Double-shell SnO$_2$/CeO$_2$:Yb,Er hollow nanospheres as an assistant layer that suppresses charge recombination in dye-sensitized solar cells$^\dagger$

Rongfang Zhao,$^{a,b}$ Dongmei Tang,$^a$ Qianhui Wu,$^a$ Wenlong Li,$^a$ Xiue Zhang,$^a$ Rong Guo,$^a$ Ming Chen$^{a,*}$ and Guowang Diao$^{a,*}$

Double-shell SnO$_2$/CeO$_2$:Yb,Er hollow nanospheres (HNSs) are prepared using SiO$_2$ as a template. Firstly, CeO$_2$:Yb,Er nanoparticles (NPs) were coated on the surface of SiO$_2$ to generate core–shell SiO$_2$@CeO$_2$:Yb,Er nanospheres. Then the SiO$_2$ cores were removed accompanied by SnO$_2$ deposition to form heterogeneous double-shell SnO$_2$/CeO$_2$:Yb,Er HNSs during a hydrothermal process. It can be seen from the structure analysis that the deposition of the SnO$_2$ shell as the framework supports the CeO$_2$:Yb,Er shell. When SnO$_2$/CeO$_2$:Yb,Er HNSs act as an assistant layer in dye-sensitized solar cells (DSSCs), the photoelectric conversion efficiency (PCE) is enhanced to 8.66%. Open-circuit voltage decay confirms that the lifetime of photogenerated electrons in the cells is prolonged. Double-shell SnO$_2$/CeO$_2$:Yb,Er HNSs might efficiently suppress the recombination of photoproduced electrons–holes, extend the electron lifetime, and further improve the photoelectric conversion performance of DSSCs.

1 Introduction

The depletion of natural resources, coupled with the ever-growing consumption of fossil fuels and an increase in global pollution, has boosted great efforts to seek renewable and sustainable energy sources. Solar cells are very appealing devices for energy conversion targeted at photoelectric conversion. Dye-sensitized solar cells (DSSCs), as they are economical, have facile fabrication approaches and have an environmentally green nature, have attracted tremendous scientific and industrial attention in the past two decades.

Normal DSSCs are composed of a photoanode, an electrolyte, and a counter electrode. The photoanode is formed with metal oxide that is sensitized by dye molecules, such as TiO$_2$, SnO$_2$, ZnO, Nb$_2$O$_5$, etc.$^3$–$^5$ TiO$_2$ is one of the most common metal oxides because of its easy preparation, band alignment, and chemical stability.$^6$–$^9$ However, the intrinsic properties of TiO$_2$ and the charge recombination in the photoanode limit the enhancement of the photoelectric conversion efficiency (PCE) of DSSCs. Researchers pay close attention to enhancing the separation efficiency of electrons and holes by designing various photoanode materials. The fabrication of TiO$_2$ composite photoanodes by doping a suitable semiconductor as an assistant layer is a common method. CeO$_2$ or its composites are used as a kind of assistant material for DSSCs.$^{10}$–$^{13}$ In our previous work, Yb and Er doped CeO$_2$ with a band gap of 2.8 eV, as a promising assistant layer, is investigated to enhance the PCE of DSSCs.$^{14}$–$^{15}$ However, CeO$_2$ displays poor conductivity and a low electron migration rate via energy band and state density analysis. SnO$_2$ as a well-known transparent conductive oxide for nanoelectronics is usually used in DSSCs due to its high electron mobility,$^{16}$–$^{18}$ and for promoting the fast diffusion transport of photoinduced electrons.$^{19}$–$^{21}$ Many studies have demonstrated that the performance of combined SnO$_2$ and CeO$_2$ can be applied in gas sensing.$^{22}$–$^{26}$ However, few studies focus on building a composite of SnO$_2$ and CeO$_2$ as an assistant photoanode material for DSSCs to improve the separation of electrons and holes.

In this paper, we synthesized double-shell SnO$_2$/CeO$_2$:Yb,Er hollow nanospheres (HNSs) using SiO$_2$ nanospheres as a template. When SnO$_2$/CeO$_2$:Yb,Er HNSs are used as an assistant layer in DSSCs, the PCE of the DSSCs is increased to 8.66%. With the assistant effect of SnO$_2$/CeO$_2$:Yb,Er, the lifetime extension of photoproduced electrons was confirmed by open-circuit voltage decay, which is conducive to enhance the performance of DSSCs.

2 Experimental

2.1 Synthesis

All of the reagents used in the experiment were acquired from Sinopharm Chemical Reagent Co. Ltd (China), were of analytical...
grade and were used as received without further purification. The synthesis route is as shown in Fig. 1.

**Preparation of SiO$_2$ nanospheres.** 1.6 mL TEOS dissolved in 44 mL ethanol was labeled as solution A, 10 mL NH$_3$.H$_2$O dissolved in 44 mL ethanol was solution B, and 2 mL TEOS dissolved in 88 mL ethanol was labeled as solution C. The three solutions were preheated in 45 °C water. Solution A and solution B were added to a three-mouth bottle with mechanical stirring at 45 °C at constant temperature. After 30 min, 8 mL NH$_3$.H$_2$O was added to the three bottles, then solution C was added to the system. After 2 h, the reaction was stopped and the solid was collected by centrifugation.

**Preparation of SiO$_2$@CeO$_2$:Yb,Er nanospheres.** 0.2 g of the SiO$_2$ nanospheres was fully dispersed in 1 mL 1 M Ln(NO$_3$)$_3$ (Ln = Ce, Yb, Er) ethanol solution (the molar ratio, Ce : Yb : Er = 96.7:0.3:3), then 0.1 g PVP was added under magnetic stirring, until it became a milky, transparent, and viscous paste. It was evenly coated on aluminum foil and dried in an oven, then calcined at 700 °C in air, to obtain the SiO$_2$@CeO$_2$:Yb,Er core–shell nanospheres.

**Preparation of SnO$_2$/CeO$_2$:Yb,Er hollow nanospheres.** Under supersonic, 20 mg of the SiO$_2$@CeO$_2$:Yb,Er nanospheres was dispersed in 20 mL ethanol, and then 1 mL 10 mg mL$^{-1}$ K$_2$SnO$_3$ solution and 0.6 g urea were added. The reaction then proceeded at 170 °C in a 40 mL reactor for 2 h and the product was collected by centrifugation to obtain the SnO$_2$/CeO$_2$:Yb,Er hollow nanospheres.

### 2.2 Fabrication of cells

The photoanode film was prepared by mixing P25 (Degussa), terpineol and ethyl cellulose dissolved in ethanol solution. Then, the slurry was screen-printed on an FTO substrate. After coating, the electrode was treated at 450 °C for 30 min. This step was repeated five times. SnO$_2$/CeO$_2$:Yb,Er HNSs were added into the ethanol solution containing terpineol and ethyl cellulose to form the slurry, which was pasted onto the TiO$_2$ transparent layer (as shown in Fig. S1, ESI†). Finally, the composite photoelectrode was sintered in a tube furnace at 450 °C. After cooling to room temperature, the electrode was immersed into N719 dye solution for 24 h. A platinum counter electrode on FTO glass was prepared by the conventional thermal decomposition method using an H$_2$PcI$_3$ precursor. The liquid electrolyte contained LiI (0.1 M) and I$_2$ (0.05 M). The dye-sensitized composite photoanode, electrolyte and platinum counter electrode formed a modified sandwich cell.

### 3 Results and discussion

#### 3.1 Materials characterization

The structure and morphology of the products were observed using transmission electron microscopy (TEM). Fig. 2a displays the SiO$_2$ nanospheres with a uniform size of about 180 nm and shows their good monodispersity. In Fig. 2b, it can be clearly seen that the CeO$_2$:Yb,Er nanoparticles (NPs) grew on the surface of the SiO$_2$ nanospheres to form the core–shell SiO$_2$@CeO$_2$:Yb,Er nanospheres. Subsequently, during the hydrothermal reaction progress, the generation of SnO$_2$ was accompanied by the dissolution of SiO$_2$ cores to obtain double-shell SnO$_2$/CeO$_2$:Yb,Er HNSs with a thickness of about 20 nm as shown in Fig. 2c–e. In the control, without the treatment of the hydrothermal reaction, pure CeO$_2$:Yb,Er cannot form hollow nanospheres, but it generates an aggregation of nanoparticles (Fig. S2, ESI†), which indicates that the shell SnO$_2$ acts as the framework to support the double-shell structure of SnO$_2$/CeO$_2$:Yb,Er HNSs. The HRTEM (Fig. 2f) shows an interplanar spacing of 0.310 nm belonging to the (111) crystallographic plane. Ce, Yb, Er, and Sn were measured by EDS as shown in Fig. 2g. EDS spectroscopy line scanning spectra (Fig. 2h) and HAADF-STEM element mapping images (Fig. 2i–m) reveal the hollow structure and the hypodispersion of every element for SnO$_2$/CeO$_2$:Yb,Er HNSs.

The XRD pattern (Fig. S3, ESI†) revealed that the peaks at 28.68°, 33.28°, 47.84°, 56.78°, and 59.60° are assigned to the (111), (200), (220), (311), and (222) planes indexed to fluorite cubic CeO$_2$. Only one diffraction peak belonging to SnO$_2$ was detected. XPS spectra (Fig. 3) demonstrated the surface elemental composition. In the survey spectrum (Fig. 3a), the peaks of Ce, Er, Sn, and...
O are clearly observed. The peaks at 900.28, 882.38, 907.58, 888.78, 916.68, and 898.28 eV (Fig. 3b) are attributed to Ce$^{4+}$, while the characteristic peaks of Ce$^{3+}$ ions (904.45 and 885.90 eV) are not observed. Therefore all Ce element exists as Ce$^{4+}$ in SnO$_2$/CeO$_2$:Yb,Er HNSs. Fig. 3c shows two peaks at 167.5 eV and 184.5 eV, which demonstrate that Er and Yb as Er$^{3+}$ and Yb$^{3+}$ exist in CeO$_2$. In Fig. 3d, two peaks at 487.10 and 495.57 eV display a distance binding energy of 8.5 eV, which confirms that Sn has a valence of +4 in SnO$_2$.

---

**Fig. 2** TEM images of (a) SiO$_2$ nanospheres, (b) SiO$_2$@CeO$_2$:Yb,Er nanospheres, (c and d) TEM images, (e and f) HRTEM images, (g) EDS, (h) EDS spectroscopy line scanning spectra of SnO$_2$/CeO$_2$:Yb,Er HNSs, (i) HAADF-STEM element mapping images of (j) Ce, (k) Sn, (l) Er and (m) Yb.

**Fig. 3** XPS spectra of (a) SnO$_2$/CeO$_2$:Yb,Er HNSs, high-resolution XPS spectra of (b) Ce, (c) Yb, Er 4d and (d) Sn 3d.
3.2 Photovoltaic and electrochemical performance

The characteristic current–voltage curves ($J-V$) of DSSCs are given in Fig. 4, and the main performance parameters are listed in Table 1. To investigate the influence of SnO$_2$/CeO$_2$:Yb,Er HNSs on DSSCs, we fabricated four kinds of DSSC. SnO$_2$ HNSs (the morphology is as shown in Fig. S4, ESI†), CeO$_2$:Yb,Er NPs (the morphology is as shown in Fig. S1, ESI†), and SnO$_2$/CeO$_2$:Yb,Er HNSs were used as assistant layers. They were named as C2, C3 and C4, respectively. The control cell was a conventional DSSC (C1). The control cell displayed the smallest current density ($J_{sc}$) of 13.99 mA cm$^{-2}$ and the lowest PCE (6.52%). However, when SnO$_2$/CeO$_2$:Yb,Er HNSs were introduced into the photoanode, C4 showed the largest $J_{sc}$ (16.54 mA cm$^{-2}$) and the highest PCE (8.66%). Compared with the control cell, the corresponding values of $J_{sc}$ and PCE increased to 18.23% and 32.82%, respectively. In addition, for C2 and C3, the performance parameters of the two DSSCs both improved compared to C1, indicating that the SnO$_2$ HNSs and CeO$_2$:Yb,Er NPs can promote the photoanode properties. Moreover, the FF of C4 is higher than that of C3, demonstrating that SnO$_2$ is conducive to separate photogenerated electrons–holes due to its high electron mobility.

The incident photon-to-current conversion efficiency (IPCE) was investigated to further analyze the photovoltaic performance of the four DSSCs, as shown in Fig. 5. The IPCE values of the four DSSCs increased in the order $P_{25}$ (SnO$_2$/CeO$_2$:Yb,Er HNSs) $>$ $P_{25}$ (CeO$_2$:Yb,Er NPs) $>$ $P_{25}$ (SnO$_2$) $>$ $P_{25}$. The most obvious increase of the IPCE value in C4 is mainly ascribed to the synergistic effect of SnO$_2$ and CeO$_2$, which can enhance the electron mobility of the photoanode assistant layer, efficiently suppress the recombination of photoproduced electrons–holes, and further promote the value of IPCE.

Fig. 6 and Fig. S5 (ESI†) show Nyquist plots and the equivalent circuit of the four DSSCs. The semicircle in the high-frequency region represents the charger transfer ($R_{ct}$) impedance. The semicircle observed in the low frequency region is assigned to the Nernst diffusion resistance ($R_d$) of the I$_3^-$/$I^-$ redox couple in the electrolyte. As shown in Table 1, C4 possesses the smallest $R_{ct}$ and $R_d$ values of 10.50 and 2.99 $\Omega$, and the control cell displays the largest $R_{ct}$ and $R_d$ values of 19.52 and 14.44 $\Omega$. The comparison shows that the transfer resistance of the electrons in the DSSCs with SnO$_2$/CeO$_2$:Yb,Er HNSs as the composite photoanode is smaller than the DSSCs fabricated with pure SnO$_2$ or CeO$_2$:Yb,Er NPs as the assistant material of the photoanode, which is advantageous to the rapid transmission of CeO$_2$:Yb,Er in the thin film. This is helpful for the effective separation of photogenerated electrons and holes, as the photoelectric conversion efficiency of C4 has been improved significantly under the synergistic effect of SnO$_2$ and CeO$_2$:Yb,Er, which is consistent with the photoelectric test results.

It has become popular to characterize recombination in a DSSC by means of a characteristic time constant that is usually
called the electron lifetime, \( \tau_n \). A widely used \( V_{oc} \) decay method is based on the reciprocal time derivative of the open-circuit voltage decay (OCVD). 28 OCVD spectra are used to study transient photoconductivity and recombination kinetics. The illumination was turned off using a shutter after the cell was irradiated with AM1.5 solar light for 20 s to reach a steady voltage to record the OCVD. The electrode lifetime \( \tau_n \) was obtained by the thermal voltage as in eqn (1) 29,30

\[
\tau_n = -\frac{k_B T}{e} \left[ \frac{dV_{oc}}{dt} \right]^{-1}
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( e \) is the positive elementary charge, and \( dV_{oc}/dt \) is the derivative of the open circuit voltage transient. The data shown in Fig. 7(a) display four OCVD curves based on different cells. It is interesting that the \( V_{oc} \) values of C3 and C4 display a little increase of about 0.02 V, which may be attributed to the existence of CeO2:Yb,Er. When \( V_{oc} \) decays to the stable state, the order of the \( V_{oc} \) values is C4 > C3 > C2 > C1 at 30 s after turning off the illumination. Fig. 7(b) shows the electron lifetime values calculated from Fig. 7(a) using eqn (1). Under the same potential, C2 has a slightly longer lifetime than C1. Especially in the region of 0.3–0.5 V, the lifetime of C4 is longer than those of C2 and C3 owing to the electron pathway provided by the SnO2/CeO2:Yb,Er assistant layer. The results indicate that the synergistic action of SnO2 and CeO2:Yb,Er suppresses charge recombination and improves the performance of DSSCs.

4 Conclusion

In summary, heterogeneous double-shell SnO2/CeO2:Yb,Er hollow nanospheres (HNSs) were successfully synthesized using a template method and a subsequent hydrothermal process. When SnO2/CeO2:Yb,Er HNSs are introduced into the photoanode, the cell shows the largest Jsc (16.54 mA cm\(^{-2}\)) and the highest PCE (8.66%). Compared with the control cell of conventional DSSCs, the corresponding values of Jsc and PCE increase to 18.23% and 32.82%, respectively. By analysing the lifetime of the photogenerated electrons by open-circuit voltage decay, it was shown that the cell fabricated with P25 (SnO2/CeO2:Yb,Er HNSs) has the longest electron lifetime under the same potential, which indicates that the synergistic action of SnO2 and CeO2:Yb,Er should suppress charge recombination and improve the efficiency of DSSCs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 21773203), the Natural Science Foundation of Jiangsu Province (BK20161329), and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

References

1. Y. Wang, Z. Li, Y. Tian, W. Zhao, X. Liu and J. Yang, J. Mater. Sci., 2014, 49, 7991–7999.
2. B. O’Regan and M. Graetzel, Nature, 1991, 353, 737–740.
3. Y. Huang, H. Xu, H. Yang, Y. Lin, H. Liu and Y. Tong, ACS Sustainable Chem. Eng., 2018, 6, 2751–2757.
4. Y. Huang, K. Li, Y. Lin, Y. Tong and H. Liu, ChemCatChem, 2018, 10, 1982–1987.
5. F. Xie, Y. Li, J. Dou, J. Wu and M. Wei, J. Power Sources, 2016, 336, 143–149.
6. H. A. Moghaddam, S. Jafari and M. R. Mohammadi, New J. Chem., 2017, 41, 9453–9460.
7. Y. Liu, K. Lan, A. A. Bagabas, P. F. Zhang, W. J. Gao, J. X. Wang, Z. K. Sun, J. W. Fan, A. A. Elzatahry and D. Y. Zhao, Small, 2016, 12, 860–867.
8. Y. Liu, R. C. Che, G. Chen, J. W. Fan, Z. K. Sun, Z. X. Wu, M. H. Wang, B. Li, J. Wei, Y. Wei, G. Wang, G. Z. Guan, A. A. Elzatahry, A. A. Bagabas, A. M. Al-Enizi, Y. H. Deng, H. S. Peng and D. Y. Zhao, Sci. Adv., 2015, 1, 8.
9. A. Li, T. Wang, X. Chang, W. Cai, P. Zhang, Z. J. Zhang and J. Gong, Chem. Sci., 2016, 7, 890–895.
10. J. Bai, X. Sun, G. Han and G. Diao, J. Alloys Compd., 2017, 722, 864–871.
11 H. Yu, Y. Bai, X. Zong, F. Q. Tang, G. Q. M. Lu and L. Z. Wang, *Chem. Commun.*, 2012, **48**, 7386–7388.

12 J. Roh, S. R. Hwang and J. Jang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 19825–19832.

13 Y. Huang, B. Long, M. Tang, Z. Rui, M.-S. Balogun, Y. Tong and H. Ji, *Appl. Catal., B*, 2016, **181**, 779–787.

14 R. Zhao, L. Huan, P. Gu, R. Guo, M. Chen and G. Diao, *J. Power Sources*, 2016, **331**, 527–534.

15 J. Bai, R. Zhao, G. Han, Z. Li and G. Diao, *RSC Adv.*, 2015, **5**, 43328–43333.

16 A. L. Aldaba, D. Lopez-Torres, C. Elosua, J. L. Auguste, R. Jamier, P. Roy, F. J. Arregui and M. Lopez-Amon, *Sens. Actuators, B*, 2018, **257**, 189–199.

17 G. B. Hong and C. J. Jiang, *J. Nanosci. Nanotechnol.*, 2018, **18**, 5020–5025.

18 K. P. Regan, J. R. Swierk, J. Neu and C. A. Schmuttenmaer, *J. Phys. Chem. C*, 2017, **121**, 15949–15956.

19 Z. H. Dong, H. Ren, C. M. Hessel, J. Y. Wang, R. B. Yu, Q. Jin, M. Yang, Z. D. Hu, Y. F. Chen, Z. Y. Tang, H. J. Zhao and D. Wang, *Adv. Mater.*, 2014, **26**, 905–909.

20 A. Pang, X. Sun, H. Ruan, Y. Li, S. Dai and M. Wei, *Nano Energy*, 2014, **5**, 82–90.

21 A. Ashok, S. N. Vijayaraghavan, G. E. Unni, S. V. Nair and M. Shanmugam, *Nanotechnology*, 2018, **29**, 8.

22 Z. H. Bakr, Q. M. Wali, J. Ismail, N. K. Elumalai, A. Uddin and R. Jose, *Electrochim. Acta*, 2018, **263**, 524–532.

23 L. Chen, J. Xu, Z. X. Li and J. B. Xia, *Sol. Energy*, 2017, **155**, 593–600.

24 P. Chesler, C. Hornoiu, V. Bratan, C. Munteanu, G. Postole, N. I. Ionescu, T. Juzsakova, A. Redey and M. Gartner, *React. Kinet., Mech. Catal.*, 2015, **117**, 551–563.

25 J. Liu, M. Dai, T. Wang, P. Sun, X. Liang, G. Lu, K. Shimanoe and N. Yamazoe, *ACS Appl. Mater. Interfaces*, 2016, **8**, 6669–6677.

26 J. Mazloom, F. E. Ghodsi, F. Z. Tepehan, G. G. Tepehan and I. Turhan, *J. Sol–Gel Sci. Technol.*, 2018, **86**, 51–62.

27 G. Park and Y. Kang, *Nano Res.*, 2018, **11**, 1301–1312.

28 J. Bisquert, F. Fabregat-Santiago, I. Mora-Sero, G. Garcia-Belmonte and S. Gimenez, *J. Phys. Chem. C*, 2009, **113**, 17278–17290.

29 J. Bisquert, A. Zaban, M. Greenshtein and I. Mora-Sero, *J. Am. Chem. Soc.*, 2004, **126**, 13550–13559.

30 A. Zaban, M. Greenshtein and J. Bisquert, *ChemPhysChem*, 2003, **4**, 859–864.