High-Efficiency Dye-Sensitized Solar Cells Based on Kesterite Cu₂ZnSnSe₄ Inlaid on a Flexible Carbon Fabric Composite Counter Electrode

Yanan Zhang,* Pengfei Wang, Tengyue Zhang, and Bingwang Gou

ABSTRACT: Composite counter electrodes have been shown to be a practical and effective strategy in dye-sensitized solar cell (DSSC) application. In this work, we designed and prepared a single-crystal Cu₂ZnSnSe₄ (CZTSe) plate structure on flexible carbon fabric as a DSSC cathode, which combines the best of the two worlds, namely, the superior catalytic activity and hierarchical microstructure of kesterite CZTSe and the high conductivity and expanded framework of carbon fabric. The composite counter electrode presented a power conversion efficiency of 8.45% and a long-term bending reservation. The remarkable device property is due to the high catalytic activity, good adherence to conductive matrix grains, effective electron migration, and quick iodide species diffusion of the novel cathode. Our results suggest that the CZTSe@carbon fabric composite could be a high-efficiency Pt-free cathode in DSSCs.

1. INTRODUCTION

As a core component in dye-sensitized solar cells (DSSCs), the cathode should possess two basic characteristics of high conductivity and catalytic activity toward I⁻/I₃⁻ redox couple, responsible for transfer of the electrons from the external circuit to the redox electrolyte and then catalysis of the reduction of the redox species.¹⁻³ In recent research related to DSSCs, especially in counter electrodes (CEs), many studies were devoted to acquire high-efficiency and long-term stable DSSC devices based on Pt-free CEs. Therefore, several feasible approaches have been developed, such as (1) choosing alternative carbon,⁴⁻⁵ conductive polymer,⁶ and inorganic transition-metal compound (TMC) catalytic materials⁷⁻¹⁰ and (2) incorporating a TMC or conductive polymer with carbon-based materials, for instance, carbon fibers,¹¹ carbon nanotubes,¹²,¹³ graphene,¹⁴ reduced graphene oxide,¹⁵,¹⁶ carbon black,¹⁷ and carbon fabric (CF).¹⁸⁻²⁰ CF, having benefits of large exposed area, high-conductivity, flexibility, stability, lightweight, and good corrosion resistance toward electrolytes, has been generally applied to flexible and all-weather energy devices, such as supercapacitors,¹¹ lithium-ion batteries,¹² and DSSCs. Herein, combination of the advantages of CF and the kesterite Cu₂ZnSnSe₄ (CZTSe) compound, in which this selenide demonstrates superior catalytic activity toward the I⁻/I₃⁻ redox couple and is reported to achieve a DSSC efficiency of 7.56%,²¹ we designed and prepared an innovative multigrade structure, through seeding of the CZTSe plate structure on flexible CF. The designed composite cathode may present three values. First, low-cost network architecture CF served as a high-speed road to collect photoelectrons, in view of its intrinsic corrosion resistance, flexibility, high electrical conductivity, excellent mechanical strength, and commercial potentiality. Second, the kesterite CZTSe plate structure composed of single-crystalline inlaid on CF acted as the catalytic medium, promoting the reduction of ionic I₃⁻ and increasing the active points. Third, through in situ solvothermal treatment, the catalytic material well-bonded to the CF substrate, lowering the nonactive interface impedance dramatically and then accelerating the transfer of photoelectrons between the interfacial layer of the CF substrate and catalytic material.

2. RESULTS AND DISCUSSION

As shown in Figure 1a,b, every carbon fiber on CF is fully covered with compact and uniform copper, zinc and tin (CZT) clusters after the feasible electrodeposition. Using selenium powders acting as the active selenium source, the irregular and
overlapped CZTSe plate is synthesized by employing the metallic Cu, Zn, and Sn as the precursor supply. The CZTSe plate, with ca. 20 nm thickness and ca. 300–750 nm width, is firmly distributed all over the surface of carbon fiber (Figure 1). Figure 1. FE-SEM results and element mapping images of the elements. (a,b) SEM images of CZT inlaid on the carbon framework. (c,d) SEM images of the CZTSe plate structure grown on CF. (e) Element mapping images of Cu, Zn, Sn, and Se.

Figure 2. (a) XRD profiles of CF, (b) XRD profiles of CZTSe@CF CE, (c) Raman spectra of CF, and (d) Raman spectra of CZTSe@CF CE.
1c,d). This unique planar structure, providing more active area for migration of the electrolyte and photoinduced electrons rapidly and effectively, can be favorable for a better catalytic performance. In such solvothermal treatment systems, added selenium powders are decomposed to Se$^{2-}$ or other active selenide species. The Se$^{2-}$ cations released in the solvent react with the CZT precursor to form metal selenide and eventually convert to kesterite CZTSe phase.$^{24}$ In particular, all the four compound elements are uniformly distributed onto each carbon fiber (Figure 1e). Furthermore, because of “self-
assembly” and “oriented attachment”, adjacent CZT metallic particles finally generate a straight interface and structure with similar crystal orientation.

The crystallographic structures and phase purity of blank CF and acquired CZTSe@CF CE were characterized by X-ray diffraction (XRD). As shown in Figure 2b, the pattern demonstrates that only one crystal structure exists in the plate structure inlaid on CF. Both the diffraction peaks located at 2θ and 43° correspond to a blank CF framework. The rest of the diffraction peaks, which are located at 27.3, 36.7, 46.5, and 55.1°, are indexed to the kesterite CZTSe crystal planes of (112), (105), (204), and (312) (JCPDS 70-8930), respectively. The XRD spectra of the kesterite CZTSe phase are consistent with those of Cu2SnSe3 (JCPDS 65-7524), cubic Cu2Se (JCPDS 88-2043), and sphalerite ZnSe (JCPDS 37-1463). To get more insight into the phases present on the fabric, the detailed structural information of the catalytic material is obtained from Raman spectrum on macroscopic scale. In Figure 2d, the peaks at 195 and 244 cm⁻¹ correspond to kesterite CZTSe, while the peaks from Cu2SnSe3 (180, 236, 251 cm⁻¹), CuSe(264 cm⁻¹), ZnSe (205, 252 cm⁻¹), and SnSe2 (186 cm⁻¹) phases are not present in the composite CE. By eliminating the existence of other ternary or binary selenide compounds, the spectrum also confirms the formation of high crystal kesterite CZTSe on CF after the facile solvothermal reaction.

The valence states of the four elements in the CZTSe phase were analyzed by X-ray photoelectron spectroscopy (XPS), and two peaks are observed in Figure 3a. One is located at 933.15 (2p3/2), and the other is located at 952.62 eV (2p1/2) with a split orbit of 19.47 eV. These peaks confirm the formation of Cu(I) ion.39 In Figure 3b, the peaks located at 1019.58 (2p3/2) and 1042.59 eV (2p1/2) are ascribed to the Zn(II) valence state in CZTSe@CF CE. In Figure 3c, peaks located at 484.14 (3d5/2) and 492.59 eV (3d3/2) divided from Sn 3d, with a split orbit value of 8.45 eV, indicate the formation of Sn(IV) but not Sn(II). As observed in Figure 3d, a wide peak located at 52.53 eV (3d5/2) indicates the appearance of Se 3d.

The detailed structure information of the CZTSe plate was further investigated by transmission electron microscopy (TEM) analysis (see Figure 4). The side length of the plate-shaped CZTSe is about 380 nm. From Figure 4b, we can find a few diffraction dots of the kesterite structure CZTSe from (112) and (200) planes. Single crystal of the plate is characterized by good crystallinity. In addition, the pure kesterite CZTSe phase is further confirmed without any mixed impure phases. This single-crystal feature can be assumed to increase the higher chemical catalytic activity by promoting photoelectron transport. High-resolution TEM (HRTEM) images of good crystallographic faces are exhibited in Figure 4c,d, which correspond to (112) planes of CZTSe (JCPDS 26-70-8930); the lattice spacing is measured to be 0.32 nm.

Figure 5 shows the J–V characteristics for DSSCs with CF, Pt, and different CZTSe@CF CEs on different solvothermal time periods under simulated sunlight irradiation (100 mW/cm²).

Composite CZTSe CEs owning higher JSC exhibit much outstanding device property, than blank CF frameworks with the η value as low as 2.92 ± 0.26%. Compared with other CEs with secondary selenide, when substituting 18 h for the CZTSe@CF CE, the DSSCs based on 18 h CE present the JSC and η of 16.42 mA/cm² and 7.20%, respectively, which are slightly lower than those of the DSSCs of CZTSe@CF. The fill factor (FF) values are closely related to the Rsh of the DSSC. A lower Rsh value at the CE/electrolyte interface can create a higher FF. Compared to blank CF electrode, the FF value of CZTSe@CF increases from 42.56 to 59.55%. The FF value reflects the internal resistance of the cell device, including contact resistance between the catalytic material and substrate, resistive contact between conductive CF, bulk resistance of CE materials, transport resistance in the photoanode, and migration resistance at the cathode—electrolyte interface. Above all, the CZTSe@CF CE owning higher JSC and FF values displays quicker charge transfer at the CE/electrolyte interface and better catalytic ability. In this fashion, the concentration gradients in the electrolyte, internal resistances, and recombination rates decrease. The synergistic effect of this device property based on this hybrid composite cathode is probably related to its unique structural morphology and high catalytic feature.

The electrochemical performance of the CZTSe@CF electrode was investigated by cyclic voltammetry (CV) measurements, with the aim to illustrate the electrocatalytic activity of the hybrid cathode. The CV curves of CF, Pt, and CZTSe@CF cathodes, recorded at a scan rate of 150 mV/s, are shown in Figure 6. It is known that the kinetic process of the catalytic reaction is closely related to the active site number and electron migration rate constant. In these curves, two pairs of oxidation/reduction peaks are displayed, verifying good electrocatalytic property toward the I⁻/I₃⁻ redox couple. In CV curves, peak-to-peak separation (ΔEp) and peak current density (Ip) are always utilized to compare the catalytic performances of CEs. A higher Ip and a lower ΔEp certify a better electrocatalytic activity for the I⁻/I₃⁻ reduction reaction. The corresponding data of ΔEp are summarized in Table 2. As listed in Table 2, the CZTSe@CF CE has lower ΔEp value compared with the Pt electrode, demonstrating that the catalytic process can be enhanced by utilizing the CZTSe@CF CE. The higher Ip of the CZTSe@CF CE indicates its good electrocatalytic ability as an efficient cathode in DSSCs.
redox peaks at more positive potentials, marked by peak II and peak II’, correspond to the oxidation of $I^{-}$ to $I_{3}^{-}$, and the redox peaks at more negative potentials, labeled by peak I and peak I’, correspond to the reduction of $I_{3}^{-}$ to $I^{-}$. Apparently, the peak I for the CF framework is not significantly observed, implying that the oxidized iodide is not easily reduced and then reproduced on the CF cathode. The peak I for the CZTSe@CF CE is observably bigger than that for blank CF, indicating more catalytic reaction sites in the CZTSe@CF structure. Given all this, when the CF framework serves as a conductive network and the CZTSe plate acts as the catalytic reduction media, the flexible composite CE proves to display remarkable catalytic ability.

The catalytic ability was further discussed according to the electrochemical impedance spectroscopy (EIS) measurement; see Figure 7a. Typically, the electrocatalytic ability of a CE could be illustrated by series resistance ($R_s$), charge-transfer resistance ($R_{Ct}$), and electrochemical double-layer capacitance ($C_{μ}$) value. The extracted data are summarized in Table 2. $R_s$ refers to series resistance represented by the intercept on the real axis, and $R_{Ct}$ means the charge-transfer resistance at the CE/cathode interface for $I_{3}^{-}$ reduction. Compared to blank CF and the Pt electrode, CZTSe@CF shows a minimal $R_s$ (10.15 $Ω$/cm$^2$) and $R_{Ct}$ (2.42 $Ω$/cm$^2$). The small value of the flexible composite cathode, improving the photoelectron transfer from the external circuit or holes to the cathode, verifies a firm action between the CZTSe and CF substrate. According to the above photovoltaic performance, smaller $R_s$ also leads to higher FF and $J_{SC}$ value of the device. The smallest $R_{Ct}$ value of the CZTSe@CF electrode presents an acceleration of high electron transfer at the interface of the CE/electrolyte, leading to higher $J_{SC}$ and FF. The bigger area of peak I for the CZTSe@CF sample also indicates a larger specific surface area of the cathode and more catalytic active sites.

Furthermore, the CZTSe@CF CE can promote electron transportation from the external circuit to the CE/electrolyte interface. Therefore, a lifetime of the electrons ($τ_e$) at the CE/electrolyte interface is a significant parameter to estimate the electrocatalytic activity of the CE. $τ_e$ can be calculated according to the equation, $τ_e = 1/2\pi f_{max}$ where $f_{max}$ is the frequency corresponding to the maximum Bode phase (Figure 7b) at high frequency. As shown in Table 2, the $τ_e$ value of Pt is 4.27 ms, shorter than that of the CZTSe@CF CE of 5.30 ms.

Table 1. Photovoltaic Parameters for DSSCs Assembled with CF, Pt, and Different CZTSe@CF CEs Based on Different Solvothermal Time Periods (Indexed as 6 h et al.)

| CE               | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF (%) | PCE (%) |
|------------------|----------------------|--------------|--------|---------|
| CF               | 9.73 ± 0.21          | 0.76 ± 0.02  | 42.56 ± 0.27 | 2.92 ± 0.26 |
| 6 h              | 13.97 ± 0.57         | 0.77 ± 0.03  | 46.83 ± 0.32 | 5.04 ± 0.24 |
| 12 h             | 11.66 ± 0.43         | 0.77 ± 0.02  | 63.60 ± 0.25 | 5.75 ± 0.21 |
| 18 h             | 16.42 ± 0.24         | 0.74 ± 0.01  | 59.40 ± 0.19 | 7.20 ± 0.22 |
| Pt               | 15.21 ± 0.14         | 0.76 ± 0.01  | 65.60 ± 0.12 | 7.57 ± 0.10 |
| CZTSe@CF         | 18.93 ± 0.22         | 0.75 ± 0.01  | 59.55 ± 0.13 | 8.45 ± 0.17 |

Table 2. Electrochemical Parameters of CF, Pt, and CZTSe@CF Symmetrical Cells

| CE               | $ΔE_p$ (V) | $R_s$ ($Ω$/cm$^2$) | $R_{Ct}$ ($Ω$/cm$^2$) | $τ_e$ (ms) |
|------------------|------------|-------------------|-----------------------|------------|
| CF               | 10.43      | 4.78              |                       |            |
| CZTSe@CF         | 0.61       | 10.15             | 2.42                  | 5.30       |
| Pt               | 0.65       | 10.82             | 5.12                  | 4.27       |

Figure 6. CV curves of the CF, Pt, and CZTSe@CF cathode.

Figure 7. (a) Nyquist EIS plots and (b) corresponding simulated Bode phase plots for the $I_{3}^{-}/I^{-}$ symmetrical cells based on the CF, Pt, and CZTSe@CF CE.
Consistent with the previous CV data, the CZTSe@CF CE exhibits a low rate of charge recombination of electrons and $I_3^-$ species and a quick diffusion rate of electrons.

Tafel polarization measurements are employed to confirm the electrocatalytic activities and interfacial charge-transfer properties of the CZTSe@CF CE (Figure 8). Tafel polarization plots exhibit the relationships for logarithmic current density as a function of potential for CF, Pt, and different solvothermal time CZTSe@CF. As shown in Figure 8, Tafel polarization analysis shows that the CF coated with the pure CZTSe plate possesses the highest exchange current density ($J_0$) among the assembled CEs, which means that this catalytic material has a quicker electron migration capability on the CE/electrolyte interface. The higher $J_0$ value is attributed to three rare characters: single crystallinity CZTSe material possesses excellent electrocatalytic activity; the expanded CZTS structure provides a feasible transport tunnel for $I_3^-/I^-$ diffusion throughout the CZTSe material; tight bonding between the CZTSe catalyst and conductive carbon fiber avoids diffusive barrier, ensuring a fluent electron transport. $J_0$ value has a relationship with $R_{ct}$ (charge-transfer resistance for electrolyte), according to following equation

$$J_0 = \frac{RT}{nFRC_l}$$

where $R$ is the gas constant, $T$ is absolute temperature, $n$ is the electron number in the electrochemical reaction, $F$ is Faraday’s constant. Limiting diffusion current density ($J_{lim}$) can be also acquired from the Tafel curve at high potential. $J_{lim}$ value relates to the diffusion coefficient of $I_3^-/I^-$ couples in the electrolyte. As expressed in eq 2, the $J_{lim}$ value of the CZTSe@CF composite is as high as 1.37 mA/cm$^2$, superior to that of Pt (1.16 mA/cm$^2$) and other electrodes. This Tafel polarization characterization is well-asserted with previous EIS and CV data.

$$D = \frac{J_{lim}}{2nFC}$$

3. CONCLUSIONS

In summary, a novel and effective composite cathode based on kesterite CZTSe plate structure grown on flexible conductive carbon-cloth was prepared by electrodeposition and a feasible solvothermal treatment method. The DSSCs constituted by flexible the CZTSe@CF CE possess a power conversion efficiency as high as 8.45 and ~100% PCE value maintained after 500 cyclic bending tests. The designed three-dimensional CZTSe@CF cathode, without any post-treatment has proven to be useful in the area of photovoltaics and even can be extended to supercapacitors and lithium ion battery application.

4. EXPERIMENTAL METHODS

4.1. Orthotopic Growth of the Kesterite CZTSe Plate Structure on CF.

The kesterite CZTSe plate structure was orthotopically seeded on flexible CF homogeneously by means of electrodeposition strategy first, followed by adopting a mild solvothermal treatment, regarded as the CE for DSSCs. In the electrodeposition phase, metallic precursor particles of CZT were deposited on CF simultaneously. The CF was first precleaned by ultrasonic degreasing in ethanol for 10 min and then dried at room temperature. Then, 6 mM copper sulfate pentahydrate ($CuSO_4\cdot5H_2O$), 35 mM zinc sulfate monohydrate ($ZnSO_4\cdotH_2O$), 4 mM tin sulfate ($SnSO_4$), and 100 mM sodium citrate dihydrate ($Na_3C_6H_7O_6\cdot2H_2O$) were dissolved in deionized water under stirring until a uniform electrolyte solution was obtained. Then, 2 × 5 cm$^2$ of CF was collected, and CZT precursor particles were electrodeposited on it under −1.17 V (vs SCE) for 1200 s. After electrodeposition, the sample was alternately rinsed by distilled water and ethanol three times. Subsequently, the obtained sample was transferred into a Teflon-lined autoclave, containing 5 mM excessive selenium powders and 50 mL of ethanol. The autoclave was subsequently kept at 200 °C for one day to make sure CZT precursors had completely reacted with the selenium source. Then, the coated carbon cloth was cleaned by ethanol and dried at 70 °C in air. No more post-treatments were performed on the obtained CZTSe@CF composite.

4.2. Fabrication of DSSCs.

DSSCs were fabricated by inducing a TiO$_2$ photoanode and a CZTSe@CF composite cathode. An ionic liquid electrolyte was placed into the interspace between the photoanode and cathode and sealed by a ∼100 μm hot-melt glue. The TiO$_2$ photoanode preparation is described below. An ozone-treated fluorine-doped tin oxide (FTO) glass was kept in 0.1 M TiCl$_4$ solution at 85 °C for 1 h. A commercial TiO$_2$ slurry was then deposited on the mentioned FTO glass via the spin-coating technique at 1000 rpm. The TiO$_2$-coated sample was slowly heated up to 450 °C at 5 °C/min in air and then annealed at 450 °C for 1 h to obtain a ∼35 μm porous TiO$_2$ layer. After thermal annealing, the sample was immersed in TiCl$_4$ aqueous solution again to obtain more TiO$_2$ tiny clusters on the surface. Thereafter, the 85 °C heated glass was soaked in 1 mM N719 dye solution from Dyeso for a duration of 24 h. In the cathode preparation process, the CZTSe@CF composite was stuck on a polytetrafluoroethylene membrane, serving as the flexible CE immediately. To make a conductive wire, a carbon fiber was lined through the hole of above CF. All the assembly fabrication was conducted in dark conditions at room temperature.

4.3. Material and Electrochemical Characterization.

The phase structure information of CZTSe materials was characterized by an X-ray diffractometer and a confocal 488 nm Ar-ion laser Raman microscope. The morphological features of the composite CE were observed via field-emission
scanning electron microscopy (FE-SEM) and TEM incidental with selected-area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy mapping. The valent state and detailed structural properties of the acquired compound were analyzed by XPS. The J–V curves of the DSSC devices were recorded through illumination of an assembled solar cell under incident light (100 mW/cm², collected with a standard Si cell) using a Newport solar simulator. The electrochemical properties of the cathodes were investigated by CV measurement, Tafel polarization, and EIS curves, adopting a Chenhua CHI 650E electrochemical workstation. The CV test was conducted in acetonitrile solution, consisting of 0.5 M LiClO₄, 5 mM I₂, and 25 mM LiI in a three-electrode system at a scan speed of 50 mV s⁻¹. The as-prepared cathode served as the working electrode, and an 8 cm² Pt sheet was the counter electrode. The reference electrode was an Ag/Ag⁺ couple. The frequency was controlled in the range from 0.05 to 10⁶ Hz. The impedance spectra were investigated for a symmetrical cathode. The active area of the symmetrical cathode was limited to be 0.20 cm². In detail, the Tafel polarization and EIS spectral line were acquired by introducing a perturbation amplitude of 5 mV. The frequency was controlled from 0.05 to 10⁶ Hz. The impedance spectra were investigated and fitted by Z-View simulation software, applying a related equivalent circuit as models.

### AUTHOR INFORMATION

#### Corresponding Author

Yanan Zhang — College of Materials Science & Engineering, Nanjing Tech University, Nanjing 211816, China; orcid.org/0000-0002-7128-8852; Phone: +86-19951797205; Email: zyn3648@163.com

Authors

Pengfei Wang — College of Materials Science & Engineering, Nanjing Tech University, Nanjing 211816, China

Tengyue Zhang — China Research and Development Academy of Machinery Equipment, Beijing 100089, China

Bingwang Gou — Science and Technology on Combustion and Explosion Laboratory, Xi’an Modern Chemistry Research Institute, Xi’an 710065, P R China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03686

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors are thankful for the financial support from the Natural Science Foundation of Jiangsu Province (BK20180698).

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