure of Y\(_2\)O\(_3\) since the ionic radii and coordination numbers of both Er and Y cations are very similar. The signals of Au and TiO\(_2\) were too weak to detect in the XRD pattern of SYE/A@T owing to their low content and relative low crystallinity within the composite.

3.2. Photoluminescence property

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>FF (%)</th>
<th>(\eta) (%)</th>
<th>(\eta) (% ((\lambda &gt; 800 \text{ nm})))</th>
<th>Dye adsorption ((\times 10^{-3}) mol m(^{-2}))</th>
<th>(R_{ct}) ((\Omega))</th>
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<tr>
<td>Pure TiO(_2)</td>
<td>0.707</td>
<td>15.89</td>
<td>60.28</td>
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<td>0.046</td>
<td>2.15</td>
<td>10.93</td>
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<td>13.06</td>
<td>62.23</td>
<td>5.35</td>
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<td>2.03</td>
<td>26.82</td>
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<td>SYE/A@T</td>
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<td>19.01</td>
<td>61.02</td>
<td>8.05</td>
<td></td>
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<td>SY/A@T</td>
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<td></td>
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<td>22.27</td>
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<td>SYE/A@T</td>
<td>0.694</td>
<td>20.94</td>
<td>59.48</td>
<td>8.64</td>
<td>0.232</td>
<td>2.27</td>
<td>15.38</td>
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</table>

The photoluminescence spectra of the as-synthesized SYE, SYE/A together with SYE/A@T excited with a \(\lambda = 980\) nm laser, as displayed in Fig. 3a, reveal the influence of Au NPs and TiO\(_2\) shell on...
the emission band of the fluorphore overlapping with the plasmonic resonance frequency of the metal nanostructures, it is reported to be able to increase the emission rate and thus enhance the emission efficiency due to the coupling of the UC emission with the plasmonic resonance [43]. UV–vis absorption spectrum of the Au NPs (Fig. 3b) clearly exhibits that the plasmonic resonance frequency of the Au NPs overlaps well with the green emission bands of SYE (525 nm and 560 nm), which allows the effective coupling of plasmonic resonance with UC emission and hence leads to an increment of the emission intensity. Such increased emission intensity via combination of SYE and Au NPs could ensure sufficient excitation for UC, and hence greatly enhance the final sunlight harvesting in N719 and improve the photoelectric conversion efficiency of DSSCs. Note that the Au NPs plasmonic resonance couples better with the green emission than the red, therefore the enhancement factor of the green emission is larger than that of the red one, as shown in Fig. 3c. Thus, UV–vis absorption spectra together with PL spectra verify that the SPCE plays a dominated role in the enhancement of UC emission. Furthermore, from the PL spectra it can be also found that TiO2 shell causes a slightly decrease of the emission intensity of SYE/A. Such phenomenon might be attributed to two possible reasons. On one hand, TiO2 has a higher phonon energy (about 600 cm⁻¹) than Y2O3 (about 550 cm⁻¹), leading to extra energy loss associated with the increasing probability of multiphonon nonradiative transition [44,45]. On the other hand, the rough TiO2 shell can scatter part of incident NIR light and simultaneously absorb part of emissive visible light, hence resulting in the decrease of utilization of the NIR light.

3.3. Photovoltaic performance of DSSCs

In order to evaluate the optical properties and performances of DSSC doped with SYE/A@T, different double-layered photoelectrode films by printing a UC-TiO2 (200 nm) scattering layer (SL) on the top of a TiO2 (20 nm) transparent layer (TL) were constructed. As shown in Fig. S3, the thicknesses of TL and SL are measured to be 11 μm and 4 μm, respectively. For clarity, photoelectrode sample corresponding to the photoelectrodes added with SYE, SY/A@T, SYE@T, and SYE/A@T, respectively. For comparison, a pure TiO2 photoelectrode (denoted as pure TiO2) was also made in parallel. The photocurrent density-voltage (J-V) curves of all the DSSCs are shown in Fig. 4, and their photovoltaic parameters are summarized in Table 1. As can be seen, the pure TiO2 cell exhibits a short-circuit current density (Jsc) of 15.89 mA cm⁻² and a photoelectric conversion efficiency (η) of 6.77%, and the cell SYE shows the lowest Jsc of 13.06 mA cm⁻² and η of 5.35%. As for SYE/A@T cell, the photovoltaic performance is improved and the highest Jsc of 20.94 mA cm⁻² and η of 8.64% are achieved, which are 27.6% and 61.5% enhancements of η as compared with pure TiO2 and SYE cells, respectively.

3.4. Scattering properties of photoelectrodes

To find out the reasons of the photovoltaic enhancement associated with the morphology as well as the components of the Au/TiO2-modified UC composites, we measured UV–vis diffuse reflectance spectra of above photoelectrodes in the wavelength region of 400–800 nm, and the results are shown in Fig. 5. Comparing with pure TiO2 film, all the UC-composite-doped photoelectrode films exhibit a remarkable improvement in light reflection over the entire region. Similarly, the reflectance of the photoelectrode increases with the increase of adding amount of SYE/A@T, as shown in Fig. S2a. These results reveal that the micron-sized UC composites can act as stronger light scattering centers than submicron-sized TiO2 (200 nm) can. However, SYE cell
perform much worse than SYE@T cell, SYE/A@T cell, and even pure TiO2 cell. The low performance of SYE indicates that the introduction of bare UC materials makes negative effect on the DSSC performance. Such a negative effect might be associated with poor electron transport ability and poor dye-loading ability of bare SYE. In contrast, the SYE@T cell exhibits much better performance than the SYE cell. Therefore, the coated TiO2 shell play an important role on the photoelectric behaviours of DSSC.

3.5. Electron transport and dye-loading abilities of photoelectrodes

To investigate the influence of TiO2 shell out of SYE core on the photoelectric behaviours of DSSC, electrochemical impedance spectroscopy (EIS) was employed to examine the SYE, pure TiO2 and SYE@T cells [46]. As shown in Fig. 6a, all the three plots exhibit two distinguishable semicircles, which are associated with the electrochemical reaction at the electrolyte/counter electrode interface in the 103 Hz range (Rct1) and at the TiO2/dye/electrolyte interface in the 10−1 to 103 Hz range (Rct2) from left to right, respectively [47]. The electron transport property in the photoanode can be judged by Rct2, which is defined by the diameter of the low-frequency semicircle [48,49]. According to the fitted values of Rct2 listed in Table 1, it can be seen that the impedance drastically increases from 10.93 Ω for the pure TiO2 cell to 26.82 Ω for the SYE cell, implying a weak charge transport within the SYE cell. It may be attributed to the serious charge recombination effect and poor charge transport ability of bare SYE in the photoanodes, and hence a low electron diffusion and collection efficiency in the SYE cell [50]. Compared with the SYE cell, the impedance for the SYE@T cell dramatically decreased to 14.75 Ω, implying that the negative charge recombination originating from micron-sized SYE was remarkably reduced and the electron transport was improved by coating a TiO2 shell. However, the charge transport in the SYE@T cell is still more difficult than in the pure TiO2 cell, that is, introducing SYE@T cell still increases the impedance of photoanode film. Moreover, UV−vis absorption spectra of dye solution desorbed from the above N719-sensitized photoanodes were also measured to investigate the influence of TiO2 shell on dye-loading ability, as shown in Fig. 6b, and the corresponding dye-loading amounts results are listed in Table 1. It can be seen that the introduction of bare SYE severely reduce the dye-loading amount of photoanode. After being coated with TiO2 shell, the SYE@T as well as SYE/A@T could adsorb more dye molecules than SYE, attributed to the nanoporous structure of TiO2 shell. That is, with the increase of SYE/A@T weight ratio, more and more dye molecules are adsorbed into the photoanode film, which can be identified by the dye-loading amount results in Fig. S2b. The increase in dye-loading amount can enhance the amount of photo-generated electrons and thereby contribute to a better photovoltaic performance of DSSCs.

3.6. Light-harvesting ability of photoelectrodes

Comparing the SYE@T cell with SYE/A@T cell, we can find a discernable difference in photovoltaic performance, indicating that Au NPs also play a notable role in improving the photovoltaic property of SYE/A@T. To understand the function of Au NPs, the light-harvesting ability of unsensitized SYE/A@T photoelectrodes with different adding amount of SYE/A@T were investigated by measuring the absorption spectra within the visible and NIR range of 400−1000 nm, as displayed in Fig. 7a. The percentages varying from 10% to 25% correspond to different mass-fractions of SYE/A@T with respect to scattering layer. Obviously, the absorption of the SYE/A@T is increasing with the increase of adding amount of SYE/A@T within the visible and NIR range of 400−1000 nm. Note that for all the SYE/A@T, the absorption increase within NIR region, especially in the wavelength around 980 nm indicates more NIR light could be exploited and transferred into absorbable photons for dye via UC process. As demonstrated in Fig. 4b, the η of SYE/A@T cell under NIR irradiation (λ > 800 nm) is much higher than that of pure TiO2. However, this increase owing to UC effect under NIR irradiation cannot account for the total increase of η from the pure TiO2 to SYE/A@T (compare Fig. 4a and b). Thus, it means that the extension of light-harvesting band to NIR region caused by plasmon-enhanced UC effect makes an almost negligible contribution to the total increase of η of SYE/A@T. Moreover, an absorption enhancement in the wavelength around 515 nm owing to the LSPR effect of Au NPs is discerned for all the SYE/A@T [42]. It is worth noting that such absorption of Au NPs within SYE/A@T (Fig. 7a) shows a slight red shift versus the absorption the pure Au NPs displayed in Fig. 3b, which is arising from the aggregation of Au NPs [42,43]. Under sunlight irradiation, the plasmon-induced electrons in the Au NPs of SYE/A@T could move through Au-TiO2 interface into the conduction band of TiO2 [51]. Therefore, the absorption enhancement in the wavelength of about 515 nm is thought to be beneficial for the enhancement of DSSC performance by attaching Au NPs.

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Voc (V)</th>
<th>Jsc (mA cm−2)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>Dye adsorption (× 10−3 mol m−2)</th>
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<tr>
<td>Pure TiO2</td>
<td>0.707</td>
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<td>6.77</td>
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<td>58.04</td>
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4. Conclusions

In summary, 3D starlike core-shell-structured Y2O3:Er/Au@TiO2 composite was prepared and demonstrated effective upconversion and light scattering when applied in DSSC. The TiO2 shell out of the upconversion core remarkably reduced the charge recombination on the surface of SYE and simultaneously enlarged the dye-loading amount. In addition, the LSPR effect originating from Au NPs can...
not only intensify the upconversion emission intensity via SPCE, but also enhance the light absorption around wavenumber of 515 nm. At the optimum mixing weight ratio of 23%, an efficiency of 8.64% was obtained, which was a significant improvement of 27.6% compared with the pure TiO2 cell. Our work provides a feasible strategy to prepare an upconversion composite with plasmon-enhanced emission and enable this composite to accommodate the DSSCs system and improve the conversion efficiency of DSSCs.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2016.03.032.

References