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Screen-printed Cu_2S-based Counter Electrode for Quantum-dot-sensitized Solar Cell

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Cu_2S-based counter electrodes screen-printed on different substrates for CdS/CdSe quantum-dot-sensitized solar cells are reported. The photovoltaic conversion efficiency of 3.71% was obtained with Cu_2S counter electrode deposited on conductive substrate due to low charge-transfer resistance. By addition of conductive carbon material, a cell with Cu_2S/C composite counter electrode screen-printed on insulated glass substrate displayed an efficiency of 3.37%. These results showed the potential application of such Cu_2S-based counter electrode for large-scale quantum-dot-sensitized solar cells in the future.

In recent years, quantum-dot-sensitized solar cells (QDSCs) have attracted great attention due to the remarkable merits of quantum dots (QDs).[1] QDSC usually adopts a sandwich structure consisting of three parts: the photoanode decorated with QDs, the counter electrode (CE), and the electrolyte between two electrodes. Up to now, QDSC research is still under development, and much efforts focus on how to improve the assembly of QDs onto the TiO_2.[1] In fact, CE is an equally important part of QDSC, which is responsible for electron transfer from the external circuit back to the redox electrolyte and catalyzing the reduction reaction of the S_x^{2-} species in the electrolyte.[2,3] In order to further improve the cell performance of QDSC, intense investigations have been devoted to CEs, including seeking new catalytic materials and various substrates.[2–4] Besides Pt CE,[2,3] Au,[2] carbon,[3,4] and Cu_2S[5,6] CEs have also been studied. Among all these materials, Cu_2S exhibits relatively high electrocatalytic activity toward polysulfide redox system (S_2^{-}/S_x^{2-}).[5–7] Researchers have attempted in situ-prepared Cu_2S CEs on brass sheet[5] and flexible graphite paper,[6] and good photovoltaic performance of QDSCs was obtained. However, these in situ-prepared CEs are still unsatisfactory for their utilization, especially cell sealing and the application for large-scale QDSCs. Therefore, an innovative strategy for highly efficient and easily fabricated Cu_2S counter electrodes is in urgent need now.

In this study, we developed screen-printable Cu_2S-based pastes to fabricate counter electrodes for CdS/CdSe quantum-dot-sensitized solar cells. Furthermore, by combining the conductive carbon material, the electric conductivity of Cu_2S film has been improved so that the F-doped SnO_2 conducting glass (FTO) substrate can be replaced by insulated glass, and the Cu_2S/C composite counter electrode can still perform well in QDSC.

The 10-μm thick nanoporous TiO_2 films (Degussa, P25) were deposited on FTO (15 Ω/sq) by screen-printing. The CdS/CdSe quantum dot decoration on TiO_2 film was realized by a chemical bath with detailed description elsewhere.[8,9] After QDs fabrication, surface passivation with ZnS was conducted twice by following the literature.[9,10] Polysulfide electrolyte in aqueous solution of Na_2S (1M) and S (2M) was used as redox agent. Cu_2S paste for CE was prepared as follows. First, 0.01 mol of $Cu(NO_3)_2$ was dissolved in 50 mL of diethylene glycol (DEG) solution by vigorous stirring and heated up to 180 °C. Then, 0.005 mol of thioacetamide in 20 mL of DEG was added drop by drop, and the mixture was kept stirring at this temperature for 3 h.[11] After cooling down to room temperature, the Cu_2S precipitate was centrifuged, washed with ethanol three times, and finally dried at 60 °C in vacuum. 0.5 g of the as-prepared Cu_2S powder was ball-milled with 5 mL of terpineol, 0.1 g of ethyl cellulose, and 0.3 mL of titanium isopropoxide for 8 h to afford the paste. The paste was coated on FTO to give Cu_2S film by screen-printing. The film was dried at 80 °C, and then it was sintered at 400 °C for 20 min to get the Cu_2S CE (thickness 7 μm). For the composite Cu_2S/C CE, carbon powder (hybrid of graphite and carbon black, weight ratio 9:1) was dispersed in DEG in the first step before $Cu(NO_3)_2$ was added, and the following procedures were the same. To assemble a cell, electrolytes were placed on the sensitized photoanode, and counter electrode was clipped firmly to make a sandwich structure QDSC. A 50-μm silicone film was used as a spacer between two electrodes. The active area of the cell was 0.15 cm^2.

Figure 1 illustrates the XRD (M18X-AHF, MAC Science) pattern of synthesized Cu_2S sample. The peaks of corresponding crystal planes are indexed in the figure, matching to the cubic phase Cu_2S (JCPDS card No. 84-1770). The SEM (FEI, XL30 S-FEG) images of Cu_2S counter electrode are shown in Figures 2a–2c with increasing magnifications. Obviously, the

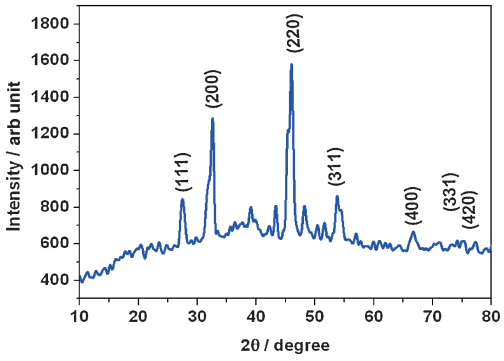


Figure 1. XRD pattern of synthesized Cu_2S powder.

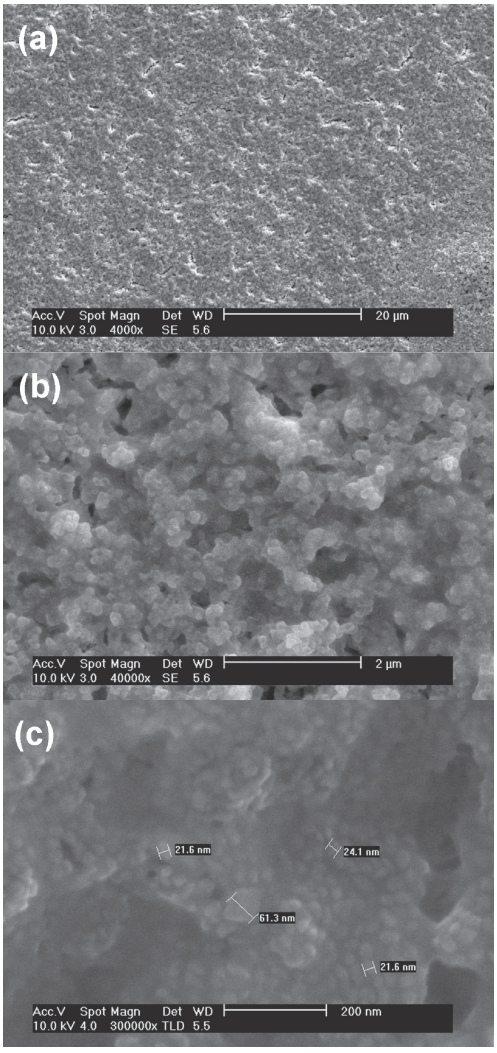


Figure 2. The SEM images of the surface of Cu_2S film on FTO counter electrode with increased magnifications.

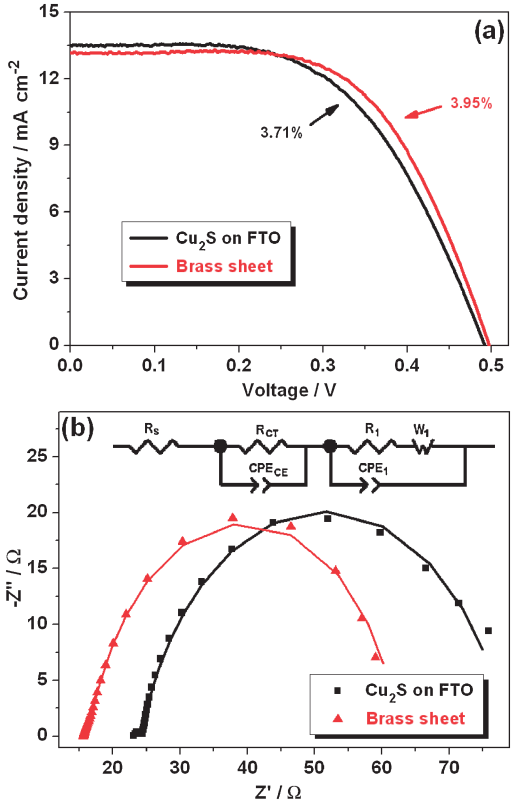
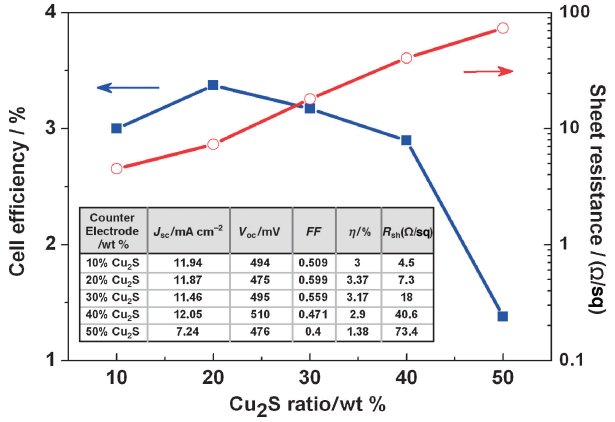


Figure 3. (a) *I–V* characteristics for QDSCs with two kinds of counter electrodes under illumination of AM1.5. (b) Nyquist plots (scattered) and their fitting results (line) of QDSCs with two kinds of counter electrodes under bias of V_{oc} (under illumination of AM1.5). The inset shows the equivalent circuit. R_{CT} and R_1 represent the charge-transfer resistance at counter electrode and photoanode, respectively; CPE_{CE} and CPE_1 describe the constant phase element at these two electrodes, respectively; W accounts for finite-length Warburg diffusion; and R_s is the series resistance in the cell.

electrode surface was smooth in a large area in Figure 2a, guaranteeing the uniformity of film thickness. Magnified image of the morphology revealed the microstructure of the Cu_2S film. The noticeable feature of the microstructure was the large number of nanoscale holes between the Cu_2S submicrometer particles in the film, which would enlarge the effective surface area for charge exchanging. Amazingly, deeper observation proved that the Cu_2S particles themselves were covered with numerous 20 nm-sized nanocrystals on the surface. Such kind of a structure would further increase the surface area of the Cu_2S film, which was advantageous for the reduction reaction at the CE.

Two kinds of CEs were used in the *I–V* test (Princeton Applied Research, Model 263A) to compare their performance: Cu_2S film on FTO and the in situ-prepared Cu_2S on brass sheet, and the results are shown in Figure 3a. For FTO group, the photovoltaic conversion efficiency (η) was 3.71%, with 13.52 mA cm^{-2} of photocurrent density (J_{sc}), 492 mV of open circuit voltage (V_{oc}), and 0.558 of fill factor (*FF*). In comparison, QDSC with brass sheet CE obtained J_{sc} of 13.16 mA cm^{-2}, V_{oc} of 497 mV, *FF* of 0.603, and η of 3.95%. Apparently, the performances of these two CEs were very similar, and the slight difference in *FF* probably originated from the distinction of substrate conductivity. The Nyquist plots (Zahner, IM6ex) of electrochemical impedance spectroscopy (EIS) in Figure 3b confirmed this. By the equivalent circuit simulation, the calculated values of R_s were 23.27 and 15.56 Ω for QDSC with FTO and brass sheet substrate, respectively. On the other hand, the charge-transfer resistances (R_{CT}) were 0.133 and 0.254 Ω cm^2 for FTO and brass group, respectively. The low R_{CT} values further proved the excellent activity of these two electrodes, which means that Cu_2S was the ideal candidate material for the QDSC counter electrode.

Furthermore, Cu_2S/C composite CEs were deposited on insulated glass substrate to replace the expensive FTO. Figure 4 showed the QDSC performance with such composite CEs (film thickness 13 µm) of different Cu_2S weight percentage and the film sheet resistance (R_{sh}). By optimizing the Cu_2S and carbon powder weight ratio, premium result of 3.37% for η was obtained for this novel QDSC with TCO-free counter electrode of 20 wt % Cu_2S. These results here proved that the substitution



Counter Electrode /wt %	J_{sc}/mA cm^{-2}	V_{oc}/mV	FF	η/%	R_{sh}(Ω/sq)
10% Cu_2S	11.94	494	0.509	3	4.5
20% Cu_2S	11.87	475	0.599	3.37	7.3
30% Cu_2S	11.46	495	0.559	3.17	18
40% Cu_2S	12.05	510	0.471	2.9	40.6
50% Cu_2S	7.24	476	0.4	1.38	73.4

Figure 4. Cell performance of QDSCs using a series of counter electrodes deposited on insulated glass substrate and their sheet resistance (R_{sh}).

Table 1. The sealed cell efficiency on day 0 and day 7

	Efficiency/%						
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Day 0	3.26	3.27	2.44	3.23	3.58	3.37	3.21
Day 7	3.01	2.75	2.08	2.46	2.99	2.72	2.68
Ratio	0.923	0.842	0.853	0.759	0.836	0.809	0.835

of TCO with bifunctional Cu_2S/C composite was feasible in application. Meanwhile, it was also worth noting that the ingredient percentage was important because the relationship between conductivity and catalytical activity was a trade-off in such a composite CE. Thus, in order to maximize the cell efficiency, cautions must be taken to balance these two properties.

As to the stability of the Cu_2S counter electrode, our preliminary results in Table 1 (Ratio = efficiency(day7)/efficiency(day0)) indicate that the Surlyn®-sealed cells are basically stable for a week time (at room temperature without light soaking). Further stability tests, such as light soaking and relatively high temperature test, will be clarified in the future.

In conclusion, we fabricated a screen-printable Cu_2S-based counter electrode for quantum-dot-sensitized solar cells. The photovoltaic conversion efficiency of 3.71% was obtained with FTO substrate. Significantly, by adding the conductive carbon material, Cu_2S/C composite counter electrode can be deposited on insulated substrate without FTO, indicating the potential application of this novel TCO-free counter electrode for low-cost large-scale QDSC.

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