Copper nanowires on Recycled Conducting Glass for DSSC Electrodes

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ABSTRACT

A simple method for recovery of conducting glass from thin film transistor liquid crystal display (TFT-LCD) wastes for low-cost dye-sensitized solar cell (DSSC) electrodes has been investigated. The indium tin oxide (ITO), TFT array, and color filter glasses separated with two parallel aluminum plates moved in opposite directions in the ethanol solution were recovered. Since the recovered color filter contains a much less indium than the others, recovery of indium from the color filter wastes may not be economically attractive. To enhance conductivity of the recovered color filter glass for DSSC electrodes, Cu@C core-shell nanoparticles (prepared by carbonization of Cu^{2+}-β-cyclodextrin at 573 K) were used to construct Cu nanowires on the recovered glass by spin coating. The carbon-shell of Cu@C was removed by steam reforming at 573 K. The cinversion efficiency of the DSSC utilizing Cu nanowires on electrodes can be increased by at least 12%. Notably, the total material cost of a DSSC can be reduced substantially by utilization of the recovered glass for DSSC electrodes.

Keywords: Recycling, conducting glass, dye-sensitized solar cells, Cu nanowire.

1 INTRODUCTION

Thin film transistor liquid crystal display (TFT-LCD) planes are widely used in notebook/personal computers, televisions and cell phones. About 25,000 tons per year of TFT-LCD wastes including glass, plastic, printed circuit board and electrical wires are to be recycled in Taiwan [1, 2]. The transparent conductive oxide (TCO) glass substrate is generally coated with indium tin oxide (ITO) thin film. Indium is a precious metal, and the average price is between 360-400 USD/kg in 2009 [3]. Therefore, recovery of ITO glass can be very cost-effective. Indium may be recovered using di-2-ethylhexyl phosphoric solutions with an indium recovery rate of nearly 90% [4]. Park and coworkers recovered indium from LCD powders by a chloride volatilization process using PVC as a chlorination agent [5]. About 92% of indium in the glass scraps could be dissolved in acid solutions containing nitric and hydrochloric acids ($HCl:HNO_3:H_2O$=45:5:50) [6]. Lin and Coworker [7, 8] crushed the recycled glass to an uniform particle size for producing glass-ceramic building bricks. Wang [9] used the glass in substituting of cement in mortar. However, recovery of indium from TFT-LCD wastes may need further energy-intense purification as well as the secondary waste treatments.

Recently, ZnO, TiO_2, silicon, and CdTe nanowires are widely used in photoelectronic applications, because of the variable ratios of length and diameter, ultra-high specific surface area and anti-reflection [10]. Jiang and coworks prepared wide-size CuO nanowires by controlling temperature and time of the crystal growth rate [11]. Vayssieres synthesized ZnO nanowires having a size range of 10-20 nm [12]. Nickle nanowires with controllable width and length channels were prepared using anodic aluminum oxide templates [13]. By a metal-organic chemical vapor deposition method, InP core-shell nanowires were prepared for solar cells [14]. Sputtering gold nanoparticle thin film on a silicon substrate could form nanowire possessing p-type silicon core, which can enhance light absorbance [15].

Generally, about 30% of the total cost for a dye-sensitized solar cell (DSSC) is attributed to the conducting glass. Therefore, in the present work, a simple method for recovery of conducting glasses from TFT-LCD wastes for DSSC electrodes was investigated. To enhance conversion efficiency (η) of a DSSC, Cu nanowires were coated on the recovered glasses which have a low conductivity.

2 EXPERIMENTAL

The TFT-LCD wastes were provided by a TFT-LCD manufacturing plant in Taiwan. The TFT-LCD contains layers of polarizing film, liquid crystal, color filter and TFT array glass substrate coated with ITO. The color filters and TFT array glass substrates were separated from TFT-LCD planes. The glasses sandwiched with two parallel aluminum plates were moved in opposite directions in the ethanol and acetone (1:1) solution assisted with supersonic vibration for 40 min to separate polarizing films and liquid crystal materials. The glass was shredded into a size of 2 cm×2 cm. Before utilized in DSSC electrodes, the recovered glasses were cleaned in neutral detergent, acetone and isopropanol with ultrasonic-assisted dissolution.

The concentrations of indium, tin and copper in the recovered ITO glass were analyzed by inductively coupled plasma equipped with a mass spectrometer (ICP-MS, PE-SCIEX ELAN 6100 DRC). Conductivity of the recovered glasses was measured by a four-point probe (KEITHLEY 2400).

To synthesize nanosize-controllable Cu@C core-sell particles, β-cyclodextrin (CD) (wako) and copper(II)

nitrates (J.T. Baker) were mixed at a copper-to-carbon (in CD) molar ratio of 13 [18, 19]. The Cu^{2+}-CD complexes were dried at 353 K for 8 h to form Cu^{2+}-CD powders which were deposited on the recovered conducting glass substrates by spin coating at 1000 rpm. The Cu^{2+}-CD complex/glass was carbonized at 573 K for 2 h in high-purity nitrogen gas (99.99%) to form Cu@C nanowires. The carbon-shell of the Cu@C nanowires was removed by steam reforming ($Cu@C+H_2O \rightarrow Cu+CO+H_2$) at 573 K for 30 min. Chemical structure of copper in Cu@C coated on the glass was analyzed by thin-film X-ray diffraction spectroscopy (D8 DISCOVER) scanned from 0 to 60° (2θ) at a scan rate of 0.05°/min. Images of Cu and Cu@C nanoparticles were measured on an environmental scanning electron microscope (ES-SEM, FEI Quanta 400 F).

The DSSC photoelectrode was prepared by a TiO_2 paste and $Ti(OPr)_4$ precursor solution, which were dropped on the recycled glass substrates by spin coating under 800 rpm. The coated glass was dried and scratched out for a working area of 0.25 cm^2, preheated at 323 K for 15 min and calcined at 723 K for 30 min. The TiO_2 coated glass was immersed in N719 (Ruthenium 535-bis TBA, Solaronix) (3×10^{-4} M) solution for 24 h in the dark. The counter electrode was prepared by deposition of $H_2PtCl_6 \cdot 6H_2O$ (Alfa Aesar) (5×10^{-3} M) onto the glass which was coated with Cu@C nanowires by spin coating at 1,500 rpm. The electrode was dried at 353 K for 10 min, and calcined at 673 K for 10 min.

The two electrodes were sandwiched with a 60 μm spacer of hot-melt thermal foil (Solaronix). The electrolyte containing 0.1 M of LiI (Aldrich), 0.05 of M I_2 (Riedel-de Ha¨en), 0.6 M of DMPII (Solaronix), and 0.5 M of 4-tert-butylpyridine (Aldrich) in acetonitrile solution was injected into the channel between two electrodes and sealed with AB epoxy. The photovoltaic performances of the DSSCs were measured by a 300 W xenon arc lamp solar simulator (NEWPORT, 91160A) combined with an AM 1.5 Globe filter (ORIEL, 59044). The DSSCs were illuminated with a light power of100 mW/cm^{-2} which was calibrated with a reference solar cell and meter (ORIEL, 91150) in the dark.

3 RESULTS AND DISCUSSION

The concentrations of indium, tin, and copper in the recycled ITO, TFT array and color filter glass are shown in Table 1. It is clear that the color filter contains a much less indium than the others. Recovery of indium from the color filter wastes may not be economically attractive. The color filter glasses are generally coated with color filter films (red, green and blue) and a shading layer (black matrix) [19]. Thus, relatively low optical transmission and high resistivity of the recovered color filter may be the main drawbacks for its utilization in optical-electronic devices (see Table 1).

The thin-film XRD patterns in Fig. 1 show intense peaks at 11, 16, 32, and 41° (2θ), which are associated with the existence of indium-tin oxide crystallines on the recovered ITO and TFT array glasses. However, on the color filter, the indium-tin oxide crystalline is not found. Generally, using known technology, high purity indium can be recovered from ITO and TFT array glass wastes. Nevertheless, direct utilization of the recovered conducting glasses in optical-electronic devices such as DSSCs may be cost-effectively feasible. Table 2 shows the photovoltaic performances (determined with the AM 1.5 Globe filter solar simulator) of the DSSCs using the recovered conducting glasses on the electrodes. It seems that the recovered ITO glass can be used as the DSSC electrodes having 0.76 V in the open-circuit voltage (V_{OC}), 8.37 mA/cm^2 in the short-circuit current density (J_{SC}), and 0.62 in the fill factor (*FF*), and a desired η of 3.94%. However, the recovered TFT array or color filter glass has a low η (in Table 2). To enhance η of a DSSC utilizing the recovered glass such as the color filter, a construction of conducting wires on the high resistivity glass for the DSSC electrodes has been carried out.

In separate experiments, a simple method for preparing size-controllable core-shell nanoparticles such as Cu@C has been developed [16]. To construct Cu nanowires on the glass, the Cu@C core-sell nanoparticles were prepared at a copper-to-carbon (in CD) molar ratio of 13. After carbonization in high purity nitrogen atmosphere at 573 K for 2 h, core-shell nanoparticles can be yielded. The ES-SEM image of the Cu@C coated on the color filter glass is shown in Fig. 2(a). It is clear that the Cu@C nanoparticles are well dispersed on the glass. It is also worth noting that the carbon-shell which protects the core metals from being oxidized or aggregated can be removed by steam reforming ($C+H_2O \rightarrow CO+H_2$) at the temperature of 573 K. In Fig. 2(b), Cu nanowires on the color filter glass are observed by ES-SEM. The thin-film XRD pattern of the steam reformed Cu@C on the color filter glass is shown in Fig. 1(d). Mainly Cu_2O is found in the Cu nanowires. The average diameter of the Cu_2O nanoparticles estimated using the Scherrer equation is 21 nm approximately.

4 CONCLUSION

Conducting glasses including ITO, TFT array, and color filter can be recovered from TFT-LCD wastes for utilization in low-cost DSSC electrodes. Unlike ITO and TFT array, the recovered color filter having relatively unfavorable indium content, low optical transmission and high resistivity has been suffered from limited applications. Cu nanowires have, therefore, been coated on the recovered color filter glass to enhance it conductivity for DSSC electrodes. The conversion efficiency of the DSSC assembled with the recovered color filter containing Cu nanowires can be increased by at least 12%. It is worth noting that the total material cost of a DSSC may be reduced substantially by utilization of the recovered glass in DSSC electrodes.

	In	Sn	Cu	Optical transmission	Resistivity
ITO	306	33	5	84	15-17
TFT array	266	127	37	70	97-100
Color filter	78	47	241	33	680-690

Table 1: Concentrations (mg/kg) of key elements, optical transmission (%) (under AM 1.5, 100 mW/cm^2) and resistivity (ohm) (measured by a four-point probe) in recycled ITO, TFT array and color filter glass substrates.

Electrodes	J_{SC} (mAcm^{-2})	**Voc (V)**	***FF***	**η (%)**
ITO	8.37	0.76	0.62	3.94
TFT array	3.46	0.69	0.41	0.97
Color filter	0.99	0.69	0.25	0.17
Cu nanowires/ color filter	0.91	0.81	0.26	0.19

Table 2: Photovoltaic performances for DSSC. *J*sc: short circuit current density; Voc: open circuit voltage; *FF*: fill factor; η: conversion efficiency.

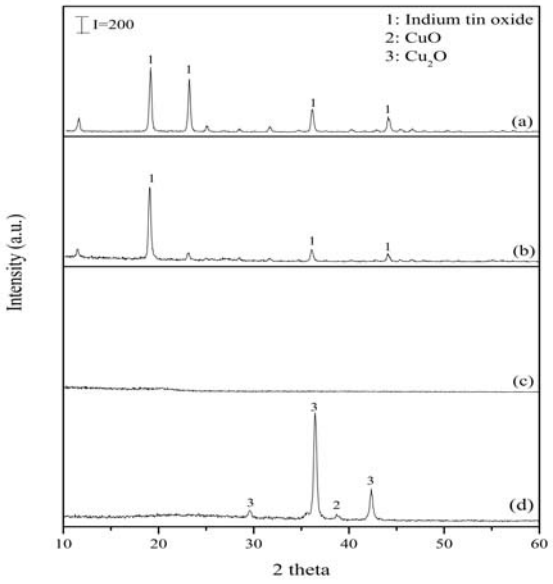

Figure 1: Thin film XRD patterns of (a) ITO, (b) TFT array, (c) color filter, and (d) Cu nanowires/color filter.

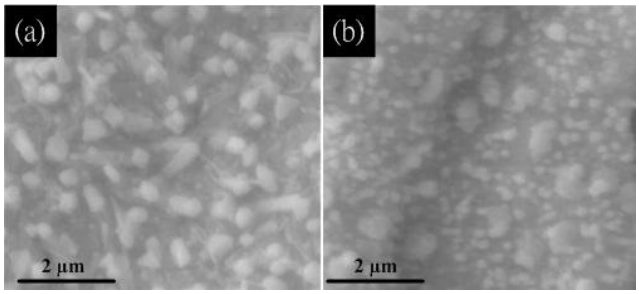

Figure 2: ES-SEM images of (a) Cu@C nanoparticles and (b) Cu nanowires formed from steam reforming.

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