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Growing n-Cu_2O Thin Films on Transparent ITO Substrate to Replace the Opaque Copper Metal Substrate for Dye-Sensitized Solar Cells

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ABSTRACT

The world is facing the problem of fossil fuel shortage, and increasing crude oil prices. Hence, sustainable energies such as hydropower, wind power, geothermal power, solar power, and biomass are in the main focus in the energy research. The Dye-sensitized solar cells (DSSCs), classified as the third-generation photovoltaic offer a low-cost and nontoxic device, with functionalities such as flexibility and transparency. At present, titanium dioxide (TiO_2) is used as one of the electrode materials in DSSC. Among other different metal oxide materials, copper-base dioxide materials are of great interest in this context. To-date, most of the time, the Cu_2O working electrodes are fabricated on copper metal substrate. This only allows the devices to be back illuminated, which result in reducing the photo-response. Thus, the study presented here is focused on developing a nano-porous Cu_2O layer on a transparent substrate (ITO glass) with different methods, and study their optoelectronic properties in the aim of utilizing these electrodes in photovoltaic or opto-electronic device applications.

1. INTRODUCTION

Nowadays the whole world pays attention to the problem of fossil fuel shortage, and increasing crude oil prices. As a result, sustainable energies have been more focused in current fields in research. Hydropower, wind power, geothermal power, solar power, and biomass processing are few examples of the sustainable energies. Solar energy is one of the resources in archiving the target of a clean energy future. Everyday sun gives more energy (~$1.73*10^{11}$ MW) than the need on the Earth (~$1.73*10^{6}$MW)[1]. Solar panels convert this energy upon shining sunlight and convert them into electrical energy (electricity). There is no depletion in the incoming solar energy and this energy conversion process environmentally

The development of solar cell technology is been divided in to three generations. The first generation is the very costly single crystal silicon (Si) based solar cells, then the second generation is the low-cost thin film solar cell, but the materials used here are toxic and carcinogenic, and disposal of the devices are harmful for the environment. The Dye-sensitized solar cells (DSSCs) are classified as third-generation organic solar cells because they offer al low-cost and use anoxic materials in production. Additionally, they provide the functionalities such as flexibility and transparency, which are not offered by the first two generation devices [2]. Moreover, the ability that the DSSCs could be fabricated at low cost, in different colors, on a transparent glass or on flexible substrates have a huge potential in the commercial market, specially for “low-density” applications such as rooftop solar collectors and other small electronic gadgets. Another important feature is its operational hours at both ambient light and full sun condition without much impact on efficiency and also its ability to work at wider angles; when the other traditional solar cells would fail at illumination below a certain

range in incident angle. Hence, the DSSCs could operate around 10 to 14 h in a day (depending on the latitude and the season) whereas the traditional silicon solar cells merely operate for 6 to 8 hours (under the same conditions)[3].

When the operation of a DSSC is considered, the light passes through transparent anode and excites the dye molecules. The excited dye molecule injects electrons into the nanoparticle layer which acts as an n-type semiconductor. The electrons flow through the external circuit to the cathode and then flow into the hole-collector, which is an electrolyte regenerating the dye back to its ground state.

At present, titanium dioxide (TiO_2) or a p-type semiconductor. Then the hole-collector transports the electrons back to the dye molecules, is used as one of the electrode materials in DSSC. Other oxide semiconductor materials too, are studies as possible electrode material to be use in DSSC such as Cu_2O, Nb_2O_5, ZnO, SnO_2 etc.[4]. Among different metal oxide materials, Cu based materials are of great interest because of their wide range of applications. There are many reasons to select Cu_2O absorber layers for solar cells. In general, they are non-toxic, have low band gap values and can be easily adjusted by altering the composition[3]. They have high absorbance coefficient and can be prepared at low cost in simple method. To-date, most of the time, the Cu_2O working electrodes are fabricated on copper metal substrate. This only allows the devices to be back illuminated, which result in reducing the photo-response of the device. This study is focused on developing a nano-porous layer of Cu_2O on a transparent substrate (ITO glass) with different methods. Material properties of such films were studied and compared with the properties of a Cu_2O thin film grown on a copper metal substrate.

2. METHODOLOGY

For this study, cuprous oxide layers were grown using three methods and tested with dyes for their performance by measuring photocurrent and photo-voltage, in a device configuration ITO/{Cu}/n-Cu_2O/Dye/hole-collector/{ITO} or platinum film (Dye is Rhodamine-B). When the copper metal (identified as {Cu} in the above configuration) is in the cell, ITO glass is used as the counter electrode and the devices are illuminated through the back contact.
The dye coating on the thin films were done by dipping the prepared copper oxide thin films in concentrated dye solutions, in ethanol, for about 24 hours. Finally, the dye coated electrode was washed with distilled water to remove any excess dye molecules that were not properly anchored on to the electrode, and allowed them to dry with ambient air/temperature. As hole collectors, CuI or CuSCN were used for solid state devices and the I^-/I^{-3} redox couple was used as the electrolyte in the electro-chemical devices. Following methods were used in fabricating the Cu_2O films for the working electrode.

2.2 Thermal Oxidation Method

In the first method used to prepare the copper oxide thin film, an ITO glass was cleaned with acetone, and a piece of metallic copper sticker was pasted on the glass substrate. Thereafter, the surface of the copper metal tape was cleaned, with dilute nitric acid and washed with distilled water. Finally, it was boiled in copper sulphate solution until copper oxide film of considerable thickness grows on copper tape. Here the Cu_2O films is grown on the copper substrate, the performances and properties of this sample was

kept as the control to compare the results of the electrodes made by the other two methods.

2.3 Electro chemical deposition method

In the second method, the copper oxide nano-films were deposited electrochemically. Here, a two-electrode system with negative 0.5V potential between the working and counter electrodes were used. The cuprous oxide was coated on the working electrode, of a cleaned ITO glass. The counter electrode was a platinum electrode. A platinum sheet in 3mm× 3mm size was well polished and placed as a counter electrode. Current was allowed to flow between the working electrode and the counter electrode. The copper oxide source here is the electrolyte.
The electrolyte was prepared with 0.1M of copper sulphate pentahydrate (pure) and 0.1M of tartaric acid, mixed in 1:1 ratio in volume. A solution of 1M of NaOH was used to adjust the pH of the electrolyte, at 11, to form Cu_2O. The temperature of the bath was maintained at room temperature for slow deposition. The films were deposited for a period of 1 hour [5].

2.4 Nano particle depositing Method

In the third method, a 1 ml of 0.1M copper chloride was mixed with 95.5 ml of distilled water, then 2 ml of 1 M sodium hydroxide solution was added to the above solution while stirring at room temperature, using a magnetic stirrer. Then 0.87 g of sodium dodecyl sulphate (SDS) was added while continues stirring. Finally, a 1.5 ml of 0.2 M hydroxylamine solution was quickly added while shaking the solution vigorously and the resulted solution was left for ageing and to form copper oxide nanoparticles for ~2 hrs [6]. Finally, to deposit the copper oxide thin film, an ITO glass, which was cleaned by acetone, was placed at the bottom of the beaker to slowly deposit the cuprous oxide nano particles. At the end they were dried in an oven at 65 C.

3. RESULTS AND DISCUSSION

Figure 1 (a) depicts the XRD spectra of the copper oxide thin film, grown on a copper foil. The peaks at the 30.065°, 36.951°, 42.80°, and 61.92° positions of 2-theta values represents the existence of following different plans which are Cu_2O (111), Cu_2O (200), and Cu_2O (220) in the film. Additionally, there a planes of copper metal observed in the XRD due to the effects of copper substrate, The I-V characteristics of a device in the configuration ITO/Cu/n-Cu_2O/Dye/Electrolyte/ITO is shown in Figure 1b, implies a feasibility of fabrications of a substantial photovoltaic device using this nano- particle Cu_2O film.
The XRD of Cuprous oxide layer prepared by Nano particle method and electrochemical method are depicted in Fig. 2 (a) and 2(b) respectively. As can be seen in the Fig. 2(a) the thin film made with the nano-particle method only consist with Cu_2O poly crystals. The poly-crystalline nature of the film is confirmed by the existence of different planes namely, Cu_2O (111), Cu_2O (200), and Cu_2O (220) on the electrode. In contrast in the electrode made with the electro deposition techniques, in addition to Cu_2O, the CuO crystals are also formed on the electrode33°45', and 51°26' are correspond to CuO (-111), CuO (002) and CuO (020) respectively. Additionally, the same planes as of above, that of Cu_2O were observed of the electrodeposited electrode.. The peaks at 2*theta = 26°26',

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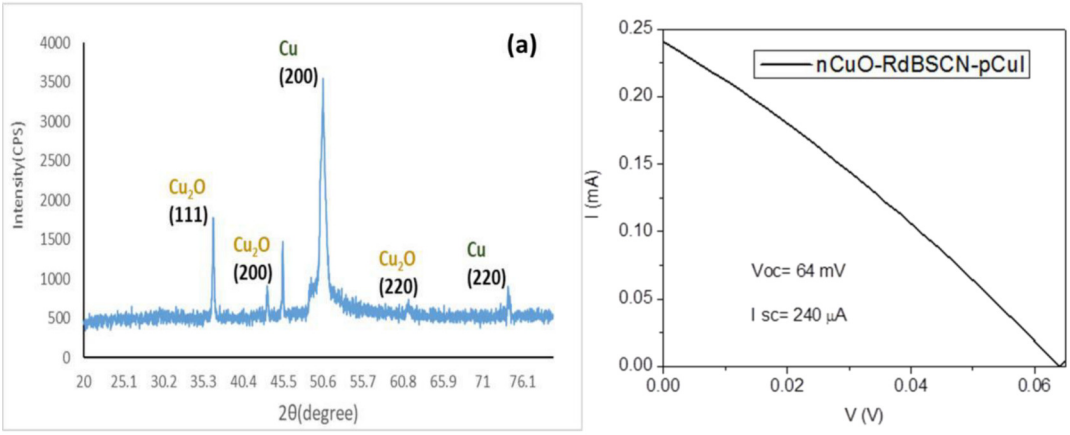

Figure 1: (a) The XRD spectra of the copper oxide thin film, grown on a copper foil, and **(b)** the I-V characteristics of a device in the configuration ITO/Cu/n-Cu_2O/Dye/CuI/ITO.

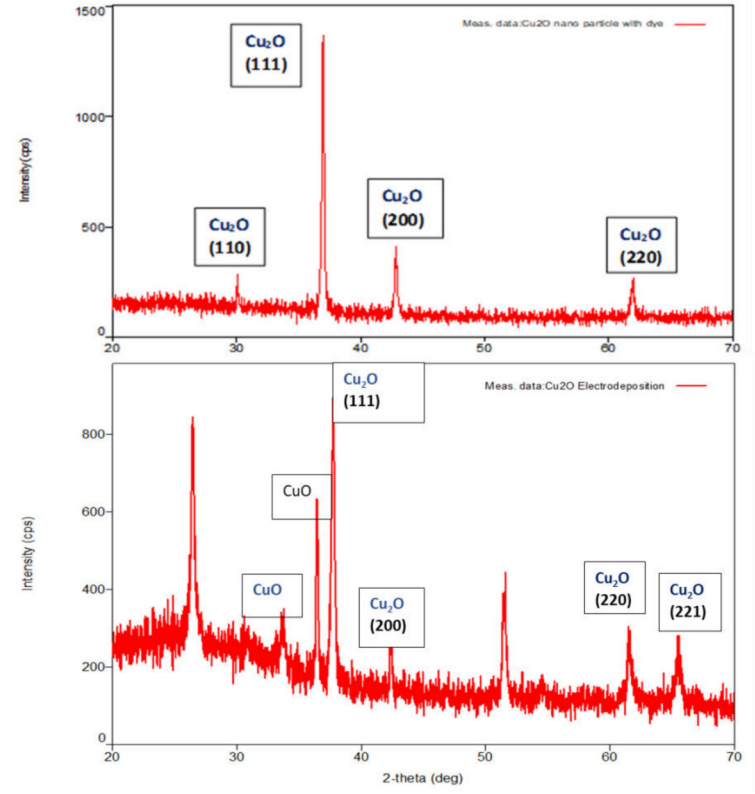

Figure.2: The XRD spectra of the working electrodes made by (a) nano-particle method and (b) electrochemical method.

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The inverse square capacitance vs. voltage plot for the electrode made by nano-particle method is shown in Figure 3. The plot implies the material to be n-type semiconductor. In contrast the data obtained for the electro-deposition method was in conclusive. The determination of the conductivity type for the electrodeposited electrode was not possible. It can be assumed that the CuO crystals exists in the film acts as a p-type material and the Cu_2O act as a n-type material, then the existence of mixture of both n- and p-type materials have led to inconclusive result in clear determination of the conductivity type of the electrodeposited film.

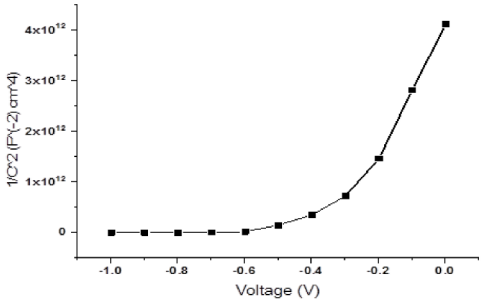

Figure 3: The invers square capacitance (1/C^2) vs. voltage (V) plot for the electrode made by nano-particle method. The positive slope implies the material been having n-type semiconducting properties.

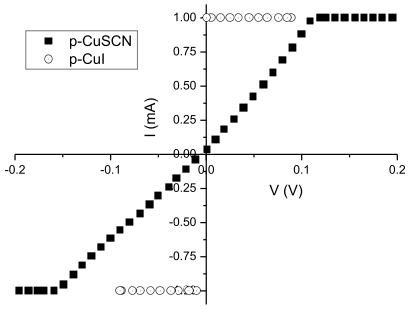

Figure 4: The dark I-V curve for the device configuration ITO/n-Cu_2O/Dye/CuI/ITO (filled squires) and ITO/n-Cu_2O/Dye/CuSCN/ITO (open circles).

The Figure 4 shows the dark I-V characteristic curves for the device configuration ITO/n-Cu_2O/Dye/CuI/ITO and ITO/n-Cu_2O/Dye/CuSCN/ITO. Where the Cu_2O thin films were fabricated using the nano-particles method. The liner behaviour in the I-V characteristic implies short circuit in the device. The short circuit can be occurred in the device due to voids in the Cu2O thin film, which allows the hole collector material (CuI or CuSCN in this samples) been penetrated through the Cu_2O layer and getting direct contact with the ITO glass in the working electrode.

Even though the solid-state type device (using CuI or CuSCN as hole collector) have made the device to be short circuited, when using the I^-/I_3^- redox couple electrolyte, there have been some promising photo-current, ~1 mA/cm^2. This photo current was

rapidly degrading as of the chemical reactions with the copper oxide nanoparticles. Additional studies are needed in finding a more suitable electrolyte to be used with the Cu_2O nanoparticle, in aim of developing a stable electrochemical DSSC with Cu_2O electrode.

4. CONCLUSION

Cuprous oxide electrodes were grown using three methods and these electrodes were tested for here electronic properties as single electrodes and, in a device configuration ITO/{Cu}/n-Cu_2O/ Rhodamine b Dye /hole-collector/{ITO} or platinum for their performance as a photo-voltaic device. The electrodes made with nano-particle deposition have shown a n-type semiconductor behaviour. But as a p-n junction device, under the above device configuration, the device failed to perform. The preliminary studies indicate short-circuiting of the device, due to low density and voids and pin holes generated in the film.

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