Fabrication of Cu$_{1.8}$S/CuS nanoplates counter electrode via alternating current etching for quantum dots-sensitized solar cells

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We demonstrate a method for fabricating a Cu$_{1.8}$S/CuS nanoplate counter electrode (CE) via the alternating current (AC) etching of brass. The photoelectrochemical performance and electrocatalytic properties of Cu$_{1.8}$S/CuS CE with a η value of 3.22% are much higher than those of Pt and conventional Cu$_2$S CEs. Furthermore, it offers a simple and low-cost method for producing Cu$_S$ counter electrodes in the future.

1. Introduction

In the past few years, quantum dot-sensitized solar cells (QDSCs) have attracted considerable attention. QDSCs have emerged as a promising candidate for the development of next generation solar cells because of their acceptable power conversion efficiency, ease of fabrication, and low production cost. QDSCs are based on the photosensitization of wide band gap semiconductor photoanodes (TiO$_2$, ZnO, SnO$_2$, etc.) with quantum dots (QDs) (such as CdS, CdSe, and PbS [ref. 5 and 6]), which make it possible to tune the absorption threshold by choosing the dot diameter, provide high luminescence efficiency and more stability than dyes.

The counter electrode (CE) is a critical component in QDSCs, where electrons are injected into a polysulfide electrolyte. In DSSCs, Pt is usually used as the CE owing to its stability and high catalytic activity for the reduction of I$_3^-$, $\text{I}_2$. However, Pt is not very catalytic in a polysulfide electrolyte. This is because the sulfur present in the polysulfide electrolyte chemisorb on platinum surfaces and induce poisoning effects toward the electrode performance, which results in low fill factors and conversion efficiency.

In order to increase the efficiency of QDSCs, metal sulfides, such as cobalt sulfide (CoS)$_x$, iron sulfide, lead sulfide (PbS), nickel sulfide (NiS)$_x$, Cu$_2$ZnSnS$_4$, and copper sulfide (Cu$_S$ and CuS) have been employed as efficient CEs in the fabrication of QDSCs containing polysulfide electrolyte as a redox couple. Among them, Cu$_S$ and CuS have been most commonly and efficiently used as CEs for QDSCs in recent years. Most recently reported Cu$_S$ CEs are made by exposing the Cu metal to a sulfide solution. The black Cu$_S$ film is easy to peel off from the Cu substrate, but the tendency of a continual reaction with a polysulfide electrolyte on a Cu substrate is the serious drawback of this method, which may make Cu$_S$ CE unstable. Other methods of fabricating Cu$_S$ or CuS include chemical bath deposition and hydrothermal methods. The advantage of using these methods could be used to prepare pure Cu$_S$ or CuS with fewer crystal defects, but these methods need high-level equipment, high experimental conditions and complex processes. Furthermore, these methods using FTO as a carrier may decrease the interfacial binding force between FTO and the film. The adhesion intensity of the electrocatalytic active materials on the FTO substrate were as the counter electrode is a very important factor for determining the η of QDSCs. If the materials cannot stick to the FTO substrate, they may be released into the electrolyte, which depresses the stability of CE and solar cells.

In the present study, we developed a new method via AC etching of brass to obtain a Cu$_{1.8}$S/CuS nanoplate CE on a Cu micro-nanostructure. A Cu$_{1.8}$S/CuS film by an in situ reaction was synthesized based on the Cu micro-nanostructure that could allow an effective control of the surface morphology and film thickness through AC etching. It is obvious that the large specific surface areas of Cu$_{1.8}$S/CuS nanoplates improve the electrocatalytic activity for the polysulfide electrolyte. The interfacial binding force and conductivity of the Cu$_{1.8}$S/CuS film on the brass substrate are obviously superior to a Cu$_S$ film on FTO. At the same time, AC etching is simple to operate, uses less equipment and is low-cost. In addition, the photoelectrochemical performance of Cu$_{1.8}$S/CuS CE is much higher than Pt and Cu$_S$.

2. Experimental section

2.1. Preparation

2.1.1. Preparation of Cu$_{1.8}$S/CuS counter electrode. Brass was used as the substrate and a polysulfide electrolyte (the aqueous solution of 2 M Na$_2$S and 3 M S) was used as the reaction solution. First, brass plates containing 64 wt% Cu
36 wt% Zn were ultrasonically cleaned in acetone and deionized water in sequence. They were then mechanically polished by 180# water proof emery paper and rinsed thoroughly with deionized water. Moreover, two polished brass plates were dipped in a 5 M phosphoric acid (A.R.) solution as electrodes. An AC voltage (20 V and 50 Hz) was applied to the two electrodes for different durations. After rinsing with deionized water and ethanol, the etched brass plates were dipped in a polysulfide electrolyte for 5 min.

2.1.2. Preparation of photoelectrode. P25 TiO2 nanoparticles were used to prepare a photoelectrode using the doctor-blade technique.19 and the thickness of the TiO2 porous film was about 11–12 μm. After that, the TiO2 porous films were sintered at 450 °C for 30 min. The TiO2 porous films were then successively dipped in 0.5 M Cd(NO3)2–methanol for 5 min, rinsed with methanol, dipped in an aqueous solution of 0.5 M Na2S for 5 min and the SILAR cycle was repeated 3 times at room temperature. The TiO2/CdS electrodes were dipped in 0.5 M Cd(NO3)2–methanol for 5 min at room temperature, rinsed with deionized water and then immersed in an aqueous solution of Na2SeSO3 for 1 h at 50 °C. Finally, the TiO2/CdS/CdSe electrodes were dipped in the ethanol solution of 0.5 M Zn(NO3)2 for 5 min, rinsed with deionized water, dried with an drier, and then dipped in an aqueous solution of 0.5 M Na2S for 5 min.12

Sulphur sublimed (A.R.), sodium sulfide (A.R. Na2S–9H2O) and polyethylene glycol (M.W. 20 000) were purchased from Beijing Yili Fine Chemicals Co., Ltd (China). Selenium powders (A.R.) and ethanol were supplied by Beijing Chemical Works (China). Cadmium nitrate (A.R. Cd(NO3)2–4H2O), sodium sulfite (A.R. Na2S–9H2O) and zinc nitrate (A.R. Zn(NO3)2–6H2O) were purchased from Tianjin Jinke Fine Chemicals Co., Ltd (China).

2.2. Characterization
The surface morphology and composition of the samples were evaluated by scanning electron microscopy (SEM, JSM-6010LA) equipped with an EDS system and transmission electron microscopy (TEM, F20) equipped with an energy dispersive X-ray (EDX) spectroscopy system. Atomic force microscopy (AFM, Veeco DI, USA) was used to measure the surface roughness. The X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku D/MAX-RB diffractometer with monochromatized Cu Kα radiation (λ = 1.5418) at a scan rate of 6° min−1. The digital photographs were obtained using a digital camera (Olympus E-PL1, Japan).

The photocurrent–voltage (J–V) of the QDSCs was recorded under illumination with a xenon lamp (500 W). The illumination intensity was 100 mW cm−2 and the range of wavelengths was 380–700 nm. A two-electrode photoelectrochemical cell was constructed and the electrolyte was an aqueous solution containing 2 M Na2S and 3 M S.19 A CHI 600A electrochemical analyzer was applied to record the J–V curves under illumination with an active area of 1 cm2.

Electrochemical impedance spectra (EIS) and Tafel polarization measurements with a scan rate of 10 mV s−1 were conducted in a symmetrical dummy cell fabricated with two identical CEs using a CHI 600A electrochemical analyzer in dark. The measured frequency for EIS ranged from 10 mHz to 1 MHz and the amplitude was set to 10 mV. The spectra were fitted by ZSimpWin software.

3. Results and discussion
Fig. 1 illustrates the preparation of Cu1.8S/CuS CE. First, we obtain the Cu micro-nanostructure through AC etching of brass. In this progress, zinc strips from the surface of the brass and can form a porous structure, which clearly increases the specific surface area. The etched brass is then dipped in polysulfide electrolyte for 5 min and we obtain the CE with nanopolates.

SEM was used to evaluate the surface morphology of the samples at different preparation stages. Fig. 2(A–C) shows the digital photographs of the bare, etched and sulfurized brass, respectively. It can be readily indicated that bare brass becomes red after AC etching and becomes black after immersion in a polysulfide electrolyte. Furthermore, the black film on the brass is stable after a long period of time.

Before etching, brass has a coarse morphology with many obvious scratches due to mechanical polishing [Fig. 2(a)]. After etching for a period of time, the etched brass presents a hierarchical microstructure with a pinecone-like morphology [Fig. 2(b)]. When the etched brass plates are immersed in the polysulfide electrolyte, nanoplates can be observed on the sulfurized brass [Fig. 2(c)]. At higher magnification, we can clearly see nanoplates with a scaly structure. In Fig. 2(D), the film layer structures are not evenly distributed and there are many large pores. Fig. 2(E) indicates that the thickness of the black film is about 4–7 μm.

To study the growth process from a pinecone-like morphology to a nanoplate morphology, different morphologies were obtained after different growth times, as shown in Fig. 3. After immersing for 1 s, the original pinecone-like morphology changed and some needle-like whiskers emerged. By extending the immersion duration to 30 s, the buds bloomed like flowers and the nanoplate structure appeared. As immersion was further extended to 5 min, as shown in Fig. 3(d), a typical nanoplate morphology was formed. The nanoplate structure changed slightly after the immersion duration was extended to 1 h.

Fig. 4 shows XRD patterns of the samples at different preparing stages. The peaks at 42.3°, 49.3°, 72.2° and 87.5° correspond to the diffraction peaks of Cu1.8S/Zn0.36 (JCPDS no. 121–41–40).
50-1333), respectively. After AC etching, new peaks corresponding to the diffraction peaks of Cu (JCPDS no. 04-0836) appeared at 43.3°, 50.4° and 74.1° 2θ, indicating that the surface of the sample is mainly composed of Cu after AC etching.

It is known that when brass is in a corrosive medium, it is prone to “dezincification”, which means that zinc can be preferentially released because zinc is more active than copper. Corrosion can be accelerated when brass plates are immersed in the phosphoric acid solution and under an AC voltage. Under an AC voltage, each brass plate can alternately be an anode and cathode. The instant electrode reactions are shown below:

Instant anode: \( \text{Zn} \rightarrow 2e^- + \text{Zn}^{2+} \)

Instant cathode: \( 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \uparrow \)

The formation of Cu micro-nanostructure is attributed to the interaction of the AC electric field with the anode and cathode. Fig. 4 clearly shows that the sulfurized brass has the peaks for Cu\(_{7.2}\)S\(_4\) (JCPDS no. 24-0061) and CuS (JCPDS no. 06-0464).

Furthermore, the black film was removed from the brass substrate, powered and then deposited on a TEM nickel grid. The resulting HRTEM images are shown in Fig. 5. The observed lattice spacing of 0.304 nm and 0.321 nm correspond to the (102) plane of CuS and the (111) plane of Cu\(_{1.8}\)S, respectively. Both the HRTEM image and XRD pattern confirm that the black film is composed of Cu\(_{1.8}\)S and CuS.

To evaluate the performance of Cu\(_{1.8}\)S/CuS as the CE of QDSCs, we employed TiO\(_2\)/CdS/CdSe/ZnS as the photoelectrode. The \( J-V \) curves of different counter electrodes were recorded, and are shown in Fig. 6. A Pt sheet was used as the Pt CE, while a Cu\(_2\)S CE was prepared by immersing a pure Cu sheet in a polysulfide electrolyte for 5 min. The values of \( J_{sc}, V_{oc}, \text{ff}, \) and \( \eta \) calculated from \( J-V \) curves are listed in Table 1.
In Fig. 6(A), QDSCs based on Pt CE show very low photo-electrochemical performance with a $\eta$ of about 0.63%. The low performance of Pt CE is due to the very low catalytic property of Pt in a polysulfide electrolyte, resulting from the strong absorption of $S_{2}/S_{0}$ on the surface, which reduces the surface activity of Pt.24 As a result, a really low $ff$ (0.33) is achieved by QDSCs based on Pt CE. Cu$_{2}$S CE is well known to exhibit high electrocatalytic activity in a polysulfide solution, which improves the $ff$ and $\eta$ of QDSCs.10,12,13,19 Here, using Cu$_{2}$S as a CE boosts the $ff$ and $\eta$ to about 0.41 and 1.43%. For Cu$_{1.8}$S/CuS, it is interesting to find its $\eta$ (3.22%) is much higher than that of Cu$_{2}$S CE. The root-mean-square roughness ($R_{ms}$) values determined from the atomic force microscope (AFM) topography images were 189 nm (Cu$_{2}$S) and 229 nm (Cu$_{1.8}$S/CuS). Therefore, Cu$_{1.8}$S/CuS nanoplates show a larger specific surface area than Cu$_{2}$S based on $R_{ms}$ and AFM images [Fig. 6(C and D)]. These results imply that charge-transfer resistance at the electrode/electrolyte interface would be lower in the case of Cu$_{1.8}$S/CuS CE, because this CE would have more electrocatalytic active sites for the reaction of the polysulfide ($S^{2-}/S_{0}^{2-}$) redox couple in the electrolyte.27 In Fig. 6(B), the values of $V_{oc}$, $J_{sc}$ and $\eta$ were obtained from the $J$–$V$ curves every three hours. After 30 h, the photovoltaic parameters, $J_{sc}$, $V_{oc}$, and $\eta$, were 13.98 mA cm$^{-2}$, 0.49 V and 3.07%, respectively, indicating that $J_{sc}$, $V_{oc}$ and $\eta$ values retained 96%, 88% and 95% of their initial values. The decay of $V_{oc}$ was much more significant. This is because the film of the

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<th>CE</th>
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<th>$J_{sc}$</th>
<th>$ff$</th>
<th>$\eta$</th>
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**Table 1** Parameters calculated from the $J$–$V$ curves of the QDSCs based on different CEs.
photoanode gradual fell off from ITO during in the polysulfide electrolyte. Compared with the reported Cu$_2$S CEs (Table 1), Cu$_{1.88}$/CuS CE exhibits excellent photoelectrochemical performance that is close to RGO-Cu$_2$S CE (nanoplate morphology). Therefore, the J–V results suggest that Cu$_{1.88}$/CuS exhibits excellent electrocatalytic activity for the polysulfide electrolyte and is suitable as the efficient CE of QDSCs.

Besides the immersion time in a polysulfide electrolyte, the AC etching voltage is another important parameter that has a significant influence on the characteristics of the Cu$_{1.88}$/CuS. As seen in Fig. 7, the surface of brass has not undergone complete dezincification to fabricate Cu micro-nanostructures at a lower voltage. With the increasing voltage, the reaction rate increases rapidly and Cu nanoparticles start to aggregate (Fig. 7(E)). Therefore, the brass surface cannot fabricate Cu micro-nanostructure with a higher or lower voltage. Besides the immersion time in a polysulfide electrolyte, the AC etching voltage is another important parameter that has a significant influence on the characteristics of the Cu$_{1.88}$/CuS. As seen in Fig. 7, the surface of brass has not undergone complete dezincification to fabricate Cu micro-nanostructures at a lower voltage. With the increasing voltage, the reaction rate increases rapidly and Cu nanoparticles start to aggregate (Fig. 7(E)). Therefore, the brass surface cannot fabricate Cu micro-nanostructure with a higher or lower voltage.

EIS was used to investigate the charge transfer resistance ($R_{ct}$), which is related to the electrocatalytic activity of the different CEs. Fig. 8(A) shows Nyquist plots of the QDSCs using Cu$_{1.88}$/CuS, Cu$_2$S and Pt CEs. The charge transfer resistance, $R_{ct}$, corresponding to charge exchange between the different counter electrodes and the polysulfide electrolyte is derived from the semicircles in the Nyquist plots. For Pt, $R_{ct}$ is very large, about 3212 Ω, demonstrating sluggish kinetics. This is further attested by no evident diffusion component in the Nyquist plot. $R_{ct}$ for Cu$_2$S is about 43.05 Ω, which is much smaller than that for Pt. In addition, Cu$_{1.88}$/CuS exhibits a smaller value of 5.18 Ω. Note that an efficient QDSSC usually exhibits a low $R_{ct}$ value. From the $J$–$V$ and Table 1, the electrocatalytic activity in polysulfide electrolyte are in the order, Cu$_{1.88}$/CuS > Cu$_2$S > Pt, which is consistent with the $R_{ct}$ results obtained from EIS. The inset in Fig. 8(A) shows that $R_{ct}$ for Pt is 3.52 Ω, which is much larger than that for Cu$_2$S ($R_{ct}$ = 2.82 Ω) and Cu$_{1.88}$/CuS ($R_{ct}$ = 1.23 Ω). QDSC with an electrode with a greater $R_{ct}$ value provides smaller $J_{sc}$ values. From Table 1, Cu$_{1.88}$/CuS exhibited a $J_{sc}$ value of 14.50 mA cm$^{-2}$, which was much larger than the Pt CE (4.40 mA cm$^{-2}$) and Cu$_2$S CE (8.13 mA cm$^{-2}$). These results prove that the smaller $R_{ct}$ and $R_{s}$ of Cu$_{1.88}$/CuS CE show lower charge transfer resistance and superior electrocatalytic activity.

Based on the EIS results, it should be expected that Cu$_{1.88}$/CuS exhibits much higher photoelectrochemical performance than Pt and Cu$_2$S. Therefore, theoretical calculations and Tafel polarization measurements were further carried out in the dummy cell used in the EIS experiments to prove this. It is known that the exchange current density ($J_0$), which is equal to $J_0 = RT/nF$ce,$^{36}$ is directly related to the electrochemical catalytic activity of the electrode, where $R$ is the gas constant, $T$ is the absolute temperature in K, $n$ is the number of electrons involved in the electrochemical reduction reaction, $F$ is the Faraday constant, and $R_{ct}$ is the charge transfer resistance. $^{31}$ From EIS, $R_{ct}$ are in a consistent order of Cu$_{1.88}$/CuS < Cu$_2$S < Pt, so we can obtain the exchange current density ($J_0$) in a consistent order of Pt < Cu$_2$S < Cu$_{1.88}$/CuS by theoretical calculations. At the same time, Fig. 8(B) shows the logarithmic current density (log $J$) as a function of the voltage ($V$) for the oxidation/reduction of the $S^{2-}$/S$_2^2$ couple. The exchange current densities ($J_0$), which can be estimated from the extrapolated intercepts of the cathodic branches of the corresponding Tafel plots, are in a consistent order of Pt < Cu$_2$S < Cu$_{1.88}$/CuS. These results confirm that electroactive materials with a higher exchange current density

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**Fig. 7** SEM images at different etching voltages (A) 10 V, (B) 15 V, (C) 20 V, (D) 25 V, (E) 25 V and (F) J–V curves obtained based on different voltages.
require a lower activation energy, and it is much easier for Cu$_{1.8}$S/CuS to catalyze the reduction of S$^2^-$/S$^0$. The electrochemical performance of QDSCs and Tafel polarization show good consistency with the corresponding photovoltaic performance of QDSC devices based on different CEs, in which the QDSCs based on Cu$_{1.8}$S/CuS CE shows the highest performance.

4. Conclusion

In this study, we demonstrated that Cu$_{1.8}$S/CuS as CE exhibits excellent electrochemical catalyze activity and remarkable stability in catalyzing the reduction of S$^2^-$/S$^0$. The electrochemical performance of QDSCs based on Cu$_{1.8}$S/CuS CE (ff = 0.41 and $\eta = 3.22\%$) was much higher than that of Pt and Cu$_2$S CEs. At the same time, it is a simple and efficient method for fabricating nanoplates based on the Cu micro-nanostructure by the AC etching of brass. Our results show that the Cu$_{1.8}$S/CuS CE can be suitable for replacing the most expensive Pt CE and other copper sulfide electrodes derived from copper and brass sheets.

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