

# Stability of CdS-coated TiO<sub>2</sub> solar cells

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**Abstract** The obstacle to realize the large-scale production of dye-sensitized solar cells (DSSCs) is its long-term stability and reliability problem. One of the main causes of the instability of DSSCs is the use of liquid electrolytes. In addition, exploring nano-sized particles of CdS as an alternative sensitizer for organic dye in dye-sensitized solar cells have attracted great interest due to the high cost and the instability of the organic dye. Our study has found that the CdS-coated TiO<sub>2</sub> cell degrades rapidly in the liquid electrolytes even under dark environment. In this work, a solid-state solar cell structure of Glass/FTO/TiO<sub>2</sub>/CdS:Cu/FTO/glass was successfully made with an efficiency of 0.7%. CdS:Cu served as both the p-type conductor and absorber. No efficiency was obtained for cell structures of glass/FTO/TiO<sub>2</sub>/CdS/FTO/glass. This indicates the effectiveness of hole conducting behavior of CdS:Cu. This is the first time that this type of solid-state solar cell is reported and improved stability is demonstrated.

**Keywords** Dye-sensitized solar cell · Solid state · CdS · Stability

## Introduction

Dye-sensitized solar cell (DSSC) has been widely studied in the past 10 years because of its low cost and potential high energy conversion efficiency. The highest energy conversion efficiency obtained is 11.5% (2009) under AM

1.5 G simulated sunlight made from mesoporous TiO<sub>2</sub> films absorbed ruthenium dye and I<sub>3</sub><sup>-</sup>/I<sup>-</sup> liquid electrolytes [1]. However, the use of organic dye and liquid electrolytes has been the grand challenge in the long-term stability of the DSSC technology. A few solid-state inorganic p-type semiconductors were used as hole collectors to replace liquid electrolytes, such as CuI [2, 3], CuBr [4], CuSCN [5, 6], NiO [7] and CuAlO<sub>2</sub> [7], but their efficiency is very poor despite their good pore filling. The main reason is that the conductivity of these p-type conductors is low [8–10]. p-type Cu-doped CdS was made with simple chemical bath method with good conductivity (2 S/cm) in 1993 [11] and has been demonstrated on the homojunction CdS/CdS:Cu diode. CdS:Cu is a better p-type conductor than CuI ( $\sigma_H \sim 0.01 \text{ S cm}^{-1}$ ), and its crystal size can be as small as nanosize which will provide good pore filling. In addition, semiconductors such as CdS [12–14], CdSe [15], PbS [16] have been used to replace the expensive organic dyes as alternative sensitizers. CdS is one of the most commonly used alternative sensitizers due to its several advantages. For example, its optical properties and the band gap can be adjusted by the particle size [17]; it has better UV stability than organic dyes [18] and it has reduced dark current [19]. However, the current efficiency of CdS-sensitized solar cell is still low. The highest efficiency of CdS-sensitized TiO<sub>2</sub> solar cell is 1.84% [17, 20, 21] and the cell is very unstable. In addition, the authors did not report the efficiency of any control sample. The CdS-sensitized cell efficiency can be improved to 2.8% [22] by adding CdSe. However, adding CdSe complicates the sensitizing process. The poor cell efficiency and its instability in I<sub>3</sub><sup>-</sup>/I<sup>-</sup> electrolytes have limited the application of CdS in DSSC solar cells. Researchers have attributed the low efficiency to the poor pore penetration of CdS into TiO<sub>2</sub> or ZnO network [23, 24]. In this work, a CdS process is developed and achieved a solar cell efficiency of

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2.46% ( $V_{oc}=0.69$  V,  $J_{sc}=6.54$  mA/cm<sup>2</sup>, F.F.=0.55). This is the highest reported efficiency of using CdS alone as sensitizer (active area of 0.16 cm<sup>2</sup> under AM 1.5). This process can be easily modified to achieve p-type Cu-doped CdS (CdS:Cu) which allows the manufacturing of a simple solid-state CdS-coated nanocrystalline TiO<sub>2</sub> solar cells. A solid-state solar cell structure of Glass/FTO/TiO<sub>2</sub>/CdS:Cu/FTO/glass was successfully made with an efficiency of 0.7%. Compared to the solid-state DSSCs made from CuI [2, 3], CuBr [4], CuSCN [5, 6], NiO [7], and CuAlO<sub>2</sub> [7], this type of solar cell has very simple controllable structure and does not use the expensive dye and Pt catalyst. The CdS:Cu serves as both the absorber and hole conductor. Even though the efficiency of this type of solar cell is still lower than that of CuI, CuBr, and CuSCN and further optimization of CdS:Cu is needed to improve the cell performance, the demonstrated stability of this type of solar cell indicates that this novel cell structure and new hole conductor (CdS:Cu) could be promising approaches to achieve stable solid-state DSSCs.

## Experimental

### TiO<sub>2</sub> electrode

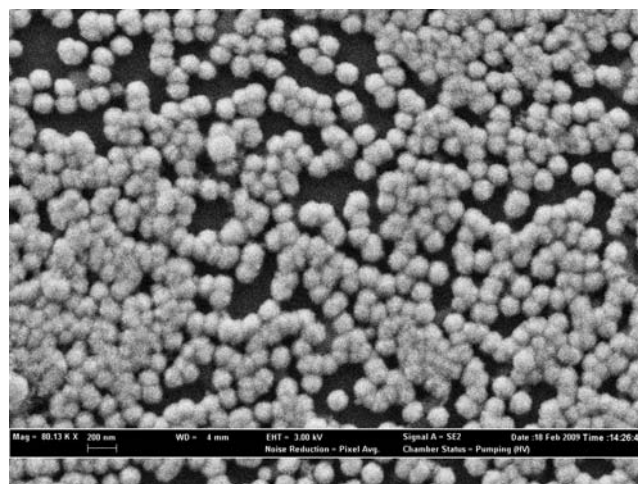
Commercial TiO<sub>2</sub> (3 g; P<sub>25</sub>, Degussa AG, Germany) was mixed with acetylacetone, Triton X-100 and water [25]; 10% PEG 20,000 (by weight) was subsequently added in the paste. TiO<sub>2</sub> pastes were then spread on SnO<sub>2</sub>:F-coated (FTO) glass substrate using a doctor blade method. The film was annealed in 450 °C for 30 min in air. The thickness of TiO<sub>2</sub> is about 10 μm.

### CdS deposition

TiO<sub>2</sub>-coated FTO was put into the solution of 0.015 M CdCl<sub>2</sub> 50 ml, 1.5 M thiourea 25 ml, and ammonium hydroxide 62.5 ml mixed in 366 ml water. The solution pH was around 11.5 [26]. The reaction was carried out at 60°C for 20 min with slow stirring. The as-grown sample exhibited nanoparticle structure with particle size of 100 nm (Fig. 1).

### Solar cell fabrication

Electrolyte was made with 0.1 M LiI (Aldrich), 0.05 M I<sub>2</sub> (Aldrich), 0.6 M tetrabutylammonium iodide (Fluka), and 0.5 M *tert*-butylpyridine (Aldrich) in dry acetonitrile (Fluka) [27]. The counter electrode was made of Pt-coated FTO glasses [28]. The active area of the cell is 0.16 cm<sup>2</sup>. AM 1.5 solar simulator (100 mW·cm<sup>-2</sup>) was used as illumination source and  $I-V$  curves were obtained with a digital source meter (Keithley 2,400, Keithley Instruments). The measurement is calibrated with commercial Si refer-



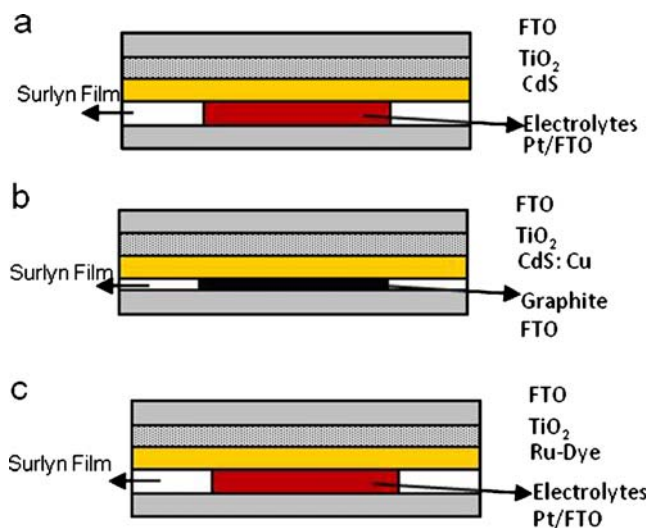
**Fig. 1** SEM images of CdS on glass

ence solar cell. Two configurations of solar cell structure are investigated in this study. One is the CdS-coated TiO<sub>2</sub> solar cell with liquid electrolytes (Fig. 2a). Another is CdS-coated TiO<sub>2</sub> solid-state solar cells (Fig. 2b). The solid-state solar cell does not require the use of Pt catalyst since the liquid electrolyte is not employed. A control sample made with the standard Ru-dye is shown in Fig. 2c.

## Results and discussion

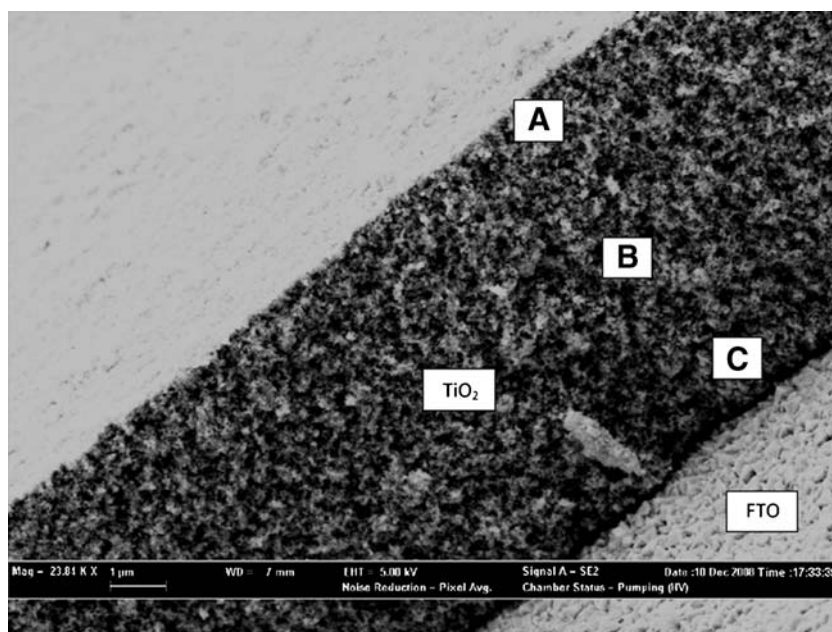
### CdS morphology and CdS penetration into TiO<sub>2</sub> network

Figure 3 shows the cross section of the CdS/TiO<sub>2</sub>/FTO/glass. The energy-dispersive X-ray spectroscopy (EDS) was



**Fig. 2** Three solar cell configurations investigated in this work **a** CdS-coated TiO<sub>2</sub> solar cell with liquid electrolytes **b** Solid-state CdS-coated TiO<sub>2</sub> solar cell **c** Control sample of Ru-dye-sensitized TiO<sub>2</sub> solar cell with liquid electrolytes

**Fig. 3** Cross section of CdS on TiO<sub>2</sub> and the EDS testing points



Testing Points	S/Ti (Mole Ratio)	Cd/Ti (Mole Ratio)	S/Cd (Mole Ratio)
A	0.04	0.04	0.87
B	0.04	0.03	0.89
C	0.02	0.03	1.74

taken for locations A, B, and C along the cross section as shown in Fig. 3. As we can see, the sulfur ion has better penetration into the TiO<sub>2</sub> film than Cd ion which might be due to the relative larger particle size of CdS. This suggests that further reduction in CdS particle size is required to improve the pore penetration. Nevertheless, the efficiency of the solar cell obtained by this CdS with liquid electrolytes (structure shown in Fig. 2a) is 2.46% ( $V_{oc}=0.69$  V,  $J_{sc}=6.54$  mA/cm<sup>2</sup>, F.F.=0.55). This is the highest reported efficiency of using CdS alone as sensitizer. Compared to the control sample (structure shown in Fig. 2c) efficiency of 7.88% ( $V_{oc}=0.73$  V,  $J_{sc}=19.22$  mA/cm<sup>2</sup>, and F.F.=0.56), the low  $J_{sc}$  is the major factor contributing to the poor cell performance which might be due to the poor CdS penetration into TiO<sub>2</sub> film and inefficient light absorption of CdS compared to the dye.

**Investigation of CdS-coated solar cell stability**

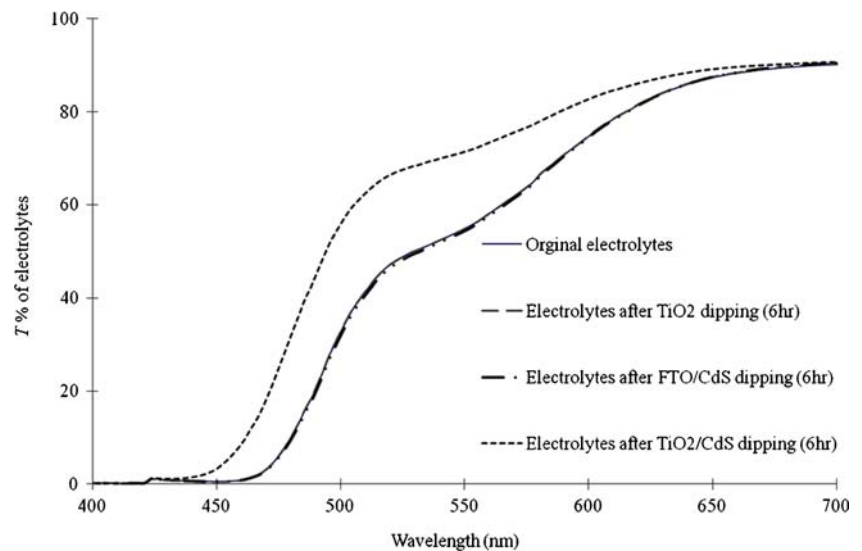
In order to test the stability of CdS-coated solar cell, solar cells with liquid electrolytes (structure shown in Fig. 2a) were sealed and kept in the dark for 6 h. The cells suffered significant  $J_{sc}$  degradation as seen in Table 1 (the first two rows of “w/o barrier”). To explain this, we need to understand the chemical reactions among the three compo-

nents of CdS, TiO<sub>2</sub>, and liquid electrolytes. Samples of FTO/CdS, FTO/TiO<sub>2</sub> and FTO/TiO<sub>2</sub>/CdS were immersed into 5 mL electrolytes (1/25 diluted with acetonitrile) for 6 h in the dark. UV–Vis data of the electrolyte solution shown in Fig. 4 was measured before and after the dipping of samples. FTO/TiO<sub>2</sub> and FTO/CdS do not show any UV–Vis degradation (overlapping of UV–Vis curves with that of original electrolytes) in electrolytes after 6 h which means that the reaction can be neglected when only having TiO<sub>2</sub> or CdS alone on FTO in electrolytes. FTO/TiO<sub>2</sub>/CdS (the top dashed line in Fig. 4), on the other hand, showed the dramatic change in UV–Vis. This indicates that TiO<sub>2</sub> may serve as an oxidizer for CdS and accelerate the reaction between CdS and electrolytes. Thus, a compact barrier layer of TiO<sub>2</sub> film less than 2 μm (Fig. 5a) is

**Table 1** Stability study of CdS-sensitized TiO<sub>2</sub> liquid electrolytes solar cells with (W/) and without (W/O) TiO<sub>2</sub> barrier layer

TiO <sub>2</sub> film	Time (h)	Efficiency (%)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	F.F.
W/O barrier	0	2.46	0.69	6.54	0.55
W/O barrier	6	0.52	0.81	3.82	0.17
W/barrier	0	2.41	0.67	6.79	0.53
W/barrier	6	1.09	0.85	3.05	0.43

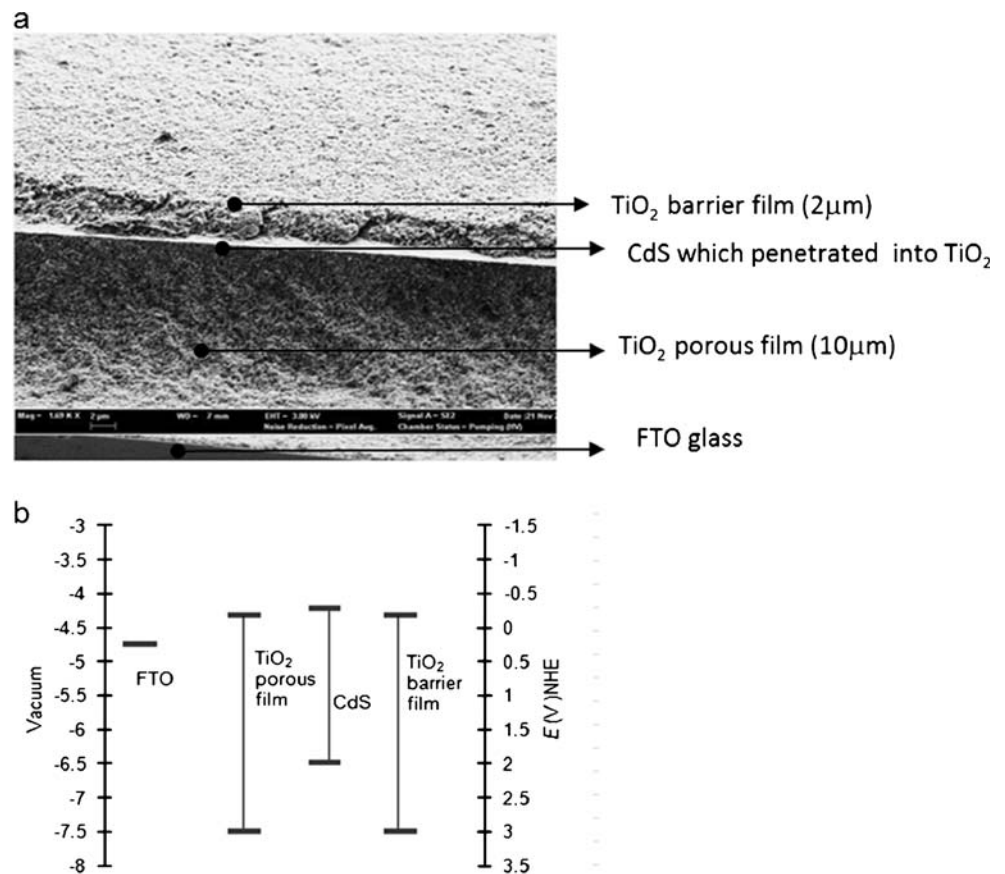
**Fig. 4** Transmittance data of electrolytes before and after 6 h reaction

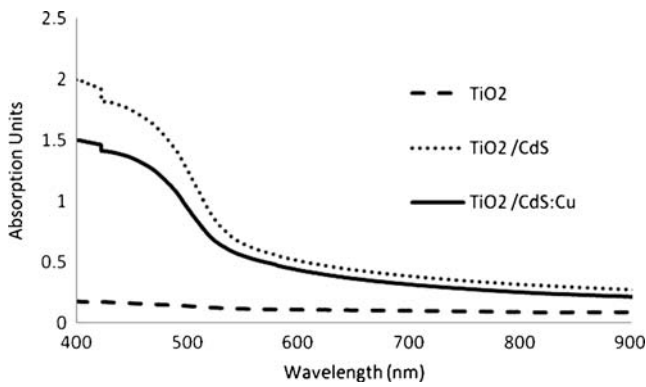


deposited on porous  $\text{TiO}_2$  to have structure of  $\text{TiO}_2/\text{CdS}/\text{TiO}_2$ . To make  $\text{TiO}_2$  barrier film, 3 g commercial  $\text{TiO}_2$  ( $\text{P}_{25}$ , Degussa AG, Germany) was ground in a porcelain mortar with a small amount of water 1 mL containing acetylacetone 0.1 mL (about two drops) to prevent reaggregation of the particles. After the powder had been

dispersed by the high shear forces in the viscous paste, it was diluted by slow addition of water (4 mL) under continued grinding. When  $\text{TiO}_2$  barrier film was applied, the  $J_{sc}$  degradation slowed down as seen in Table 1 (the last two rows of “w/barrier”). The  $\text{TiO}_2$  barrier film does not block hole transport from electrolytes to CdS possibly

**Fig. 5** SEM image of  $\text{TiO}_2$  barrier film of  $\text{TiO}_2/\text{CdS}/\text{TiO}_2$  and band diagram of different layers in the solar cell [29]





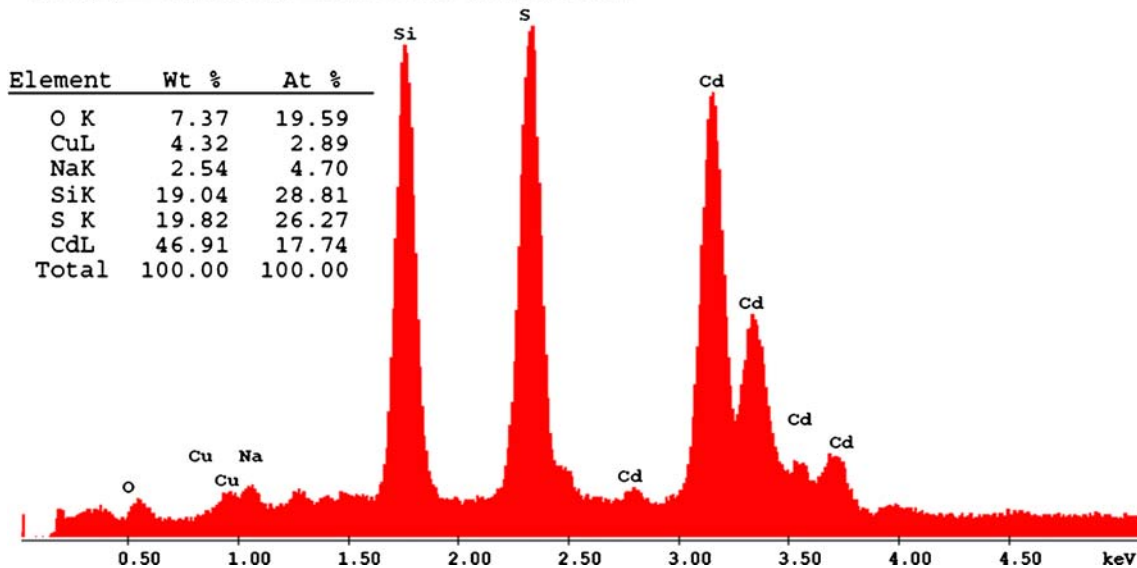
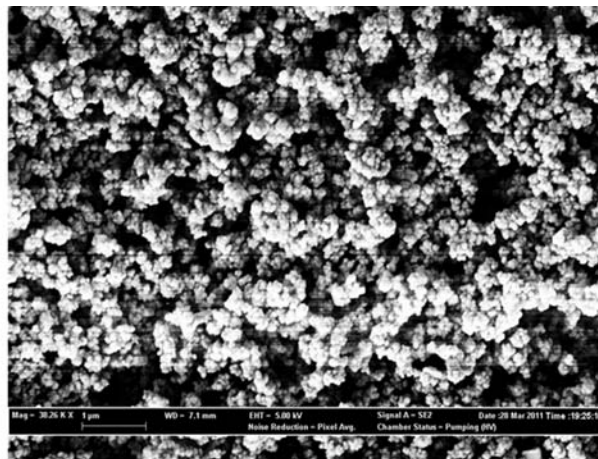
**Fig. 6** The absorption spectrum of TiO<sub>2</sub> before and after CdS and CdS:Cu deposition

because the  $E_{vb}$  of TiO<sub>2</sub> (3.0 NHE) is lower than CdS (2.0 NHE) [29] (Fig. 5b). The solar cell performance data in Table 1 has demonstrated the modest effectiveness of the TiO<sub>2</sub> barrier layer.

Solid-state CdS-coated solar cell

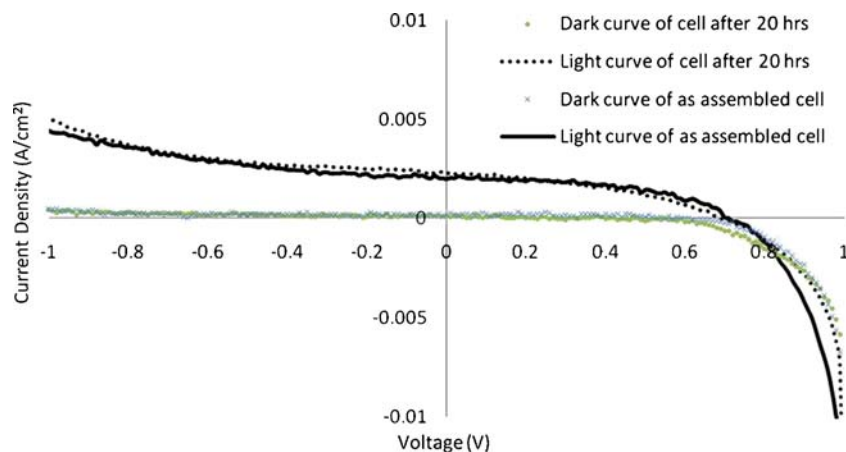
Using TiO<sub>2</sub> barrier layer only demonstrated modest cell stability. Since the accelerated reaction between TiO<sub>2</sub> and CdS occurs at the presence of liquid electrolytes, a solid-state CdS-coated TiO<sub>2</sub> solar cells (structure shown in Fig. 2b) is attempted. To make CdS:Cu on TiO<sub>2</sub>, TiO<sub>2</sub>-coated FTO was immersed in the solution of 0.015 M CdCl<sub>2</sub> 50 ml, 1.5 M thiourea 25 ml and ammonium hydroxide 62.5 ml mixed in 366 ml water. 5 mol% CuCl was added as Cu source. The pH of the solution was around 11.5. The reaction was carried out at 60 °C for 20 min and with slow stirring.

Solid-state solar cell structure using CdS:Cu as both sensitizer and hole conductor was obtained with cell efficiency of 0.7% ( $J_{sc}$ =2.04 mA/cm<sup>2</sup>,  $V_{oc}$ =0.68 V and F.F.=0.51). The  $I$ - $V$  curve is shown in Fig. 8. A thin layer of graphite is used as the contact between CdS:Cu and FTO. This is the first time this type of solid-state TiO<sub>2</sub> nanocrystalline solar cell is made. No cell efficiency was found for cells with FTO/TiO<sub>2</sub>/CdS/



**Fig. 7** a SEM plane view of CdS:Cu and b EDS of CdS:Cu

**Fig. 8**  $I$ - $V$  curves of the solid-state CdS:Cu devices as assembled (0.7%;  $J_{sc}$ =2.04 mA/cm<sup>2</sup>,  $V_{oc}$ =0.68 V, and F.F.=0.51) and after 20 h (0.68% with  $J_{sc}$ =2.34 mA/cm<sup>2</sup>,  $V_{oc}$ =0.68 V, and F.F.=0.42)



FTO structure. This indicates the hole conducting behavior of CdS:Cu. The absorption spectrum of TiO<sub>2</sub> before and after CdS and CdS:Cu deposition is presented in Fig. 6. The decreased light absorption of CdS:Cu could be caused by the increased particle size of CdS:Cu (SEM shown in Fig. 7a) compared to CdS (SEM shown in Fig. 1). The EDS data shown in Fig. 7b indicates that the Cu dopant concentration is about 3 at% in CdS:Cu film. Thus, if the light absorption of CdS:Cu could be improved by reducing the CdS:Cu particle size, the efficiency of solid-state CdS-coated TiO<sub>2</sub> solar cell will be increased. This solid-state CdS-coated TiO<sub>2</sub> solar cell has demonstrated much better stability for days. The cell efficiency is 0.68% with  $J_{sc}$ =2.34 mA/cm<sup>2</sup>,  $V_{oc}$ =0.68 V, and F.F.=0.42 after 20 h as shown in Fig. 8. Further optimization is needed to improve the  $J_{sc}$  by optimizing the CdS:Cu deposition process to reduce the particle size of CdS:Cu.

## Conclusions

In this study, a solar cell efficiency of 2.46% was achieved for CdS-coated TiO<sub>2</sub> solar cell. However, the cell was found to be unstable due to the reaction with electrolytes. Adding TiO<sub>2</sub> barrier layer can improve the cell stability to some extent. A complete solid-state CdS-coated solar cell using CdS:Cu as both hole conductor and sensitizer was made, improving cell stability dramatically. The solid-state solar cell efficiency was 0.7%. This is the first time this type of solid-state TiO<sub>2</sub> nanocrystalline solar cell is made.

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