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The synergistic effect of the combination of conductive carbon and Bi$_2$S$_3$ can significantly improve the photovoltaic performance of the DSSCs.
Facile synthesis of Bi$_2$S$_3$-C composite microspheres as low-cost counter electrodes for dye-sensitized solar cells

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Porous bismuth sulfide-carbon (Bi$_2$S$_3$-C) composite microspheres were synthesized via a facile solvothermal route and served as a low-cost counter electrode material for Pt-free dye-sensitized solar cells (DSSCs). The electrochemical performance analysis indicates that the Bi$_2$S$_3$-C electrode has lower charge transfer resistance on the electrolyte/electrode interface, smaller Nernst diffusion impedance of iodide in electrolyte and higher catalytic ability than bare Bi$_2$S$_3$ electrode. After optimization the content of carbon, the DSSC with the Bi$_2$S$_3$-C counter electrode exhibit an excellent power conversion efficiency of 6.72%, which is comparable to that of the Pt-based DSSC (6.74%).

Introduction

In the past decade, dye-sensitized solar cells (DSSCs) have attracted extensive attention due to their easy fabrication, low-cost and environment friendliness.\(^1\)\(^,\)\(^2\) Generally, a typical DSSC is composed of a dye sensitized photoanode,$^3$\(^,\)\(^4\) a liquid electrolyte with iodide/triiodide (I$_2$/I$_3^-$) redox couples and a catalytic counter electrode (CE). As an indispensable component of DSSCs, CEs collect electrons from external circuit and promote the reduction of triiodide. The conventional CEs are magnetron sputtering deposited or thermally decomposed Pt on rigid fluorine-doped tin oxide (FTO) substrates, which have shown remarkable electrocatalytic activity for the regeneration of iodide from triiodide. However, the high price of metal Pt restrains the large-scale manufacturing of DSSCs. Therefore, it is necessary to explore low cost and effective non-Pt CEs.

Fortunately, many economic materials have shown excellent catalytic performance as Pt CEs, such as carbonaceous materials,$^5$\(^,\)\(^6\) conducting polymers$^{10,12}$ and metal nitrides, oxides and sulfides.$^{13-21}$ Among them, metal sulfides gained more attention due to their facile preparation conditions and relatively low toxicity.

As a well-known layered semiconductor, bismuth sulfide (Bi$_2$S$_3$) has many widely applications in electronic and optoelectronic devices,$^{22}$ hydrogen storage materials$^{23,24}$ and lithium ion batteries.$^{25,26}$ Particularly, Bi$_2$S$_3$ is considered as a potential material for photoelectrochemical solar cells by virtue of its small band gap, high absorption coefficient and reasonable energy conversion efficiency.$^{27}$ However, to our knowledge, few researches have reported on the application of Bi$_2$S$_3$ as CEs in DSSCs except for the works by Liu’s group$^{28,29}$ and Li’s group.$^{30}$ In 2012, Liu et al. compared the catalytic activities of different facets within Bi$_2$S$_3$ through density functional theory computations. Then, they successfully synthesized flower-like Bi$_2$S$_3$ nanostructures with predominantly exposed (130) and (211) facets and obtained photovoltaic efficiencies of 3.5% and 1.9% within these differently faceted Bi$_2$S$_3$ based DSSCs, respectively. Subsequently Li et al. prepared Bi$_2$S$_3$ microspheres grown on the graphene by two-step solvothermal method and used as CE for the DSSC system. The power conversion efficiency of Bi$_2$S$_3$/graphene hybrid material boosted to 5.5%.$^{31}$ This remarkable improvement of the conversion efficiency is mainly due to the efficient electron transport network provided by graphene. In fact, many efforts have recently been devoted to investigate the synergistic effect in the combination of nanomaterials and carbon materials. For example, Ma’s group reported two composites of MoC and WC embedded in ordered carbon materials and employed them as the CE materials for DSSCs. The results indicated that both of them have superior catalytic performance to the expensive Pt CE.$^{32}$ Li et al. also presented an improved photovoltaic efficiency of DSSC with TiN nanoparticles and carbon black composite as CE.$^{33}$ And then, Yue et al. utilized high porous Mo$_2$C-C hybrid film as the Pt-free CE materials for DSSC and achieved a high photovoltaic efficiency of 7.69%.$^{34}$ Besides, Wang et al. synthesized a carbon-coated WS$_2$ material using a simple method. The DSSC assembled with this carbide-based CE also showed fantastic photovoltaic performance.$^{35}$

Herein, a composite material of Bi$_2$S$_3$ and conductive carbon was prepared by a one-step solvothermal route, and investigated...
as CEs for Pt-free DSSCs. As far as we know, this is the first report on the utilization of Bi$_2$S$_3$-C composite material as CEs for DSSCs. Based on the beneficial synergistic effect of Bi$_2$S$_3$ and carbon, the DSSC assembled with this composite material CE exhibits excellent electrocatalytic activity and achieves a high photovoltaic conventional efficiency of 6.72%. Compared with Li et al. study, our present work has several advantages, namely 1) replace graphene with carbon to improve the conductivity in preparation process, which means the complex preparation process of graphene is avoidable; 2) use a facile one-step solvothermal approach instead of two-step solvothermal approach; and 3) derive more excellent catalytic material than Bi$_2$S$_3$/graphene composite.

**Experimental**

**Synthesis of Bi$_2$S$_3$ and Bi$_2$S$_3$-C composite materials**

The Bi$_2$S$_3$-C composite materials were prepared by using analytical-grade bismuth nitrate (Bi(NO$_3$)$_3$·$5$H$_2$O) and L-cysteine (C$_6$H$_{12}$NO$_7$S), without further purification. The typical synthesis procedure as follows: 2 mM Bi(NO$_3$)$_3$·$5$H$_2$O and 6 mM L-cysteine were dissolved in 30 mL anhydrous ethanol and continuously stirred for 2 h to form a homogeneous solution. Afterward, 5 mg, 10 mg, 20 mg and 30 mg glucose powder were added into the solution, followed by further stirred for another 30 min. The solution was transferred to a 50 mL Teflon-lined stainless steel autoclave, maintained at 150 °C for 24 h, and then cooled to room temperature naturally. The black precipitate was collected by centrifugation, washed several times using deionized water and anhydrous ethanol to remove the possible remaining cations and anions, and then dried in an oven at 60 °C for 8 h for further characterization purposes. The final samples were denoted to Bi$_2$S$_3$-0.39-C, Bi$_2$S$_3$-0.77-C, Bi$_2$S$_3$-1.53-C and Bi$_2$S$_3$-2.28-C, respectively. The values 0.39, 0.77, 1.53, and 2.28 represent the contents of carbon are 0.39 wt.%, 0.77 wt.%, 1.53 wt.%, and 2.28 wt.% in the composite materials, respectively.

Pure Bi$_2$S$_3$ were synthesized according to the same method of preparing Bi$_2$S$_3$-C composites, but only replaced glucose with 0.3 g surfactant PVP 40000.

**Fabrication of counter electrodes**

To prepare CEs, 0.1 g Bi$_2$S$_3$ and Bi$_2$S$_3$-C powders were respectively mixed with 0.025 g Polyethylene glycol, and then dispersed into 4 mL anhydrous ethanol followed by stirring to form a fluid mixture. Afterward, a film was made using the doctor-blade technique on FTO conductive glass. The films were annealed at 430 °C for 1 h at the protection of argon atmosphere, and then the CEs were obtained. As a comparison, Pt CEs were purchased from Wuhan Georgi science instrument Co. Ltd. (Wuhan, Hubei, China).

**Assembly of DSSCs**

Firstly, the TiO$_2$ photoanodes were soaked overnight in the N-719 dye solution (0.3mM in the solvent of ethanol). TiO$_2$ photoanodes were obtained from Dalian HeptaChroma Solar Technology Development Co. Ltd (Dalian, Liaoning, China). Then, the dye-sensitized TiO$_2$ photoanodes were washed with anhydrous ethanol and dried in the hot air. Finally, the TiO$_2$ photoanodes were fabricated with the prepared CEs with the injection of redox shuttle electrolyte (0.5M LiI, 0.05M I$_2$, 0.6M 1-propy1-1, 3-dimethylimidazolium iodide and 0.5M 4-tert-buty1pyridine with acetonitrile as the solvent). The effective areas of all cells are 0.5 ×0.5 cm$^2$.

**Characterizations and measurements**

The compositions of the as-synthesized samples were characterized by X-ray diffraction (XRD) under a Rigaku D/Max-2500 X-ray diffractometer with Cu K$\alpha$ radiation ($\lambda$= 0.154056 nm). The Raman spectra were recorded with a laser confocal micro Raman spectrometer (Invia-Reflex, Renishaw, UK) at 532 nm with a 100X objective. The sizes and morphologies of Bi$_2$S$_3$ and Bi$_2$S$_3$-C samples were investigated by scanning electron microscopy (SEM; S-4800, Hitachi, Japan) equipped with energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM; JEM-2100, JEOL, Japan). Nitrogen adsorption and desorption isotherms were measured on a Tristar II 3020 automated surface area and pore analyzer. The electrocatalytic activity of the various CEs were characterized by Cyclic voltammetry (CV) tests, which were implemented on an electrochemical workstation (ZAHNER ZENNIUM CIMPS-1, Germany) equipped with a three-electrode system in an anhydrous acetonitrile solution consisting of 0.1 M LiClO$_4$, 10 mM LiI, and 1 mM I$_2$ at a scan rate of 50 mV·S$^{-1}$. The Electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements were executed on symmetric cells containing two identical electrodes, using an impedance measurement unit of workstation in the frequency range 0.1·$10^6$ Hz with an ac amplitude of 10 mV. The photocurrent density-voltage (J - V) curves were measured using a Keithley 2410 digital source meter under the illumination of AM 1.5G simulate solar light (100 mW·cm$^{-2}$), which was calibrated by a Si reference cell beforehand. All the measurements were performed at ambient temperature.

**Results and discussion**

**Characterization of the as-synthesized materials**

Fig.1 shows the XRD diffraction patterns of Bi$_2$S$_3$ and Bi$_2$S$_3$-C nanomaterials synthesized by facile solvothermal process. All of the diffraction peaks in both patterns can be readily assigned to the orthorhombic phase Bi$_2$S$_3$ (PDF# 17-0320). The derived lattice constants are $a = 1.1149$ nm, $b = 1.1126$ nm, and $c = 0.3985$ nm, which are in good coincidence with the reported values for Bi$_2$S$_3$ ($a = 1.1149$ nm, $b = 1.1304$ nm, and $c = 0.3981$ nm).

Comparing the XRD patterns of Bi$_2$S$_3$ and Bi$_2$S$_3$-C materials in detail, we found non-existence of the Carbon-related characterized peaks in Bi$_2$S$_3$-C XRD pattern, denoting the amorphous carbon derived from glucose.

To further confirm the microstructure of carbon, Raman spectroscopy was executed on the pristine Bi$_2$S$_3$ and Bi$_2$S$_3$-C composite materials. As shown in Fig. 2, both of the samples present scattering bands at 138, 259, 348, 510, 651 and 956 cm$^{-1}$. Except for the peak at 138 cm$^{-1}$, all other peaks are well consistent with the reported results of Bi$_2$S$_3$ nanocrystals.
Typically, the presence of the peak at 138 cm\(^{-1}\) stems from the contribution of surface optical phonon modes.\(^{38}\) From the partial enlarged drawing of Bi\(_2\)S\(_3\)-C Raman spectra (Inset of Fig.2), it can be found that two weak peaks appeared at 1355 and 1574 cm\(^{-1}\). These two new peaks are corresponding to so-called D and G bands of carbon, respectively.\(^{26,39}\) Energy dispersive spectroscopy (EDS) shown in Fig. S1 confirms the presence of C, S and Bi elements in Bi\(_2\)S\(_3\)-C microspheres.

The morphologies of the solvothermal synthesized Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_3\)-C samples were investigated by SEM, as shown in Fig. 3 and Fig. S2. The bare Bi\(_2\)S\(_3\) (Fig. 3a) is composed of tremendous nanoparticles. In comparison, the facile synthesized Bi\(_2\)S\(_3\)-C composite product, as shown in Fig. 3b and Fig. 3c, exhibits the form of homogeneous porous microspheres with diameters of 2-3um. Furthermore, owing to the distribution of innumerable nanoparticles within the Bi\(_2\)S\(_3\)-C microspheres (Fig. 3d), this composite structure possesses a very large specific surface area.

In order to determine the microstructure of Bi\(_2\)S\(_3\)-C composite, TEM measurement was performed as shown in Fig.4. Fig. 4(a) shows that the diameter of Bi\(_2\)S\(_3\)-C microspheres is about 2.5 μm. From Fig. 4(b), it can be clearly seen that the synthesized Bi\(_2\)S\(_3\)-C microsphere possesses a highly porous structure. The high resolution TEM (HRTEM, Fig.4(c) and (d)) images reveal that the Bi\(_2\)S\(_3\)-C composite has good crystallinity and the lattice spacing of about 0.309 nm, which corresponds to the (211) facet. Besides, on the Bi\(_2\)S\(_3\) particle surface there is an inhomogeneous coating layer, which is probably amorphous carbon derived from degradation of glucose.

The porous character of the Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_3\)-C was analyzed by N\(_2\) absorption and desorption measurements. As shown in Fig. 5, both of them exhibit a typical absorption-desorption isotherm of type IV. The Bi\(_2\)S\(_3\)-C composite possesses an ultrahigh BET surface area of 76.88 m\(^2\)g\(^{-1}\), which is close to that of Bi\(_2\)S\(_3\) (77.31 m\(^2\)g\(^{-1}\)). In addition, from the pore size distribution curves (inset of Fig. 5), they both have broad pore size distribution, from several nanometres to about 100 nm. The average pore diameter of the Bi\(_2\)S\(_3\) is 14.6 nm with a pore volume of 0.282 cm\(^3\)g\(^{-1}\), while the average pore diameter of the Bi\(_2\)S\(_3\)-C microspheres increases to 14.9 nm with a pore volume of 0.286 cm\(^3\)g\(^{-1}\). The high surface area and rich mesopores structure of Bi\(_2\)S\(_3\) and Bi\(_2\)S\(_3\)-C indicate that they are desirable for electrode materials because they can provide efficient electronic transportation channels during the oxidation-reduction process.

**Photovoltaic performance of DSSCs**

Fig. 6 and Fig. S3 present the photocurrent density-voltage (J-V) curves of DSSCs based on various CEs under the stand illumination (100 mW·cm\(^{-2}\)). The corresponding photovoltaic parameters, such as the open-circuit voltage (V\(_{oc}\)), short-circuit current density (J\(_{sc}\)) and fill factor (FF), are summarized in Table 1. The conversion efficiency (\(\eta\)) of the DSSCs were calculated.
Fig. 5 N₂ absorption-desorption isotherms of the Bi₃S₃ and Bi₃S₃-C. Inset shows the corresponding BJH pore size distribution curves.

Fig. 6 Photovoltaic characteristics of the DSSCs using various CEs.

according to Eq. (1) and (2):

\[
\eta(\%) = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100\% \tag{1}
\]

and

\[
FF = \frac{V_{max} \times J_{max}}{V_{sc} \times J_{sc}} \tag{2}
\]

As shown in Table 1, the DSSC with the bare Bi₃S₃ CE exhibits an inferior photovoltaic conversion efficiency of 5.56% due to its poor electrocatalytic activity. However, after the optimization, the DSSC fabricated with Bi₃S₃-C microspheres CE presents a \( V_{oc} \) of 0.750 V, \( J_{sc} \) of 14.45 mA cm⁻², and \( FF \) of 0.62, resulting in a promising conversion efficiency of 6.72%, which is very close to that of DSSC with traditional Pt CE (6.75%). Considering the detailed parameter of \( FF \), we found that the addition of glucose in the preparation process of CEs leads to large differences in \( FF \) of DSSCs. As CEs for the DSSC, the Bi₃S₃-C exhibits much higher \( FF \) than the pure Bi₃S₃, which indicates the superiority of the former. The enhanced \( FF \) value may result from the positive synergistic effect between the Bi₃S₃ and amorphous carbon in the Bi₃S₃-C CEs. Therefore, the cooperation of Bi₃S₃ and amorphous carbon can effectively improve the catalytic performance of Bi₃S₃-C.

Electrochemical properties of CEs

In the following, the cyclic voltammetry (CV) tests, electrochemical impedance spectra (EIS) measurements, and Tafel polarization curves were used to investigate the electrocatalytic activities of various CEs.

Firstly, CV tests were carried out in a three-electrode system with the Pt sheet as CE, various CEs as working electrode and saturated calomel electrode as reference electrode. Fig. 7 and Fig. S4 show the CVs of various CEs in redox couple \( \Gamma / \Gamma^- \) system. Two typical pairs of oxidation and reduction peaks are observed for all CEs. The left pair in low potential range is assigned to the redox reaction Eq. (3) and the right pair in the high potential range is corresponded to the redox reaction Eq. (4):

\[
\Gamma^- + 2e^- \leftrightarrow 3\Gamma^- \tag{3}
\]

\[
3\Gamma_2 + 2e^- \leftrightarrow 2\Gamma^- \tag{4}
\]

As can be seen in Fig. 7, the Bi₃S₃ and Bi₃S₃-C electrodes exhibit obvious cathodic peaks similar to that of the efficient Pt electrode, suggesting that the Bi₃S₃ and Bi₃S₃-C electrodes have similar catalytic ability to the Pt electrode. In addition, the reduction current peaks of Bi₃S₃-C electrode are higher than that of pure Bi₃S₃ electrode, which match well with the results of \( J-V \) curves and further confirm the higher catalytic activity of the former.

To further investigate the catalytic activities for regeneration of the redox couple \( \Gamma / \Gamma^- \) on the aforementioned CEs, EIS measurements were conducted in symmetrical cells fabricated with two identical CEs (CE/electrolyte/CE). As shown in Fig. 8 and Fig. S5, two typical semicircles are observed in the higher and lower frequency regions. The high-frequency intercept on the \( Z' \) axis is generally assigned to the Ohmic series resistance (\( R_\| \)). The left semicircle is attributed to the charge-transfer resistance (\( R_\varepsilon \)) and the constant phase element (CPE) at the CE/electrolyte interface, while the right semicircle is consistent with the Nernst diffusion impedance (\( Z_\varepsilon \)). The corresponding EIS parameters are listed in Table 1. The Bi₃S₃ electrode possesses a large \( R_\| \) of 8.78 Ω cm⁻². But after the addition of the carbon, the Bi₃S₃-C composite CEs demonstrate the lower \( R_\varepsilon \). It’s interesting that the \( R_\varepsilon \) of the Bi₃S₃-C CEs decreases gradually with increasing the dosage of carbon from 0.39 wt.% to 1.53 wt.%, and then increases with further increasing the carbon content. The change tendency of \( R_\varepsilon \) in the Bi₃S₃-C electrodes with different carbon contents is in agreement with that of other carbon-based materials, such as MoS₂/C,² MoS₂/G,⁴² CoS₂/G⁴⁵ and WS₂/MWCNT.⁴⁴ This phenomenon may be due to the excessive amounts of carbon reduces the catalytic activity of the Bi₃S₃-C. Ultimately, the sample of Bi₃S₃-1.53-C exhibits the smallest \( R_\varepsilon \) (2.26Ω cm⁻²) among all composite electrodes. This indicates that less resistance is required for the transfer of electrons from the surface of Bi₃S₃-1.53-C electrode to the electrolyte. In addition, the Bi₃S₃-C electrodes has smaller \( Z_\varepsilon \) than that of the pristine Bi₃S₃ electrode, which indicates that the Bi₃S₃-C composite can provide more efficient electrolyte diffusion channel for \( \Gamma^- \). Therefore, Bi₃S₃-C composite materials exhibit much higher catalytic activity than pure Bi₃S₃ material used as the CE for the DSSC, which is in agreement with the...
results from above J-V and CV experiments.

**Table 1** Photovoltaic and EIS parameters of the different CEs

<table>
<thead>
<tr>
<th>CEs</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω·cm$^{-2}$)</th>
<th>$R_w$ (Ω·cm$^{-2}$)</th>
<th>$Z_w$ (Ω·cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$S$_3$</td>
<td>0.718</td>
<td>13.68</td>
<td>0.57</td>
<td>5.56</td>
<td>6.30</td>
<td>8.78</td>
<td>1.04</td>
</tr>
<tr>
<td>Bi$_2$S$_3$-0.39-C</td>
<td>0.729</td>
<td>14.03</td>
<td>0.58</td>
<td>5.89</td>
<td>7.31</td>
<td>5.42</td>
<td>1.03</td>
</tr>
<tr>
<td>Bi$_2$S$_3$-0.77-C</td>
<td>0.744</td>
<td>14.14</td>
<td>0.60</td>
<td>6.36</td>
<td>7.18</td>
<td>3.65</td>
<td>0.80</td>
</tr>
<tr>
<td>Bi$_2$S$_3$-1.53-C</td>
<td>0.750</td>
<td>14.45</td>
<td>0.62</td>
<td>6.72</td>
<td>7.22</td>
<td>2.26</td>
<td>0.39</td>
</tr>
<tr>
<td>Bi$_2$S$_3$-2.28-C</td>
<td>0.725</td>
<td>13.92</td>
<td>0.58</td>
<td>5.88</td>
<td>7.43</td>
<td>6.74</td>
<td>0.80</td>
</tr>
<tr>
<td>Pt</td>
<td>0.757</td>
<td>13.82</td>
<td>0.64</td>
<td>6.75</td>
<td>4.10</td>
<td>1.67</td>
<td>0.30</td>
</tr>
</tbody>
</table>

![Fig. 8](image1) Electrochemical impedance spectra of different CEs. Inset figure is the equivalent circuit model.

Finally, Tafel polarization analysis was executed using symmetric cells similar to the one used in above EIS experiments. Fig. 9 shows the Tafel polarization curves for the Bi$_2$S$_3$, Bi$_2$S$_3$-C and Pt electrodes. In general, exchange current density ($J_0$) and limiting diffusion current density ($J_{lim}$) are closely related to the catalytic activity of the catalysts. In Fig. 9, the Bi$_2$S$_3$-C composite electrode shows a larger slope in the anodic and cathodic branches than the Bi$_2$S$_3$ electrode, suggesting a higher $J_0$ in the Bi$_2$S$_3$-C electrode surface. Obviously, the slope of Pt electrode is the highest one, implying that the highest $J_0$ and best catalytic activity of Pt electrode among these CEs. Furthermore, $J_0$ can also be estimated by Eq. (5):

$$J_0 = \frac{RT}{nF R_s}$$

(5)

where $R$ is the gas constant, $T$ is the absolute temperature, $F$ is Faraday’s constant and $n$ represents the number of electrons involved in the reduction of $I_{3^-}$ at the electrode. The tendency of $J_0$ for three CEs calculated according to above equation coincide well with that obtained from the Tafel polarization curves. In addition, the Tafel curves also include the information of $J_{lim}$, which can be expressed by Eq. (6):

$$J_{lim} = 2nFCD/l$$

(6)

where $C$ is the $I^-/I_{3^-}$ concentration, $D$ is the diffusion coefficient of the $I_{3^-}$ in electrolyte and $l$ is the spacer thickness. From Eq. (6), a higher $J_{lim}$ indicates a larger diffusion coefficient $D$ of the $I_{3^-}$ in electrolyte at same potential. Meanwhile, a CE with a faster diffusion rate of the $I_{3^-}$ represents its smaller Nernst diffusion impedance $Z_w$ in the electrolyte. Apparently, the order of $J_{lim}$ is Pt > Bi$_2$S$_3$-C > Bi$_2$S$_3$ in Fig. 9, which is completely consistent with the order of $Z_w$ in EIS spectra. This result suggests that Bi$_2$S$_3$-C nanocomposites possess a higher catalytic activity for the reduction of $I_{3^-}$ than Bi$_2$S$_3$.

Fig. 9 shows the possible synergistic effect on the improved electrocatalytic ability of the Bi$_2$S$_3$-C composite. The grain boundary in the CEs assembled by Bi$_2$S$_3$ nanoparticles may cause the poorly efficient migration of electrons, due to the electron scattering in this crystal boundary. In the Bi$_2$S$_3$-C composites, this electron scattering may be overcome by the conductive carbon that covers the Bi$_2$S$_3$ particles. In addition, when the electrons flow into the CEs, they are easily shuttled to the intrinsically electrocatalytic Bi$_2$S$_3$ by taking advantage of the fast electron transport network of carbon. As a result, the excellent conductivity of the amorphous carbon and the superior electrocatalytic activity of the Bi$_2$S$_3$ can provide low $R_w$ at the interface between the CE and electrolyte for the $I^-/I_{3^-}$ redox reaction. Notably, the excessive amounts of carbon could reduce the catalytic activity of the Bi$_2$S$_3$-C. With the excessive increase of the carbon contents, the amorphous carbon heavily surrounds Bi$_2$S$_3$ nanoparticles in a microsphere of Bi$_2$S$_3$-C composite, leading to the isolation of Bi$_2$S$_3$ from redox couple $I^-/I_{3^-}$ system, reducing the catalytic activity of the Bi$_2$S$_3$ and $R_w$ enhanced. The two effects compete with other. Consequently, the Bi$_2$S$_3$-1.53-C CE has the fastest electron-transfer kinetics than other CEs due to the synergistic effect from the conductive network of carbon and the intrinsically catalytic Bi$_2$S$_3$, and the DSSCs with it obtain the highest conversion efficiency.

**Conclusion**

In this study, a nanocomposites of Bi$_2$S$_3$-C was successfully prepared by a facial one-step solvothermal method. The compositions and morphologies of Bi$_2$S$_3$-C composite material were observed by XRD, Raman, SEM, TEM and EDS. In addition, J-V curves, CV, EIS and Tafel polarization experiments have demonstrated the superiority of the composite electrode, which is mainly due to the positive synergistic effect in the...
combined Bi$_2$S$_3$-C composite, including improved electrical conductivity and enhanced electrocatalytic activity for I$_3^-$ reduction. As a result, the DSSCs fabricated with the Bi$_2$S$_3$-C CE obtained a high conversion efficiency of 6.72 % by the optimization of the carbon content in composite materials, which increased by more than 20% compared with that of bare Bi$_2$S$_3$ CE, suggesting Bi$_2$S$_3$-C composite materials is a potential alternative to expensive Pt for the low-cost DSSCs.

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