Carbon fiber/Co$_9$S$_8$ nanotube arrays hybrid structures for flexible quantum dot-sensitized solar cells†

Wenxi Guo, Chang Chen, Meidan Ye, Miaoqiang Lv and Changjian Lin*

Recently, hybrid carbon materials and inorganic nanocrystals have received an intensive amount of attention and have opened up an exciting new field in the design and fabrication of high-performance catalysts. Here we present a novel kind of hybrid counter electrode (CE) consisting of a carbon fiber (CF) and Co$_9$S$_8$ nanotube arrays (NTs) for fiber-based flexible quantum dot-sensitized solar cells (QDSSCs). The growth mechanisms of Co(CO$_3$)$_{0.35}$Cl$_{0.20}$OH$_{1.10}$ nanowire arrays (NWs) on the CFs were discussed, and the catalytic activity of the CF, Pt and Co$_9$S$_8$/CF hybrid structure (Co$_9$S$_8$@CF) were elucidated systematically as well. An absolute energy conversion efficiency of 3.79% has been demonstrated under 100 mW cm$^{-2}$ AM 1.5 illumination by using Co$_9$S$_8$@CF as a CE. This work not only demonstrates an innovative approach for growing cobalt sulfide NTs on flexible substrates that can be applied in flexible devices for energy harvesting and storage, but also provides a kind of hybrid structure and high-efficiency CE for QDSSCs.

Introduction

Quantum dot-sensitized solar cells (QDSSCs) have attracted intensive attention in scientific and industrial fields due to their high molar extinction coefficient, spectral tunability by particle size, ease of fabrication, and low cost.$^{1-4}$ Theoretically, the conversion efficiency of QDSSCs may reach 44% which is considerably higher than that of dye-sensitized solar cells (DSSCs).$^5$ However, with the development of DSSCs, more and more strategies have been introduced to improve the photovoltaic performance of DSSCs.$^6-9$ So far, most reported efficiency values of QDSSCs are lower than those of DSSCs for various reasons, including their narrow absorption range and charge recombination.$^{10-15}$ As an important component in QDSSCs, counter electrodes (CEs) play a crucial role in collecting electrons from the external circuit and reducing polysulfide ($S^{2-}/S_{2-}$) electrolytes.$^{16-21}$ Due to the sulfur atom present in polysulfide electrolyte being easily absorbed onto the surface of the Pt CE, metal sulfides including Cu$_2$S,$^{16,17}$ CoS,$^{16,20}$ PbS,$^{16,21}$ and Cu$_2$S/reduced graphene oxide composite,$^{22}$ etc. have been widely exploited. However, most of the aforementioned works are based on powdered disordered metal sulfides, which are poor in contact between the conductive substrate and the metal sulfide film.$^{24-27}$ What is more, the poor light transmittance of the metal sulfides means that the QDSSCs can only work under front-illumination which restricts the substrate sources of the photoanode.

To grow 1D metal sulfides onto flexible conductive substrates and strengthen the adaptability of QDSSCs, here we design a spiral-shaped flexible QDSSC (the structures and working

Fig. 1 Design and principle of the fiber-shaped QDSSC. (a) CdS and CdSe QDs co-sensitized TNARs film on the spiral Ti wire is used as the photoanode of the QDSSCs, and the carbon fibers with Co$_9$S$_8$ NTs are used as the CE of the QDSSC. (b) Detailed structure and working principle of the fiber-shaped QDSSCs.
Experimental section

Fabrication of TNARs on spiral Ti wire

A 0.20 mm-diameter and 20 cm-long Ti (99.6% purity) wire was rolled up to form a spiral Ti electrode of 0.50 mm inner diameter. TNARs on the spiral Ti wire were fabricated by electrochemically anodizing the spiral Ti wire in ethylene glycol solution containing 0.3 wt% NH₄F and 2 vol% H₂O with Pt as the CE. Before anodization, the spiral Ti wires were ultrasonically cleaned in acetone, water, and ethanol consecutively, and then dried in air. The prepared Ti wire was first anodized at 50 V for 6–8 h. The resulting NT film around the spiral Ti wire was then removed by a ultrasonic in acetone for a few minutes, leaving hexagon-like footprints around the wire. A second anodization was then performed under the same conditions for about 7 h and the black Se powder was almost reacted. After cooling to room temperature, the obtained Na₂SeSO₃ aqueous solution was filtered to remove the unreacted Se. Cd(NO₃)₂ aqueous solution (0.08 M) was prepared as the Cd source. The CBD process of CdSe QDs was conducted in a mixture of Na₂SeSO₃ solution and the Cd(NO₃)₂ solution mentioned above with a volume ratio of 1 : 1 under 5 °C for 10–40 h.

Fabrication of Co₉S₈ NTs@CFs CE

A thin film of Co₂(CO₃)₉Cl₂(OH)₁₀ nanowire arrays (NWs) (~5 μm long) was grown on the CF substrate using CBD as previously reported by Ho et al., the CF substrate was fixed on a glass slide and put upside-down in a closed bottle with an aqueous solution comprised of urea (6.25 wt%) and of CdCl₂·6H₂O (0.15 M) at 90 °C for 3 h. After the CBD process, the obtained film on the CFs was converted into Co₉S₈ NTs by soaking it in a closed bottle containing Na₂S aqueous solution (0.01 M) at 120–160 °C for 8–16 h. After this conversion process, the obtained film was washed with deionized water (DIW) and dried at 60 °C, followed by annealing at 400 °C for 2 h in nitrogen to form the crystal phase with relatively high crystal purity, and the Co₉S₈ NTs@CFs CE was thus obtained.

Characterization

The morphology and structure of the prepared nanostructures of TiO₂ and Co₉S₈ were examined by scanning electron microscopy (SEM-Hitach 4800), and transmission electron microscopy (TEM-JEM 2100). The phase identification of the Co₉S₈ NTs and precursor were conducted by X-ray diffraction (XRD) using a PANalytical X'Pert PRO diffractometer. The light absorption of the TiO₂ films with QDs was measured by UV-visible spectroscopy (Varian; UV-Visible spectrophotometer, Cary 5000). Cyclic voltammetric (CV) measurements were performed using an Autolab electrochemical workstation, and conventional three-electrode system. One of the various CEs of QDSSCs, a platinum sheet, and a saturated calomel electrode (SCE) were used as the working electrode, CE, and reference electrode, respectively. The methanol and DIW (3 : 7 v/v) mixed solution containing 0.5 M Na₂S, 0.2 M S, and 0.2 M KCl was used as the electrolyte for all CV measurements. The CV curves were recorded at a scan rate of 50 mV s⁻¹, and the Tafel polarization curves were obtained by using an Autolab electrochemical workstation at 5 mV s⁻¹, with a two-electrode system. The two electrodes used in symmetrical cells were identical which were separated by a semipermeable membrane. The electrolyte used for the symmetrical cells was the same as that used for CV.
measurements. Electrochemical impedance spectroscopy (EIS) was carried out using an AUTOLAB model PGSTAT 30 (ECO Chemie B.V.) equipped with a Frequency Response Analyzer (FRA) module (Autolab, Eco-Chemie). The frequency range explored was 100 kHz to 0.1 Hz and the corresponding ac amplitude was 10 mV. The impedance spectra were analyzed using an equivalent circuit model. A Solux solar simulator was used as calibrated with a Daystar meter to simulate sunlight for an illumination intensity of 100 mW cm$^{-2}$. The solar cell was irradiated using a solar simulator (300 W model 91260, Newport) with an AM 1.5 spectrum distribution calibrated against an NREL reference cell to simulate accurately a full-sun intensity (100 mW cm$^{-2}$).

**Results and discussion**

Fig. 2a–c are the FESEM images of the TNARs@Ti wire obtained after a two-step anodization, showing typical morphology and structures. From Fig. 2a and 2b, it can be observed that the Ti wire is rolled up and wound into a spiral shape, where the diameters of the Ti wire and spiral ring are about 0.20 mm and 0.50 mm, respectively. After a two-step anodization, uniform TNARs with similar structures on the top of the Ti wire were obtained (the top view and the cross-section view are shown in Fig. 2c), and the average inner diameter and length of the NTs are about 100 nm and 14 µm, respectively. Compared with the morphology of the TiO$_2$ NTs obtained after a one-step anodization in ethylene glycol electrolyte as revealed in Fig. S1 (ESI†), the TiO$_2$ NTs prepared by a two-step anodization show much more perfect morphology without any visible defects on the surface, which is beneficial for electron transport, QDs deposition and electrolyte infiltration.$^{37,38}$

In this study, CdS and CdSe QDs were successively deposited on the TiO$_2$ NTs as photosensitizers by a CBD method. Due to the complementary band gaps of the CdS (2.31 eV) and CdSe (1.77 eV) QDs,$^{39}$ the combination of the two sensitizers would maximize the absorption of solar light.$^{39,40}$ Fig. 2d displays the SEM image of a CdSe/CdS@TiO$_2$ NTs film on the Ti wire, and as can be seen from the top-view of the TNARs, QDs are well-distinguished and their inner pores are not blocked after deposition of the QDs. Obviously, this TNARs’s architecture facilitates the multi-layer deposition of QDs without blocking the inner-pores. The top view and cross-section view (Fig. 2d) clearly demonstrate that the wall thickness of the TNARs continuously increases from 25 nm to 50 nm. The CdSe/ CdS@TiO$_2$ NTs film was further investigated by using TEM and

![Fig. 2](image.png)  
**Fig. 2** SEM and TEM images of the photoanode for QDSSCs. (a–c) SEM top-view images at different magnifications of TNARs on the spiral Ti wire by a two-step anodization. Inset in (c) shows the cross-sectional view; (d) is the SEM top-view image of CdSe and CdS QDs-coated TNARs; inset: cross-sectional view of the CdSe and CdS QDs-coated TNARs; (e) optical photo of the CdSe and CdS QDs-coated TNARs; (f and g) TEM and corresponding HRTEM images of the CdSe and CdS QDs-coated TNARs. The inset in (f) is the selected area electron diffraction (SAED) pattern of the CdSe and CdS QDs-coated TNARs.

![Fig. 3](image.png)  
**Fig. 3** (a and b) SEM top-view images at different magnifications of Co(CO)$_{3}$Cl$_{3}$ NWs grown on the CFs by CBD method at 90 °C for 3 h; (c–e) SEM top-view images at different magnifications of Co$_{9}$S$_{8}$ NTs grown on the CFs by hydrothermal and template methods at 150 °C for 8 h, the inset in (c) is the EDX spectrum of the corresponding Co$_{9}$S$_{8}$ NTs.
the results are shown in Fig. 2f and 2g. The high-magnification TEM images demonstrate that the sizes of the QDs are in the range of 5–15 nm. The observed lattice spacing of 0.372 nm, 0.335 nm and 0.355 nm in the image corresponded to the (100), (111) and (101) plane of CdSe, CdS and TiO2, respectively.41 The corresponding EDX spectrum (ESI, Fig. S2†) reveals that the obtained thin films are composed of Ti, O, Cd, Se and S. It is apparent, from the UV-vis diffuse reflection spectra of the TNARs and corresponding QDs-sensitized TNARs (ESI, Fig. S3†), that the CdS-sensitized TNARs samples exhibited a higher light absorption between wavelengths of 200 and 450 nm whereas the CdSe and CdSe co-sensitized TNARs samples exhibited a higher light absorption in both the UV and visible light regions. This is ascribed to the light trapping of the multi-layer composite structures and the complementary effect in the visible light harvest of low band gap QDs.42,43

To grow cobalt sulfide NTs on the CFs, a facile two-step hydrothermal method was developed. First of all, as the sacrificial template, cobalt oxide NWs grew on the CFs by a hydrothermal reaction at 90 °C K for 3 h. As can be seen from the digital photograph (ESI, Fig. S4†), the color of the CFs turned red and a thin film was obviously observed on the fibers. Fig. 3a and 3b show the corresponding SEM images of the red film on the CFs. As can be seen from Fig. 3a, the entire surfaces of the CFs are covered very uniformly by the NWs that are dense and well-organized. Fig. 3b gives a clear view of the NWs, which shows that the NWs are needle-like, with diameters of 100–350 nm, and lengths of 2–5 μm. The phase and purity of the as-obtained samples were examined by XRD shown in Fig. 4. As revealed in pattern [a], all of the diffraction peaks of the red film can be indexed to Co(CO3)0.35Cl0.20(OH)1.10 according to Joint Committee on Powder Diffraction Standards (JCPDS card, file no. 38-547), which is consistent with the result reported by Wang et al.44 The corresponding EDX spectrum (Fig. S5†) further reveals that the prepared thin films are composed of Co, O, C and Cl.

According to the XRD pattern (ESI Fig. S6†), the shells have an amorphous structure. Apparently, there is no lattice match between the Co(CO3)0.35Cl0.20(OH)1.10 NWs and the CF substrate. Therefore, it is impossible for the Co(CO3)0.35-Cl0.20(OH)1.10 NWs to grow on the fiber surface through epitaxial growth. For a better understanding of the growth mechanism of the Co(CO3)0.35Cl0.20(OH)1.10 NWs, controlled experiments were carried out by varying the hydrothermal reaction time. Fig. S7† (ESI) displays the SEM images of the Co(CO3)0.35Cl0.20(OH)1.10 NWs grown on the CFs for different times. At the beginning, no NWs were observed on the CFs, and the bare CFs displayed a smooth circular cylindrical outline of about 8–10 μm in diameter. As the hydrothermal reaction time was increased to 45 min, some needle-like NWs (shown in the Fig. S7b†) appeared, scattered on the surface of the CFs. According to our previous works,44,45 the formation mechanism of the Co(CO3)0.35-Cl0.20(OH)1.10 NWs may be summarized here: as a homogeneous precipitation agent, urea would produce OH− and CO32− anions by hydrolysis in an aqueous solution. The dissociative OH−, Cl− and CO32− would react with the Co2+ cations to generate Co(CO3)0.35Cl0.20(OH)1.10 crystals. The formation reactions may be expressed as follows:\textsuperscript{46}

\begin{align*}
\text{Co(NH}_3\text{)}_2 + \text{H}_2\text{O} &\leftrightarrow \text{CO}_2 + 2\text{NH}_3 & (1) \\
\text{NH}_3 + \text{H}_2\text{O} &\leftrightarrow \text{NH}_4^+ + \text{OH}^- & (2) \\
\text{CO}_2 + \text{H}_2\text{O} &\leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+ & (3) \\
\text{Co}^{2+} + 0.35\text{CO}_3^{2-} + 1.1\text{OH}^- &+ 0.2\text{Cl}^- \leftrightarrow \text{Co(CO}_3)_{0.35}\text{Cl}_{0.20}\text{(OH)}_{1.10} & (4)
\end{align*}

Upon increasing the reaction time, more and more Co(CO3)0.35Cl0.20(OH)1.10 crystals form in the solution. When the concentrations of urea and cobalt chloride are moderate, the degree of supersaturation for Co(CO3)0.35Cl0.20(OH)1.10 crystals is strictly controlled at a low level. It is difficult for Co(CO3)0.35Cl0.20(OH)1.10 polycrystalline clusters to form in the solution by homogeneous nucleation as the low degree of supersaturation favors heterogeneous nucleation on the surface of the CFs. A few scattered, bud-like nanorods formed on the surface of the CFs by heterogeneous nucleation could be observed by SEM which is shown in Fig. S8a† (ESI). These bud-like nanorods served as the seeds to guide the subsequent growth of Co(CO3)0.35Cl0.20(OH)1.10 NWs, and once the nucleus formation on the CFs, the growth speed increases rapidly and abundant NWs completely spread across the substrate as time progresses. When the growth time was extended to more than 90 min, a dense Co(CO3)0.35Cl0.20(OH)1.10 NWs film was observed which is shown in Fig. S7f and S7d† (ESI).

In addition, the morphology of Co(CO3)0.35Cl0.20(OH)1.10 can be tuned by the concentration of the reactants that profoundly influence the crystal growth mechanism. Herein, we changed the concentration of the reactants to see their effect on the growth of the Co(CO3)0.35Cl0.20(OH)1.10 nanostructures. When the concentrations of urea and CoCl2·6H2O were low, no NWs were found on the CFs, as the degree of the supersaturation for Co(CO3)0.35Cl0.20(OH)1.10 was too low for heterogeneous nucleation on the surface of the CFs. By contrast, when the concentrations of the reactants are fold increased, well defined NWs cannot be developed on the CFs. Instead, over 20 μm thickness Co(CO3)0.35Cl0.20(OH)1.10 nanoflowers and nanospheres were observed on the surface of the CFs (ESI Fig. S8b†). It is easy to
understand that fold increasing the concentration of reactants would lead to a burst of homogeneous nucleation, then the supersaturated \( \text{Co(CO}_3\text{)}_{0.35}\text{Cl}_{0.20}\text{(OH)}_{1.10} \) nuclei tended to aggregate to minimize the surface energy, and thus, a large number of polycrystalline clusters form in the solution by homogeneous nucleation. Subsequently, these clusters were deposited on the surface of the CFs and acted as nucleating centers for further growth of the nanorods. Since there was no crystal plane trend for these clusters, the nanorods inevitably grow along any direction and further self-assemble into microspheres or tufted nanoﬂowers.

The synthesized \( \text{Co(CO}_3\text{)}_{0.35}\text{Cl}_{0.20}\text{(OH)}_{1.10} \) NWs were used as templates and transformed into cobalt sulfide NTs in \( \text{Na}_2\text{S} \) aqueous solution. After 8 h of hydrothermal treatment in \( \text{Na}_2\text{S} \) solution at 150 °C, the red ﬁlm on the CFs became black (ESI, Fig. S4†). The morphology of the as-prepared samples was examined by SEM in Fig. 3c and 3d. It is apparent that the as-prepared sample is similar to the precursor in morphology. However, a SEM image (Fig. 3e) with higher magniﬁcation shows that the arrays are transformed into NTs instead of NWs, where the open ends of the NTs can be clearly seen from some of the broken NTs. Compared with the precursor, the surface of the NTs are much rougher. TEM and HRTEM were used to further examine the morphology and microstructure of the prepared NTs. Fig. 5a shows a TEM image of the obtained nanotubes, where a clearly hollow structure reveals that the template was successfully removed since the shapes of the voids in the NTs are very similar to the precursor NWs. From Fig. 5c, the HRTEM image of a NT, it can be observed that the interplanar spacing is 0.242 nm, corresponding to the separation between the (400) lattice planes of \( \text{Co}_9\text{S}_8 \). The selected area electron diffraction (SAED) pattern of this NT (Fig. 5b) shows several diffraction rings, which can be indexed as the (440) and (311) lattice planes of \( \text{Co}_9\text{S}_8 \). It is noteworthy that, due to the low surface tension between the CF surface and the \( \text{Co}_9\text{S}_8 \) NTs, the film adhesion is so good that the NTs did not peel off, even when we further prolonged the reaction time.

Fig. 4b shows a typical XRD pattern of the sample obtained by reacting the \( \text{Co(CO}_3\text{)}_{0.35}\text{Cl}_{0.20}\text{(OH)}_{1.10} \) NWs with \( \text{Na}_2\text{S} \) solution. All of the reﬂection peaks marked in this pattern can be indexed to the face-centered cubic \( \text{Co}_9\text{S}_8 \). No distinct diffraction peaks correspond to the \( \text{Co(CO}_3\text{)}_{0.35}\text{Cl}_{0.20}\text{(OH)}_{1.10} \), indicating that most of the precursor NWs were transformed into \( \text{Co}_9\text{S}_8 \) NTs. The \( \text{Co}_9\text{S}_8 \) sample was further investigated by EDX, and only Co and S were found from the spectrum in the inset of Fig. 3c.

For comparison, different electrodes including CF, Pt and \( \text{Co}_9\text{S}_8@\text{CFs} \) were then exploited as photoanodes to assemble the QDSSCs. The photocurrent density–voltage (\( J–V \)) curves of the QDSSCs under a light intensity of 100 mW cm\(^{-2} \) are shown in Fig. 6a, where the plot of current density against voltage (\( J–V \) curve) shows an open-circuit voltage (\( \text{V}_{\text{OC}} \)), short-circuit current density (\( J_{\text{SC}} \)), fill factor (FF), and energy conversion efficiency

\[
\eta = \frac{FF \times \text{V}_{\text{OC}} \times J_{\text{SC}}}{P_{\text{in}}}
\]

where \( P_{\text{in}} \) is the incident light power density. The photovoltaic parameters are listed in Table 1, from which it is apparent that the QDSSCs with \( \text{Co}_9\text{S}_8@\text{CFs} \) show a much better cell performance than the others, especially for the values of \( J_{\text{SC}} \) and FF. The largely enhanced \( J_{\text{SC}} \) and FF values indicate that the rate of hole recovery at the \( \text{Co}_9\text{S}_8@\text{CFs} \) electrode–electrolyte interface is more rapid than that of the other two CEs. A 3.79% efficiency was successfully demonstrated with the \( \text{Co}_9\text{S}_8@\text{CFs} \) electrode, about 130% and 724% times higher than those for Pt and CF CEs based QDSSCs, respectively.
To further recognize the high catalytic activity of the Co$_9$S$_8$@CFs electrode, cyclic voltammetry (CV) was performed to study the electrocatalytic abilities of the various CEs. The measured CV curves of the CEs are shown in Fig. 6b. The electrochemical behavior of the CEs, Pt foil and Co$_9$S$_8$@CF electrodes for the $S^{2-}$/S$_2^{2-}$ redox couple was investigated from $-1.5$ V to $0.1$ V at a scan rate of $50$ mV s$^{-1}$. During regeneration in the QDSSCs, the oxidized species, S$_x^{2-}$, had to be reduced to $S^{2-}$ on the CE (S$_x^{2-}$ + 2e$^-$ $\rightarrow$ S$_{x-1}^{2-}$ + S$^{2-}$). Compared with the Pt and CF electrodes, Co$_9$S$_8$@CF provided a conspicuously larger current density at the reduction potential range, suggesting the higher catalytic activity for reducing the S$_2^{2-}$/S$^{2-}$. During $-0.7$ to $-0.9$ V, before hydrogen evolution, both the reduction current density of the CFs and Pt are lower than $-0.6$ mA cm$^{-2}$ which is much smaller than that for the Co$_9$S$_8$@CF (9.27 mA cm$^{-2}$ at $-0.9$ V), revealing the poor electrocatalytic activity to the S$_2^{2-}$/S$^{2-}$ redox couple. According to the literature, the higher reduction rate at surface of the CE will provide a higher value of $J_{\text{sc}}$, where the results agree with the obtained cell efficiency and $J_{\text{sc}}$, as shown in Table 1.

The electrochemical impedance spectroscopy (EIS) measurements were also further performed to evaluate the electrocatalytic activity of the CEs by measuring the charge-transfer resistance ($R_{ct}$), which is closely associated with the catalytic activity of the CEs. Fig. 7a shows the Nyquist plots of the Pt, CF and Co$_9$S$_8$ CEs, and the equivalent circuit as shown in the top-left inset may be proposed to fit the Nyquist plots, where $R_s$ is the solution resistance; $R_{ct}$ and $Q_{dl}$ represent the charge-transfer resistance and the double-layer capacitance of the electrode–electrolyte interface, respectively. Due to the heterogeneousness on the surface of the electrodes, the double layer does not behave as an ideal capacitor, and thus, the constant phase element (CPE) is frequently used as a substitute for the capacitor in an equivalent circuit to fit the impedance behavior of the electrical double layer more accurately. The impedance ($Z_{\text{CPE}}$) and capacitance ($C_{\text{CPE}}$) of the CPE are defined as follows:

\[
Z_{\text{CPE}} = (Y_0(j\omega)^n)^{-1} \quad (5)
\]
\[
C_{\text{CPE}} = (Y_0\omega_m^{-n+1})/\sin(n\pi/2) \quad (6)
\]

where $Y_0$ is the magnitude of the CPE and $n$ is defined as the phenomenological coefficient which indicates the deviated degree of the capacitance from the ideal condition. The parameter $\omega_m$ is the frequency at which the phase angle is at a maximum. According to the above proposed equivalent circuit and the definitions of eqns (5) and (6), the series resistance ($R_s$), the values of $R_{ct}$, $R_{ct}$, the capacitance of the CPE, $Y_0$, and $n$ could be obtained, as listed in Table 1. Compared to the values of $R_{ct}$, the values of $R_s$ are very small and all of them are less than $10$ $\Omega$, indicating the $R_{ct}$ is the most important influencing factor for the catalytic activity of the CEs. It is apparent that the value of $R_{ct}$ of the Co$_9$S$_8$@CF hybrid electrode (95.8 $\Omega$) is much smaller than that of the Pt (3548 $\Omega$) and pure CF electrodes (4862 $\Omega$). The lower $R_{ct}$ indicates that the charge transfer became more effective at the electrolyte–CE interface, thus resulting in the acceleration of $S_x^{2-}$ reduction by the CEs. Consequently, the CE with a lower $R_{ct}$ value indicates a higher catalytic activity for $S_x^{2-}$ reduction. According to the previous works, the lower $R_{ct}$ value could provide a higher FF value when the electrode is applied in QDSSCs, and the tendency of the $R_{ct}$ totally agrees with the tendency of the FF as listed in Table 1.

The Tafel polarization curves are also usually adapted to study the electrocatalytic activity of the CEs for QDSSCs by studying the extrapolated intercepts of the anodic and cathodic branches. Fig. 7b presents the Tafel curves of the three different symmetrical cells, from which it is apparent that the value of the intercept of the anodic and cathodic branches for the Co$_9$S$_8$@CF hybrid CEs is much larger than those for the other two. It is well known

<table>
<thead>
<tr>
<th>CEs</th>
<th>$R_s$ ((\Omega) cm$^2$)</th>
<th>$Y_0$ (10$^{-5}$ F cm$^{-2}$ S$^{-1}$)</th>
<th>$n$</th>
<th>$C_{\text{CPE}}$ ((\mu F))</th>
<th>$R_{ct}$ (k(\Omega) cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
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<tbody>
<tr>
<td>Pt</td>
<td>2.957</td>
<td>1.301</td>
<td>0.8842</td>
<td>279.3</td>
<td>3.548</td>
<td>0.40</td>
<td>10.55</td>
<td>0.38</td>
<td>1.65</td>
</tr>
<tr>
<td>CF</td>
<td>5.997</td>
<td>2.217</td>
<td>0.8753</td>
<td>520.3</td>
<td>4.862</td>
<td>0.48</td>
<td>3.66</td>
<td>0.26</td>
<td>0.46</td>
</tr>
<tr>
<td>Co$_9$S$_8$@CF</td>
<td>8.232</td>
<td>22.31</td>
<td>0.5683</td>
<td>690.6</td>
<td>0.0958</td>
<td>0.37</td>
<td>17.95</td>
<td>0.57</td>
<td>3.79</td>
</tr>
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</table>
that the extrapolated intercepts of the anodic and cathodic branches can be used to estimate the value of the exchange current density \( J_0 \), and \( J_0 \) can also be evaluated by the equation of \( J_0 = R T n F R_{ct} \), where \( R \) is the gas constant, \( T \) is the temperature, \( F \) is the Faraday constant, and \( n \) is the number of electrons exchanged in the reaction at the electrolyte interface. This is to say, the \( R_{ct} \) is inversely proportional to \( J_0 \) and the lower \( R_{ct} \) and higher \( J_0 \) could provide a higher electrocatalytic activity of the CEs. It can be observed from Table 1 that the tendencies of \( R_{ct} J_0 \) and FF totally agree with each other.

**Conclusion**

In summary, we have developed an innovative and cost-effective approach to fabricate the Co\(_9\)S\(_8\) NTs@CFs hybrid CE for enhancing the performance of QDSSCs. The first step involves the direct growth of dense single-crystal Co\((CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}\) NWs on the CEs using a facile hydrothermal method. The second is to transform the Co\((CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}\) NWs into Co\(_9\)S\(_8\) NTs in Na\(_2\)S aqueous solution. Compared to the traditional CEs of CFs and Pt, the Co\(_9\)S\(_8\)@CFs electrode shows a much higher charge exchange in the reaction at the electrolyte interface, that is to say, the Co\(_9\)S\(_8\) NWs can be used to estimate the value of the exchange current density (\( J_0 \)).

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**Notes and references**