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Optimizing Photovoltaic Performance in p-Cu2O/n-TiO2 Heterojunction Solar Cells: The Impact of Annealing Temperature, Layer Thickness, and Carbon Doping

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Abstract

This study analyzes the photoresponse behavior and optimizing the efficiency of p-Cu_2O/n-TiO_2 heterojunction solar cells. The impact of annealing temperature, layered thickness, and carbon doping on the optical and electrical characteristics of the solar cells was investigated. The findings reveal that the annealing temperature continuously affects the optical absorption and energy gap of Cu_2O, with the best performance at 250°C. Increasing the layer thickness of Cu_2O resulted in further improvement in absorption and efficiency. It was also found that doping carbon into TiO_2 lowered the energy gap, increasing efficiency. The maximum efficiency of 0.003593% was obtained with carbon-doped TiO_2. This work guides optimizing the design of heterojunction solar cells for better photovoltaic performance.

Keywords: Photoresponsive Materials, Heterojunction Solar Cells, Cu_2O, TiO_2, Carbon Doping, Annealing

INTRODUCTION

Developing dye-sensitized solar cells (DSSCs) is an innovative solution for the problems linked with silicon-based solar cells because of their low cost and uncomplicated production methods (Grätzel, 2003). Unfortunately, the cost-effective nature of DSSCs still lacks the required efficiency, paving the way for research into other structures and materials. This challenge can be addressed by creating heterojunction solar cells, which integrate p-type and n-type semiconductors to enhance charge carrier separation within the device, thus resulting in better efficiency (Fujishima, Zhang, & Tryk, 2007). The p-Cu_2O/n-TiO_2 heterojunction configuration was studied, with Cu_2O serving as the p-type semiconductor and TiO_2 as the n-type semiconductor.

Makhlouf et al. (2017) notes cuprous oxide (Cu_2O) is regarded as a p-type semiconductor due to its direct band gap of approximately 2 eV, high absorption capabilities, as well as its abundance and non-toxic nature (Makhlouf et al., 2017). On the other hand, Muniz et al. (2011) states titanium dioxide (TiO_2), an n-type semiconductor widely used in solar cells, is known for its excellent stability, low cost, and electron transport properties (Muniz et al., 2011). TiO_2 has also been successfully implemented in nanocomposite form, such as ZnO/TiO_2, to improve dye-sensitized solar cell (DSSC) performance, particularly when combined with natural dyes like mangosteen peel extract (Dwi, Utomo, Nur, & Wihadi, 2022).The synergetic effects of these two semiconductors are expected to be more beneficial when used as a p-Cu_2O/n-TiO_2 heterojunction, increasing the photovoltaic performance (Qin et al., 2019). Furthermore, in an effort to enhance the charge transport properties and overall photovoltaic efficiency, TiO_2 will be doped with carbon.

Norazlina et al. (2021) outlined the use of electrodeposition and hydrotermal techniques and how these conventional methods are the primary focus of other studies. This research is unlike others as it incorporates the Chemical Bath Deposition (CBD) technique, which is low cost, low temperature, and suited for uniform and adhesive semiconductor thin films (Arsad et al., 2023). CBD also has strong contenders in thin film solar device mass production due to its ease in scaling and process control (Febriyanti, 2021).

The distinct contribution of this study stems from the methodical focus on the impacts of annealing temperature, thickness of the layer, and carbon doping on the performance of p-Cu_2O/n-TiO_2 heterojunction solar cells manufactured by chemical bath deposition

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(CBD). Unlike undoped structures and set-processing parameter focus, this study attempts to optimize the fabrication parameters to improve the efficiency of the device. In addition, by adding carbon as a dopant into the Cu homoide layer, we propose a new alerternative for increasing the conductivity and carrier mobility in Cu/TiO heterojunctions, which has not been studied in detail before.

The most important parts of this work are (1) the application of a low-cost CBD method for heterojunction fabrication, (2) the study of the effects of post-deposition annealing and doping and their effects on performance, and (3) optimization of the resulting solar cells. With this work, it is hoped that the technological advancement of photovoltaics further drives development and leads to the creation of highly-efficient, environmentally friendly, and cost-effective technologies.

METHODOLOGY

Material and Instrumentals

All chemicals utilized in this study were of analytical grade and were not further purified. Key chemical reagents were FTO glass substrates, $CuSO_4$, $Na_2S_2O_3$, NaOH, Ti(III) chloride, NH_4OH, PVA, KI, I_2, and acetonitrile. A natural dye was isolated from the peels of mangosteen (Garsinia mangostana).

A temperature-controlled hot plate was employed for synthesis and deposition as well as for solution preparation using a magnetic stirrer and cleaning substrates using an ultrasonic cleaner. Annealing treatments were done using a laboratory oven. Thin film deposition of TiO_2 was performed by the doctor blade method. Characterization of the resulting TiO_2 and Cu_2O films was performed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), in that order, to evaluate crystallinity and surface morphology respectively. Optical property characterization was done using UV-Visible spectrophotometry. The photovoltaic performance of the fabricated solar cells was evaluated in a simple circuit with external sunlight or artificial lamp sources as power supplies, measuring voltage and current output.

Methods

Synthesis of Cu_2O and TiO_2 Nanoparticles

TiO_2 nanoparticles were synthesized using a co-precipitation technique. The precursor employed was $TiCl_3$; the TiO_2 obtained was then subjected to calcinating over 2.5 hours at 450°C to anatase the phase (Dwi Fahyuan, Farid, & Sarina Pakpahan, 2015). Carbon doping of 14 percent weight was introduced in the solution of TiO_2, which was deposited employing the doctor blade on the FTO substrate (Yao et al., 2018). Additionally, to prepare the TiO_2 paste for deposition on the FTO glass, a sol-gel method was used. The sol-gel method was chosen due to its simplicity and ability to control nanoparticle size and crystallinity, as has also been reported in ZnO-based materials for electrochemical applications (Febriyana & Setiarso, 2024).

The Cu_2O thin films were produced using the CBD (Chemical Bath Deposition) method. A 1M NaOH solution was kept at 60 °C and copper thiosulfate solution was made from $CuSO_4$, then stirred for 120 minutes with $Na_2S_2O_3$. The substrates were dipped alternately in NaOH and copper thiosulfate for 30 seconds each, a total of 10, 20 to 50 cycles was done, followed by annealing at 200-300 °C (Maddu, Sirait, Tri, Dan, & Zuhri, 2007).

Steps in the Production of Heterojunction Solar Cells

The fabrication procedures involved synthesizing the p-Cu_2O/n-TiO_2 heterojunction solar cells by depositing TiO_2 and Cu_2O layers on FTO (fluorine-doped tin oxide) substrates. The photoanode was sensitized by mangosteen peel extract anthocyanin dye at ~70 °C for 24 hours. The counter electrode was the deposition of 2B graphite and candle soot on FTO glass and mixed with carbon.

An electrolyte consisting of KI/I_2 dissolved in acetonitrile was made and used for assembling the DSSC in a sandwich configuration. The structure of the sandwich layer arrangement in the DSSC can be seen in Figure 1. Performance testing was carried out under sunlight and artificial lamp illumination by measuring current and voltage through a variable resistor.

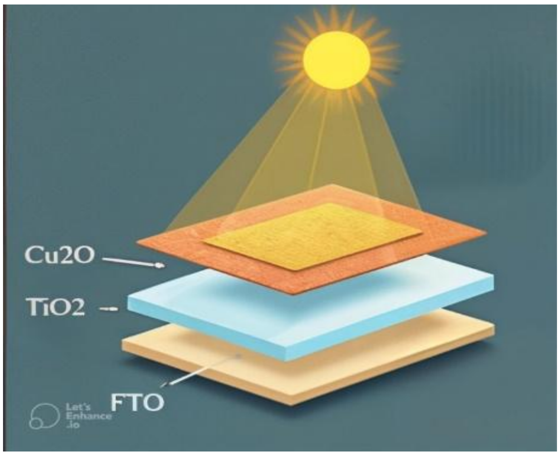

Figure 1. Schematic illustration of a thin-film heterojunction solar cell composed of FTO glass, TiO_2, and Cu_2O layers

The construction of the solar cells was done in a sandwich-like fashion, with the TiO_2 layer dyed facing the carbon-coated counter electrode (Cahaya, Prajitno, & Puspitasari, 2018).

Characterization and Testing

The synthesis characterization was done using X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Vis spectroscopy. The photoreactive performance was evaluated using a halogen lamp, with the efficiency of the solar cell being determined by recording the current-voltage (I-V) characteristics (Sawicka-Chudy et al., 2019).

Data Analysis

The efficiency of a Dye-Sensitized Solar Cell (DSSC) is generally evaluated by its power conversion efficiency (η), which describes the amount of incident light energy transformed into electric energy. The following equation describes how the efficiency is computed.:

$$\eta = \frac{Voc\ X\ Jsc\ X\ FF}{Pin} X\ 100 \qquad (1)$$

RESULTS AND DISCUSSION

Morphology and Elemental Mapping of Cu2O/TiO2 Heterojunction

The EDX performed showed that the major constituent was copper with an atomic percentage of 73.18% while titanium was only 3.37%. The atomic percentage data is presented in Table 1.

Table 1. TiO2/Cu2O mapping

Element	Weight total %	Atomic total (%)
OK	7,23	23,45
CuK	89,66	73,18
TiK	3,11	3,37

The EDX results confirm the pseudomorphic transformation of deposited TiO_2 onto Cu_2O thin film when the film is heated to higher temperatures in the presence of oxygen forming Cu_2O thin films of titanium oxide (Liao et al., 2018). This change happens because interdiffusion and surface reactions at higher temperatures create a mixed interface or layered structure between TiO_2 and Cu_2O, thus enhancing fabrication. It has been shown that at high annealing temperatures, titanium is diffused into the Cu_2O layer where it reacts with available oxygen, forming Ti-rich oxide phases whilst maintaining the film's morphology (Yurddaskal, Dikici, & Celik, 2016).

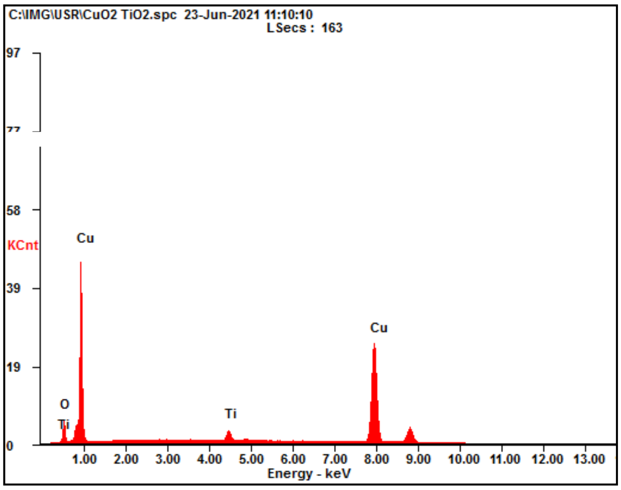

Figure 2. EDX analysis of Cu_2O and TiO_2 layers indicating the presence of Cu, Ti, and O elements

Figure 2 shows the thin film structure by p-n heterojunction which indicates that it is possible for effective charge separation required for solar cell operations (Yao et al., 2018b)

Impact of the Cu_2O Annealing Temperature on Its Attributes

The optical and structural properties of the Cu_2O were highly affected due to the annealing temperature. From the absorbance data within the scope of 300–900 nm illustrated in Figure 3, it can be seen that absorption was highest at 200°C with a gradual decrease at higher temperatures. This is because, at temperatures beyond 250°C, the Cu_2O gives rise to CuO, which decreases the absorption coefficient and increases the energy gap (Raship, Sahdan, Adriyanto, Nurfazliana, & Bakri, 2017).

This change results from the thermal oxidation of the Cu^+ ions into Cu^{2+}, resulting in a phase change from Cu_2O to CuO, which has a higher bandgap and different optical properties. Bai et al. (2018), also reported similar findings where they observed reduction of optical absorption along with a shift of band gap with increasing annealing temperature associated with formation of CuO (Bai, Ma, Dai, & Shi, 2018). These transformations, wherein the material loses the ability to strongly absorb light, are critical for photovoltaic or photocatalytic applications.

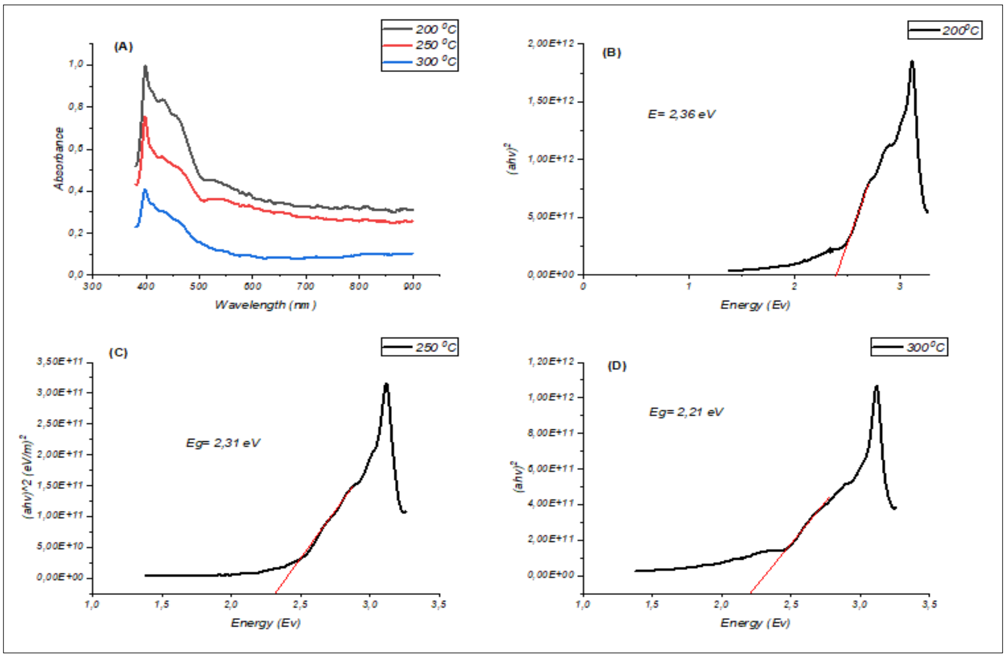

Figure 3. UV-Vis absorption spectra and Tauc Plot of Cu_2O with different annealing temperatures

According to Tauc plot analysis (Figure 3), the energy gap of Cu_2O decreased from 2.36 eV at 200°C to 2.21 eV at 300°C. This reduction is compatible with the formation of CuO since CuO has a lower bandgap than Cu_2O (Pratista, Gunawan, & Widodo, 2020). It was noted that the optimal annealing temperature for Cu_2O was 250°C, where the material had a high absorption value but a lower energy gap (Qin et al., 2019).

Influence of Layer Thickness on the Efficiency of the Solar Cell

The number of deposition cycles controlled the thickness of the Cu_2O layer. As shown in Figure 4, the absorption increased with thickness, achieving a peak at 50 cycles. The increased number of Cu_2O atoms increases photon absorption and electron-hole pair generation (Tivanov, Moskalev, Kaputskaya, & Żukowski, 2016).

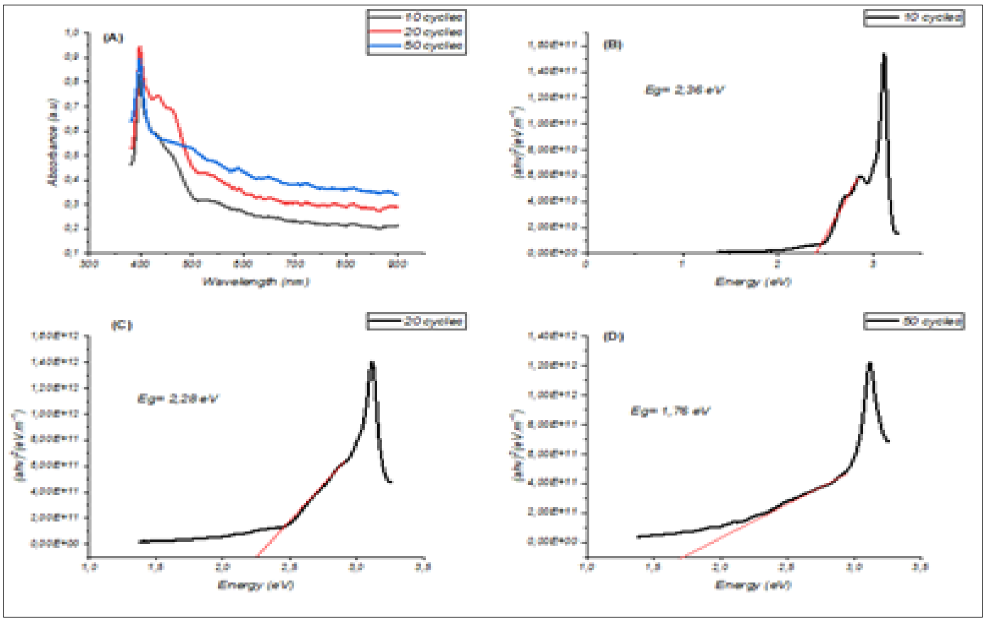

Figure 4. UV-Vis absorption spectra and Tauc Plot of Cu_2O for different layer thicknesses

The solar cell's efficiency also increased with thickness, reaching a peak of 0.002238% at 50 cycles (Table 2). However, recombination losses may ensue beyond this thickness value, thereby diminishing the overall efficiency (Enebe, Lukong, Mouchou, Ukoba, & T-C, 2022)

Table 2. Figure of merit F of solar cells with varying Cu_2O thicknesses

Cycles	Voc (V)	Jsc (A/m^2)	Fill Factor	η (%)
10	0.2024	0.34	0.163915	0.00145
20	0.2325	0.32	0.215013	0.002066
50	0,2574	0.39	0.172614	0.002238

Influence of Carbon Doping on the Properties of Titanium Dioxide

In order to assist in improving the conductivity of TiO_2, carbon doping was brought in to decrease the energy gap. The absorption capacity of carbon-doped TiO_2 was greater than that of pure TiO_2, especially in the visible region, as seen in Figure 4. This is due to carbon's inclusion of mid-gap states that increase energy harvesting photons (Li et al., 2020; Ye, Liu, Tian, Peng, & Zan, 2013).

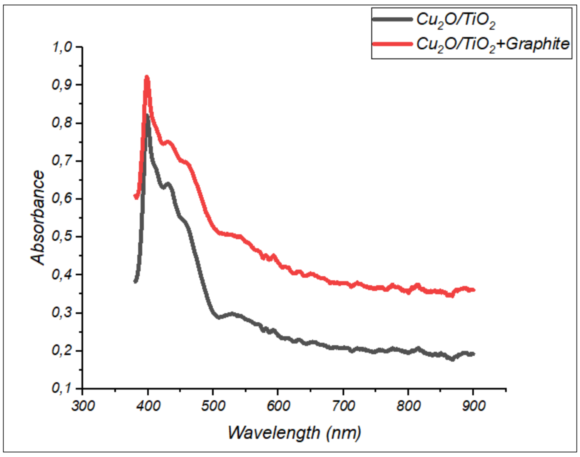

Figure 5. UV-Vis spectra of carbon-doped TiO_2 and pure TiO_2

The energy gap of TiO_2 reduced from 2.97 eV to 2.6 eV post carbon doping, based on Tauc plot analysis. The drop in energy gap is in line with previous research showing that the incorporation of carbon into the structure of titanium dioxide enhances its photocatalytic efficiency (Kumar et al., 2022). This observation is also consistent with studies on TiO_2 composites for dye degradation, where the surface characteristics and TiO_2 distribution significantly influenced the photocatalytic effectiveness (Tumbel, Wuntu, & Abidjulu, 2015)

The maximum theoretical efficiency of the solar cell increased from 0.002066% to 0.003593% after carbon doping (Table 3). This improvement results from increased electron transport and diminished recombination losses in the carbon-doped TiO_2 layer (Wisz et al., 2021).

Table 3. Efficiency of solar cells with and without carbon doping

Sample	Voc (V)	Jsc (A/m^2)	Fill Factor	η (%)
Cu_2O-TiO_2	0.2325	0.32	0.215013	0.002066
Cu_2O-TiO_2+Grafit	0.2645	0.35	0.300491	0.003593

CONCLUSION

This experiment highlights the promising photovoltaic performance of p-Cu_2O/n-TiO_2 heterojunction solar cells. Significant changes in the optical and electrical properties of the solar cells were noted with varying annealing temperatures, layer thickness, carbon doping and the lowering of the TiO_2 to Cu_2O (TCOS) ratio. The optimal annealing temperature for Cu_2O was 250°C, while the most excellent efficiency was noted at 50 cycles of the Cu_2O layer with carbon-doped TiO_2. This study helps optimize the heterojunction solar cells for future use.

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