Low-Cost Dye-Sensitized Solar Cells Based on Interconnected FTO-Activated Carbon Nanoparticulate Counter Electrode Showing High Efficiency

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Abstract: The development of low-cost DSCs (Dye-sensitized solar cells) based on activated carbon counter electrodes is described. Although, the use of activated carbon in CEs (Counter electrodes) has been documented, the efficiencies obtained in such solar cells have been low, particularly, due to low electrical conductivity of such counter electrodes. Our design of the counter electrode eliminates this problem by using an in-situ formed FTO (Fluorine-doped tin oxide)-activated carbon composite on FTO surface as the CE. The FTO particles are prepared by atomized spray pyrolysis method from a spray solution containing dispersed activated carbon particles. The CE thus prepared has a reasonable electronic conductivity and the composition of the spray solution was optimized to give the highest conversion efficiency and the thickness of the CE was optimized by controlling the spray duration and deposition temperature. The best DSC based on AC-FTO CE has a JSC of 18.98 mA·cm-2, a VOC of 0.709 V, and a FF (Fill factor) of 0.563 giving a conversion efficiency of 7.6%. The data for Pt-FTO CE based DSC are a JSC of 18.78 mA·cm-2, a VOC of 0.732 V, and a FF of 0.688 with a conversion efficiency of 9.5%.

Key words: DSCs (Dye-sensitized solar cells), activated carbon counter electrode, spray-pyrolysis, fluorine-doped tin oxide.

1. Introduction

Research on DSCs (Dye-sensitized solar cells) has been in forefronts ever since their first report by O’Reagan and Grätzel, in 1991 [1]. Several innumerable modifications have been effected to improve the solar light to electricity conversion efficiency by improving all the components of the device. The CE (Counter electrode) contributes significantly to the cost of the device since the usual CEs require platinum even though lightly platinized FTO (Fluorine-doped tin oxide) is used. Search for cheaper materials to replace prohibitively expensive platinum has been carried out by many researchers and several alternatives have recently been proposed. These include CNTs (Carbon nanotubes) [2-5] activated carbon [6, 7], graphite [8], nanocarbon [9], carbon black [10, 11], conducting polymers [10-12], and graphene [13]. The efficiencies of these devices range from 3% to 7% at AM 1.5 illumination and are below the maximum reported efficiency for the Gratzel type DSC (Dye-sensitized solar cells) (15%) under otherwise identical conditions. Nevertheless, since 40% of the cost of DSC production goes to fabricate CE, the lower efficiency obtained by using much cheaper CE can be compensated by the lower cost in mass production of DSCs for practical applications when cheaper CEs are used. The maximum reported efficiency for the AC (Activated carbon) CE based DSC so far reported is 6.6% [7].

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Among these alternative materials, carbon-based counter electrodes have shown promising results. Carbon-based materials have attracted a great attention due to their low-cost, high corrosion resistance, high catalytic activity, high thermal stability, good electrical conductivity, as well as high natural abundance. Kim et al. have prepared a counter electrode based on graphite fiber sheet with poly (3, 4-ethylenedioxythiophene) polymer by spin-coating and the DSC based on this CE has shown a power conversion efficiency of 8.05% where Pt-based cell has shown 7.41% under identical conditions [14]. In this work, the cyclic voltammetric data have shown higher reduction current for the carbon-based electrode when compared to that of FTO-Pt based electrode and the fact has been attributed to the high surface activity of the former electrode. Lim et al. have reported a TiO$_2$/carbon black counter electrode using particles in the nanometer range. A 7.4% of power conversion efficiency for the DSC constructed has been reported where Pt-based DSC had shown 7.7% under the same conditions [11]. This work has clearly shown the possibility of using semiconductor/carbon based composite as an effective counter electrode in DSCs. Huang et al. have reported a CE with layer-by-layer carbon nanotubes and FTO and the DSCs with these counter electrodes have shown higher fill factors similar to those of the Pt-based DSCs, and have clearly shown that the spray pyrolysis technique is more suitable to fabricate such layer-by-layer type of counter electrodes [15]. Gao et al. have also investigated adhesion properties of carbon-based counter electrodes. They have shown an improvement in the mechanical properties of the carbon dye-based counter electrode due to the addition of conductive carbon paste, which is a combination of carbon particles and thermoplastic resins [16]. Bu et al. have reported a transparent carbon based counter electrode fabricated on FTO substrate using an in-situ carbonization method. Here, a Triton-X100 based carbon precursor was spin-coated on FTO glass and sintered at 500 °C in an argon atmosphere to form carbon nanoparticles on the surface of the FTO [17]. This counter electrode has been employed in the bifacial transparent DSC and the device had a power conversion efficiency of 6.07% where the Pt-based DSC has shown 6.89% under identical conditions.

In this publication, we report a comprehensive study of DSCs whose counter electrodes are made from AC and FTO composite co-deposited on glass, by optimizing the parameters of the thin film deposited on FTO glass surfaces. The optimized parameters include deposition temperature, amount of activated carbon used in the thin film, the film thickness and the morphology of the film. DSC performances of all these devices are reported and compared with those of the Gratzel type cell that utilizes lightly platinized FTO CE.

2. Experimental Methods

2.1 Preparation of AC/FTO Dispersion

First, 1.40 g of SnCl$_4$·5 H$_2$O (Wako Chemicals, Japan, 99%) was added to 40.0 cm$^3$ of ethanol (Sigma-Aldrich, 95%) and the mixture was ultrasonicated for 15 min to obtain a clear solution. Then, 0.24 g of saturated aqueous solution of NH$_4$F (Sigma-Aldrich 99%) was added to the above solution and the mixture was sonicated for further 15 minutes to form an FTO precursor solution. Then, to a separate mortar required amount of AC was added and ground well for 5 minutes with a small amount of the FTO solution. In order to optimize the sintering temperature, 0.10 g of AC was used. After the optimization of the sintering temperature, the amount of AC was varied as 0.200, 0.400, 0.600, 0.800 and 1.000 g in separate preparations. Then, the whole of the FTO solution was added to the mortar, in each case, and the dispersion was transferred in to a beaker and ultrasonicated for 15 minutes.

2.2 Deposition of AC/FTO Composite on FTO Substrate and Characterization

First, the FTO plates were cut into 1 cm × 2 cm
pieces and cleaned using ultrasonication in a detergent added isopropanol bath. Then, the plates were thoroughly washed and dried. 1 cm × 1 cm section of each plate was covered using an aluminium foil. The AC/FTO dispersion was then spray-pyrolyzed on to the heated FTO substrate at 300 such that after every 10.0 mL spray of the precursor solution, the plates were sintered in an oven for 3 min. To optimize the sintering temperature, the temperature was varied from 300-600 using separate plates in each study. This process continued until the formation of thick black film on the substrate. Finally, the aluminium foils were removed and plates were sintered at the above temperatures for 5 min and the loose crust on the surface of the film was wiped out using cotton wool. The catalytic behavior of the I$^3_-$ reduction on the counter electrodes was investigated by cyclic voltammetry by using electrodes of active area of 1 cm × 1 cm, at a scan rate of 100 mV·s$^{-1}$, in an acetonitrile solution containing 10 mM LiI, 1 mM I$^2_-$ and 0.1 M NaClO$_4$ electrolytes. The reference and counter electrodes are SCE (Saturated calomel electrode) and a Pt-gauze, respectively. All the potentials given are with respect to SCE. The optimized AC/FTO electrode was characterized using XRD (Siemens X-Ray Diffractometer D5000, Cu K$_\alpha$, $\lambda = 1.54056$ Å) for its crystal structure.

2.3 Preparation of the TiO$_2$ Colloidal Solution

Titanium tetraisopropoxide (20.0 cm$^3$, Kanto Chemicals Co. Inc., Japan, 97%) and acetic acid (2.5 cm$^3$, Wako Chemicals, Japan, 99.7%) were mixed with 25.0 cm$^3$ of ethanol (Hayman, United Kingdom, 99.9%) and subsequently steam was passed through the solution for 2 min. Rapid hydrolysis of titanium tetraisopropoxide and the expulsion of ethanol by steaming then produces a transparent solid mass consisting of TiO$_2$ nanoparticles. The solid mass was ground with 50.0 cm$^3$ of de-ionized water in a motor for several minutes and subsequently autoclaved at 150 °C for 3 h.

2.4 Preparation of Dyed-TiO$_2$ Based Working Electrode

To a 20.0 cm$^3$ of the TiO$_2$ colloidal solution prepared as detailed in section 2.3, 5.5 cm$^3$ of acetic acid (Wako Chemicals, Japan, 99.7%), 20.0 cm$^3$ of ethanol (Hayman, United Kingdom, 99.9%) and five drops of Triton X-100 (Sigma, USA) were added and well stirred. The resulted colloidal solution was ultrasonicated for 15 minutes, and the suspension thus resulted was spread on to FTO substrate by the spray pyrolysis technique at 150 °C. This TiO$_2$-coated FTO plate was sintered at 500 °C for 30 min in air and allowed to gradually cool down to about 80 °C. Then warm plate was kept soaked in a 0.3 × 10^{-3} M solution of the cis-diisothiocyanato-bis(2, 2'-bipyridyl-4, 4'-dicarboxylato) ruthenium (II) bis (tetrabutylammonium) dye (N 719, Solaronix SA, Switzerland) in a 1:1 v/v mixture of acetonitrile (Sigma-Aldrich, USA, 99.8%) and t-butyl alcohol (Fluka, USA, 99.5%) for 12 h. The plate was withdrawn from the dye solution, rinsed with acetonitrile and dried in an air flow.

2.5 Construction of the Dye-Sensitized Solar Cell and Characterizations

AC/FTO counter electrode was placed on the above dyed-working electrode and the free space between the two electrodes was filled with the liquid electrolyte containing I$^-$ and I$^3_-$ redox couple (0.1 M LiI, 0.05 M I$_2$, 0.6 M dimethylpropylimidazolium iodide and bipyridine in acetonitrile) to complete the DSC configuration where the active cell area was 0.25 cm$^2$. For comparison DSC based on Pt/Cr mirror type counter electrode was also constructed in a similar manner. Several DSCs were prepared by varying the sintering temperature of the FTO-AC coated CE and also by varying the amount of AC in the precursor solution of the CE fabrication at the optimum temperature which was determined by measuring the I-V characteristics using Solar Simulator (PECcell-L01, Japan) under AM 1.5 illumination.
3. Experimental Results

3.1 Characterization of FTO/AC-FTO Counter Electrode

As depicted in Section 2.2, catalytic activities of the AC/FTO counter electrode on the reduction of I$_3^-$ and oxidation of I$^-$ have been investigated by CV (Cyclic voltammetric) studies. The respective cyclic voltammograms of the AC/FTO and Pt-Cr-mirror electrodes are shown in the Fig. 1. The voltammograms clearly show two redox reactions. The peaks for the reduction and oxidation of iodide/triiodide half-reactions of the AC/FTO electrode and Pt/Cr-mirror electrode appear at –0.184 V / +0.339 V and –0.285 V / +0.430 V, respectively. The peaks corresponding to the AC/FTO electrode show higher current densities than those of the FTO/Pt-Cr-mirror counter electrode, indicating higher catalytic activity of the former electrodes for I$_3^-$ reduction and I$^-$ oxidation. Also the shift in the peak positions needing extra over-potentials in both half-reactions when compared to the peak potentials of Pt-based CE is possibly due to the higher sheet resistance of the AC/FTO electrode (~60 $\Omega/\square$) compared to that of the Pt/Cr-mirror electrode (less than 5 $\Omega/\square$). Increasing AC content in the composite tend to increase the catalytic activity but decreases electrical conductivity and on the other hand increasing FTO content will increase conductivity but decrease catalytic activity. As such a compromise is needed to get optimum properties.

SEM images of the AC-FTO film on FTO which was prepared at 500 are shown in the Fig. 2 (i). These films were obtained before wiping the film with cotton wool. The top surface seems to contain a considerable amount of loose crust and the thickness of the film together with the loose crust is 6 $\mu$m as revealed by the cross-section SEM [Fig. 2 (i-a)]. As such, the film was wiped using cotton wools to remove the loose crust and SEM images were taken after removing the loose crust. These images are shown in Fig. 2 (ii)-a. Clearly, the morphology of the film is much smoother when the loose crust is removed and the thickness of the film now reduces to ~3 $\mu$m [Fig. 2 (ii)-b]. The SEM images also show that the morphology of the film is highly porous before wiping but is highly dense when the loose crust is removed.

![Fig. 1](image.png)  
Fig. 1  The cyclic voltograms of AC/FTO and Pt/Cr-mirror type electrodes in 10 mM LiI, 1 mM I$_2$ and 0.1 M NaClO$_4$ in an acetonitrile electrolyte, at 100 mV-s$^{-1}$. Reference and counter electrodes are Saturated Calomel Electrode and Pt-gauze electrode, respectively.
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Fig. 2  The SEM images of the carbon/FTO composite film prepared on FTO glass at 500 °C, (i) Before wiping the film to remove loose crust and (ii) after wiping the film and thereby removing the loose crust.

Fig. 3  The XRD pattern of the AC/FTO counter electrode prepared at 500.

Since the AC/FTO film thickness is well over 1 μm, the XRD of the film will not be affected by the underneath FTO film since the depth of penetration of X-rays is much less than the thickness of the film. The XRD spectrum of AC-FTO film prepared at 500 is shown in the Fig. 3. The peaks correspond to the
JCPDS Card No. 41-1445 and intense peaks are shown at 2-theta values of 26.61° (110), 33.89° (101), 37.95° (200), 51.78° (211), 54.76° (220), 61.87° (310), 65.94° (301), 71.28° (202), and 78.71° (321). This confirms the formation of FTO during this fabrication.

3.2 DSC Performance

The $J-V$ characteristics of the DSCs constructed using AC/FTO counter electrodes are shown in the Table 1. The highest performance was observed for the DSC fabricated using the CE sintered at 500 °C. In our previous studies, we have shown that at least a 450 °C of temperature is required to form FTO. The $J-V$ data show that although the DSCs give impressive $V_{oc}$ with reasonable fill factors, the $J_{sc}$ values are lower than those obtained using Pt-based CE. Therefore, in order to improve the electron flow inside the cell, the amount of catalytic centers in the CE should be improved. With that intention in mind, we have varied the AC amount in the precursor solution and CEs containing different amounts of AC were fabricated and used in the assembly of DSCs. Their $J-V$ characteristics are shown in Table 2. The DSC assembled using the CE prepared from 0.400 g of AC per 40.0 mL of FTO precursor solution which was sintered at 500 °C has shown the highest power conversion efficiency of 7.6%, where the Pt/Cr mirror type counter electrode based DSC has shown 9.4% under the same conditions. DSCs with these carbon-FTO based counter electrodes have shown low fill factors compared to those of the Pt-based counter electrodes. This seems to be a major problem associated with these novel and low-cost counter electrodes although carbon materials tend to show superior catalytic properties towards $I_3^−$ reduction.

Here, the fill factor has been improved to 0.56 where it is expected to have good interconnection between the AC particles through the FTO grains. Also the AC/FTO layer has shown good adhesion properties towards the FTO substrate and it is also important to reduce the internal resistance in the counter electrode materials since the sheet resistance of ~ 60 Ω/□ was obtained for this CE whereas that of Pt-Cr one is below 5 Ω/□. Nevertheless, the lower conversion efficiency may compensate the lower production cost of the DSC when Pt is replaced by AC.

The best $J-V$ curves of the DSCs fabricated using AC/FTO counter electrode and Pt/Cr mirror type counter electrode are shown in the Fig. 4. It is clear that the two DSCs show comparable $J_{sc}$ values; AC/FTO being slightly better. However, $V_{oc}$ of the AC/FTO based

<table>
<thead>
<tr>
<th>Sintering temperature/°C</th>
<th>$J_{sc}$/mA·cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>11.64</td>
<td>0.637</td>
<td>0.430</td>
<td>3.2</td>
</tr>
<tr>
<td>400</td>
<td>11.54</td>
<td>0.694</td>
<td>0.534</td>
<td>4.3</td>
</tr>
<tr>
<td>500</td>
<td>12.81</td>
<td>0.703</td>
<td>0.522</td>
<td>4.7</td>
</tr>
<tr>
<td>600</td>
<td>12.66</td>
<td>0.698</td>
<td>0.524</td>
<td>4.6</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>AC amount (g/40 mL)</th>
<th>$J_{sc}$/mA·cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC/FTO</td>
<td>0.20</td>
<td>16.20</td>
<td>0.714</td>
<td>0.540</td>
<td>6.2</td>
</tr>
<tr>
<td>AC/FTO</td>
<td>0.40</td>
<td>18.98</td>
<td>0.709</td>
<td>0.563</td>
<td>7.6</td>
</tr>
<tr>
<td>AC/FTO</td>
<td>0.60</td>
<td>19.85</td>
<td>0.697</td>
<td>0.438</td>
<td>6.1</td>
</tr>
<tr>
<td>AC/FTO</td>
<td>0.80</td>
<td>18.84</td>
<td>0.690</td>
<td>0.453</td>
<td>5.9</td>
</tr>
<tr>
<td>AC/FTO</td>
<td>1.00</td>
<td>18.27</td>
<td>0.662</td>
<td>0.340</td>
<td>4.1</td>
</tr>
<tr>
<td>Pt/Cr mirror</td>
<td>-</td>
<td>18.78</td>
<td>0.732</td>
<td>0.688</td>
<td>9.4</td>
</tr>
</tbody>
</table>
DSC is slightly lower. Comparison of the $V_{OC}$ of AC/FTO based DSCs show that $V_{OC}$s decrease as the AC content of the film and the thickness are increased. The increased electrical resistance of the CE renders it difficult for the oxidation of I, as manifested by CV studies explained above, thus slowing down the removal of oxidized dye species. This will increase the recombination and hence the lowering of the Fermi level thus contributing to decrease the $V_{OC}$. The fill factors of the DSCs decrease as the thickness of the CE is increased. Increased resistance of the CE contributing to increased overall resistance of the DSCs may account for this behavior. The FF is lower in the best DSC based on AC-FTO when compared to that of Pt-Cr-FTO based DSC. These two limitations contribute to overall decrease in the conversion efficiency of the former device.

So far, in the literature, the researchers have deposited various carbon materials onto the FTO substrate. That approach is proper if the carbon material is also electronically conducting, for e.g., graphite, graphene or carbon nanotubes. However, when activated carbon is used and the FTO layer is covered with a thick AC layer the CE becomes insulated and consequently performance of the device is lowered. In our approach, we have deposited AC along with the FTO solution, thereby forming AC-FTO film during the deposition and by annealing the composite film at 500 °C. This process has the advantages due to following reasons. The AC nanoparticles formed in our method get interconnected with the help of FTO particles and hence the overall resistance of the CE is significantly lowered from the situation where the FTO layer is covered with an AC layer. This may explain the comparatively high conversion efficiency of 7.6% obtained for our DCS based on AC-FTO counter electrode. The decrease in the conversion efficiency due to the replacement of expensive Pt-Cr CE by low-cost AC-FTO CE is only 19% and this may compensate for the much lower cost of the DSC based on AC-FTO CE.

4. Conclusions

Activated carbon-FTO based counter electrode was fabricated and DSCs were fabricated using such counter electrodes in place of expensive platinum-FTO counter electrode. The DSC performance of the former was optimized by changing the composition of the...
precursor solution in the atomized spray pyrolytic deposition of the composite, deposition temperature and the spray duration. The best DSC has a conversion efficiency of 7.6% while that of the Pt-FTO based one is 9.4% under otherwise identical conditions. Although the cheaper counter electrode based DSC yields similar \( J_{SC} \) and somewhat higher \( V_{OC} \), slightly poor fill factor is responsible for the lower performance. Studies are underway to improve fill factor. The lower efficiency may be offset by the lower cost of the devices when cheaper counter electrodes are used.

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**References**


