Electrochemically Assisted Deposition of Indium Tin Oxide for Use in Quantum Dot Sensitized Solar Cells

Barclay Randall, Toshia Wrenn, Dr. Sandra Rosenthal
Vanderbilt University, Chemistry Department, Nashville, TN

Abstract

Indium tin oxide (ITO) was used as a hole conductor for quantum dot sensitized solar cells (QDSSC) and optimization of the deposition of ITO was investigated. To determine optimal voltage for electrochemically assisted deposition (EAD) of ITO, linear sweep voltammetry was employed. The results showed a cathodic voltage of 0.8V is an optimal voltage for the reactions needed to facilitate ITO deposition. To determine an optimal time for deposition of ITO, EAD of ITO was performed on multiple titanium foils for various times. The optimal time was determined to be around 300 seconds as determined by using scanning electron microscopy (SEM) to look at the morphology of the film deposited. QDSSCs were created by anodization of titanium to produce titanium oxide nanotubes, sensitization by chemical-linking of cadmium selenide quantum dots to the nanotubes, and EAD of ITO. Devices were subjected to EAD of ITO for 60s, 120s, and 300s. Energy dispersive X-ray spectroscopy (EDX) of this device showed that there was significantly more indium and tin throughout the device area of the 300s device than either the 60s or 120s film, indicating that the 300s device has the largest active area. In agreement with the EDX findings, photovoltaic efficiency of these devices showed that the device that underwent EAD for 300s had the highest efficiency.

Purpose

-Indium tin oxide was used as a solid hole conductor to increase the longevity of quantum dot sensitized solar cells
- Quantum dot sensitized solar cells could be much less costly than traditional solar cells
-Electrochemically assisted deposition (EAD) could be a much more industry friendly alternative

Introduction:

The device design is based on the Gratzel Cell, with a few main differences.
•instead of titanium nanoparticle network, a vertically-aligned array of nanotubes is used
•instead of a dye, quantum dots are the light harvester
•instead of a liquid electrolyte, indium tin oxide is used

Methodology

Anodization:

Anodic oxidation (or anodization)[1] is used to produce titanium oxide nanotubes directly onto the surface of a titanium foil.

Quantum Dot Synthesis[4]:

Solvothermal reaction of cadmium oleate with selenium: tributylphosphine produces cadmium selenide quantum dots with maximum absorbance at 568nm.

Chemical Linking[5]:

Chemical Linking is the process that deposits cadmium selenide quantum dots onto the devices. The quantum dots act as a light harvester for the devices.

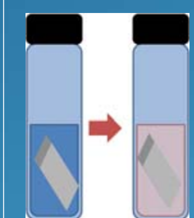

Fig 1a)
• 10% Mercaptopropionic acid in methanol- 24 hrs
•CdSe Quantum Dots in hexanes- 72 hrs

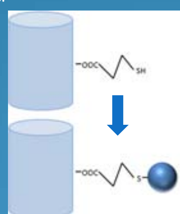

Fig 1b)
- Carboxylic acid links to the nanotubes
- Thiol group binds to quantum dot

Electrochemically assisted deposition:

Electrochemically assisted deposition[2, 3] or EAD is the main focus of research

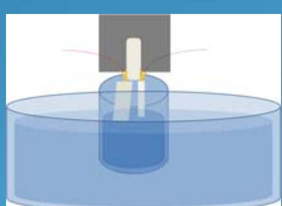

Fig 1c) EAD Set-up
Solution:
10mM $In(NO_3)_3$,
1M KNO_3,
4.6mM HNO_3,
and 1mM $SnCl_4$
Water Bath Temperature:
80°C
Reference Electrode:
Ag/AgCl

Localized pH increase:

$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O$
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Precipitation of Indium Tin Hydroxide Complexes:

$[(HO)_{4-n}Sn(H_2O)]_m\ In_n(H_2O)_{5n}]^{2n+} \xrightarrow{H_2O\ pH>2.3} In_nSn_mO_x(OH)_y(s) + H^+$

Annealing

Tube Furnace 350°C for 1 hr
-Convert Indium tin hydroxide to indium tin oxide
-Crystallize nanotubes into anatase titanium dioxide

Time Trials

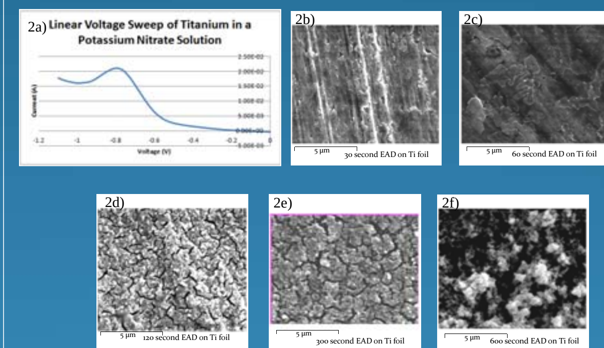

Fig. 2)
a) Linear sweep voltammetry was used in order to discover an optimal voltage of –0.8V for deposition.
b) SEM image of a titanium film that underwent EAD for 30 seconds
c) EAD 60 seconds
d) EAD 120 seconds
e) EAD 300 seconds
f) EAD 600 seconds

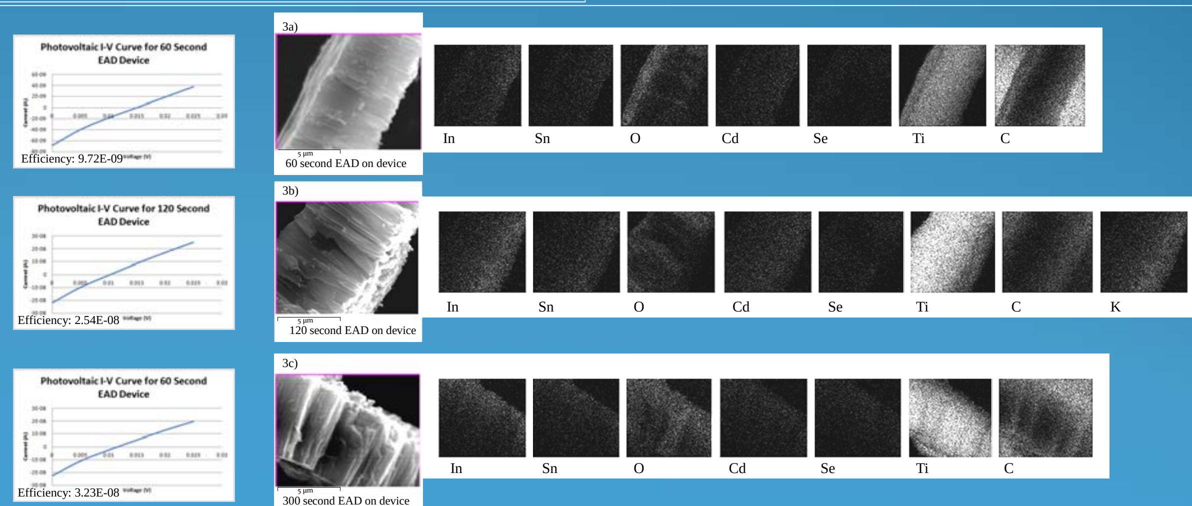

Fig. 3)
a) 60s EAD QDSSC photovoltaic response curve, SEM side view image, and EDX results
b) 120s EAD QDSSC photovoltaic response curve, SEM side view image, and EDX results
c) 300s EAD QDSSC photovoltaic response curve, SEM side view image, and EDX resutls

Conclusions:

The optimal parameters for electrochemically assisted deposition were investigated.
-Optimal voltage was determined to be -0.8V by linear sweep voltammetry
- Time trials concluded that 300s of EAD produced the film with the best morphology
-Energy dispersive X-ray spectroscopy (EDX) indicates that 300s of EAD produces devices with the largest working area
-300s EAD QDSSC- most efficient device due to larger working area

Future Directions:

-The annealing process could be investigated
-Time spent annealing
-Temperature
-Diameter of nanotubes could be investigated for any correlation to efficiency of devices
--Anodization voltage

Acknowledgements:

The author would like to show his appreciation for financial assistance to TN-SCORE grant number DMR 0907619 and for the use of VINSE resources.

Citation:
[1]Shiqi Li et al.. J. Phys. Chem. C **2009**, 113, 12759-12765
[2]Nina I. Kovtyukhova et al. Chem. Mater. **2010**, *22, 4939-4949*
[3]S. Manara, F. Paolucci et. al Inorganica Chemica Acta 361 **2008** 1634-1645
[4]Sandra Rosenthal. Surf. Sci. Rep., vol. 62, no. 4, pp. 111–157, 2007.
[5]Istva´n Robe et al. J. AM. CHEM. SOC. 2006, 128, 2385-2393