Earth-abundant Fe$_{1-x}$S@S-doped graphene oxide nano–micro composites as high-performance cathode catalysts for green solar energy utilization: fast interfacial electron exchange

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In the process of conversion of solar energy into electricity and fuel, efficient electrocatalysts are indispensable. Rieske iron–sulfur protein and FeS catalysts play an important role in natural photosynthesis (NPS), and in artificial photoelectrochemical cells, respectively. Nano–micro composite catalysts (NMCCs) possess not only high catalytic activity but also fast electron transport. Herein, we prepared a nano–micro composite (NMC) of Fe$_{1-x}$S nanoparticles decorated on sulfur-doped graphene oxide (S-GO) sheets (namely, Fe$_{1-x}$S@S-GO–NMC) to be used as a cathode in dye-sensitized solar cells (DSCs). The GO effectively inhibits the aggregation of Fe$_{1-x}$S nanoparticles. Notably, DSCs based on an Fe$_{1-x}$S@S-GO–NMC cathode achieved a high solar-to-electrical conversion efficiency up to 7.23%. The conversion efficiency is, to our knowledge, one of the highest efficiencies for DSCs based on an FeS or FeS$_2$ cathode. Although the Fe$_{1-x}$S@S-GO–NMC exhibited a low thermodynamic possibility for redox reactions, it showed a higher kinetic rate than that of Pt for the charge transfer between the reaction medium and the cathode. This indicates that a fast electron exchange process occurs at the interface between the reaction and the cathode. The value of the time constant (τ) corresponding to the charge exchange resistance based on Fe$_{1-x}$S@S-GO–NMC (0.0215 ms) was smaller than that obtained with Pt (0.261 ms). Therefore, we ascribed the superior performance of the photoelectrochemical device based on Fe$_{1-x}$S@S-GO–NMC to its good electrocatalytic performance. The results are of great interest for fundamental research and for practical applications of FeS and FeS$_2$ and their composites in the solar splitting of water, artificial photoelectrochemical cells, and electrocatalysts.

Introduction

With the continuous increase in consumption of fossil energy, environmental pollution$^1$ and the energy crisis$^2$ are becoming more and more stringent. As an alternative, considerable efforts have been devoted to developing new renewable and clean energy resources.$^3$ The effective development and use of these energy sources can greatly reduce the dependence on fossil fuels, which will consequently reduce environmental pollution. The use of renewable energy sources, such as wind energy, hydro energy, or geothermal energy, is restricted by specific regional conditions. Solar energy offers the advantage of being available everywhere and at a lower cost. Therefore, the effective transformation and utilization of solar energy is a very promising direction in prospect. Solar energy can be converted into heat,$^4$ electrical energy,$^5$ or chemical energy (oxygen and carbohydrates are produced from water and carbon dioxide using sunlight).$^6$ In the process of conversion of solar energy into electricity and fuel, efficient electrocatalysts are essential.$^7$ For example, in a dye-sensitized solar cell and a quantum dot solar cell, redox mediators (sulfur, iodine, cobalt, ferrocene) are recycled by efficient electrocatalysts.$^8$ In the process of water-splitting, the role of an efficient electrocatalyst is also indispensable.$^9$

The Rieske iron–sulfur protein plays an important role in natural photosynthesis (NPS).$^{10}$ In addition, FeS has great potential in dye-sensitized solar cell applications and quantum dots-sensitized solar cells (QDSCs). Quan et al. reported the application of three-dimensional (3D) FeS nanospheres as
electrocatalysts for the $S^{2-}/S_n^{2-}$ redox reaction in quantum dots-sensitized solar cells: a power conversion efficiency (PCE) of 3.34% was achieved. FeS was deposited on 3D carbon scaffolds to develop electrocatalysts for the $S^{2-}/S_n^{2-}$ redox reaction in quantum dots-sensitized solar cells, demonstrating a power conversion efficiency of 4.58%. QDSCs based on an FeS/nickel foam counter electrode achieved a PCE of 4.39%. Recently, Wu and Batmunkh demonstrated the application of a hybrid electrocatalyst SGN-FeS (sulfur-doped graphene with FeS2 microspheres) and polypyrrole/FeS in DSCs. An SGN-FeS2 and polypyrrole/FeS-based device displayed PCEs of 7.48% and 8.1%, respectively. In addition, the performance of carbon (such as graphene)-based cathodes in DSCs was also good.

Nano–micro composite catalysts (NMCCs) not only give higher catalytic activity but also fast electron transport. Herein, we report the one-pot hydrothermal synthesis of a nano–micro composite (NMC) composed of Fe$_1$-$x$S nanoparticles decorated on sulfur-doped graphene oxide (S-GO) sheets (namely, Fe$_1$-$x$S@S-GO-NMC). The graphene oxide substrate in NMC inhibited the aggregation of Fe$_1$-$x$S nanoparticles. Notably, DSCs based on an Fe$_1$-$x$S@S-GO–NMC cathode achieved a high solar-to-electrical conversion efficiency up to 7.23% with an open circuit voltage ($V_{OC}$) of 0.72 V, a short circuit current density ($J_{SC}$) of 14.08 mA cm$^{-2}$, and a fill factor (FF) of 0.72. We ascribe the superior performance of an Fe$_1$-$x$S@S-GO–NMC based photoelectrochemical device to its excellent electrocatalytic performance.

**Experimental section**

**Preparation of Fe$_1$-$x$S agglomerated particles**

Typically, 0.003 mol of FeCl$_3$-6H$_2$O were dissolved in 30 mL of deionized water by vigorous agitation. 0.045 mol of thiocetamide (TAA) were dissolved in 30 mL of deionized water by vigorous agitation. The above two solutions were mixed. The mixture was stirred for 0.5 h at room temperature and then transferred into a Teflon-lined autoclave. After being heated at 200 °C for 15 h, the product was naturally cooled to room temperature. The product was washed three times with water and ethanol.

**Preparation of Fe$_1$-$x$S nanoparticles fixed on S-doped graphene oxide (GO) sheets (namely, Fe$_1$-$x$S@S-GO)**

Graphene oxide (GO) was prepared using a modified Hummers’ method. The specific synthesis method can be seen in our previous paper. The obtained GO precipitates were dispersed in deionized water to obtain a 1 wt% GO dispersion. 2 g of 1 wt% GO dispersion were dispersed in 10 mL of deionized water by ultrasound. 0.81 g of FeCl$_3$-6H$_2$O were dissolved in 30 mL of deionized water by vigorous agitation. Different quantities (0.2340, 1.1348, 2.2546, 3.3847, 4.5045 g) of TAA were dissolved in 20 mL of deionized water by vigorous agitation. The above three solutions were mixed. The mixture was stirred for 0.5 h at room temperature and then transferred into a Teflon-lined autoclave. After being heated at 200 °C for 15 h, the product was naturally cooled to room temperature. The product was washed three times with water and ethanol.

**Results and discussion**

In our experiments, Fe$_1$-$x$S@S-GO-NMC was prepared using a simple one-pot solvothermal approach, as shown in Fig. 1. The amounts of FeCl$_3$ and TAA in solution were 0.003 and 0.045 mol. Meanwhile, Fe$_1$-$x$S particles were prepared as a reference. Details of the synthesis process are reported in the experimental section. The SEM images shown in Fig. 2a illustrate that Fe$_1$-$x$S agglomerated particles were seriously agglomerated. Fig. 2b shows that the agglomeration of Fe$_1$-$x$S particles resulted in a non-uniform size (within the range of 500 nm to 2 microns) of the block or caking. The agglomerated Fe$_1$-$x$S blocks or cakings cover many catalytically active sites on the surface of each Fe$_1$-$x$S nanoparticle. In addition, the massive grain boundaries in the Fe$_1$-$x$S blocks could possibly inhibit electron transport. These two factors may be the reason for the poor performance of previously reported devices based on pure FeS. We tried to inhibit the aggregation of Fe$_1$-$x$S nanoparticles with GO. Fig. 2c
shows the 2D structure of GO prepared using the modified Hummers’ method. The surface of GO flakes up to ten microns is very smooth with only few wrinkles. In the case of a conductive film or a composite substrate, the large size of GO is beneficial to reducing the boundaries in the thin film and helps to limit the recombination of the electrons at the boundaries, and thus increases the conductivity. The TEM images of Fe_{1-x}S@S-GO–NMC (Fig. 2d and e) show that Fe_{1-x}S nanoparticles were dispersed on the GO surface. Fig. 2e shows the sizes of Fe_{1-x}S nanoparticles dispersed on the RGO surface within the range of 40 nm to 350 nm. Thus, the GO effectively inhibits the aggregation of Fe_{1-x}S nanoparticles. XRD patterns

Fig. 1  Schematic diagrams illustrating the simple one-pot hydrothermal approach for preparing Fe_{1-x}S nanoparticles fixed on sulfur-doped graphene oxide (S-GO) sheets (namely, Fe_{1-x}S@S-GO–NMC).

Fig. 2  (a) SEM images of as-prepared Fe_{1-x}S agglomerated nanoparticles; (b) Size distribution of as-prepared Fe_{1-x}S agglomerated particles; (c) SEM images of as-prepared 2D GO sheets; (d) TEM images of as-prepared Fe_{1-x}S nanoparticles fixed on sulfur-doped graphene oxide (S-GO) sheets (Fe_{1-x}S@S-GO–NMC); (e) size distribution of Fe_{1-x}S nanoparticles fixed on sulfur-doped graphene oxide (S-GO) sheets; (f) XRD patterns of as-prepared Fe_{1-x}S@S-GO–NMC powder.
of Fe$_{1-x}$S@S-GO–NMC (Fig. 2f) show that Fe$_{1-x}$S@S-GO–NMC displays.

FeS–FeS$_2$ hybrid crystalline structure. Diffraction peaks at 30.0’, 30.8’, 33.8’, 43.6’ and 53.3’ were attributed to the (100), (002), (101), (102) and (110) planes, respectively, of the standard FeS nanocrystals with a hexagonal (P6$_3$/mmc) structure (JCPDS#75-0602). Diffraction peaks at 28.5’, 33.0’, 37.2’, 40.7’, 47.4’ and 56.2’ could be indexed to the (111), (200), (210), (211), (220) and (311) planes, respectively, of the standard FeS$_2$ nanocrystals with a cubic [Pa-3(205)] structure (JCPDS#42-1340).

To further determine the structure and composition of Fe$_{1-x}$S@S-GO–NMC, we conducted X-ray photoelectron spectroscopy (XPS) tests. The results are shown in Fig. 3. The full range of the XPS spectra of Fe$_{1-x}$S@S-GO–NMC, S-GO and GO is shown in Fig. 3a. The mole ratio of FeCl$_3$/TAA = 1/15, so the excess TAA will react with GO to form S-GO. The obvious peaks at 162.4 and 168.7 eV in the S 2p spectra of Fe$_{1-x}$S@S-GO–NMC can be attributed to S in the FeS–FeS$_2$ hybrid crystalline structure. In addition, shoulder peaks at 163.8 and 164.9 eV in the S 2p spectra of Fe$_{1-x}$S@S-GO–NMC (as shown in Fig. 3b) can be observed. In order to assign shoulder peaks at 163.8 and 164.9 eV in the S 2p spectra of Fe$_{1-x}$S@S-GO–NMC, we have synthesized S-GO with graphene oxide and TAA under the same experimental conditions as for Fe$_{1-x}$S@S-GO–NMC. The obvious S 2p peaks at 163.8 and 164.9 eV can also be observed in the S 2p spectra of S-GO, as shown in Fig. 3b. Thus, shoulder peaks at 163.8 and 164.9 eV in the S 2p spectra of Fe$_{1-x}$S@S-GO–NMC confirmed the formation of sulfur-doped graphene oxide in Fe$_{1-x}$S@S-GO–NMC. A complex energy distribution of Fe 2p photoelectrons was obtained and is shown in Fig. 3c. The spectrum could be fitted using the “XPS peak” software with Gaussian functions after subtraction of a Shirley background.  

| Peak  | Position | Index | Area |
|-------|----------|-------|------|
| Peak 1 | 707.3 | FeS$_2$ 2p$_{3/2}$ | 1205 |
| Peak 2 | 712.1 | FeS 2p$_{3/2}$ | 15003 |
| Peak 3 | 720.6 | FeS$_2$ 2p$_{3/2}$ | 3808 |
| Peak 4 | 725.4 | FeS 2p$_{3/2}$ | 17210 |

In order to demonstrate the hypothesis that an Fe$_{1-x}$S@S-GO–NMC cathode has a good electrocatalytic performance, we

![Fig. 3](image-url)
investigated the electrocatalytic performance and the electron transfer of Fe$_{1-x}$S@S-GO. Fe$_{1-x}$S@S-GO ink was fabricated into a thin film electrode by spraying it onto a FTO/glass substrate. In our previous report, we optimized the catalyst loading in similar nano–micro composite catalysts (Fe$_3$O$_4$@RGO). For Fe$_3$O$_4$@RGO, a layer thickness of 16 µm is best. So we control the layer thickness of our cathode at 16 µm. Meanwhile, pyrolytic platinum was prepared for use as a cathode reference. Pyrolytic platinum was fabricated on FTO/glass by pyrolysis of a 0.16 wt% H$_2$PtCl$_6$ aqueous solution. The obtained 1µm was sintered at 450 °C for 1 h. For EIS and Tafel characterizations, symmetrical cells were assembled using two identical cathodes filled with I$_3^-/I^-$ electrolytes and spaced by 40 µm tape, as shown in Fig. 4a. The active area of the symmetrical cell was 0.64 cm$^2$. The exchange current density ($J_0$) in the Tafel region (as shown in Fig. 4b) is very closely related to the kinetic rate of charge transfer between the reaction medium and the cathode. Tafel polarization curves of symmetrical cells fabricated with two identical cathodes (mole ratios of FeCl$_3$/TAA = 1/1, 1/5, 1/10, 1/15, 1/20) are shown in Fig. 4b. $J_0$ for the cathode material synthesized with a mole ratio of FeCl$_3$/TAA = 1/1 was 1.04 mA cm$^{-2}$, which is lower than that based on Pt (1.16 mA cm$^{-2}$). When the mole ratio of FeCl$_3$/TAA was increased to 1/5, 1/10, 1/15 and 1/20, the values of $J_0$ also increased. The results indicated that the element of S-GO (formed by reaction between excess TAA and GO) in Fe$_{1-x}$S@S-GO–NMC was beneficial for improving the kinetic rate of charge transfer between the reaction medium and the cathode. For Fe$_{1-x}$S@S-GO–NMC synthesized with a mole ratio of FeCl$_3$/TAA = 1/15, the $J_0$ (2.28 mA cm$^{-2}$) in the Tafel zone which resulted was remarkably higher than that of Pt (1.16 mA cm$^{-2}$), indicating a faster electron exchange at the interface between the reaction medium and the cathode. The larger $J_0$ well explains the high photovoltaic activity observed with the Fe$_{1-x}$S@S-GO–NMC cathode. The Fe$_{1-x}$S@S-GO–NMC cathode delivered a higher photocurrent density (13.0 ± 1.0 mA cm$^{-2}$) compared to Pt (12.1 ± 0.6 mA cm$^{-2}$), as shown in Table 2. Thus, the Fe$_{1-x}$S@S-GO–NMC cathode allows for an accelerated

![Fig. 4](image-url)
electron transfer and for the regeneration of the redox mediator; this property in turn increases the solar-to-electrical conversion efficiency of the corresponding photovoltaic devices. Fig. 4c shows cyclic voltammograms of Fe\textsubscript{1−x}S@S-GO–NMC synthesized with a mole ratio of FeCl\textsubscript{3}/TAA = 1/15 and Pt for the I\textsuperscript{−}/I\textsuperscript{3} redox couple. Curves obtained with the Fe\textsubscript{1−x}S@S-GO–NMC and a Pt cathode exhibited two pairs of redox peaks. The redox peak at low potential was ascribed to the reaction: I\textsuperscript{3}− + 2e\textsuperscript{−} → 3I\textsuperscript{−}.\textsuperscript{25} The reduction potential and the oxidation potential obtained with Fe\textsubscript{1−x}S@S-GO–NMC were 0.085 V (vs. Ag/AgCl in saturated potassium chloride) and 0.369 V (vs. Ag/AgCl in saturated potassium chloride), respectively. The reduction potential and oxidation potential obtained under the same conditions with Pt were 0.078 V and 0.281 V. The separation between anodic and cathodic peaks (ΔE) is inversely proportional to the thermodynamic possibility of the above redox reaction. Interestingly, the ΔE value for Fe\textsubscript{1−x}S@S-GO–NMC (0.454 V) was higher than that for Pt (0.203 V), which may explain why the photovoltaic devices based on an Fe\textsubscript{1−x}S@S-GO–NMC cathode delivered a lower fill factor (0.72 ± 0.02) compared to the Pt cathode (0.78 ± 0.01), as shown in Table 2. EIS was carried out to reveal the inherent interface resistance, as shown in Fig. 4d. The arc at high frequency depends on the charge transfer resistance (R\textsubscript{ct}) at the interface between the cathode and the electrolyte. This parameter reflects the performance of the cathode material. The point of intersection between the plot at high frequency and the real

| Cathode | V\textsubscript{oc} (V) | J\textsubscript{sc} (mA cm\textsuperscript{−2}) | FF | PCE (%) | R\textsubscript{s} (Ω cm\textsuperscript{2}) | R\textsubscript{ct} (Ω cm\textsuperscript{2}) | Z\textsubscript{N} (Ω cm\textsuperscript{2}) |
|---------|-----------------|-----------------|-----|----------|-------------|-------------|--------------|
| Fe\textsubscript{1−x}S@S-GO–NMC\textsuperscript{a} | 0.72 ± 0.01 | 13 ± 1 | 0.72 ± 0.02 | 6.8 ± 0.3 | 16.75 | 2.59 | 44.06 |
| Pyrolytic Pt | 0.71 ± 0.01 | 12.1 ± 0.6 | 0.78 ± 0.01 | 6.7 ± 0.4 | 32.16 | 9.17 | 132.80 |

\textsuperscript{a} Fe\textsubscript{1−x}S@S-GO–NMC were synthesized with a mole ratio of FeCl\textsubscript{3}/TAA = 1/15.

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Table 2 Average photovoltaic parameters of DSCs based on Fe\textsubscript{1−x}S@S-GO–NMC and Pt cathodes and EIS parameters of the symmetrical cells

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Fig. 5 (a) Schematic illustration and solar-to-electrical conversion properties of DSCs based on the Fe\textsubscript{1−x}S@S-GO–NMC cathode under AM1.5, 100 mW cm\textsuperscript{−2} simulated illumination. Pt-based devices are also shown as a reference (the inset table gives the values of the best photovoltaic parameters); (b) stability of the Fe\textsubscript{1−x}S@S-GO–NMC cathode measured by a three-electrode system in I\textsuperscript{3}−/I\textsuperscript{−} liquid electrolyte; (c) the values of the redox current density in each cycle of the CV plots.
axis of the Nyquist plot gives the series resistance ($R_s$). The values of the EIS parameters were obtained by fitting Nyquist plots with the Z-view software according to an equivalent circuit diagram (Fig. 4d, inset). The fitting results of the Nyquist plots are listed in Table 2. The $R_s$ of symmetrical cells based on FeS@S-GO–NMC (synthesized with mole ratios of FeCl$_3$/TAA = 1/1 and 1/15) and a Pt cathode were 16.17, 2.59 and 9.17 $\Omega$ cm$^2$, respectively. The reciprocal of the highest frequency ($f$) of the top of the arc corresponds to the charge exchange resistance representing the reaction time constant ($\tau$) of the reactant at the cathode surface. The smaller the time constant, the faster the reaction. The value (0.0215 ms) of $\tau$ obtained with the Fe$_{1-x}$S@S-GO–NMC cathode (synthesized with a mole ratio of FeCl$_3$/TAA = 1/15) was smaller than those obtained with Pt and Fe$_{1-x}$S@S-GO–NMC (synthesized with a mole ratio of FeCl$_3$/TAA = 1/1). Thus, the Fe$_{1-x}$S@S-GO–NMC (synthesized with a mole ratio of FeCl$_3$/TAA = 1/15) electrode exhibits a fast electron exchange process occurring at the interface between the reaction and the cathode. In addition, the $Z_{el}$ of symmetrical cells based on Fe$_{1-x}$S@S-GO–NMC (synthesized with a mole ratio of FeCl$_3$/TAA = 1/1) is 44.06 $\Omega$ cm$^2$, which is smaller than that of a Pt cathode (132.80 $\Omega$ cm$^2$). This indicates that the channels formed by 2D lamellar graphene are beneficial for the diffusion of the electrolyte, which makes the diffusion resistance ($Z_{diff}$) smaller. From the analysis of CV, Tafel and EIS results, we can see that the Fe$_{1-x}$S@S-GO–NMC cathode exhibited excellent electrocatalytic performance, which in turn promoted the performance of the corresponding photovoltaic devices.

The photovoltaic performance was investigated by characterizing DSCs based on an Fe$_{1-x}$S@S-GO (synthesized with a mole ratio of FeCl$_3$/TAA = 1/15) cathode under AM 1.5, 100 mW cm$^{-2}$ simulated illumination (schematic diagrams shown in Fig. 5). For each cathode, we fabricated four DSCs and determined the mean photovoltaic performance. The detailed photovoltaic parameters are summarized in Table 2. Fig. 5a shows the best photocurrent density with respect to voltage (J–V curve) for the DSCs in each group. The DSCs based on the Fe$_{1-x}$S@S-GO–NMC cathode showed a solar-to-electrical conversion efficiency of 7.23% with an open circuit voltage ($V_{oc}$) of 0.72 V, a short circuit current density ($J_{sc}$) of 14.08 mA cm$^{-2}$ and a fill factor (FF) of 0.72. The conversion efficiency based on the Fe$_{1-x}$S@S-GO–NMC cathode is nearly the same as that obtained from DSCs based on pyrolytic Pt cathodes (7.21%). Although the device is very similar to a tandem DSC, we did not obtain the value of $V_{oc}$ in the device based on the Fe$_{1-x}$S@S-GO–NMC cathode was significantly higher than from the one obtained with the reference Pt. Therefore, the excellent device performance obtained with the Fe$_{1-x}$S@S-GO–NMC cathode is ascribed to the excellent electrocatalytic activity of the composite material, which could effectively recycle the redox mediator and reduce the over-potential. In addition, an investigation of the stability of Fe$_{1-x}$S@S-GO–NMC in I$_3$–/I$^-$ liquid electrolyte was carried out, as shown in Fig. 5b and c. The changes in the potentials and current density for the redox peaks in each cycle of the CV plots were not obvious. The results showed that the Fe$_{1-x}$S@S-GO–NMC exhibited good stability in I$_3$–/I$^-$ liquid electrolyte.

Conclusions

In conclusion, we synthesized a nano-micro composite composed of Fe$_{1-x}$S nanoparticles decorated on sulfur-doped graphene oxide sheets by a one-step hydrothermal method. Compared to Fe$_{1-x}$S agglomerated particles, GO sheets in NMC obviously prevented the aggregation of Fe$_{1-x}$S nanoparticles. DSCs based on an Fe$_{1-x}$S@S-GO–NMC cathode achieved the highest reported solar-to-electrical conversion efficiency up to 7.23% for photoelectrochemical cell. The superior performance of the photoelectrochemical device based on Fe$_{1-x}$S@S-GO–NMC was attributed to the good electrocatalytic performance of the material. We hope that our work here will be of great interest for fundamental research and for practical applications of FeS or FeS$_2$ and their composites in the solar splitting of water, artificial photoelectrochemical cells, and electrocatalytic applications.

Conflicts of interest

There are no conflicts to declare.

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